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Treatment of Mixed Solvent Vapors with Hybrid System Composed of Biofilter and Photo-catalytic Reactor

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Abstract–The transient behavior of a hybrid system composed of biofilter and photo-catalytic reactor was observed at the height of each sampling port to treat waste-air containing ethanol. The biofilter packed with mixed media (of granular activated carbon and compost) was inoculated with a pure culture of *Burkholderia cepacia* G4 and *Pseudomonas putida*, while a photo-catalytic reactor was composed of 15W UV-A lamps and annular pyrex tubes packed with glass beads coated with sol type of TiO_2 before calcination. The maximum elimination capacities of toluene and ethanol turned out to be 130 g/m^3/h and 230 g/m^3/h, respectively, which were greater by 40 g/m^3/h and 130 g/m^3/h, respectively, than those from the experiments performed with a biofilter only. Thus, the maximum elimination capacities for toluene and ethanol increased by 44% and 130%, respectively, by use of a hybrid system. The photo-catalytic process contributed to the maximum elimination capacities of hybrid system on toluene and ethanol by 30.8% and 56.5%, respectively, which contributions for the elimination capacities on toluene and ethanol were allocated indirectly by 25.4% and 44.3% as well as directly by 5.4% and 12.2%, respectively. Direct contributions of photo-catalytic process were 17.5% and 21.5% to the increments of the elimination capacities on toluene and ethanol, respectively, while its indirect contributions were 82.5% and 78.5% to those on toluene and ethanol, respectively.

Key words: Hybrid System, Photo-catalytic Process, Biofilter, Toluene, Ethanol, Transient Behavior, Removal Efficiency, Elimination Capacity

INTRODUCTION

Biological processes have increasingly been used to control undesirable compounds in different kinds of wastes. Among these processes, biofiltration has emerged as a promising air pollution control technology. Biofilters excel in two main domains: in the removal of odoriferous compounds [Hirai et al., 1990; Eckhart, 1987; Lee et al., 2000; Islander et al., 1990; Oyarzun et al., 2003; Cho et al., 2000; Wani et al., 1998; Chung et al., 1996a, b, 2001] and in the elimination of volatile organic compounds [Ottengraf, 1986; Deshusses et al., 1995; Deshusses and Dunn, 1994; Deshusses and Hammer, 1993; Lim and Lee, 2003; Buchner, 1989; Leson and Winer, 1991; Sorial et al., 1995; Leson and Smith, 1997; Swanson and Loehr, 1997; Ottengraf and van den Oever, 1983; Zarook and Baltzis, 1994; Mohseni and Allen, 2000; Tang et al., 1995; Jorio et al., 1998; Hodge and Devinny, 1994, 1995; Shim et al., 1995; Arulneyam and Swaminathan, 2000; Auria et al., 1998; Christine et al., 2002; Lim and Park, 2004, 2005], primarily solvents, from waste air. It has been known that the performance of biofilter treating waste-air containing VOCs depends on their solubility in the bio-layer of a biofilter [Ottengraf and van den Oever, 1983; Zarook and Baltzis, 1994]. It was reported that removal efficiency of hydrophobic VOC (α-pinene) dropped more significantly up to 74% as the concentration of hydrophilic VOC (methanol) increased for the simultaneous biofilter-treatment of hydrophobic VOC (α-pinene) and hydrophilic VOC (methanol) than that for the sole treatment of hydrophobic VOC (α-pinene) of 91.2% [Mohseni and Allen, 2000]. Thus utilization of a biofilter has been limited in case that 1) vapors of hydrophobic VOC and hydrophilic VOC are treated simultaneously, 2) the optimum operating conditions of cultures of different microorganisms inoculated on packing media of biofilter are quite different from each other, or 3) air-polluting VOC of target is very toxic to microorganisms or is recalcitrant and non-biodegradable.Unlike ozone treatment AOP (Advanced Oxidation Process) reportedly facilitates bio-treatment by the way that it degrades non-biodegradable soluble organic compounds into small BDOC (biologically degradable organic compounds) by generating OH radicals [Fahmi et al., 2002; Scheck and Frimmel, 1995]. Since the biofilter is a reactor in which a humid polluted air-stream is passed through a porous packed bed on which pollutant-degrading microbial cultures are naturally immobilized as liquid-bio-layer and dissolve soluble organic compounds, AOP may be applied to treat polluted waste-air so as to convert non-biodegradable organic compounds into BDOC or to convert biodegradable organic compounds into more biodegradable ones and to enhance the removal efficiency and elimination capacity of traditional biofilter.

The photo-catalytic process is a very popular one of AOP, and its photo-catalyst means the catalyst that accelerates photo reaction by oxidation and reduction of organic and inorganic materials to be removed. Thus, it provides other paths of reaction mechanism than photo-reaction does in order to accelerate the rate of reaction. In a photo-catalytic reaction the surface of the catalyst can be activated and oxidation occurs by positively-charged holes, as electron acceptors, generated by exiting an electron, only if energy higher than band-gap energy is provided. In addition, the positively-charged hole

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reacts with water molecules or OH^- to generate strong oxidant OH radicals. Titanium dioxide (TiO_2) has been used as photo-catalyst that can be activated by external energy higher than band-gap energy in order to generate the hole and exited electrons for oxidative and reductive reactions, respectively. As the source of external energy, UV-light is broadly used in the study of photo-catalytic processes.

In order to perform experiments for the simultaneous treatment of hydrophobic and hydrophilic VOCs, toluene and ethanol are designated as hydrophobic and hydrophilic VOCs, respectively, since they have been emitted very frequently from various industries and their emission has been under regulatory control. As previous investigations comparable to this work, Lim and Park [2004] performed experiments to observe the transient behavior of a biofilter, treating waste-air containing ethanol, packed with mixed media (of granular activated carbon and compost) inoculated with *Pseudomonas putida* (KCTC 1768) for five stages of biofilter-run at the height of each sampling port of biofilter. Later, Lim and Park [2005] investigated the transient behavior of the biofilter in the similar manner to the previous work of Lim and Park [2004] for the simultaneous treatment of both hydrophobic VOC and hydrophilic VOC from waste-air. They investigated toluene and ethanol as hydrophobic VOC and hydrophilic VOC, respectively, in the same manner as in this work. In this present work the authors chose a photo-catalytic reactor (as AOP) combined with a biofilter to form a hybrid system. The transient behavior of the hybrid system is observed for the simultaneous treatment of both toluene and ethanol from waste-air, which has never been reported so far, and is compared to that of the previous works [Lim and Park, 2004, 2005] for the evaluation of the performance of this hybrid system.

