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# BIOFILTRATION OF GASEOUS TOLUENE USING ADSORBENT CONTAINING POLYURETHANE FOAM MEDIA

**Altangerel Amarsanaa, Won Sik Shin†, Jeong-Hak Choi, and Sang-June Choi**

Department of Environmental Engineering Kyungpook National University Taegu 702-701, Korea

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**Abstract** : In this study, conventional biofilters packed with flexible synthetic polyurethane (PU) foam carriers were operated to remove toluene from a contaminated air stream. PU foams containing various adsorbents (e.g., zeolite, sepiolite, dolomite and barite) were synthesized for the biofilter media and their adsorption characteristics of toluene were determined. Adsorption capacity of PU-adsorbent foam was in the order of PU-dolomite ≈ PU-zeolite > PU-sepiolite > PU-barite. During the biofiltration experiment, influent toluene concentration was in the range of 0-160 ppm and EBRT (i.e., empty bed residence time) was 45 seconds. Pressure drop of the biofilter bed was 4-5 mm $H_2O$/m column height. The maximum removal capacity was in the order of PU-dolomite > PU-zeolite > PU-sepiolite > PU-barite, while the complete removal capacity was in the order of PU-dolomite > PU-sepiolite > PU-zeolite > PU-barite. The better biofiltration performance in PU-dolomite foam was because PU-dolomite foam had lower density and higher porosity than the others providing favorable conditions for microbial growth. The results of biodegradation kinetic analysis showed that PU-dolomite foam had higher maximum removal rate ($V_m$ = 11.04 g toluene/kg dry material/day) and saturation constant ($K_s$ = 26.57 ppm) than the other PU foams. This supports that PU-dolomite foam was better than the others for biofilteration of toluene.

**Key Words** : Adsorbent, Biodegradation Kinetics, Biofiltration, Polyurethane foam, Sorption, Toluene

## INTRODUCTION

Biofiltration technology has a promising potential as an effective and economical treatment technology than the traditional treatment technologies for treating contaminated air stream with low concentration of odorous compounds and/or volatile organic compounds (VOCs). The fundamental principle of biofiltration of polluted air is that gaseous pollutants are destroyed in the process being converted into carbon dioxide, water and biomass by microbial metabolic reactions. During the biofiltration, polluted air is passed through the biofilter medium where the pollutant is transferred from the gas to the liquid-solid phase where they are degraded by biofilm.[1-3)]

The concept of biofiltration to treat waste gases is similar to other forms of biological wastewater 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 inert products such as carbon dioxide, water, and biosolids.

† Corresponding author
E-mail: wshin@mail.knu.ac.kr
Tel: 053-950-7584, Fax: 053-950-6579

Biofiltration primarily depends on the choice of the packing material. A proper packing material should have favorable conditions such as high porosity, appropriate pore size and suitable surface area for microbial growth and lower clogging effect that involves biofilter systems operated for long periods of time.[2-4)]

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 and polyurethane foam.[4-7,23-26)] In addition to the primary support medium, a variety of additives may be used including bulking agents, buffers, nutrients, and microorganisms.[8,27)]

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 clogging 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.[9)] 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, clogging due to excessive microbial growth in overloaded systems or systems operated for long periods of time under normal loading. 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.* developed a successful backwashing procedure for biofilters packed with ceramic pellets but the daily downtime was appreciable and full-bed fluidization was required.[10)] Holubar *et al.* controlled clogging by limiting the addition of nutrients at the expense of biofilter performance.[11)] They 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. Farmer *et al.* investigated a system of three biofilters in series where the lead biofilter receiving contaminated inflow was periodically operated.[12)] Although this decreased net biomass production in biofilters not in the lead position, clogging was still a problem. Severin *et al.* sparged air and water through a biofilter and successfully dislodged excess biosolids.[13)]

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[13,18,23,24)] while others, such as polyurethane foam, are produced from hydrophilic materials that are easily re-wetted.[4-7,15)] 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 rise reduce the air's relative humidity to less than 100%. Nutrient limitations can have a negative impact on contaminant removal.[4,13,14)] 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.[8)] 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 new biofilter medium, polyurethane foam. Moe *et al.* 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.[14] The new medium also permits use of novel nutrient addition and biosolids wasting strategies.

The chemistry of polyurethane formulation uses the reaction of organic isocyanates with compounds containing active hydrogen atoms such as polyols or polyamines. Generally, choice of the starting molecules of polyurethane foam highly affects the physicochemical properties of foam.[4,15,16] In addition, polyurethane foam may also be made from hydrophilic and sorption materials that are easily rewetted if drying occur. As a general rule, any additive such as adsorbents that can be present in the water (in solution, suspended, emulsified, etc.) can be incorporated into an aqueous phase and become an integral part of polyurethane foam through covalent bonding or physical entrapment.[16]

In this study, conventional biofilters using polyurethane foams as packing material were operated for the removal of toluene from air stream. Polyurethane foams containing various adsorbents such as zeolite, sepiolite, dolomite and barite were synthesized as biofilter media. The effects of various adsorbents on the biofiltration of gaseous toluene were investigated. The biodegradation kinetics of these systems was also analyzed.

