Influences of Aeration and Biological Treatment on the Fates of Aromatic VOCs in Wastewater Treatment Processes

Wei-Hsiang Chen[1*], Wen-Ben Yang[1], Chung-Shin Yuan[1,2†], Jun-Chen Yang[2], Qing-Liang Zhao[2]

[1] Institute of Environmental Engineering, National Sun Yat-sen University, Kaohsiung 804, Taiwan
[2] State Key Laboratory of Urban Water Resources and Environments (SKLUWRE), Harbin Institute of Technology, Harbin 150090, China

ABSTRACT

In this study, a lab-scale bioreactor experiment was conducted to investigate the fates of three aromatic hydrocarbons (benzene, toluene, and xylenes) in wastewater treatment processes, with respect to the differences among the species, together with the effects of aeration and the presence of activated sludge. The concentrations of the volatile organic compounds (VOCs) in the phases of air, water, and activated sludge in the bioreactor were analyzed to determine the respective chemical activities and to predict the possible transferring potentials of the VOCs among the three phases. Given appreciable levels of the VOCs being absorbed from the wastewater treatment plants (WWTPs) and their volatility, the directions of the transfers for these VOCs were from activated sludge to water and from water to air, indicating the importance of volatilization for the fates of VOCs in this reactor. The presence of activated sludge in the bioreactor had a positive effect on the transfers of the VOCs from air to water and from water to sludge, particularly for those VOCs with large octanol-water partition coefficients (K_{OW}). The effect of aeration on the fates of the VOCs was affected by factors including the Henry's law coefficients and K_{OW} values of the VOCs, and the presence of activated sludge in the system. For the VOCs with large Henry's law coefficients and small K_{OW} values, aeration reduced the concentration of the VOCs in the air and water phases more significantly, resulting in positive and negative impacts on the volatilization and biosorption/biodegradation of the VOCs in WWTPs, respectively, which was unexpected based on the design of the WWTPs for VOC removal.

Keywords: Aromatic volatile organic compounds; Fates; Wastewater treatment; Aeration; Biological treatment.

INTRODUCTION

Volatile organic compounds (VOCs) are organic chemicals mainly being composed of carbon atoms and can be easily emitted to the atmosphere as gases due to high vapor pressures resulting by their low boiling points. Besides natural sources such as vegetation and forest fires, VOCs are used in various industrial processes and applications by different means, such as components and starting substances in industries, and are released from these sources (Nizzetto *et al.*, 2007; Bravo-Linares and Mudge 2009; Joseph *et al.*, 2012; Han *et al.*, 2012; Hossain and Park 2012; Wang *et al.*, 2012). The main reason for VOCs being of concern is their detrimental effects on the environment and public health (Yeh *et al.*, 2011, Choosong *et al.*, 2010). For example, benzene is a chemical substance classified as a probable/

known carcinogen by the U.S. Environmental Protection Agency (USEPA) and International Agency for Research on Cancer (IARC), causing cancers on lung and kidney (USEPA 2012; IARC 2012).

Despite those natural and industrial/commercial processes acting as sources releasing VOCs into the environment, there is a growing concern regarding the emission of VOCs from wastewater treatment plants (WWTPs) (WEF-ASCE 1995; Banat and Simandl 1996; Escalas *et al.*, 2003; Oskouie *et al.*, 2008; Lebrero *et al.*, 2011). VOCs originally present in source wastewater may be released or emitted into the environment, mainly via volatilization, as they undergo various treatment technologies in WWTPs (Fatone *et al.*, 2011; Lehtinen and Veijanen 2011). Many preceding studies have documented the occurrences of VOCs emitted from wastewater treatment processes. For examples, mandated by the Clean Air Act, the public WWTPs in the U.S. need to inventory and control their emissions of hazardous air pollutants in which most of them are VOCs (USEPA, 2012). Pope and Disalvo (1995) researched the VOC emission in 14 WWTPS in the U.S. with different wastewater sources including residential and industrial sources, commercial facilities, hospitals, laboratories, and stormwater (Pope and

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Disalvo, 1995). In Canada, WWTPs were identified as one of the major sources for VOC emissions in the country (Hall Jr., 1997). VOC emissions from two WWTPs in Germany were studied with respect to the concentration distributions and the associated rates of emission from water to air (Frechen, 1992). Studies have also been conducted to examine the VOC emissions from WWTPs in Taiwan, with most of them focusing on specific industrial sources (Cheng and Chou, 2003; Chou and Cheng, 2005). In addition to WWTPs, Yeh *et al.* (2011) measured the concentrations of VOCs emitted from the wastewater in sewer systems and estimated the possible cancer risks caused by the exposure to these VOCs.