MATERIALS AND METHOD

1. Design of Hybrid System Composed of Biofilter and Photo-catalytic Reactor

An experiment to treat waste-air containing hydrophobic toluene and hydrophilic ethanol was performed to observe the transient behavior of a hybrid system composed of a photo-catalytic reactor and a biofilter. The photo-catalytic reactor was annular type of 8 cm (outer radius of annular region)×4 cm (inner radius of annular region)×47 cm (length) pyrex tubes and 15 W UV-A lamp (437 mm (length)×28 mm (ϕ)) was inserted into inner pyrex tube. Glass beads (ϕ=10 mm) were packed in the annular region of pyrex tubes. The waste-air contacting surfaces of the annular region of the pyrex tube and packed glass beads were treated by dip-coating with sol type of photo-catalyst (TiO_2) purchased from Nano-pac, were dried for 10 minutes at ambient temperature and were calcinated at 450 °C for more than 30 minutes in a furnace (Dong-Il Eng.). The processes of dip-coating and calcination were repeated three times.

The biofilter reactor was manufactured in a way that feed gas entered from the top of the biofilter composed of two acryl tubes (diameter: 5 cm, length: 25 cm) connected in series. Upper and lower reactor tubes were packed up to 18 cm and 20 cm from their bottom with media, respectively, so that total effective height of biofilter was adjusted to 38 cm. Among four sampling ports of the biofilter, the 1st one, 2nd one and 3rd one were positioned at 10 cm below top surface of the upper media, 2 cm below top surface of the lower media and 12 cm below top surface of the lower media, respectively. The fourth one was positioned at the exit of the biofilter. Therefore, the ratios of effective height to total were 0.26, 0.53, 0.79 and 1.0 for the 1st one, 2nd one, 3rd one and 4th one, respectively. In the biofilter, a mixture of equal volume of granular activated carbon and compost with the average radius of 3 mm and 0.6 mm, respectively, was used as the packing media of biofilter. Granular activated carbon chosen as supporting material of the packing media has shortcomings of frequent channeling and short circuiting with increased pressure drop resulting from microsomal growth, while it has the advantage of high buffer capacity against sudden shock loading owing to high adsorption capacity. Nutrition necessary for the growth of microorganism was provided by organic packing media, i.e., compost. In addition, buffer solution was intermittently provided from the top of the biofilter in order to maintain the optimum pH and moisture condition.

Air provided by a blower (Young Nam Yasunnaga, outlet pressure=0.12 kg_f/cm^2, maximum flow rate=43 L/min) passed through a series of three humidifier columns maintained at 40-50 °C by thermostat (Jeil Science, J-PW B2) and its relative humidity was maintained at 95-99%. Variously adjusted amount of ethanol was continuously injected by syringe pump (KD Scientific, Model: KDS200) into a heated conduit of 140 °C through which humidified air passed. Waste-air containing ethanol of variously designed concentration was artificially manufactured in this way and was provided to the top of the biofilter. Tygon tube was used to convey pure air and viton tube was used to transport manufactured waste-air containing ethanol as feed gas to the biofilter. Temperature of biofilter column was maintained near 30 °C by heating band and temperature controller and swagelok fitting was used for all fittings. A schematic diagram of the biofilter process is shown in Fig. 1.

2. Microorganism, Mixed-inoculum Preparation, Bacteria Count

Burkholderia cepacia G4 from Inje University was incubated according to the procedure as follows. The solutions, as shown in Table 1, were mixed in such a fixed proportion as [salt stock solution (100 ml)+$CaCl_2 \cdot 2H_2O$ (10 ml)+$MgSO_4 \cdot 7H_2O$ (10 ml)+sterilized

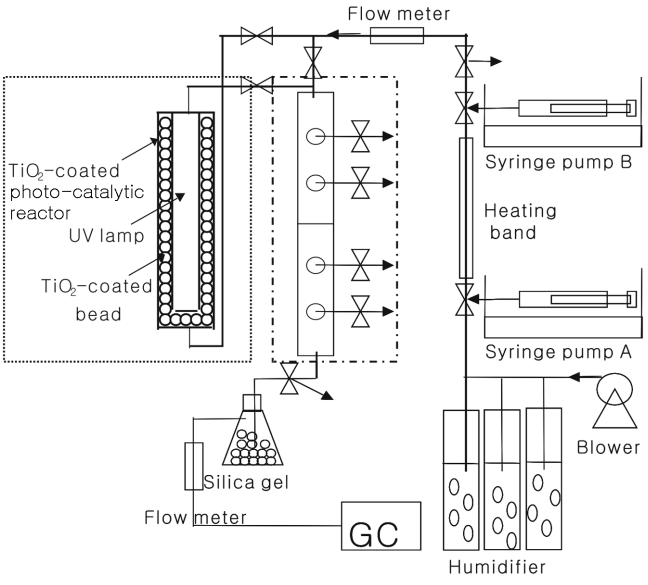

Fig. 1. Schematic diagram of hybrid system.

Table 1. Compositions of buffer and mineral solution.

Salt stock solution		Mineral solution	
Na_2HPO_4	70 g/L	$CaCl_2 \cdot 2H_2O$	1.5 g/L
KH_2PO_4	30 g/L	$MgSO_4 \cdot 7H_2O$	24.6 g/L
NaCl	50 g/L		
NH_4Cl	10 g/L		

distilled water (880 ml)] to make 1 liter of the buffer and mineral medium. Then 22 μL (5 Mm) of phenol was added. Small quantity of the medium was poured and agar was added to attach solid-medium on the surface of petri-dish where *Burkholderia cepacia* G4 was smeared. Microorganism on the petri-dish was taken by loop transfer needles, was dropped into a prepared medium in a flask was incubated under the condition of 30 °C and 200 rpm set by shaking incubator. *Pseudomonas putida* (KCTC 1768) was also incubated in the following way. Eight grams of nutrient broth purchased from Merck was dissolved in demineralized water of pH 7 and sterilized at 121 °C for 15 minutes by autoclave to make liquid-medium. The procedure to incubate *Psedomonas putida* (KCTC 1768) was the same as that of *Burkholderia cepacia* G4 except for the incubation temperature of 26 °C. Mixed culture of *Psedomonas cepacia* G4 and *Pseudomonas putida* (KCTC 1768) was inoculated, when the absorbance of each medium representing optical density measured in every 3 hr at the wave length of 600 nm by UV-spectrometer exceeded 0.8, on the packing media of biofilter by recycling the mixture of both incubated microorganisms with the mixed medium into biofilter at the rate of 0.4 ml/min for 48 hrs.