# MATERIALS AND METHODS

## Materials

Polyurethane (PU) foam used in this study was made from Hypol 3000 prepolymer (Dow Chemical Co., Midland, MI, USA). The nonionic surfactant, Tween 85 was obtained from Aldrich Chemical Co. (Milwakee, WI, USA). The adsorbents such as zeolite, sepiolite, dolomite and barite were obtained from Wangpyo Chemical Co. (Pohang, Korea). The impurities of the adsorbents were removed by washing them several times with distilled water at 60 °C. The adsorbents suspension was filtered with 0.22 μm membrane filter, and the filtrate was examined for its impurities using a UV-spectrophotometer (Hewlett Packard, 8452A, USA). The washed adsorbents were settled, dried in an oven at 60 °C for 24 hours, and stored in a brownish bottle prior to use. The physicochemical properties of the adsorbents are summarized in Table 1.

## Synthesis of PU Foam

PU foam was synthesized by slight modification of the procedure previously reported by Moe et al.[15] Surfactant solutions, ranging from 2 to 40 g/L, were prepared by dissolving Tween 85 surfactant in deionized water (DI water, resistivity $\geq$ 17.5 MΩ·cm) and cooling to 4 °C. To manufacture polyurethane foam, Hypol 3000 prepolymer was heated to 55 °C in a water bath and maintained at that temperature for at least 2 h before being combined with surfactant solution. Approximately 110 g of Hypol 3000 and 110 g of surfactant solution were added into a

Table 1. Physicochemical properties of the used adsorbents

| Properties | Zeolite | Sepiolite | Dolomite | Barite |
|---|---|---|---|---|
| Formula | $Al_2Si_3O_{10}·8H_2O$ | $Si_{12}Mg_3O_{32}·8H_2O$ | $CaMg(CO_3)_2$ | $BaSO_4$ |
| Structure | - | Orthorhombic | Trigomal | Orthorhombic |
| Mineral group | Zeolites | Silicates | Carbonates | Sulfates |
| Hardness | 3.5-4.0 | 3.5-4.0 | 3.5-4.0 | 3.0-3.5 |
| Density | 2.1-2.2 | 2.0 | 2.8-2.9 | 4.3-4.6 |
| pH | 7.0-10.0 | 9.0-10.0 | 9.0-10.0 | 6.0-10.0 |
| General contents | $SiO_2$: 71.0%<br>$Al2O_3$: 10.0% | $SiO_2$: 48.0%<br>MgO: 24.0% | CaO: 30.0%<br>MgO: 22.0% | $BaSO_4$: 94.0%<br>CaO: 0.5% |

Teflon beaker (Nalgene, USA), vigorously mixed for 20 seconds using a plastic spoon, and then poured into a 8.5 cm-id, 12-cm long cylindrical cardboard mold. As the foaming reaction progressed, polyurethane foam expanded to fill the mold. The foam was air dried before the mold was removed. Before further testing, the impermeable "skin" that formed on the outermost layer of the foam (and adhered to the cardboard mold) was removed as were the top and bottom 1 cm of each cylinder. Free surfactant was rinsed from the foam by repeatedly washing with DI water.

The procedure used to make an adsorbent containing polyurethane foam composite material was the same as that for manufacturing foam without adsorbent except that prior to adding the surfactant solution to the Hypol 3000, adsorbent was mixed into the surfactant solution (30 g/L of Tween 85 in deionized water cooled to 8 °C) by stirring vigorously with a plastic spoon for approximately 10 seconds until no adsorbent floated on the surface. The adsorbents were sieved by U.S. Mesh No. 250-350 prior to use. The resulting foam cylinders were repeatedly rinsed with distilled water by submerging in a plastic bucket containing 2 L of DI water and repeatedly squeezing (approximately 10 times). Excess water in the rinsed foams was squeezed completely, and then the foams were rinsed in a new 2 L of DI water. This rinsing process was repeated by five times. After the rinsing process the foam cylinders were dried in an oven at 60 °C for several days, and then the dried foams were placed in 1 L of glass jars filled with DI water. The water was allowed to sit for 24 h, drained and then refilled. This process was repeated for 10 times to remove surfactant.

The density of dry foam and wet foam (65% moisture content) was calculated by dividing the mass of the foam by the volume of the foam. Percent swelling in the horizontal direction and vertical direction was calculated by dividing the difference between wet dimensions and dry dimensions by the dry dimensions and multiplying by 100%. The void space in the PU-adsorbent foam was measured using water displacement. The physicochemical properties of the synthesized PU-adsorbent foams were summarized in Table 2.

## Experimental Apparatus

Figure 1 shows a schematic diagram of biofilter used for toluene removal experiment. Each glass column (8.5-cm id, 50-cm-long) was filled with 3×10 cm flexible synthetic PU foams to provide a total bed depth of approximately 30.8 cm and a total bed volume of approximately 1.7 L. Initial operating conditions of biofiltration process were summarized in Table 3.

