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Biofiltration of Gaseous Toluene Using Activated Carbon Containing Polyurethane Foam Media

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In recent decades, biofiltration has been widely accepted for the treatment of contaminated air stream containing low concentration of odorous compounds or volatile organic compounds (VOCs). 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 amounts of pulverized activated carbon (PAC) were synthesized for the biofilter media and tested for toluene removal. Four biofilter columns were operated for 60 days to remove gaseous toluene from a contaminated air stream. During the biofiltration experiment, inlet toluene concentration was in the range of 0-150 ppm and EBRT (i.e., empty bed residence time) was kept at 26-42 seconds. Pressure drop of the biofilter bed was less than 3 mm H_2O/m filter bed. The maximum removal capacity of toluene in the biofilters packed with PU-PAC foam was in the order of column II (PAC = 7.08%) > column III (PAC = 8.97%) > column I (PAC = 4.95%) > column IV (PAC = 13.52%), while the complete removal capacity was in the order of column II > column I > column III > column IV. The better biofiltration performance in column II was attributed to higher porosity providing favorable conditions for microbial growth. The results of biodegradation kinetic analysis showed that PU-PAC foam with 7.08% of PAC content had higher maximum removal rate (V_m = 14.99 g toluene/kg dry material/day) than the other PU-PAC foams. In overall, the performance of biofiltration might be affected by the structure and physicochemical properties of PU foam induced by PAC content.

Key Words : Biodegradation kinetics, Biofiltration, Powered activated carbon (PAC), Polyurethane foam, Toluene

1. Introduction

Biofiltration technology has a promising potential as aneffective 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.

Biofiltration primarily depends on the choice of the packing material. A proper packing material should have favorable conditions such as high porosity, ap-

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propriate 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[4~7,23,24]. In addition to the primary support medium, a variety of additives may be used including bulking agents, buffers, nutrients, and microorganisms[8].

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 a 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].

Packing material used in biofilter beds can be broadly categorized as either natural or synthetic. Natural media include peat, soil, compost, back, wood chips; synthetic media that have been used, which include activated carbon, ceramic, sintered glass, polystyrene beads and polyurethane foam[2~4]. A good media can be incorporated several or all of the desirable properties; these include high porosity, appropriate pore size, low density and an ability to sorb water[2~4].

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 amounts of PAC were synthesized as biofilter media. The effects of various PAC contents adsorbents on the biofiltration of gaseous toluene were investigated. The biodegradation kinetics of these systems was also analyzed.

2. Materials and Methods

2.1. Synthesis of PU-PAC Foam

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) and PAC was obtained from Duksan Pure Chemicals Co., Ltd. (Ansan, Korea).

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 ≥ 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 Teflon beaker (Nalgene, USA), vigorously mixed for 20 seconds using a plastic spoon, and then poured into a cylindrical cardboard mold (8.5 cm i.d. × 12 cm long). 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 1.

Table 1. Physicochemical properties of PU-PAC foams used

Properties	Foam I	Foam Ⅱ	Foam Ⅲ	Foam Ⅳ
Final PAC content (%)	4.95	7.08	8.97	13.52
Dry density (kg/m^3)	94.0	96.0	99.0	108.0
Density at 65% moisture content (kg/m^3)	132.0	136.0	142.0	151.0
Swelling in vertical direction at 65% moisture content	36.92	29.75	31.54	28.28
Swelling in horizontal direction at 65% moisture content	21.93	24.62	23.21	24.30
Swelling in volume at 65% moisture content	103.76	106.01	99.71	105.60
Porosity at 65% moisture content	0.77	0.82	0.77	0.78

2.2. Experimental Apparatus

Figure 1 shows a schematic diagram of biofilter used for toluene removal experiment. Each glass column (8.5 cm i.d. × 50 cm long) was filled with three cylindrical pieces of flexible synthetic PU foam (i.e., 3 × 10.1 cm height) to provide a total bed depth of approximately 30.3 cm and a total bed volume of approximately 1.7 L. The column I, II, III, and IV were packed with PU foam cylinders A, B, C, and D containing 4.95%, 7.08%, 8.97% and 13.52% of PAC by mass, respectively (Table 1). Initial operating conditions of biofiltration process were summarized in Table 2.