Microbial count fixed on packing media was determined in the following way. One gram of packing media was vortexed with 5 ml of sterilized demineralized water and it was ground in 5% paraformaldehyde solution for 48 hrs. The ground sample was 10 times diluted and was filtered with polycarbonate membrane filter (pore size=0.2 μm, ϕ=25 mm) by 1 ml at a time and the filter was dried. The dried filter was placed on slide glass and was stained by 10 μl of DAPI (4'-6-diamidino-2-phenylindole, 0.33 mg/ml) for 1 hr in dark box. After the stained filter was washed and was dried, each drop of fluoroguard-antifade-reagent was dropped on each side of the stained filter. It was covered with cover glasses and was observed by fluorescence microscope (Axiolab, Xeiss, Germany) UV filter (G365, LP395, FT420). The total bacterial number (TBN) was calculated by the formula as below:

$$\text{TBN (total bacterial number)} = \frac{A_0 \times F_1}{F_2 \times F_3}$$

A_0 : average cell number in field
F_1 : filter area
F_2 : field area
F_3 : filter sample volume

2. Analytical Methods

Concentrations of ethanol were measured in the following way at the positions of feed and four sampling ports. A gas chromatograph (Shimazu, GC-17AAFw Ver.3) equipped with flame ionization detector (FID) and SUPELCO WAX™-10 fused silica capillary column (30 m×0.53 mm×2.0 m) was calibrated with standard gas (24.8 ppmv of toluene and 515 ppmv of ethanol) purchased from RIGAS. After each 100 μL of treated gas was taken by 250 μL gas-tight-syringe (Hamilton, USA) from feed or each sampling port, it was injected through the injector. Then concentrations of toluene and ethanol were calculated at the peak of its retention time. Nitrogen (99.999%) was used as carrier gas and its flow rate was 4 ml/min. Operating temperatures of injector, oven (column) and detector were 200 °C, 90 °C and 250 °C, respectively.

3. pH, Density, Moisture

The optimum control of pH and moisture of the packing media in the biofilter reactor is definitely necessary for adequate operation of biofilter. Buffer solution was intermittently supplied at the rate of 0.4 ml/min by peristaltic pump (Masflex) to maintain the optimum pH of packing media. Each twenty gram of media sample was taken from each sampling port to place in vacuum dry oven (Sam Heung) for 24 hrs at 150 °C and to measure dried weight of the sample. The moisture content of the media was calculated by the difference of its weight between before and after drying. Density of the media was measured on the basis of equal volume mixture of granular activated carbon (25 ml) and compost (25 ml).

4. Biofilter Experiment

4-1. Process Condition

For 4 days (8 times) of biofilter operation (i.e., 1st stage of operation) air was supplied at the rate of 0.25 L/min and toluene and ethanol were injected by two syringe pumps (KD Scientific, Model: KDS200) into air passing through preheated conduit at the rate of 0.29 μL/min and 0.83 μL/min, respectively. Theoretical toluene and ethanol concentrations of manufactured waste-air were 278 ppmv and 1,450 ppmv, respectively, assuming it was ideal gas. At 2nd stage of biofilter operation (9-26 times) the same toluene and ethanol concentrations were maintained as that of 1st stage of operation. However, air supply rate and the injection rate of toluene and ethanol were increased by factor of two to be 0.5 L/min, 0.58 μL/min and 1.67 μL/min, respectively so that the inlet loads of toluene and ethanol were doubled. During 3rd stage (27 times-42 times) air-supply rate was kept the same as 0.5 L/min and ethanol injection rate was increased, by factor of 1.5, up to 2.5 μL/min, while toluene injection rate was the same as that of the 2nd stage. Therefore, the theoretical ethanol concentration was increased by a factor of 1.5 to be 2,180 ppmv in the same way as inlet load was, while the theoretical toluene concentration remained the same. At the 4th stage of operation (43 tims-58 times) toluene injection rate was increased by a factor of two up to 1.16 μL/min with the same air-supply rate so that the theoretical toluene concentration was doubled to be 556 ppmv, while process conditions on ethanol maintained the same as those of the 3rd stage of operation. At the 5th stage of operation (59 times-77 times) the injection rate of toluene and ethanol and air supply rate were increased by factor of two to be 2.32 μL/min, 5 μL/min and 1 L/min, respectively. Therefore, the concentration of toluene and ethanol remained the same as that of the 4th stage of operation to be 556 ppmv and 2,180 ppmv, respectively. However, the inlet loads of toluene and ethanol were increased by a factor of two. The operating conditions on toluene and ethanol and temperature schedule of biofilter are shown in Table 2, Table 3 and Fig. 2 where the temperature was maintained near 30 °C, respectively.

4-2. Buffer Solution

10 ml of buffer and mineral solution was provided intermittently

Table 2. Theoretical values of operating condition on toluene from each stage of hybrid system-run

Stage (times) / Theoretical value	1st stage (1-8)	2nd stage (9-26)	3rd stage (27-42)	4th stage (43-58)	5th stage (59-77)
m (μl/min)	0.29	0.58	0.58	1.16	2.32
Q (L/min)	0.25	0.5	0.5	0.5	1.0
C_{go} (ppm)	278	278	278	556	556
C_{go} (g/m^3)	1	1	1	2	2
τ (min)	2.98	1.49	1.49	1.49	0.75
Inlet load (g/m^3/h)	20.13	40.27	40.27	80.54	160

※ m: toluene injection rate at a syringe pump
Q: air flow rate
C_{go}: feed concentration
τ: EBCT (effective height: 0.38 m)

Table 3. Theoretical values of operating condition on ethanol from each stage of hybrid system-run