To date, the emissions of VOCs from WWTPs are under close scrutiny and investigation by public and local agencies worldwide. However, there is insufficient knowledge to outline clear scenarios regarding the mechanisms and kinetics involved for VOC removal in WWTPs. While biosorption and biodegradation are important factors that define the best approach for VOC treatment in wastewaters, concerns regarding the effectiveness and efficiency of VOC treatment arise as a consequence of their volatilization. Both biosorption/biodegradation and volatilization provide positive effects on reducing the concentrations of VOCs in wastewaters. Nevertheless, the resulting impacts to the environment and public health may be completely different because of the potential of overestimating the treatment efficiencies of VOCs by WWTPs when appreciable fractions of VOCs were actually removed by volatilization into the environment. This concern may be worse given the complexities of source water qualities in the heterogeneous systems of municipal WWTPs, which typically receive the combined flows of urban and industrial wastewater, rainfall runoff, and a number of additional flows.

The objective of this study was to investigate the characteristics of the fates of the VOCs with respect to the associated effects of aeration and biological treatment, two steps widely seen in conventional WWTPs. The VOCs of interest in this and many other studies included three aromatic VOCs (benzene, toluene, and total xylenes) (Cheng *et al.*, 2008; Fatone *et al.*, 2011; Lehtinen and Veijanen, 2011; Yeh *et al.*, 2011). The ubiquitous presences of benzene, toluene, and xylenes have been identified in our preceding study researching their emission rates and health risks (Yang *et al.*, 2012). Selected physicochemical parameters of these VOCs were listed in Table 1. Instead of studying the fates of the VOCs in real WWTPs in which the complexity by the

combination of water quality and operational parameters may blur the significant findings, a lab-scale reactor was designed and used in this study to simulate three treatment technologies (primary sedimentation, aerobic biological treatment, and secondary sedimentation) and investigate the impacts of aeration and biological treatment on the fates of the VOCs. The results of this study was expected to provide insight into the individual and combined effects of these two operational factors on the removal mechanisms of the VOCs in wastewater treatment processes, assisting WWTPs in developing effective strategies for VOC removal and minimizing impacts of VOC emissions from wastewaters on the environment and public health.

METHODOLOGIES

Materials

Standard solutions of three aromatic hydrocarbons including benzene, toluene, and xylene were purchased from Kermel Chemical Reagent Co., Ltd. (China) and used to qualify and quantify the concentrations of these VOCs in three different phases of air, water, and microorganisms (i.e., activated sludge). Sodium chlorite, which was used to increase the ionic strength of aqueous samples for increasing the volatility of the VOCs to enhance the following analysis, was obtained from Tianjin Benchmark Chemical Reagent Co., Ltd. (China). Membrane filters with a 0.45 μm pore size obtained from Haining Guodian Zhonglian Medical Equipment Factory (China) were used to filter aqueous samples for the following VOC analyses. All other reagents and materials not specified were of analytical grade and obtained from Tianjin Benchmark Chemical Reagent Co., Ltd., China or Agilent, U.S.

Lab-scale Bioreactor Experiment

A biological treatment reactor with a capacity of 27 L (0.3 m (L) × 0.3 m (W) × 0.3 m (H)) and three aeration pipes connected at the bottom was designed and run to simulate the wastewater treatment processes, investigating the concentration distributions and the associated fates of the VOCs in the air, water, and sludge phases. The concentration data were further applied to calculate the chemical activities of the VOCs in different phases and to predict their possible fates in WWTPs. The wastewater and activated sludge used for the bioreactor was collected from a municipal WWTP, which is located within 10 km of the downtown of Harbin City in China and with total daily design treatment capacity

Table 1. Selected physicochemical properties of the VOCs considered in this study[1].

Chemical	Melting points (°C)	Boiling point (°C)	Water solubility (g/L)	Log of octanol-water partition coefficient (dimensionless)	Henry's law coefficient (atm-m^3/mol)
Benzene	6	80	1.88	2.13	5.5×10^{-3}
Toluene	–95	111	0.53	2.72	5.94×10^{-3}
m-Xylene	–48	139	0.16	3.2	7.18×10^{-3}
o-xylene	–25	145	0.18	3.12	5.18×10^{-3}
p-xylene	13	138	0.16	3.15	6.90×10^{-3}

[1] Adapted from Agency for Toxic Substances & Disease Registry.

of 325 thousand cubic meters per day. The wastewater received by this plant contains wide ranges of VOCs, which contains approximately 95% of the wastewater from domestic sewage, with the remaining 5% from local industrial sources. The chemical oxygen demand (COD) of the wastewater flowing into the WWTP ranged from 282 to 487 mg/L during the period of sampling.

Three major treatment technologies of the WWTP were simulated by continuously running the bioreactor under varying operational scenarios at different times. The simulated scenarios included primary sedimentation without aeration for 2 hours, followed by aerobic sludge treatment process with aeration for 8 hours and secondary sedimentation without aeration in the last 2 hours. The source water for the reactor was collected from the primary effluent wastewater of the WWTP, with a head space of 9 L air volume above the waster surface in the reactor. The activated sludge was collected from the aerobic activated sludge treatment process of the WWTP and added into the bioreactor with a mixed liquor suspended solid concentration (MLSS) controlled at 3,300 mg/L. The water was aerated with varying aeration rates to control the dissolved oxygen concentration at 4 mg/L in the water. Air, water, and sludge samples were collected every hour to measure the concentrations of the VOCs in the gas, liquid, and sludge phases.