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). Aqueous toluene in a glass gas-tight syringe (Hamilton Co, Reno, NV, USA) was injected through a 32 gauge stainless steel needle (Hamilton Co, Reno, 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 flowmeters). All surfaces that contacted contaminated air were made of glass, stainless steel, Teflon™ or Viton™.

2.3. Fixed Bed Adsorption Experiment

Fixed bed adsorption of toluene on PU foam me-

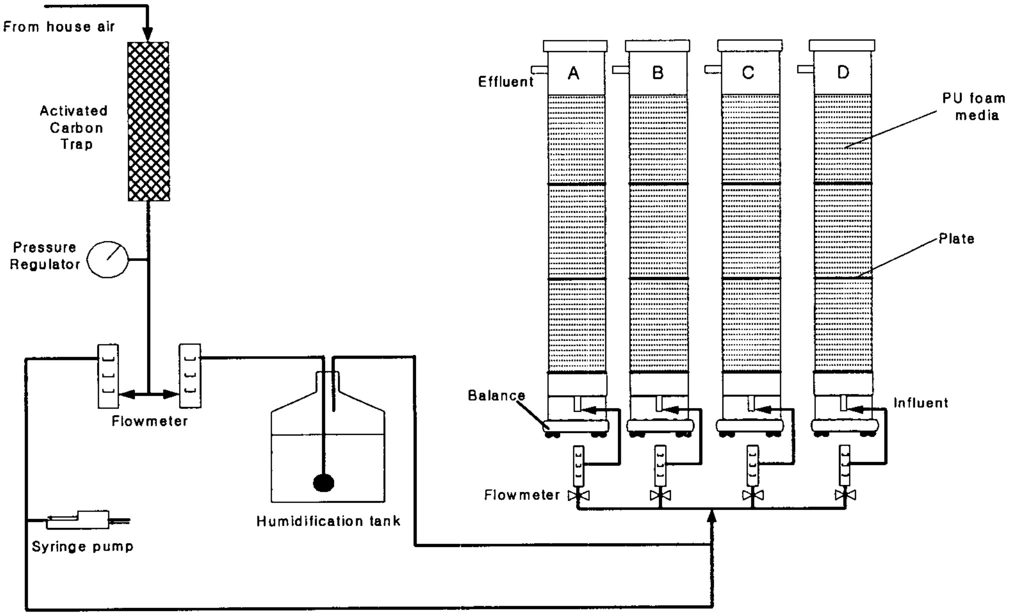

Fig. 1. Schematic diagram of laboratory biofilter system.

Table 2. Initial operating conditions of biofiltration

	Polyurethane foams containing PAC			
	Column I	Column II	Column III	Column IV
PAC content (%)	4.95	7.09	8.97	13.52
Packing weight at wet foam (g)	262.00	270.00	282.00	293.00
Packing dry weight (g)	91.00	95.00	97.00	101.00
Initial moisture content (g)				
Total	175.60	184.80	185.70	195.20
Instrument	1.53	1.28	1.40	1.88
Initial pH	6.87	6.92	6.83	6.83
Packing height (cm)	30.3	30.3	30.3	30.3
Packing volume (L)	1.70	1.70	1.70	1.70

dium 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.