Stage (times) / Theoretical value	1st stage (1-8)	2nd stage (9-26)	3rd stage (27-42)	4th stage (43-58)	5th stage (59-77)
m (μl/min)	0.83	1.67	2.5	5.0	
Q (L/min)	0.25	0.5	0.5	0.5	1.0
C_{go} (ppm)	1,450	1,450	2,180	2,180	2,180
C_{go} (g/m^3)	2.62	2.62	3.93	3.93	3.93
τ (min)	2.98	1.49	1.49	1.49	0.75
Inlet load (g/m^3/h)	52.75	105.50	158.26	158.26	316.51

※ m: ethanol injection rate at a syringe pump
Q: air flow rate
C_{go}: feed concentration
τ: EBCT (effective height: 0.38 m)

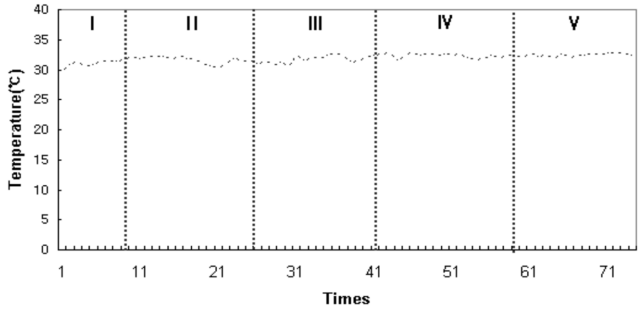

Fig. 2. Temperature schedule for the operation of hybrid system.

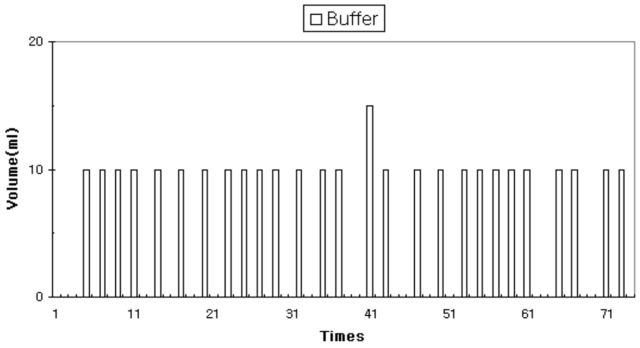

Fig. 3. Feeding schedule of buffer solution to a biofilter.

at the rate of 0.4 ml/min to the biofilter during its operation by peristaltic pump (Masterflex). Microbes were from time to time provided to the biofilter when the activity of microbes attached to media turned out to be decreased, which may be measured with the concentration of carbon dioxide.

5. Experiment of photo-catalytic reactor

Waste-air containing ethanol was treated by photo-catalytic reactor, shown as a dotted line in Fig. 1, isolated from biofilter by manipulating on-off valves. The same operating condition was applied as shown in Table 2. At each stage of photo-catalytic reactor run, the ethanol-removal efficiency of photo-catalytic reactor was measured after adsorption on the waste-air-contacting surfaces of annular region of pyrex tube and packed glass beads coated with TiO_2, reached equilibrium due to saturating the waste-air-contacting surfaces by letting waste-air pass through photo-catalytic reactor for more than 30 minutes, so that only a photo-catalytic process may be considered neglecting the effect of adsorption. Relative humidity of feeding waste-air to photo-catalytic reactor was maintained at more than 95%, which is the same humidity condition as that of the biofilter.

RESULTS AND DISCUSSION

1. Time Evolutions of Toluene Concentrations at Four Sampling Ports

The transient behavior of toluene concentrations measured at the position of feed inlet and four sampling ports of hybrid system composed of the photo-catalytic reactor and the biofilter is shown as in Fig. 4, when the biofilter where the mixed culture of *Burkholderia cepacia* G4 and *Pseudomonas putida* was inoculated, was run near 30 °C under various operating conditions as shown in Tables 2 and 3 for 39 days (total 77 times with measuring frequency of two times per day). The concentrations of toluene measured at the position of feed inlet and 1st sampling port, and 2nd, 3rd and 4th sampling port (exit) are shown as in Figs. 5 and 6, respectively. Time-evolutions

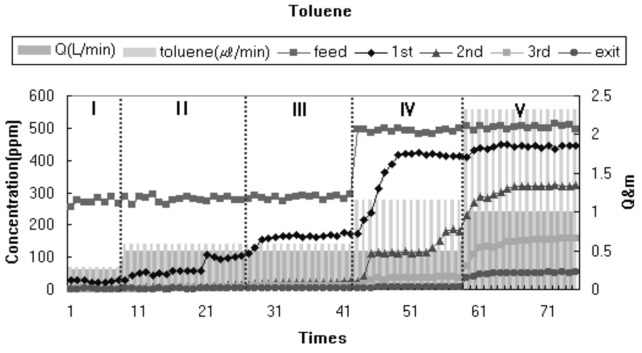

Fig. 4. Various toluene concentrations of hybrid system at each sampling port versus experimental times.

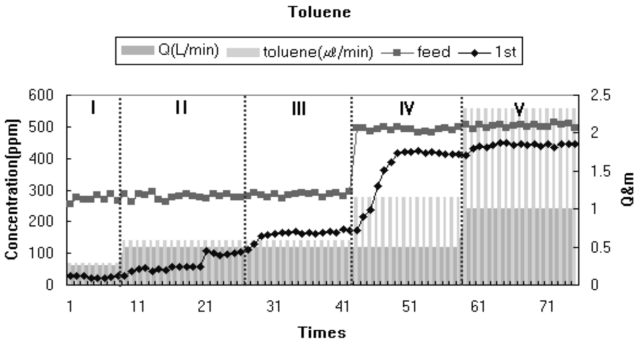

Fig. 5. Various toluene concentrations of hybrid system at feed inlet and 1st sampling port

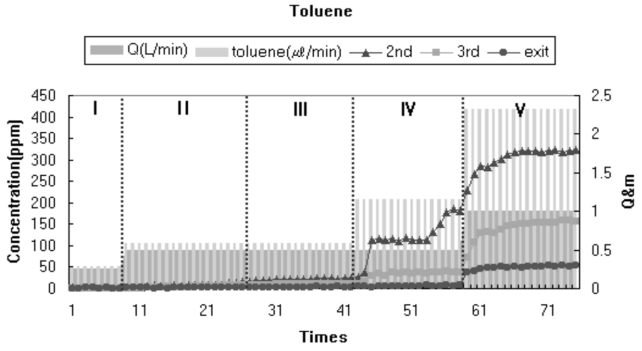

Fig. 6. Various toluene concentrations of hybrid system at 2nd, 3rd and exit sampling ports.