VOC Sampling and Analysis

Different methods were employed to collect the gas, water, and sludge samples in the bioreactor. Samplings were at lease duplicated to minimize possible errors resulted by the concentration variation amongst samples. Water samplings were performed by collecting 5 mL of wastewater after filtration with 0.45 μm pore size membrane filters and were sealed in headspace vials (5965-0051, Agilent, U.S.). Headspace gas chromatography coupled with mass spectrometry (Headspace GC/MS) was used to determine the VOC concentrations in the wastewater. The wastewater sample was placed in a closed sampling vessel and heated at 80°C for 30 minutes. The vapor produced at this temperature profile in the vessel was sampled for analysis to determine the VOC concentrations in the wastewater samples. To enhance the volatilization of VOCs to improve the sensitivity of the VOC analysis, 1 g of sodium chloride was added in the vials to increase the ionic strength of wastewater samples and decrease the solubilities of VOCs. All wastewater samples were stored at 4°C and analyzed in 72 hours after the sampling.

Air samplings in which the wastewater was continuously disturbed by aeration, air samples were collected in the middle of the bioreactor at 1 meter above the water surface, while air samples were collected at the same position but at 0.1 m above the water surface without aeration, as shown in Fig. 1. Air samples were collected by using QT-2B VOC sampler (Lianyixing Universal Equipment Co., Ltd, China) with an activated carbon-filled GH-1 adsorption tube (Yanchengrenhe Science and Technology Co., Ltd, China). The air sampling flow rate was 200 mL/min, and the sampling time was 30 minutes. After sampling, the VOCs adsorbed onto the adsorption tube were extracted by rinsing with dichloromethane for 12 hours. The extracted solutions were concentrated and stored at 4°C, followed by the analysis in 72 hours. To determine the VOC concentrations in the activated sludge of the bioreactor, 100 mL of wet activated sludge were collected, followed by slow filtration with 0.45 μm pore size membrane filters for 1 hour. The VOCs in the sludge retained on the filters were extracted by Soxhlet extraction using dichloromethane as the solvent (TWEPA, 2008). After 24 hours of Soxhlet extraction process, the extracted solution was concentrated to 1 mL and transferred into a GC vessel for the following GC-MS analysis within 72 hours.

The concentrations of the VOCs were quantified by using GC-MS (QP5050A, Shimadzu, Japan). Operational parameters and conditions were modified from a base case to determine the concentrations of benzene, toluene, and
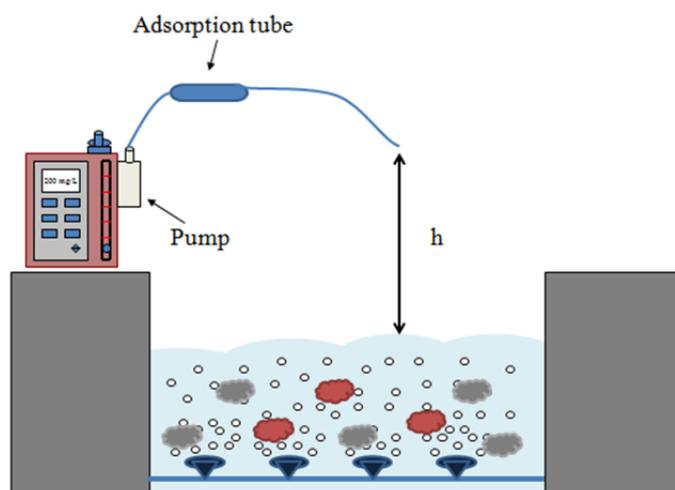
Fig. 1. A schematic figure of the air sampling conducted in the lab-scale bioreactor experiment that simulated the wastewater treatment processes in this study. The height of the sampling location, as shown as h in the figure, was varied as different treatment processes (e.g., aeration or no aeration) being simulated.

xylenes given the different physicochemical properties among these substances. For the operational parameters and conditions used for the base case, the GC was equipped with a 30 m × 0.25 mm I.D. DB-5 capillary column with 0.25 m film thickness (Agilent, U.S.). The column temperature was programmed as follows: 40°C held for 2 minutes at 10 °C/min to 160°C and at 20 °C/min to 250°C held for 12 minutes. Mass spectrometry was performed in electron ionization mode. The ion source temperature of the mass spectrometer was 230°C. The acquisition mode was to scan in the range of 50 to 400 m/z at 0.5 scan/s. For the quality control and quality assurance of the analysis, duplicate analyses were done and blank samples were analyzed for every thirty samples to obtain representative samples. The performance of the GC/MS was evaluated regularly with the standard solutions for quality control. The calibration curves of all VOCs were developed and checked before the analysis to ensure the R^2 values above the number of 0.995. The accuracy ranged from 80 to 120% for all VOCs of interest in this study, while the relative standard deviations for these VOCs were less than 20%.