2.4. Biofilter Operation

For the inoculation of microorganisms, activated sludge was obtained from the Shincheon municipal wastewater treatment plant in Daegu, Korea and the PU foam was submerged in the activated sludge (3 L) with aeration for 1 hour. Initial pH and moisture content were measured and listed in Table 2. 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-PAC foam was mixed with 95 g of distilled water and the mixture was settled for 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 (mode I), nutrient solution was added intermittently to the column reactors for the enhancement of microbial growth. For the next 40-day period (mode II-V) the drained water from the foam media was circulated through the column reactors and sometimes nutrient solution was added to prevent the packing media drying during the operation. In the last 10-day period (mode VI), 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 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 influent and effluent toluene concentrations were measured using toluene gas detection tubes (GASTEC, model 122 and 122L, Japan). The detection limit of 122 and 122L tube was 5 ppm and 1 ppm, respectively. The pressure drop and the moisture content were measured by using water manometer and load cells. The pH of the drained water was measured using a Thermo Orion pH meter (model 720A$^+$).

2.5. Biodegradation Kinetic Analysis

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

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

where C = influent toluene concentration (ppm$_v$), Z = 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 = height of packed bed, and α = conversion coefficient (kg dry material/g toluene)

$$\alpha=\frac{22.4\times\left(\frac{273+T}{T}\right)\times 10^{-6}}{M\times 1000}\times\frac{W}{V} \tag{2}$$

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 Z = 0 and C = C_e at Z = L, we obtain[18~20]:

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

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

Eq. (4) can be simplified by setting $C_{\ln}=\frac{C_0-C_e}{\ln\frac{C_0}{C_e}}$ and $R=\frac{S_a\cdot\alpha\cdot L}{F\cdot\ln\frac{C_0}{C_e}}$:

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

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

2.6. 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.

3. Results and Discussion

3.1. Adsorption Experiment

Fixed bed adsorption experiment was performed using a glass column to determine sorption capacity of the PU-PAC 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 39-42 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. The time to reach breakthrough was in the order of column I > column II > column III > column IV mainly due to difference in PAC content.

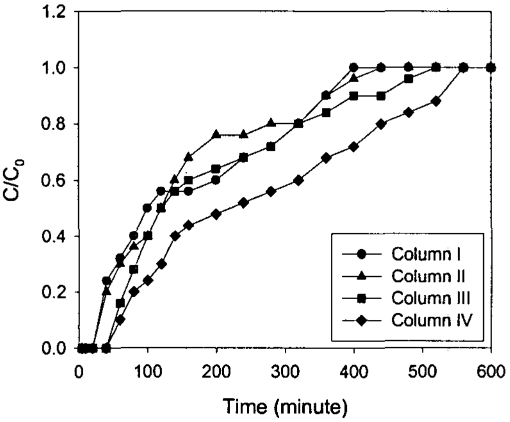

Fig. 2. Adsorption of toluene for PU-adsorbent foams. (C_0 = 50 ppm)

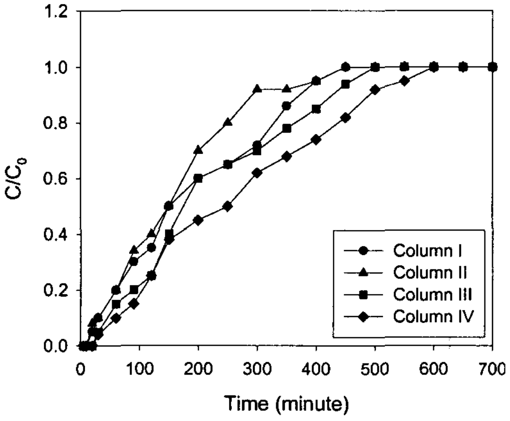

Fig. 3. Adsorption of toluene for PU-adsorbent foams. (C_0 = 100 ppm)

Table 3. Results of toluene adsorption experiment at C_0 = 50 ppm and C_0 = 100 ppm, respectively

C_0 (ppm)	Column	Mass in effluent (mg)	Gas concentration in the water* (ppm)	Mass in water* (mg)	Mass adsorbed in foam (mg)
50	Column I	960	0.47	0.54	3,039.5
	Column II	800	0.49	0.57	3,199.4
	Column III	960	0.51	0.57	5,039.4
	Column IV	600	0.55	0.63	5,399.4
100	Column I	600	1.10	1.25	5,398.7
	Column II	600	1.10	1.27	5,398.7
	Column III	480	1.13	1.27	5,518.7
	Column IV	300	1.16	1.32	5,698.7