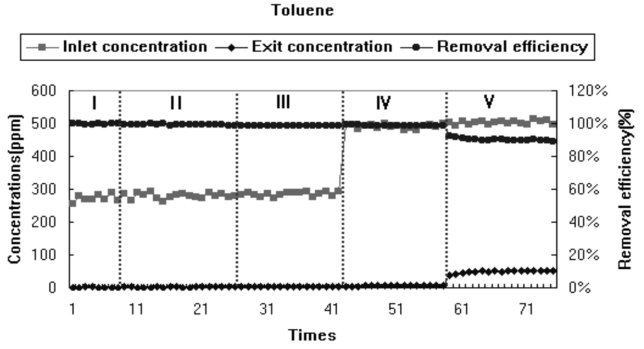

Fig. 7a. Removal efficiency, inlet and exit concentrations of hybrid system versus times.

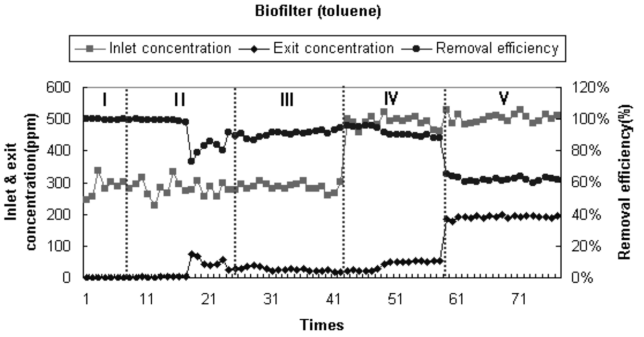

Fig. 7b. Removal efficiency, inlet and exit concentrations of biofilter system without photo-catalytic reactor versus times [Lim and Park, 2005].

of the removal efficiency and the elimination capacity of the hybrid system with the inlet load on toluene are shown as in Figs. 7a and 8, respectively, while time evolution of its removal efficiency of the biofilter system without photo-catalytic reactor from the work of Lim and Park [2005] is shown as in Fig. 7b.

During 4 days (8 times) after start-up of the hybrid system, the transient behavior of all breakthrough curves except for the 1st sampling port showed that toluene was continuously adsorbed on the media and adsorption of ethanol was under way since the theoretical inlet load of the 1st stage operation was the lowest of 20.13 g/m^3/h. At the 2nd stage of hybrid system-run (9 times-26 times), both rates of toluene injection and air supply were increased by a factor of two that toluene concentration remained same. In spite of reduced retention time due to increased rate of air-supply, removal efficiency remained almost the same of 100%, as shown in Fig. 7-1, as that at the 1st stage of operation. Increased inlet load was attributed to the fact that increased rate of air supply with same ethanol concentration resulted in reduced retention time. For the period of the 2nd stage the inlet load and removal efficiency of toluene was continued at 40.27 g/m^3/h and 100%, respectively, while its removal efficiency was 80% from the experimental result of Lim and Park [2005] where waste-air containing toluene and ethanol was treated by a biofilter only. At the 3rd stage of operation (43 tims-58 times), process conditions of toluene were maintained as the same as those of 2nd stage of operation. However the inlet load of ethanol co-feed was increased by 1.5 times. As a result the removal efficiency of toluene was still maintained at about 100% while it was 90% from

the experimental result of Lim and Park [2005]. During the 4th stage (43-58 times) of the run, retention time was maintained as the same as that of the 3rd stage and both feed concentration and inlet load of toluene were increased by a factor of two. Consequently, each breakthrough curve at each sampling port showed rapid increase and maintained new steady-state concentration, which suggested that it approached new state of saturation. It is shown in Fig. 4 that the order of saturation by adsorption from each unsteady behavior of breakthrough curve was in such way as 1st, 2nd, 3rd and 4th sampling port were in the 1st, 2nd, 3rd and 4th place, respectively. The sooner a breakthrough curve reached the status of saturation by adsorption, the higher its toluene concentration of waste-air passing through the position of its sampling port was. The removal efficiency of toluene still remained at 100% for the whole period of 4th stage with the inlet load of 80.54 g/m^3/h, while it was also still maintained at 90% from the experimental result of Lim and Park [2005].

At the 5th stage of hybrid system-run, the feed concentration of toluene was the same as that at 4th stage of run and its retention time was reduced by half so that its inlet load was increased by factor of two. During 9 days of the 5th stage the inlet load and removal efficiency continued to be 160 g/m^3/h and 90%, respectively, while its removal efficiency was about 60% according to the experimental results of Lim and Park [2005].

In time-evolution of the removal efficiency on toluene as in Fig. 7-1, it maintained almost 100%. However, it began to decrease to 90% when inlet load surpassed, as in Fig. 8, 130 g/m^3/h consistent with maximum elimination capacity shown as in Fig. 9. At the end of the hybrid system-run, the removal efficiency was decreased and maintained at 90%.

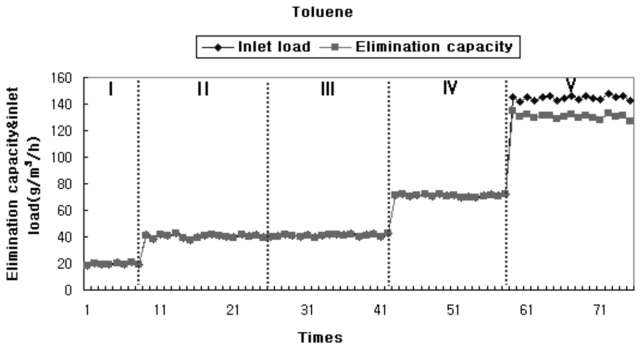

Fig. 8. Elimination capacity (g/m^3/h) and inlet load versus times.

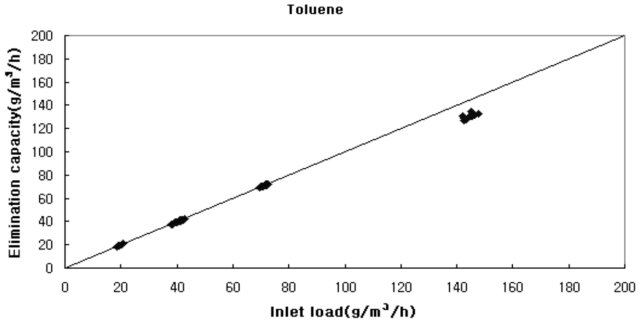

Fig. 9. Elimination capacity (g/m^3/h) versus inlet load of toluene.