Fate Prediction by the Concept of Chemical Activity

The concept of chemical activity, which compares observed concentrations with expectations from phase equilibrium considerations, was used to evaluate the possible fates of VOCs amongst the phases of air, water, and activated sludge in wastewater treatment processes. Simply speaking, it is the difference in chemical activities that determines in which direction a net flux of a compound will occur between several environmental compartments. If the chemical activity of a substance in a specific phase is greater than in the other phase, the substance will have a potential of transferring from that specific phase to the other phase. The extent of this transferring potential depends on the chemical activity difference between these two phases, and such transfer will continue until the chemical activities are equal in the interacting phases.

Evaluation of the chemical activity of a substance in any phase of interest corresponds to contrasting its concentration to whatever concentration would be expected at equilibrium with the reference state. In this study, the pure liquid VOC was chosen as the reference state, implying that the activity of the VOC is equal to 1 when it occurs at its liquid solubility. Therefore, the chemical activity of a VOC in a particular medium was calculated by applying partitioning constants that relate concentrations in non-aqueous phases (e.g., air and activated sludge in this study) to their corresponding equilibrium concentrations in water to calculate the corresponding aqueous concentrations in equilibrium with that phase and then normalizing the results to the VOC's liquid solubility. The equations used to calculate the chemical activities of the VOCs in the phases of air, water, and activate sludge were given as follows (Schwarzenbach *et al.*, 2003):

$$\text{Chemical activity of the substance i in water} = \frac{C_{iwater}}{C_{iwater,sat}} \quad (1)$$

$$\text{Chemical activity of the substance i in air} = \frac{C_{iair}}{K_H C_{iwater,sat}} \quad (2)$$

Chemical activity of the substance i in activated sludge

$$= \frac{C_{isludge}}{\rho K_{isludge} C_{iwater,sat}} \quad (3)$$

where C_{iwater}, C_{iair}, and $C_{isludge}$ represent the VOC concentration in air, water, and activated sludge, respectively [M/L^3]; $C_{iwater,sat}$ represent the saturated VOC concentration in water (or liquid solubility) [M/L^3]; K_H is the dimensionless Henry's law constant of the VOC; $K_{isludge}$ is the dimensionless partitioning constant relating the VOC concentration in activated sludge to its corresponding concentration in water; and ρ is the density of wet activated sludge, which was assumed to be equal to 1.05 g/mL in this study (Sears *et al.*, 2006).

As the information of the $K_{isludge}$ value of a chemical is not commonly available, it was assumed that the mass transfer of the VOCs between the sludge and other environmental compartments is kinetically dominated by the fractions of lipid and protein in the activated sludge, as shown in the equation below (Schwarzenbach *et al.*, 2003):

$$K_{isludge} = f_{lipid} K_{ilipid} + f_{protein} K_{iprotein} \quad (4)$$

where f_{lipid} and $f_{protein}$ denote the fractions of lipid and protein in the activated sludge on a weight basis, respectively; and K_{ilipid} and $K_{iprotein}$ represent the dimensionless partitioning constants relating the VOC concentrations in lipid and protein to its corresponding concentration in water, respectively. A one-parameter linear free energy relationship (LFER) that relates the K_{ilipid} with the corresponding octanol-water partitioning constants (K_{iow}) for apolar compounds with log K_{iow} less than 6 was used to derive the K_{ilipid} values of the VOCs of interest in this study, while another one-parameter LFER relating the logarithms of $K_{iprotein}$ with the corresponding K_{iow} values was used for prediction of the $K_{iprotein}$ values (Schwarzenbach *et al.*, 2003).

$$K_{ilipid} = 3.2 \times K_{iow}^{0.91} \quad (5)$$

$$\log K_{iprotein} = 0.7 \times \log K_{iow} \quad (6)$$

RESULTS AND DISCUSSION

Fates of the VOCs in the Wastewater Treatment Processes

Table 2 lists the concentrations of benzene, toluene, and xylenes measured in the air, water, and sludge phases of the lab-scale bioreactor experiments simulating three different scenarios (biological treatment with aeration, biological treatment without aeration, and aeration only) in three simulated treatment technologies (primary sedimentation, activated sludge treatment, secondary sedimentation) from the lab-scale experiment. The concentrations of these VOCs in the sludge phase were not available as the water was aerated without the presence of activated sludge,

Table 2. Concentrations of the VOCs analyzed in the lab-scale bioreactor experiment simulating three different wastewater treatment scenarios.