*Calculated using Henry's law

Total toluene mass adsorbed in the PU-adsorbent foam was estimated and summarized in Table 3. When the influent toluene concentration was 50 ppm, 3,040, 3,199, 5,039, and 5,399 mg of toluene was adsorbed onto the column I (PAC = 4.95%), column II (PAC = 7.09%), column III (PAC = 8.97%) and column IV (PAC = 13.52%), respectively. As expected, the adsorbed amount of toluene increased as PAC content in the PU foam increased. When the influent toluene concentration was 100 ppm, total adsorbed mass of toluene was 5,399 mg in column I, 5,399 mg in column II, 5,549 mg in column III and 5,699 mg in column IV, respectively. Total toluene mass adsorbed was increasing as the influent toluene concentration was increasing from 50 ppm to 100 ppm. However, not much difference in adsorbed toluene mass was observed in between the columns. This was because the adsorption experiment was conducted under dynamic conditions.

3.2. PU-PAC Foam Property

Physicochemical properties of the prepared PU-AC foams are summarized in the Table 1. The final content of PAC in the foam was determined by the difference between the mass of the cup after being dried in an oven at 65°C for 24 hours and the initial mass before use. The final contents of PAC in the PU foams were 4.95-13.52% of the total foam mass. Densities of dry and wet (moisture content = 65%) PU foam were calculated by dividing mass by volume. Both dry and wet density of PU foam increased as PAC content increased. Percent swelling in the vertical and horizontal direction was calculated by dividing the difference of wet and dry dimensions by the dry dimensions and multiplying by 100. The void volume in the PU foam was measured using water displacement. The porosity of PU foam at 65% moisture content was approximately 0.77 for Foam A, 0.82 for Foam B, 0.77 for Foam C, and 0.78 for Foam D, respectively. In general the performance of biofilter would be highly dependent on the porosity of the PU foam. Therefore, the porosity of PU foam was determined to measure the void space for biomass growth and for passing airflow.

3.3. Toluene Removal

The four biofilter columns packed with PU-PAC foams were operated for 60 days in 6 different modes (mode I-VI) 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. It is commonly observed that microorganisms exposed to a

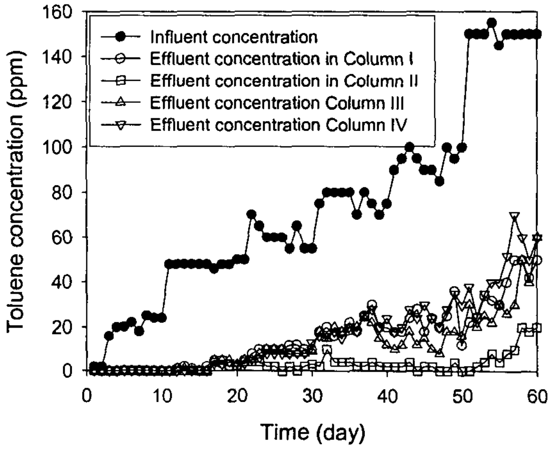

Fig. 4. Changes in toluene concentration over time.

new substrate may require acclimation periods before they start active biodegradation.[1,6] In this study, thus, the data were obtained after a 10-day acclimation period. The total gas flow rate was 2 L/min in the initial 50-day period (mode I-V) and 3 L/min for the remaining period (mode VI).

At mode I (initial 10-day operation), the inlet toluene concentration was 15-20 ppm and the outlet toluene was not detected in all columns. After mode I, the influent toluene concentration was increased gradually by increasing the syringe pump speed. At mode II, the influent toluene concentration gradually increased to 50 ppm and the effluent toluene concentration was 0-5 ppm in column I, II, and III and 0-4 ppm in column IV, respectively. At mode III, the effluent toluene concentration gradually increased as the influent toluene concentration increased to 55-70 ppm. The effluent toluene concentrations increased up to 5-12 ppm in column I, 0-4 ppm in column II, 5-10 ppm in column III, and 3-13 ppm in column IV, respectively. During the operation of mode I-III, column II showed the lowest effluent toluene concentration among the four tested columns.