Compressed air flowed through Masterflex® Norprene tubing (Cole-Parmer, Vernon Hills, IL, USA) to prevent undesired contaminations. Toluene (Aldrich Chemical Co., USA) was delivered into the column by a syringe pump (KD Scientific, Model 100, Boston, MA, USA) through a glass gas-tight syringe through a 32 gauge stainless steel needle (Hamilton Co, Reno,

Table 2. Physicochemical properties of the PU-adsorbent foam media

| | PU-zeolite foam | PU-sepiolite foam | PU-dolomite foam | PU-barite foam |
|---|---|---|---|---|
| Adsorbent content (%) | 7.58 | 7.52 | 7.65 | 7.63 |
| Dry density (kg/m$^3$) | 68.30 | 68.00 | 65.70 | 67.30 |
| Density at 65% moisture content (kg/m$^3$) | 113.67 | 117.00 | 111.30 | 112.30 |
| Swelling, at 65% moisture content | | | | |
| in vertical direction | 22.34 | 17.53 | 16.97 | 15.77 |
| in horizontal direction | 17.75 | 19.34 | 21.98 | 22.48 |
| in volume | 69.67 | 67.30 | 74.15 | 73.63 |
| Porosity | 0.77 | 0.78 | 0.80 | 0.78 |
| Specific surface area (m$^2$/g) | 0.7171 | 0.7421 | 0.0404 | 0.1895 |
| Surface area (m$^2$) | 0.0749 | 0.1161 | 0.0049 | 0.0245 |

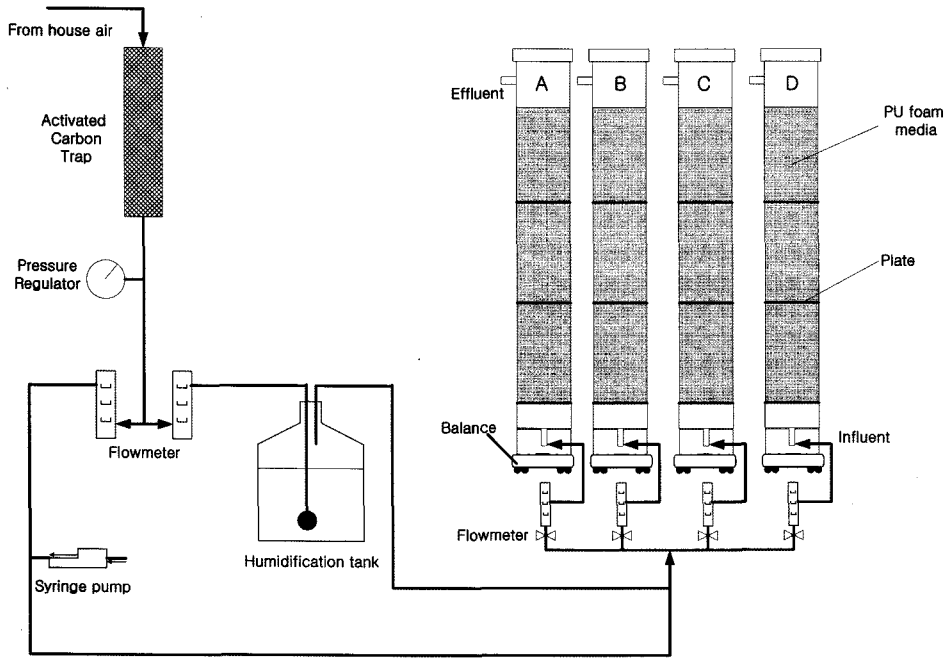


Figure 1. Schematic diagram of biofitler apparatus.

Table 3. Initial operating conditions of biofiltration

| | PU-zeolite foam | PU-sepiolite foam | PU-dolomite foam | PU-barite foam |
|---|---|---|---|---|
| Packing dry weight (kg) | 91.45 | 93.98 | 89.02 | 81.75 |
| Moisture content (%) | 66.64 | 67.91 | 65.96 | 65.08 |
| Packing weight at wet foam (kg) | 268.0 | 274.0 | 268.0 | 248.0 |
| Initial pH | 7.33 | 7.27 | 7.41 | 7.44 |
| Packing height (cm) | 30.8 | 30.5 | 30.8 | 30.8 |
| Packing volume (L) | 1.70 | 1.70 | 1.70 | 1.70 |

NV, USA) into the air stream. A pressure regulator was used to adjust the air pressure to approximately 10 psi. The airflow (total contaminated air stream) rates were measured and regulated by flowmeters (Gilmont Instruments, 150 mm scale Accucal flow meters). All surfaces that contacted contaminated air were made of glass, stainless steel, Teflon™ or Viton™.

## Fixed Bed Adsorption Experiment

Fixed bed adsorption of toluene on PU foam medium was conducted at room temperature. The moisture content of the fixed bed was adjusted to approximately 65% for a variety of influent gas flow rates and toluene concentrations. Influent toluene concentrations and influent flow rates were chosen based on their range of conditions employed in the biofiltration experiments. The experiments to determine adsorption capacity of the filter medium were conducted by setting the syringe pump and influent airflow rate at the desired levels and measuring influent and effluent toluene concentrations over time until influent and effluent concentrations were equal. Mass of toluene adsorbed to the packing medium was then estimated by subtracting the mass of effluent toluene and the mass of toluene in the water of foam from the mass of influent toluene. Henry's law was used to calculate the concentration of toluene in the water phase (Henry's law constant = 0.00664 atm-$m^3$/mol). The mass of toluene in the water phase was calculated by multiplying the concentration by the mass of water present in the wet foam.