Time (hr)	Benzene			Toluene			Xylenes		
	Water	Sludge	Air	Water	Sludge	Air	Water	Sludge	Air
				Aeration and biological Treatment					
1	22.72	4.15	1.87	21.18	3.81	1.48	25.82	8.45	1.49
2	46.89	6.36	1.28	1.42	5.14	0.97	4.77	11.43	0.78
3	23.88	19.35	1.30	1.86	9.07	1.24	2.91	3.37	0.51
4	12.02	6.25	0.93	1.24	0.78	0.95	1.30	0.91	ND
5	3.05	4.73	0.87	0.62	0.52	0.88	0.62	ND	ND
6	0.92	0.49	0.86	0.55	0.19	0.80	0.59	ND	ND
7	ND	0.16	0.82	0.18	ND	0.73	ND	ND	ND
8	ND	ND	0.74	ND	ND	0.58	ND	ND	ND
9	ND	ND	0.68	ND	ND	0.52	ND	ND	ND
10	ND	ND	0.64	ND	ND	0.41	ND	ND	ND
11	1.88	1.50	1.07	0.89	0.46	1.09	1.25	1.61	0.45
12	1.55	0.16	1.03	0.54	0.19	1.20	ND	ND	0.38
Time (hr)				Biological treatment without aeration					
1	26.29	2.60	ND	26.28	1.98	ND	33.74	5.14	ND
2	26.05	2.79	ND	25.89	2.60	ND	33.37	5.89	ND
3	25.44	12.27	ND	25.57	5.27	ND	33.19	2.11	ND
4	24.97	4.03	ND	25.18	0.50	ND	32.70	0.55	ND
5	24.66	3.22	ND	24.89	ND	ND	32.17	ND	ND
6	24.37	0.34	ND	24.59	ND	ND	31.87	ND	ND
7	24.05	0.08	ND	24.05	ND	ND	31.48	ND	ND
8	23.59	ND	ND	23.76	ND	ND	31.14	ND	ND
9	23.24	ND	ND	23.34	ND	ND	30.74	ND	ND
10	22.77	ND	ND	23.00	ND	ND	30.40	ND	ND
11	22.21	0.81	ND	22.73	0.26	ND	30.15	1.36	ND
12	21.79	0.68	ND	22.19	ND	ND	29.65	ND	ND
Time (hr)				Aeration without biological treatment					
1	26.13	ND	2.13	26.72	ND	1.34	34.36	ND	1.46
2	25.89	ND	1.80	26.29	ND	1.21	33.84	ND	0.90
3	25.48	ND	1.40	25.96	ND	1.29	33.42	ND	0.75
4	24.87	ND	1.30	25.50	ND	1.08	32.80	ND	ND
5	24.67	ND	1.13	25.31	ND	0.92	32.36	ND	ND
6	24.39	ND	0.85	25.03	ND	0.79	31.87	ND	ND
7	24.06	ND	0.80	24.47	ND	0.75	31.51	ND	ND
8	23.50	ND	0.70	24.08	ND	0.69	31.17	ND	ND
9	23.14	ND	0.56	23.58	ND	0.60	30.71	ND	ND
10	22.68	ND	0.77	22.99	ND	0.52	30.40	ND	ND
11	22.14	ND	1.09	22.68	ND	0.85	30.15	ND	0.61
12	21.52	ND	1.15	22.06	ND	4.25	29.87	ND	0.49

The units of the concentrations in the air, water, and sludge phases are 10^{-3} mg/L, mg/L, and mg/L, respectively.

whereas the gas-phase concentrations of the VOCs were not measured when the water was treated by biological treatment without aeration.

It is noteworthy that a higher benzene concentration in the liquid phase of the bioreactor with both aeration and biological treatment was observed. When the sludge was collected from the aerobic activated sludge treatment process of the WWTP and added into the bioreactor, appreciable levels of benzene may have been present. The amount of benzene contained in the sludge may transfer into the relatively less saturated water at the beginning of the experiment before aeration, increasing its water-phase concentration. However, as aeration began, the benzene

concentrations in the water and sludge were decreased and increased, respectively, possibly attributed to the enhanced activity of the sludge by aeration. These concentration profiles were further applied to calculate the respective chemical activities of these VOCs in three phases under three different scenarios and to determine their fates through the wastewater treatment processes.

Fig. 2(a) shows the estimated chemical activities of benzene in the air and sludge phases assuming that the chemical activity of benzene in the water phase was equal to 1 and only two interfaces between air and water as well as between water and sludge were present in this multimedia system. Since the chemical activity represents the proportion

of the concentration to whatever concentration would be expected at equilibrium with the reference state, a chemical activity ratio of benzene in the air or sludge phases below 1 indicated that benzene was less saturated in the air or sludge phase comparing to its reference state (the water phase), and thus was more likely to transfer from the water to air or sludge phases. On the other hand, a chemical activity ratio greater than 1 suggested the potential of benzene transferring from the air or sludge to water phases. The transferring potential is greater as the chemical activity difference between two phases becomes larger.