2. Time Evolutions of Ethanol Concentrations at Four Sampling Ports

Transient behavior of ethanol concentrations measured at the position of feed inlet and four sampling ports of the hybrid system, is shown as in Fig. 10. The concentrations of ethanol measured at the position of feed inlet and 1st sampling port, and 2nd, 3rd and 4th sampling port (exit) are shown in Figs. 11 and 12, respectively. Time-evolutions of the removal efficiency and the elimination capacity of the hybrid system with the inlet load on ethanol are shown as in Figs. 13a and 14, respectively, while time evolution of its removal efficiency of the biofilter system without photo-catalytic reactor from

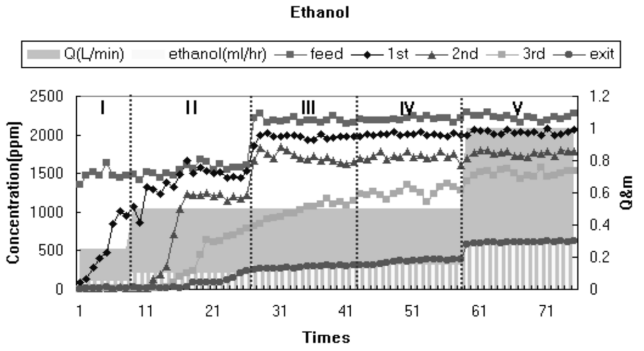

Fig. 10. Various ethanol concentrations of hybrid system at each sampling port versus experimental times.

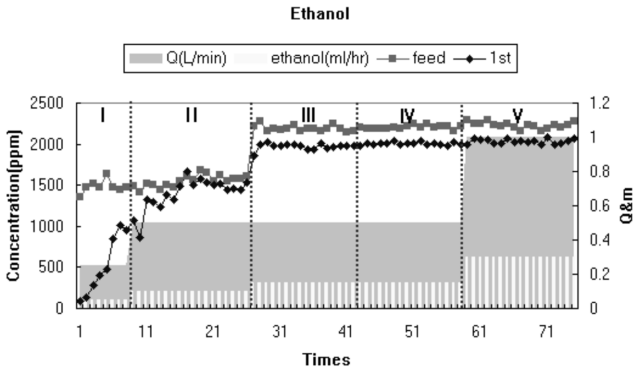

Fig. 11. Various ethanol concentrations of hybrid system at feed inlet and 1st sampling port.

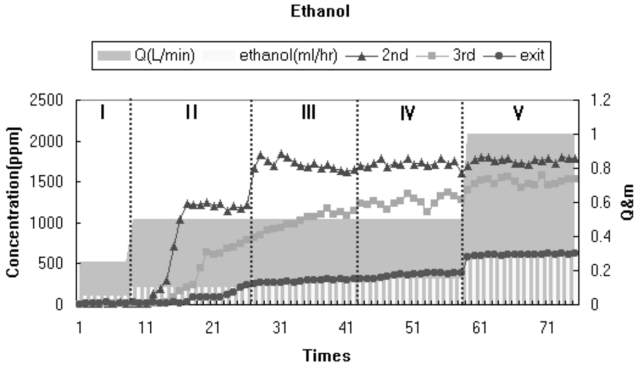

Fig. 12. Various ethanol concentrations of hybrid system at 2nd, 3rd and exit sampling ports.

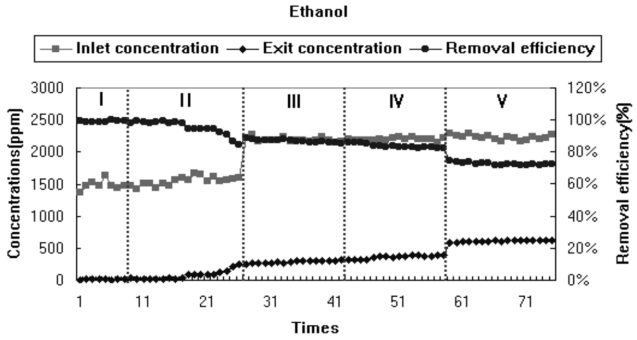

Fig. 13a. Removal efficiency, inlet and exit concentrations of hybrid system versus times.

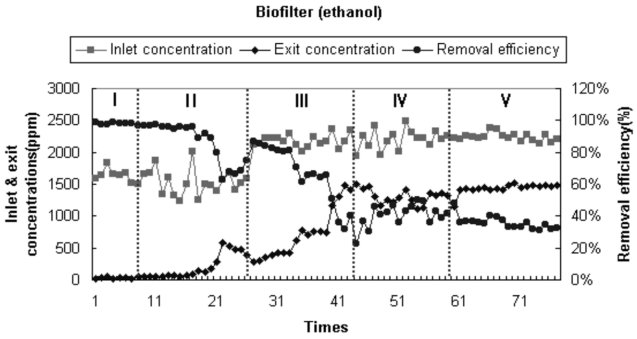

Fig. 13b. Removal efficiency, inlet and exit concentrations of biofilter system without photo-catalytic reactor versus times [Lim and Park, 2005].

the previous work of Lim and Park [2005] is shown in Fig. 13b.

During 4 days (8 times) after start-up of the hybrid system, the transient behavior of all breakthrough curves except for the 1st sampling port showed that ethanol was continuously adsorbed on the media and adsorption of ethanol was under way since the theoretical inlet load of the 1st stage operation was the lowest of 52.75 g/m^3/h. At the 2nd stage of hybrid system-run (9 times-26 times), both rates of ethanol injection and air supply were increased by a factor of two that ethanol concentration remained same. However, reduced retention time due to increased rate of air-supply resulted in less removal efficiency, as shown in Fig. 13a, than that at 1st stage of operation. Increased inlet load was attributed to the fact that increased rate of air supply with same ethanol concentration resulted in reduced retention time. For the period of the 2nd stage the inlet load and removal efficiency were continued at 105.5 g/m^3/h and more than 85%, respectively, while the removal efficiencies at the same inlet load from Lim and Park [2005] were 65% with only biofilter. It is shown in Fig. 10 that the order of saturation by adsorption from each unsteady behavior of breakthrough curve was in such way as 1st, 2nd, 3rd and 4th sampling port were in 1st, 2nd, 3rd and 4th place, respectively. The sooner a breakthrough curve reached the status of saturation by adsorption, the higher was its ethanol concentration of waste-air passing through a biofilter position of its sampling port.