## Biofilter Operation

For the inoculation of microorganisms, activated sludge was obtained from the Shincheon municipal wastewater treatment plant in Taegu, Korea and the PU foam was submerged in the activated sludge (3 L) with aerating for about 1 hour. Initial pH and moisture content were measured and showed in Table 3. The initial moisture content was measured by drying these foams at 65 °C for 48 hours. To measure the initial pH of PU foam medium, 5.0 g of PU-adsorbent foam was mixed with 95 g of distilled water and the mixture was settled for about 30 minutes.

For acclimation of the microorganisms, the influent toluene concentration was kept at 15-25 ppm for the initial 10 days. After that, the influent toluene concentration was increased gradually by increasing the injection speed of the syringe pump. Total gas flow rate was kept at 2 L/min for the 60 days of operation except 3 L/min for the last 10-day period. In the initial 10-day period, nutrient solution was added intermittently to the packing materials for the enhancement of microbial growth. For the next period of 40 days the drained water from the foam media was circulated through the column reactor. In the last 10-day period, only water was added in order to adjust moisture content of the packing materials. The nutrient solution was prepared by dissolving 8.2 g of $K_2HPO_4$, 21.4 g of $Na_2HPO_4 \cdot 12H_2O$, 26.5 g of $KNO_3$, 17.7 g of $(NH_4)_2SO_4$, 1.8 g of $FeSO_4 \cdot 7H_2O$, 0.2 mg of $MgSO_4 \cdot 7H_2O$, 0.9 mg of $MnSO_4 \cdot 7H_2O$, 1.0 mg of $NaMoO_4 \cdot 2H_2O$ and 3.0 mg of $CaCl_2$ in 1 L of distilled and deionized water.[7]

During the experimental period, water loss was measured by gravity and recovered through sprinkling the nutrient solution and/or water on the top of the column. The experiment was carried out at room temperature of 20-25 °C. The pressure drop was measured by using water manometer. The influent and effluent toluene concentrations were measured using toluene gas detection tubes (GASTEC, model 122 and 122L, Japan).

## Biodegradation Kinetic Analysis

The toluene degradation kinetics was analyzed by the Michaelis-Menten equation developed for enzyme mediated reactions.[18-20]

$$-\frac{dC}{dl} = \frac{V_m \cdot C}{K_s + C}\left(\frac{S_a}{F}\right) \cdot \alpha \tag{1}$$

where $C$ = influent toluene concentration (ppmv), $l$ = the length of column (m), $V_m$ = maximum removal rate (g toluene/kg dry material/day), $K_s$ = saturation constant (ppm), $S_a$ = cross-sectional area of column ($m^2$), $F$ = total gas flow rate ($m^3$/day), $L$ = the height of packed bed, and $\alpha$ = conversion coefficient (kg dry material/g toluene)

$$\alpha = \frac{22.4 \cdot \left[\frac{273+T}{T}\right] \cdot 10^{-6}}{M \cdot 1000} \cdot \frac{W}{V} \tag{2}$$

where $T$ = temperature (°C), $W$ = dry weight of packing material (kg), $V$ = volume of packing material ($m^3$), $M$ = the molecular weight of toluene (g/mole)

Integrating Eq. (1) under the condition of $C = C_0$ at $l = 0$ and $C = C_e$ at $l = L$, we obtain.[18-20]:

$$\int_{C_0}^{C_e}\left(\frac{K_s}{V_m} \cdot \frac{1}{C} + \frac{1}{V_m}\right) dC = -\frac{S_a \cdot \alpha}{F}\int_0^L dl \tag{3}$$

$$\frac{K_s}{V_m}(\ln C_0 - \ln C_e) + \frac{1}{V_m}(C_0 - C_e) = \frac{S_a \cdot \alpha \cdot L}{F} \tag{4}$$

Equation (4) can be simplified by setting

$$C_{\ln} = \frac{C_o - C_e}{\ln \frac{C_o}{C_e}} \quad \text{and} \quad R = \frac{S_a \cdot \alpha \cdot L}{F \cdot \ln \frac{C_0}{C_e}}$$

$$\frac{K_s}{V_m} + \frac{1}{V_m} \cdot C_{\ln} = R \tag{5}$$

From the linear plot of $C_{\ln}$ vs $R$, $V_m$ and $K_s$ were calculated from the intercept and slope of line, respectively.

### SEM Analysis

At the end of the biofiltration experiment, PU cube samples (approximately 1 cm × 1 cm × 1 cm) were taken from the filter bed media, washed twice with phosphate buffer (pH = 7.4), washed with acetone solution (30%) and then dried at 30 °C for 2 hours. The samples were finally dried in a critical point dryer (Hitachi, HCD-2, Japan). Examination was carried out in a digital scanning electron microscope (Hitachi, S-570, Japan) using an accelerating voltage by 15 kV.