As shown in Fig. 2(a), before aeration begun (in the first 2 hours), the chemical activities of benzene between the water and air phases implied the potential of benzene transferring from water to air, as expected, probably related to the high concentration of benzene in the raw influent. Limited potential of benzene transferring from sludge to water was observed. The activated sludge used in the experiment was collected from the WWTP and it was possible that recognizable fractions of VOCs such as benzene had been absorbed, giving transferring potential of the VOCs from sludge to water. As aeration started (from the 3rd hour), a significant drop of transferring potential from water to air was noticed. This was unexpected as in our early study the emission rates of VOCs predicted in the aerobic biological treatment process of the WWTP were higher than those in the primary sedimentation (Fig. 3) (Yang *et al.*, 2012). The possible explanation was that despite aeration enhanced the emission of VOCs such as benzene from water to air reducing the water-phase concentration, but also indirectly reduced the gas-phase concentrations of VOCs by mixing and dilution with fresh air. In addition, the discrepancy between the changes of emission rates and chemical activities might suggest a stronger influence of aeration on reducing the concentration in the water phase than the gas-phase concentration. As aeration continued, the water-phase concentration of benzene became low enough

and the transfer of benzene between the air and water phases was reversed and became from air to water (the 5th hour in Fig. 2(a)). Without aeration in the last 2 hours of the experiment, the transfer of benzene from water to air was observed again. Between the phases of water and sludge, the transfer of benzene was from sludge to water through the experiment, pointing out that the transfer of benzene between water and sludge was not affected by aeration and biosorption/biodegradation was not likely to be the important mechanism for benzene removal in this bioreactor or in WWTPs.

Effects of the VOC Species

Figs. 2(b) and 2(c) showed the estimated chemical activities of toluene and xylene in the air and sludge phases assuming that their chemical activities in the water phase were equal to 1, as similar as discussed above for benzene. Strong potentials of transferring from sludge to water and from water to air were noted for all three VOCs in the simulated primary sedimentation. The trends of chemical activity ratios of the VOCs between water and sludge phases (starting from the 3rd hour in Fig. 2(a) through 2(c)) showed that the effect of aeration on the transfers of the VOCs between the air and water phases varied by species. This effect increased in the order of benzene > toluene > xylenes, as the employment of aeration did not significantly change the transfer of xylenes through the experiment (Fig. 2(c)). The differences of Henry's law coefficients amongst these species (Table 1), mainly caused by the existence and number of methylene group in the chemical structure (Schwarzenbach *et al.*, 2003), may be the explanation. With a smaller Henry's law coefficient (i.e., benzene in this case), aeration may pose a stronger effect on the water-phase concentration of the compound than its air-phase concentration, subsequently reducing the potential of transferring from water to air and changing the fate of the compounds between the air and water phases (Fig. 2(a)).
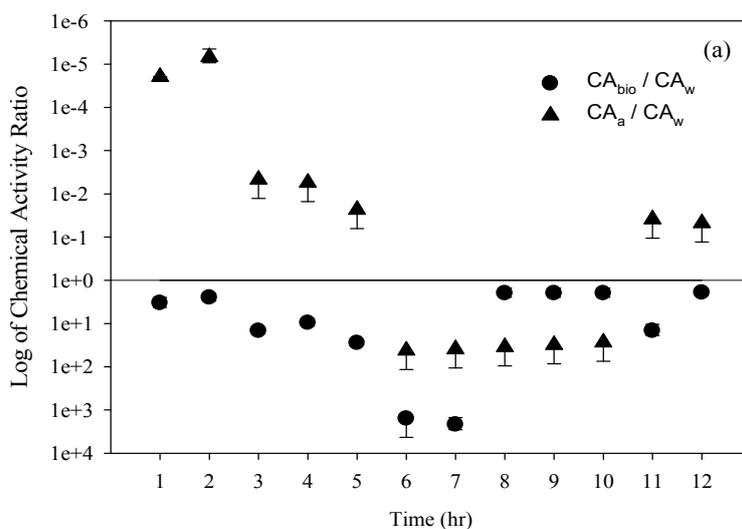
Fig. 2. Estimated chemical activities (CAs) of (a) benzene, (b) toluene, and (c) xylenes in the phases of air, water, and activated sludge under the scenario considering both biological treatment and aeration, assuming the chemical activities was equal to 1 (the straight line).
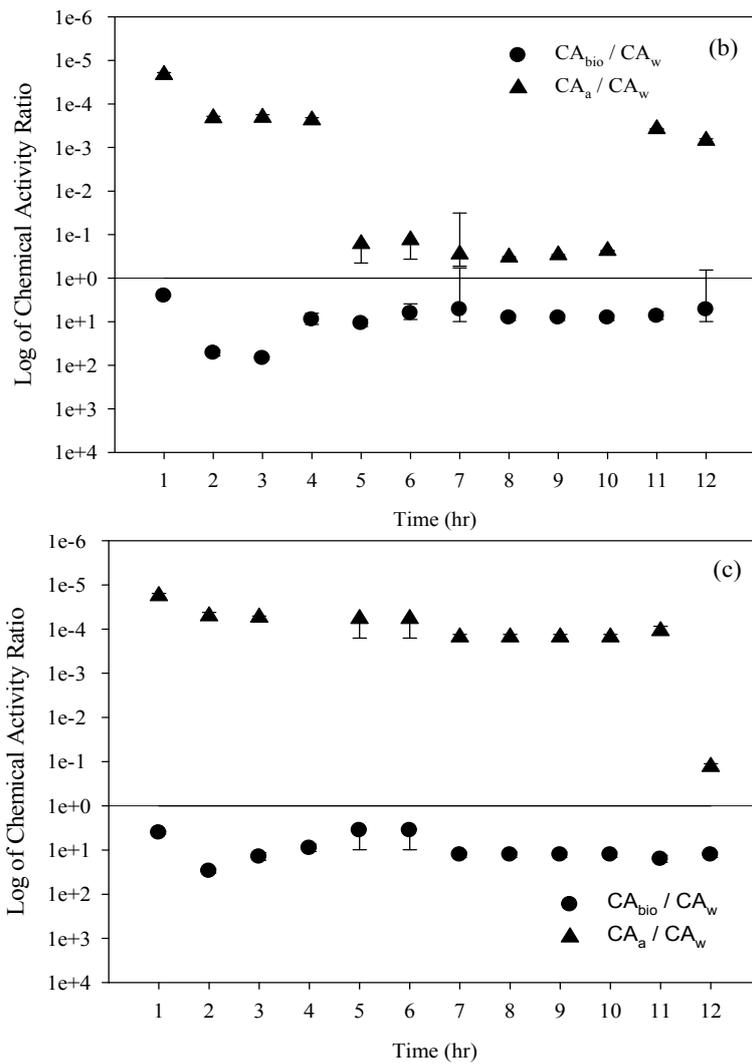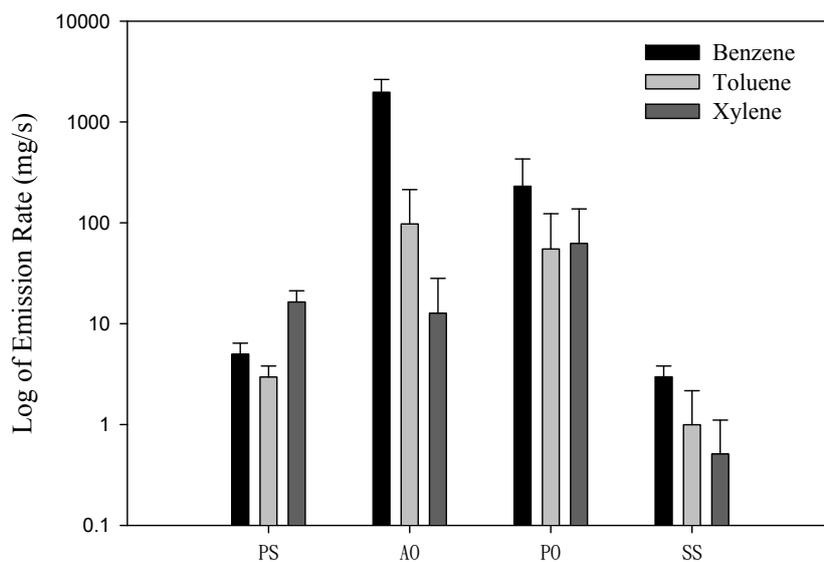
Fig. 2. *(continued).*