From mode IV, the effluent toluene concentrations increased more rapidly as the influent toluene concentration increased up to 70-80 ppm. The effluent toluene concentrations was 18-30 ppm in column I, 12-24 ppm in column III, and 15-28 ppm in column IV, respectively. However, much lower effluent concentration of 2-10 ppm was maintained in column II. At mode V, the influent toluene concentration was further increased to 85-100 ppm. The effluent concentration was kept at 0-4 ppm in column II whereas the effluent concentrations increased up to 12-36 ppm in column I, 8-18 in column III, and 18-35 ppm in column IV, respectively. At mode VI, the toluene influent concentration was further increased to 150 ppm and column II showed much lower effluent concentration (0-20 ppm) than the other columns (22-50 ppm in column I, 22-60 ppm in column III, and 25-70 ppm in column IV, respectively).

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-PAC foam media. Toluene removal efficiencies of the four biofilter columns decreased gradually as influent concentration increased. During the whole experimental period (from mode I to mode VI), the toluene removal efficiency in column II (86-100%) was consistently higher than the other columns. In the last operation mode (mode VI, influent toluene concentration = 150 ppm), the removal efficiency decreased to 66-85% in column I, 57-85% in column III, and 56-82% in column VI, respectively. Although the removal efficiency decreased as the influent toluene concentration increased for all PU-PAC foam media, the removal efficiency in column II was consistently higher than the other columns. One possible explanation for the higher removal efficiency in column II is attributed to higher porosity of PU-PAC foam used in column II than the others (Table 1). In the most cases, a homogeneous filter bed with a porosity or void volume of 40 to 80% will ensure both gas plug flow and low pressure drop[1]. 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

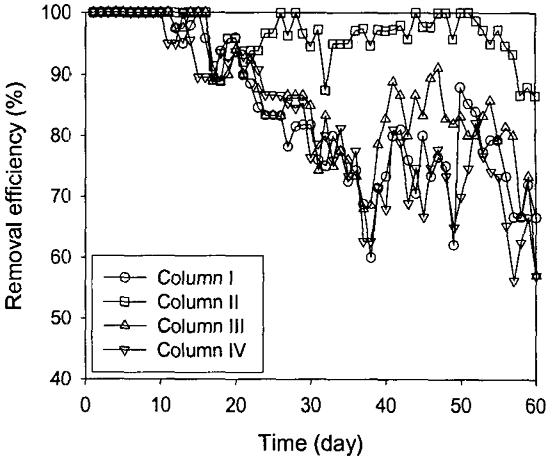

Fig. 5. Changes in toluene removal efficiency over time.

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 a limiting factor when the liquid phase is fully saturated with the contaminant[19].

During the whole experimental period, pH variation of the drained water was monitored and showed at Figure 6. The pH of drained water decreased from 7.2 to 5.5. This pH decrease is mainly due to the biological oxidation. That is to say, a toluene molecule loses an electron in an oxygen atom and carbon dioxide is produced as a result of biodegradation. The pH in a biofilter may change during operation and many of the contaminant biotransformations which occur in biofilters generate acids although a near-neutral pH (6 to 8) is required for the greatest spectrum of bacterial activity[1]. Including buffering materials such as calcium carbonate in the medium can be an effective means for controlling a near-neutral pH. In our study, column II showed nearer-neutral pH than the other columns without any buffering materials.

The pressure drop of column is related to the accumulation of biomass in the filter media. During the 60-day operation, pressure drop in all columns never exceed 3 mm H_2O/m filter bed. The pressure drop observed in this study was 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].