## RESULTS AND DISCUSSION

### Adsorption Experiment

Fixed bed adsorption experiment was performed using a glass column to determine sorption capacity of the PU-adsorbent foam under dynamic conditions. For the fixed bed adsorption experiment, the influent toluene concentration ($C_0$) was maintained at 50 and 100 ppm, respectively and EBRT was 45 seconds. Figures 2 and 3 present the results of adsorption experiments for the PU foams containing various adsorbents at the influent toluene concentration of 50 ppm and 100 ppm, respectively. Approximately 10% of the influent toluene concentration was observed in the effluent after 20 minutes and 10 minutes at influent concentration of 50 ppm and 100 ppm, respectively. As expected, the time needed to reach 10% breakthrough

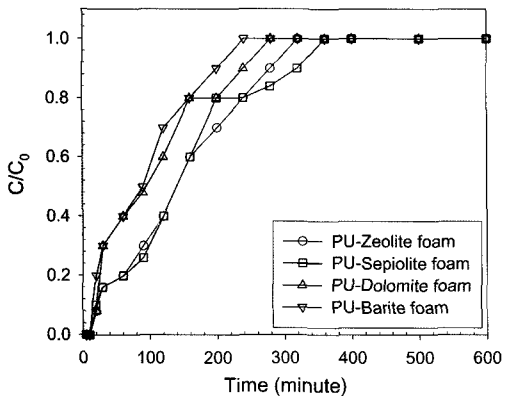


Figure 2. Adsorption of toluene for PU-adsorbent foams ($C_0$ = 50 ppm).

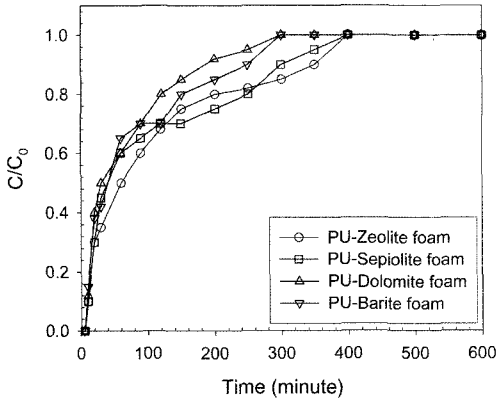


Figure 3. Adsorption of toluene for PU-adsorbent foams ($C_0$ = 100 ppm).

decreased as the influent toluene concentration increased.

Total toluene mass adsorbed in the PU-adsorbent foam was estimated and summarized in Table 4. When the influent toluene concentration was 50 ppm, 1.84, 1.80, 1.84, and 1.60 g of toluene was adsorbed onto the PU-zeoilte, PU-sepiolite, PU-dolomite, and PU-barite foam, respectively. The percent removal of influent toluene mass by the adsorption was calculated to be 92.0% in PU-zeoilte, 90.0% in PU-sepiolite, 92.0% in PU-dolomite, and 80.0% in PU-barite foam. When the influent toluene concentration was 100 ppm, total adsorbed mass of toluene was 1.80 g (PU-zeoilte), 1.80 g (PU-sepiolite), 1.76 g (PU-dolomite) and 1.70 g (PU-barite) and the percent removal of influent toluene mass was 90%, 90%, 88%, and 85%, respectively. Total toluene mass adsorbed was not increasing as the influent toluene concentration was increasing from 50 ppm to 100 ppm. This was because the adsorption experiment was conducted under dynamic conditions.

### Toluene Removal

The biofilter systems using PU foam media containing various adsorbents were operated for 60 days in 6 different modes based on the total flow rate, influent toluene concentration, and supply of nutrient solution. The influent and effluent toluene concentrations in the biofilter systems are shown in Figure 4. At mode I

Table 4. Results of toluene adsorption experiment ($C_0$ = 50 ppm)

| $C_0$ (ppm) | PU Foam | Mass in effluent (mg) | Gas concentration in the water* (ppm) | Mass in water* (mg) | Mass adsorbed in foam (mg) |
|---|---|---|---|---|---|
| 50 | PU zeolite | 160 | 0.56 | 0.64 | 1,838.7 |
| | PU sepiolite | 200 | 0.55 | 0.64 | 1,799.4 |
| | PU dolomite | 160 | 0.56 | 0.63 | 1,839.4 |
| | PU barite | 400 | 0.49 | 0.54 | 1,599.5 |
| 100 | PU zeolite | 200 | 1.10 | 1.25 | 1,798.8 |
| | PU sepiolite | 200 | 1.10 | 1.27 | 1,798.7 |
| | PU dolomite | 240 | 1.08 | 1.21 | 1,758.8 |
| | PU barite | 300 | 1.04 | 1.15 | 1,698.9 |

*Calculated using Henry's law

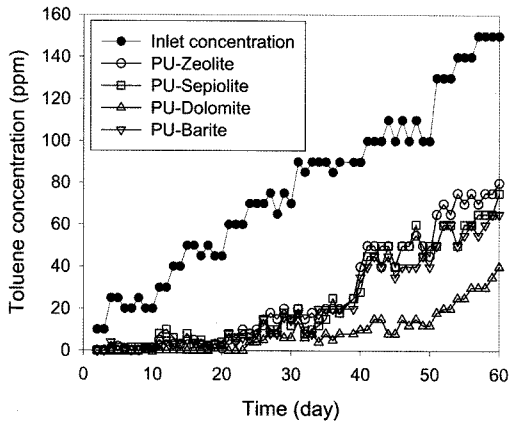


Figure 4. Changes in toluene concentration during biofiltration.