Fig. 3. Estimated emission rates of benzene, toluene, and xylenes in the selected treatment technologies of the WWTPs targeted in this study (Yang *et al.*, 2012). PS, AO, PO, and SS represent primary sedimentation, anterior and posterior aerobic sludge treatment processes, and secondary sedimentation, respectively.

Similar transferring potentials of benzene, toluene, and xylenes from activated sludge to water with limited differences were noted through the experiment (Fig. 2(a) through 2(c)). Although aeration might pose a stronger effect on the water-phase concentration of the compounds with relatively low Henry's law coefficients, the reduction of the water-phase concentration by aeration in these experiments did not significantly change the directions and potentials of the transfers of the VOCs between water and activated sludge. The slight increase of transferring potential of benzene from activated sludge to water (a smaller chemical activity ratio of sludge to the water phase starting at the 3rd hours) might result by the reducing water-phase concentration of benzene due to aeration, as described above.

Individual Effect of Biological Treatment

Fig. 4(a) through 4(c) present the experimental results of benzene, toluene, and xylenes under the scenario applying aeration without adding activated sludge into the bioreactor, respectively. Despite only the VOC concentrations in the air and water phases were analyzed, the concentration

variation of the VOCs in the air and water phases provided valuable information to understand the impact of biological treatment on the fates of the VOCs in wastewater treatment processes given that the bioreactor was a closed system with mass balance. The comparisons of Figs. 2(a) and 4(a) with Figs. 2(b) and 4(b), respectively, indicated that the biological treatment had a negligible effect on the transfers of benzene and toluene from water to air. However, the presence of activated sludge in the bioreactor significantly changed the transfer of xylenes between water and activated sludge (the comparison of Fig. 2(c) with Fig. 4(c)). Possibly attributed to the relatively higher K_{OW} value of xylenes (Table 1), the presence of activated sludge might enhance the biosorption and biodegradation of xylenes more significantly, reducing the water-phase concentration and reversing the direction of the transfer of xylenes (from water to air in Fig. 2(c) to from air to water in Fig. 4(c)).