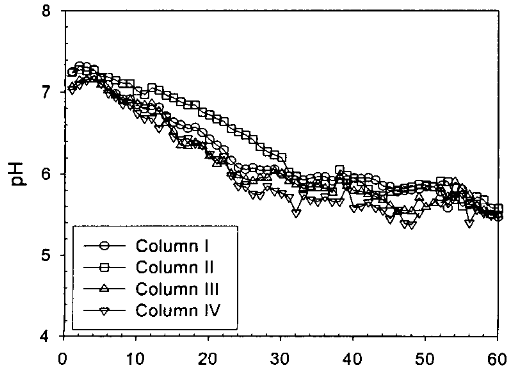

Fig. 6. Change in pH of the drained water over time.

3.4. 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 the toluene loading rate hence a 100% removal is 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 4. On the basis of both packing weight and packing volume, both maximum and complete removal capacities were the highest in column II. In column II packed with PU-PAC foam (7.08% of PAC content), the maximum removal capacity would be much larger than 9.27 g toluene/kg dry material/day if the toluene loading increased much higher than 9.46 g toluene/kg dry material/day. However, the other columns showed the maximum removal capacity of 6.13-7.36 g toluene/kg dry material/day. Consequently, the column II showed better removal efficiency than the other columns.

3.5. Biodegradation Kinetics

To determine the biodegradation kinetic parameters for the biofiltration process, the values of C_{ln} and R (Eq. 5) were calculated. The relationship between C_{ln} and R for various PU-PAC foams was shown in Figure 8. C_{ln} and R were linearly correlated for all PU-PAC 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 5. Estimation of these parameters is useful for comparing the performance of biofilters packed with PU-PAC foams with different PAC contents. As listed in Table 5, the maximum removal rate (V_m) was 8.92, 14.99, 10.38, and 7.48 g tol-

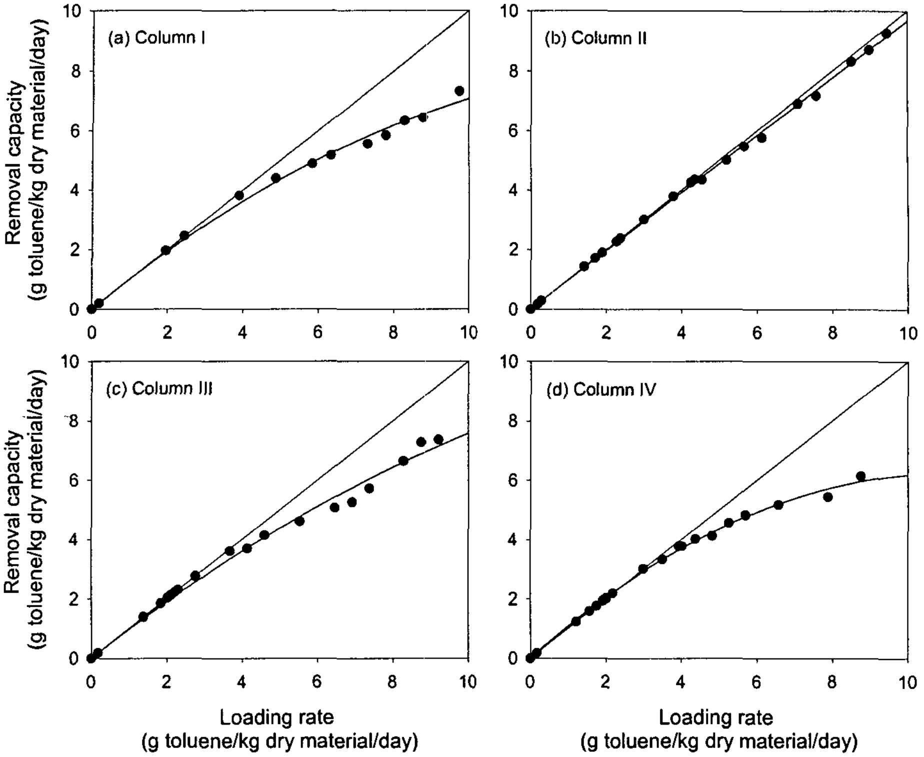

Fig. 7. Relationship between toluene removal capacity and loading rate.

uene/kg dry material/day and the saturation constant (K_s) was 29.96, 35.52, 40.16, and 26.06 ppm for column I, column II, column III and column IV, respectively. Among the four columns, similar to the experimental result of maximum removal capacity, column II packed with PU-PAC foam containing 7.08% of PAC had the highest values of the maximum removal rate (V_m = 14.99 g toluene/kg dry material/day).