(initial 10-day operation), the influent toluene concentration was 11-25 ppm and the effluent toluene concentrations were 0-2 ppm in PU-zeoilte, PU-sepiolite, and PU-dolomite and 0-4 ppm in PU-barite foam column, respectively. The influent toluene concentration gradually increased to 30-50 ppm at mode II and the effluent toluene concentrations were 1-5 ppm in PU-zeoilte, 2-10 ppm in PU-sepiolite, 0-2 ppm in PU-dolomite, and 3-5 ppm in PU-barite foam media, respectively. At mode III, the effluent toluene concentration gradually increased as the influent toluene concentration increased to 60-70 ppm. The effluent toluene concentrations increased up to 5-20, 6-18, and 4-16 ppm in PU-zeoilte, PU-sepiolite, and PU-barite foam column, respectively. However, much lower effluent concentration of 0-8 ppm was observed in PU-dolomite foam column.

From mode IV, the effluent toluene concentrations (10-40 ppm) of the columns packed with PU-zeolite, PU-sepiolite, and PU-barite foam columns increased more rapidly as the influent toluene concentration increased up to 85-90 ppm. However, still much lower effluent concentration (4-8 ppm) was maintained in PU-dolomite foam column. At mode V (the influent concentration of 100-110 ppm), the effluent concentration was kept at 8-15 ppm in PU-dolomite foam media whereas the effluent concentrations increased up to 40-55, 40-60, and 35-45 ppm in PU-zeoilte, PU-sepiolite, and PU-barite foam media, respectively. At mode VI, the effluent concentration was much lower in PU-dolomite foam (20-40 ppm) than the others (50-80 ppm) although the effluent concentration of PU-dolomite foam increased more steeply (influent concentration = 130-150 ppm).

Removal efficiency of pollutants is an important parameter influencing the degree of compliance of the control systems with emission regulations. The removal efficiency is defined as the percentage ratio of the difference between the influent and the effluent toluene concentration to the influent toluene concentration. Figure 5 shows the toluene removal efficiency of biofilter columns packed with various PU-adsorbent foam media. The toluene removal efficiencies of four column biofilters decreased gradually as influent concentration increased. From the operation mode I to mode V, however, relatively higher removal efficiency (85-100%) was sustained in the PU-dolomite foam column than the other columns. At mode V (influent toluene concentration = 100-110 ppm), the

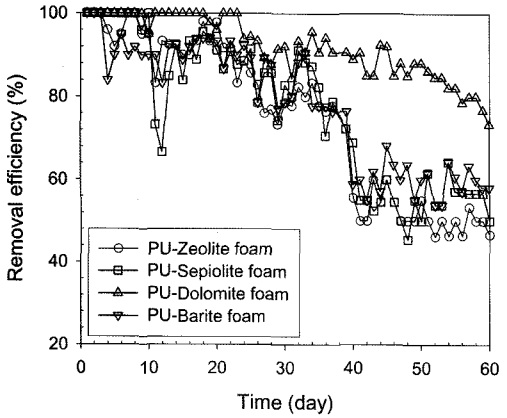


Figure 5. Changes in toluene removal efficiency during biofiltration.

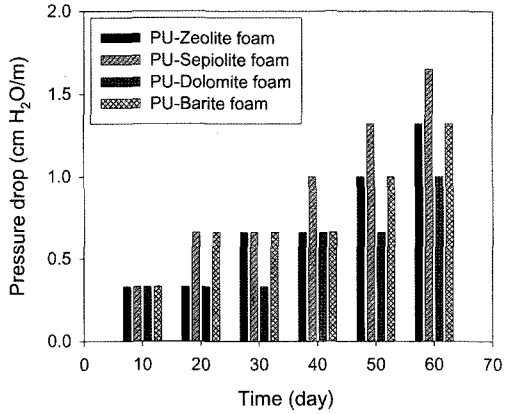


Figure 6. Changes in filter-bed-pressure drop during biofiltration.

removal efficiency of PU-zeolite, PU-sepiolite, and PU-barite foam column decreased to 50-60, 45-60, and 55-68%, respectively. In the last operation mode (mode VI, influent toluene concentration = 130-150 ppm), the PU-dolomite foam column had much higher removal efficiency (73-86%) than the others (45-65%).

Although the removal efficiency decreased as the influent toluene concentration increased for all PU foam media, the removal efficiency of PU-dolomite foam column was consistently higher than the other foam columns. In the biofiltration process, higher pollutant concentration can increase mass transfer rate from gas phase to liquid phase and then to the biofilm where the contaminants are biodegraded.[1,21] It also provides sufficient substrate accessible for microbial growth. However, it is possible that influent toluene in the gas phase is not fully transferred into the liquid phase and the biofilm and thus the toluene may not be fully degraded by the biofilm when the influent toluene concentration is too high. This is the reason why the removal efficiency decreases as the influent toluene concentration increases. The mass transfer rate can be a limiting factor when the liquid phase is not saturated with the contaminant. The biodegradation rate can also be the limiting factor when the liquid phase is fully saturated with the contaminant.[19]