During the 3rd stage (27-42 times) of hybrid system-run, the retention time was maintained the same as that of the 2nd stage of run, and both feed concentration and inlet load of ethanol were increased to 1.5 times. Removal efficiency remained at 90% for the period of the 3rd stage with the inlet load of 158.26 g/m^3/h. The value of 90% was much more enhanced than that of 40% from the work of Lim and Park [2005].

At the 4th stage of operation (43 tims-58 times), process conditions were maintained the same as those of the 3rd stage of operation, except that the inlet load of toluene co-feed was increased by factor of two. The ethanol concentrations at 1st, 2nd and 3rd and 4th sampling ports remained almost the same as in the 3rd stage. At the end of the 4th stage the removal efficiency was a little bit decreased to 85%, while that was about 40% from the result of Lim and Park [2005].

At the 5th stage of operation the feed concentration of ethanol was the same as that at the 4th stage of a run and its retention time was reduced by half so that its inlet load was increased by factor of two. Consequently, each breakthrough curve at each sampling port showed a little bit of increase and maintained a little bit higher steady-state concentration like that from the previous work of Lim and Park [2005]. During 9 days of the 5th stage the inlet load and removal efficiency continued to be 316.51 g/m^3/h and 75%, respectively, while those were 316.51 g/m^3/h and 40%, respectively, from the previous work of Lim and Park [2005].

In early time-evolution of removal efficiency as in Fig. 13a, it maintained almost 100%. However, it began to decrease when inlet load surpassed, as in Fig. 14, 230 g/m^3/h consistent with maximum elimination capacity shown as in Fig. 15.

3. Performance of Photo-catalytic Reactor

Removal efficiencies of toluene and ethanol turned out decreased as the stage-number of the photo-catalytic reactor run became higher

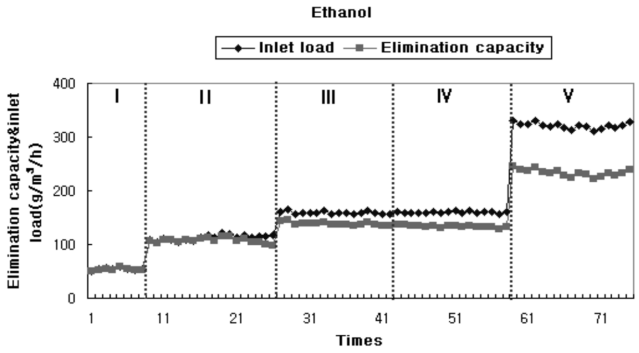

Fig. 14. Removal efficiency, inlet and exit concentrations versus times.

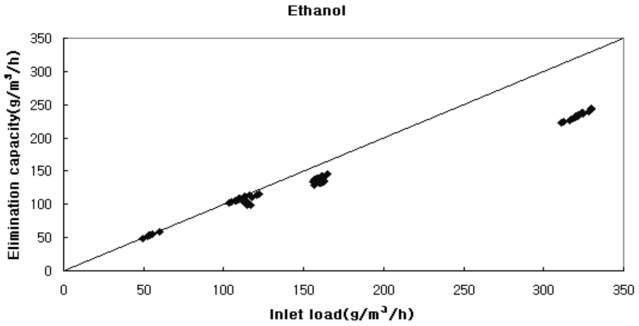

Fig. 15. Elimination capacity (g/m^3/h) versus inlet load of ethanol.

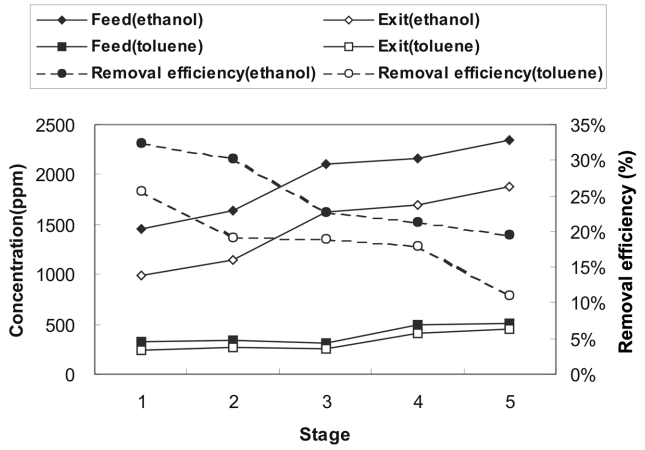

Fig. 16. Performance of photo-catalytic reactor for simultaneous treatment of ethanol and toluene at each stage.

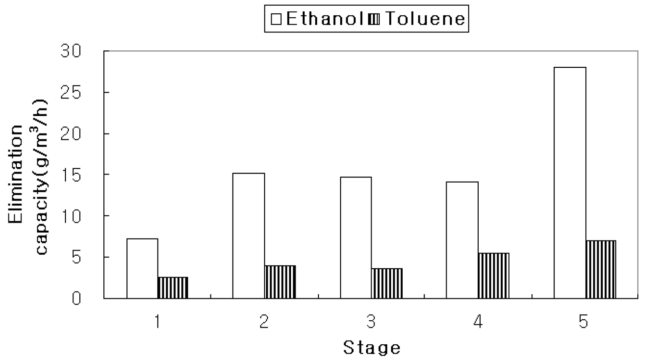

Fig. 17. Elimination capacity (g/m^3/h) of photo-catalytic reactor, for simultaneous treatment of ethanol and toluene at each stage.

as shown in Fig. 16. The removal efficiencies were about 33%, 24%, 22% and 20% at 1st, 3rd, 4th and 5th stages of the photo-catalytic reactor run, respectively, while removal efficiencies of toluene were 25%, 20%, 20%, 19% and 11% at 1st, 2nd, 3rd, 4th and 5th stages of the photo-catalytic reactor run, respectively. Elimination capacities of ethanol were *circa* 7.3 g/m^3/h, 15.2 g/m^3/h, 14.6 g/m^3/h, 14.1 g/m^3/h and *circa* 28 g/m^3/h at 1st, 2nd, 3rd, 4th and 5th stages of photo-catalytic reactor run, respectively, while elimination capacity of toluene continuously increased linearly from *circa* 2.6 g/m^3/h of 1st stage-run to *circa* 7 g/m^3/h of 5th stage-run as shown in Fig. 17.