Generally, a physical process such as adsorption occurs prior to biological degradation in biofilm when influent concentrations are lower than the satu-

Table 4. Maximum and complete removal capacities of toluene for PU-PAC columns

	Maximum removal capacity		Complete removal capacity	
	g toluene/ kg dry material/day	g toluene/m^3 dry material/day	g toluene/ kg dry material/day	g toluene/m^3 dry material/day
Column I	7.31	686.20	3.80	357.20
Column Ⅱ	9.27	889.92	4.34	416.64
Column Ⅲ	7.36	728.64	3.59	355.41
Column Ⅳ	6.13	662.04	3.32	358.56

Table 5. Maximum removal rate and saturation constant for PU-PAC columns

	Maximum removal rate (V_m)		Saturation constant (K_s, ppm)
Column I	8.92 ^{a}	838.48 ^{b}	29.96
Column Ⅱ	14.99	1439.04	35.52
Column Ⅲ	10.38	1027.62	40.16
Column Ⅳ	7.48	807.84	26.06

Units: ^{a}g toluene/kg dry material/day and ^{b}g toluene/m^3 dry material/day

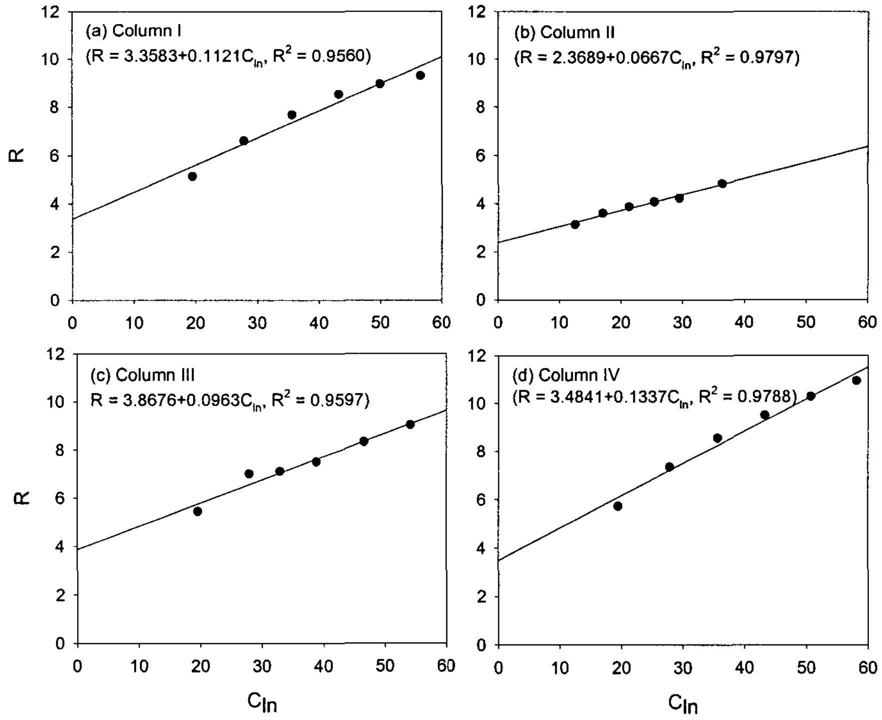

Fig. 8. Relationship between R and C_{In} for all columns.

ration 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. The biodegrdation kinetic parameters are useful for comparing the characteristics of biofilters with different packing materials. In this study, column II packed with PU foam with 7.08% of PAC content had the highest values of V_m and K_S. Whereas the column IV with the highest PAC content had the lowest values of V_m and K_S. From these results, it was concluded that the PU foam structure and properties could be more critical factors in biofiltration rather than the PAC content in the PU foam.