The changes of pressure drop in the filter bed over time were shown in Figure 6. The pressure drop of column was related to the accumulation of biomass in the filter media. During the 60-day of operation, all columns showed pressure drop between 3.3 and 16.5 mm $H_2O$/m filter bed. The pressure drops observed in this study were much lower than the typical pressure drop of 25-37.5 mm $H_2O$/m filter bed reported by Deshusses and Hamer.[22] Ergas et al. reported pressure drops of 100-600 Pa/m at corresponding superficial air velocities through the biofilter of 0.3-1.8 $m^3/m^2/min$.[5] These pressure drops were achieved by addition of perlite to the filter materials. Sorial et al. reported that as the toluene loading increased from 16.8 to 25.3 $kg/m^3$, pressure drop increased from 64 to 127 mm $H_2O$/m using diatomite as packing material.[10] In our study, pressure drop in PU-dolomite column (3.3-10.0 mm $H_2O$/m filter bed) was the lowest among the columns, while PU-sepiolite column showed the highest pressure drop of 3.3-16.5 mm $H_2O$/m filter bed.

## Toluene Removal Capacity

The appearance of continuous low removal capacity could be an indicator of poor environmental and/or operational conditions for resident microbial population.[3] Figure 7 presents the relationship between toluene removal capacity and loading rate. The solid line indicates that the removal capacity is equal to

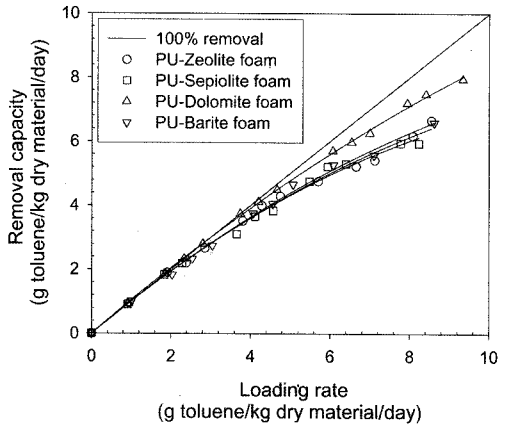


Figure 7. Relationship between removal capacity and loading rate for PU-adsorbent foams.

the loading rate of toluene hence a 100% removal was obtained. The complete removal capacity was defined as the influent toluene was completely removed and thus no effluent concentration was observed, while the maximum removal capacity was defined as the value when the removal capacity leveled off.[19] The estimated values for maximum and complete removal capacity are listed in Table 5. On the basis of both weight and volume, both of the maximum and complete removal capacities were the highest in PU-dolomite foam column.

## Biodegradation Kinetic Analysis

To determine the biodegradation kinetics parameters for the biofiltration process, the values of $C_{ln}$ and $R$ (Eq. 5) were calculated. The relationship between $C_{ln}$ and $R$ for PU-adsorbent foam was shown in Figure 8. $C_{ln}$ and $R$ were linearly correlated for all PU- adsorbent foams ($R^2 > 0.96$). From the linear relationship between $C_{ln}$ and $R$, the values of $V_m$ and $K_s$ were calculated from the slope and the intercept and listed in Table 6. Estimation of these parameters is useful for comparing the performance of various biofilters with different packing materials, structures and carrier. As can be seen from the Table 6, the maximum removal rate ($V_m$) was 6.19, 7.00, 11.04, and 7.19 g toluene/kg dry packing material/day and the saturation constant ($K_s$) was 12.65, 25.12, 26.57, and 20.92 ppm for PU-zeolite, PU-sepiolite, PU-dolomite, and PU-barite foam column, respectively. The PU-dolomite foam column had the highest values of $V_m$ and $K_s$, while the PU-zeolite foam column had the lowest.

Generally, a physical process such as adsorption occurs prior to biological degradation in biofilm when influent concentrations are lower than the saturation constants ($K_s$). Therefore the adsorption of toluene to the adsorbent containing in PU foam media may occur at early stage of the experiment. However, as the influent toluene concentration increased above the saturation constants ($K_s$), biodegradation rather than adsorption becomes a limiting factor of the biofiltration process.

## Scanning Electron Microscopy

Table 5. Maximum and complete removal capacity of toluene for PU-adsorbent foams

| PU foam | Maximum removal capacity | | Complete removal capacity | |
|---|---|---|---|---|
| PU-zeolite | 6.65[a] | 357.93[b] | 1.19[a] | 64.05[b] |
| PU-sepiolite | 5.94 | 328.45 | 1.83 | 101.19 |
| PU-dolomite | 7.94 | 415.68 | 3.74 | 195.80 |
| PU-barite | 6.59 | 317.87 | 1.01 | 48.72 |

Units: $a$ = g toluene/kg dry material/day and $b$ = g toluene/m$^3$ dry material/day

Table 6. Maximum removal rate and saturation constant

| | Maximum removal rate ($V_m$) | | Saturation constant ($K_s$, ppm) |
|---|---|---|---|
| PU-zeolite foam | 6.19[a] | 333.17[b] | 12.65 |
| PU-sepiolite foam | 7.00 | 387.06 | 25.12 |
| PU-dolomite foam | 11.04 | 577.98 | 26.57 |
| PU-barite foam | 7.19 | 346.81 | 20.92 |