4. Performance of a Hybrid System Composed of Photo-catalytic Process and a Biofilter

The maximum elimination capacities of toluene and ethanol became greater by 40 g/m^3/h and 130 g/m^3/h than those from the experiments performed with a biofilter only. Thus, the maximum elimination capacities for toluene and ethanol increased by 44% and 130%, respectively, by use of a hybrid system. At the end of a hybrid system-run the removal efficiencies for toluene and ethanol were decreased and maintained at 90% and 75%, respectively, while they were maintained at 60% and 40%, respectively, from the previous work with a biofilter only. Consequently, the use of a hybrid system improved the removal efficiencies, at the end of hybrid system-run, for toluene and ethanol by 50% and 87.5%, respectively, when those removal efficiencies measured from the experiments with a biofilter only were taken as controls. On the other hand, at the last stage of a photo-catalytic reactor run, the elimination capacities of toluene and ethanol were 7 g/m^3/h and 28 g/m^3/h, respectively, while the removal efficiencies of toluene and ethanol were 11% and 20%, respectively. Therefore, it may be concluded that the photo-catalytic process contributed to the maximum elimination capacities of hybrid system on toluene and ethanol by 30.8% and 56.5%, respectively, which contributions for the elimination capacities on toluene and ethanol were allocated indirectly by 25.4% and 44.3% as well as directly by 5.4% and 12.2%, respectively. Direct contributions of the photo-catalytic process were 17.5% and 21.5% to the increments of the elimination capacities on toluene and ethanol, respectively, while its indirect contributions were 82.5% and 78.5% to those on toluene and ethanol, respectively, as shown in Table 4.

5. Analysis of Packing Media

The density of an equal volume mixture of granular activated carbon and compost was 0.40. The pHs of packing media from 2nd and 4th sampling ports were the same, 7, as at the beginning of the biofilter experiments. However, they changed to 5.65 and 6.20 at the end of biofilter experiments. respectively. Dried weights of the media from 2nd and 4th sampling ports were 9.50 g and 9.11 g (weight of the media before drying was 20 g), by which moisture contents

Table 4. Contribution of phototocatalytic process to the performance of the hybrid system

Elimination capacity	Toluene (g/m^3/h)	Ethanol (g/m^3/h)
Maximum of the hybrid process	130	230
Maximum of the biofilter [Lim and Park, 2005]	90	100
Increment by integration of photocatalytic process	40 (100%)	130 (100%)
Direct contribution of photocatalytic process	7 (17.5%)	28 (21.5%)
Indirect contribution of photocatalytic process	33 (82.5%)	102 (78.5%)

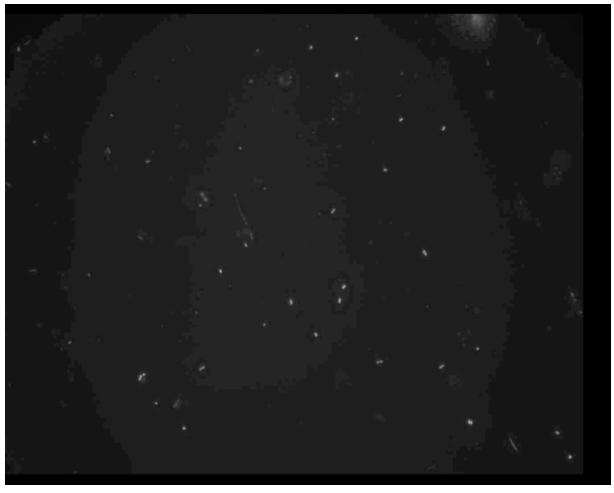

Fig. 18. Microbes observed by fluorescence microscope (16×100) (Axiolab, Xeiss, Germany).

of the media from the 2nd and 4th sampling ports turned out to be 52.50% and 54.45%, respectively.

The total bacterial numbers (TBN) for the 1st, 2nd and 3rd sampling ports turned out to 1.72×10^9/g, 9.03×10^8/g and 6.15×10^8/g, respectively. Thus, the microbial distribution in the biofilter was in the way that total bacterial number (TBN) was decreased as the effective height of the position of sampling port was increased. Microbes were observed by fluorescence microscope (16×100) (Axiolab, Xeiss, Germany) UV filter (G365, LP395, FT420) as shown in Fig. 18.

CONCLUSION

In early stage of hybrid system-run the removal efficiencies of toluene and ethanol maintained almost 100%. However, they began to decrease when their inlet loads surpassed 130 g/m^3/h and 230 g/m^3/h, respectively, consistent with the maximum elimination capacities of toluene and ethanol, which became greater by 40 g/m^3/h and 130 g/m^3/h, respectively, than those from the experiments performed with a biofilter only. Thus, the maximum elimination capacities for toluene and ethanol increased by 44% and 130%, respectively, by use of a hybrid system. At the end of the hybrid system-run the removal efficiencies for toluene and ethanol were decreased and maintained at 90% and 75%, respectively, while they were maintained at 60% and 40%, respectively, from the previous work performed with a biofilter only. Consequently, the use of a hybrid system improved the removal efficiencies, at the end of the hybrid system-run, for toluene and ethanol by 50% and 87.5%, respectively, when those removal efficiencies measured from the experiments with a biofilter only were taken as controls. On the other hand, at the last stage of photo-catalytic reactor run, the elimination capacities of toluene and ethanol were 7 g/m^3/h and 28 g/m^3/h, respectively, while the removal efficiencies of toluene and ethanol were 11% and 20%, respectively. Therefore, it may be concluded that the photo-catalytic process contributed to the maximum elimination capacities of the hybrid system on toluene and ethanol by 30.8% and 56.5%, respectively, which contributions for the elimination capacities on toluene and ethanol were allocated indirectly by 25.4% and 44.3% as well as directly by 5.4% and 12.2%, respectively. Direct contributions of the photo-catalytic process were 17.5% and 21.5% to the increments of the elimination capacities on toluene and ethanol, respectively, while its indirect contributions were 82.5% and 78.5% to those on toluene and ethanol, respectively, as shown in Table 4.

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