The toluene removal rate determined by V_m and K_s using kinetic equation, Eq. (1) for columns was depicted in Figure 9. For all materials, the toluene removal rate steeply increased as influent toluene concentration increased up to 30-40 ppm. Above 30-40 ppm, the removal rate increased steadily and finally reached to a plateau. As listed in Table 5, the results of biodegradation kinetic analysis showed that the saturation constant (K_S) was approximately 26-40 ppm. This indicates that mass transfer from gas phase to biofilm is rate-limiting factor and thus the toluene removal rate increases abruptly mainly by saturation at below saturation constant. In contrast, biodegradation becomes rate-limiting factor at concentration above the saturation constant and thus toluene removal rate increases steadily as toluene concentration

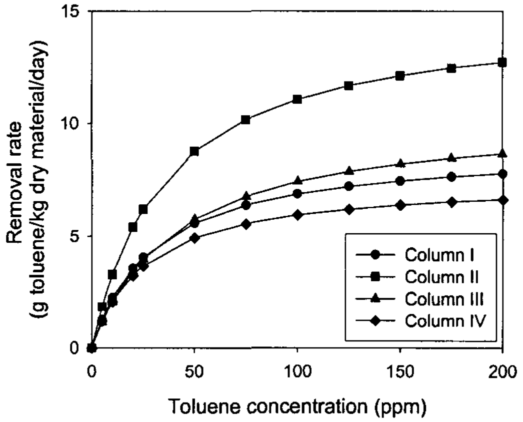

Fig. 9. Relationship between toluene removal rate and concentration.

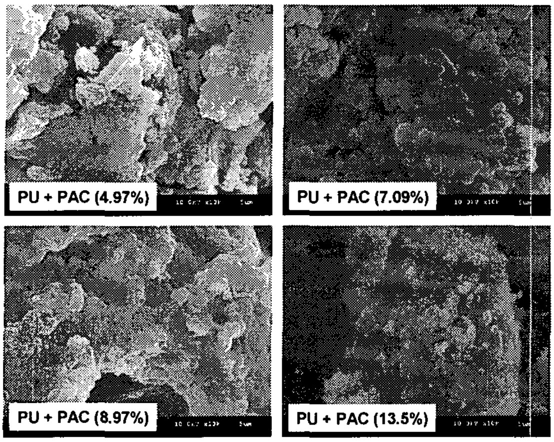

Fig. 10. SEM microphotographs of PU-PAC foams after biofiltration.

increases, finally reaching maximum removal rate. Toluene removal rate was in the order of column II > column III > column I > column IV. The toluene removal rate in column II (> 10 g toluene/dry material/day), was higher than those in other columns.

3.6. Scanning Electron Microscopy

At the end of biofiltration experiment, samples of the PU-PAC foam media were observed under scanning electron microscopy (SEM). Figure 8 shows the PU-PAC foam media with abundant growth of microorganisms after 60 days of the biofilter operation.

4. Conclusions

The following conclusions were obtained from results of this study:

1) For biofiltration experiment, the effluent toluene concentration increased as influent toluene concentration increased. However, the removal efficiency decreased gradually as influent toluene concentration increased.
2) For all PU-PAC foams, the toluene removal capacity increased as the loading rate increased, while the removal efficiency had an opposite trend. The biofilter packed with PU-PAC foam with 7.08% of PAC content showed higher toluene removal efficiency and had higher maximum and complete removal capacity than the others.
3) The results of biodegradation kinetic analysis showed that the maximum removal rate (V_m) in column II were higher than the other columns. The results of kinetic analysis indicate that the biofiltration performance is more affected by PU foam structure and properties than the PAC content in the foam.

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