Units: $a$ = g toluene/kg dry material/day and $b$ = g toluene/m$^3$ dry material/day

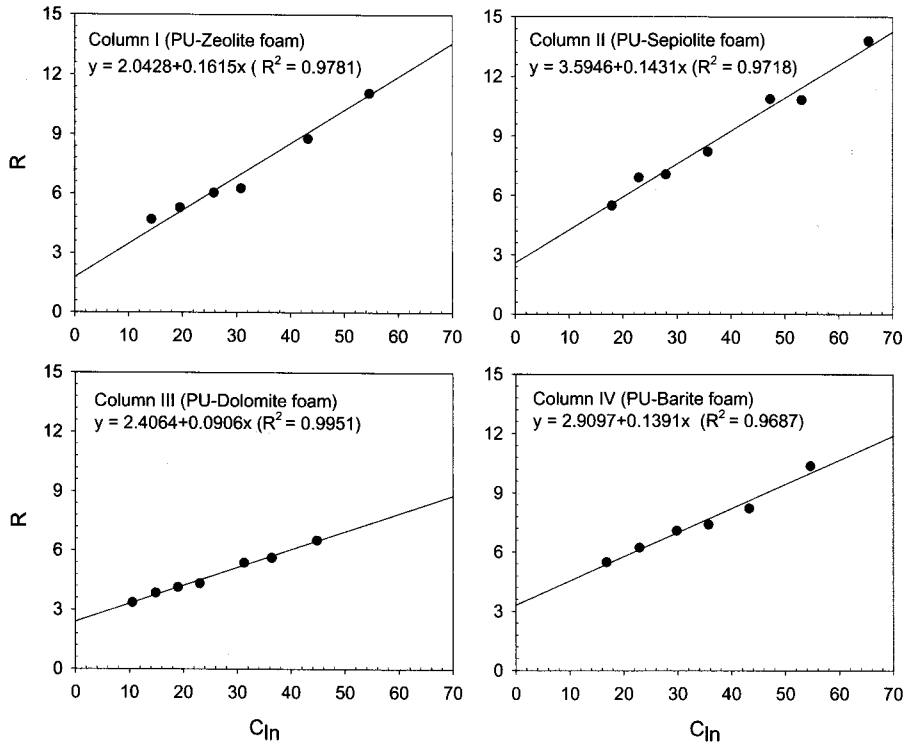


Figure 8. Relationship between Cln and R for PU-adsorbent foams.

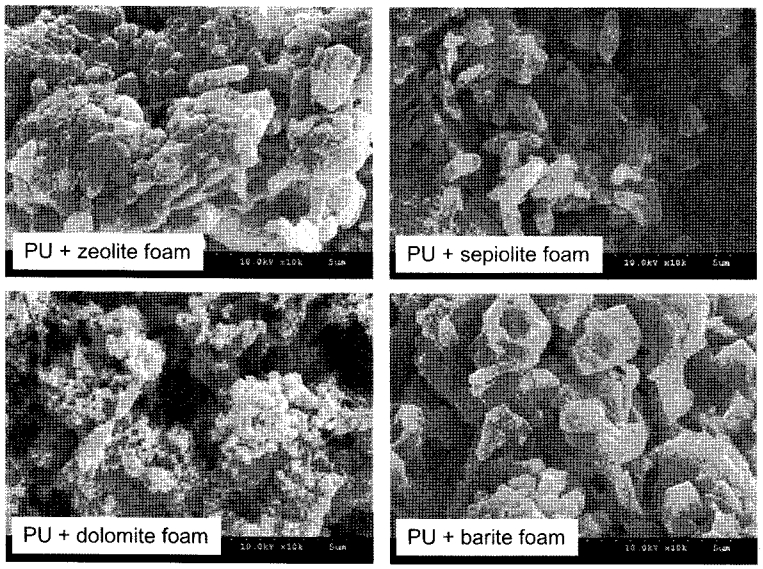


Figure 9. SEM microphotographs of PU-adsorbent foams after biofiltration.

At the end of biofiltration experiment, samples of the PU-adsorbent media were observed under scanning electron microscopy (SEM). Figure 9 shows the PU-adsorbent foram media abundant growth of microorganisms after 60 days of operation of the biofilter.

## CONCLUSIONS

The following conclusions were obtained from

results of this study:

1. For adsorption experiment, the PU-adsorbent foams adsorbed 80-92% of the total influent toluene under dynamic conditions.
2. For biofiltration experiment, the effluent toluene concentration increased as influent toluene concentration increased. However, the removal efficiency decreased gradually as influent toluene concentration increased.
3. The pressure drop increased gradually for all PU-adsorbent foam media due to biomass accumulation in the biofilter bed. The PU-dolomite foam exhibited lower pressure drop and higher removal efficiency than the other PU-adsorbent foams.
4. For all PU-adsorbent foams, the toluene removal capacity increased as the loading rate increased, while the removal efficiency had an opposite trend. PU-dolomite foam media had higher maximum and complete removal capacity than the others. The results of biodegradation kinetic analysis showed that the values of maximum removal rate ($V_m$) and saturation constant ($K_s$) of PU-dolomite foam were higher than the other PU-adsorbent foams. This confirms that PU-dolomite foam was better than the others for biofilteration of toluene.

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