Individual Effect of Aeration

The individual effect of aeration was studied by comparing the results shown in Fig. 2(a) through 2(c) with
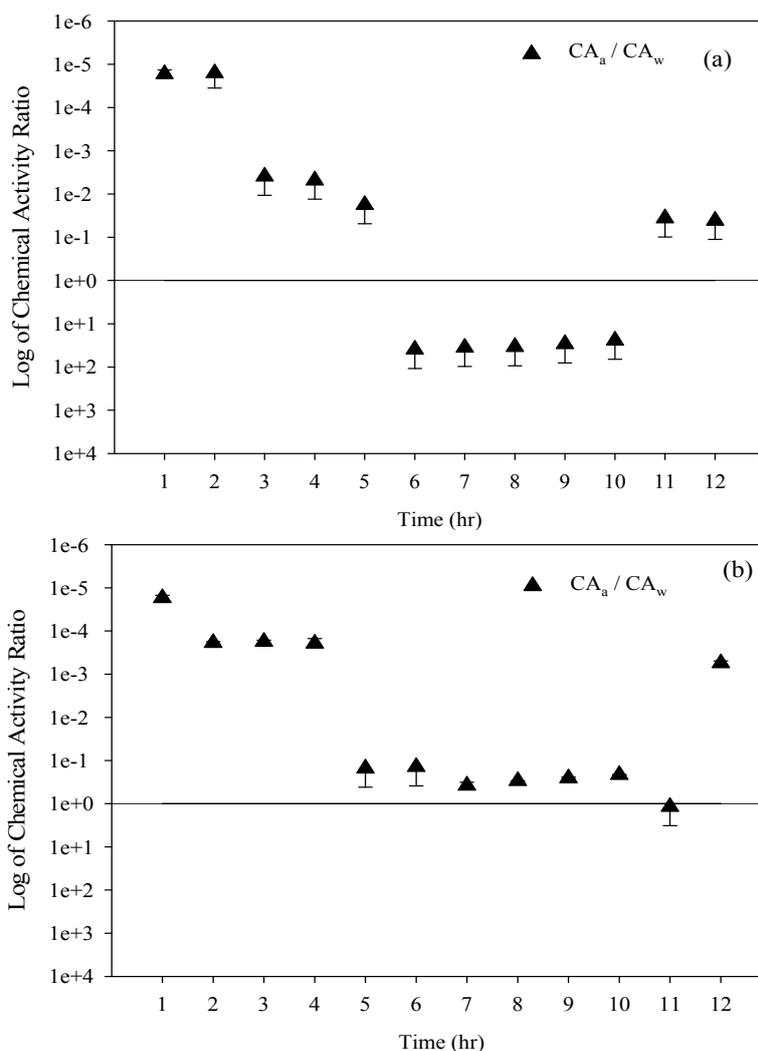
Fig. 4. Estimated chemical activities (CAs) of (a) benzene, (b) toluene, and (c) xylenes in the phases of air and water under the scenario considering aeration only, assuming the chemical activities was equal to 1 (the straight line).
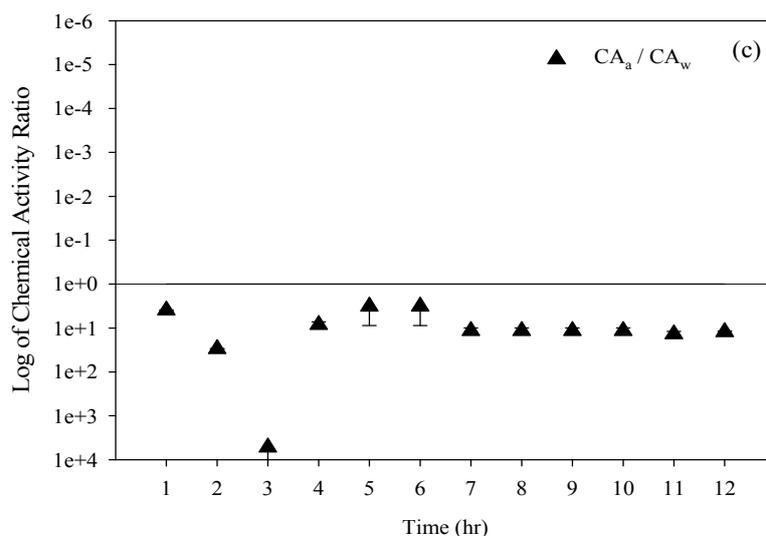
Fig. 4. *(continued).*

those in Fig. 5(a) through 5(c) for benzene, toluene, and xylenes, respectively. Interestingly, the influence of aeration on reducing the transferring potential of benzene from activated sludge to water was observed (smaller transferring potentials from sludge to air in Fig. 2(a) compared with those in Fig. 5(a) through the experiment), while the effect on those of toluene and xylenes were rather limited. It was possible in the case of benzene that the impact of aeration was stronger on reducing the water-phase concentration than on the sludge-phase concentration, potentially due to its lower K_{OW} value and thus decreasing the transferring potential from sludge to water. The effect of aeration appeared to be more difficult to predict with it simultaneously enhancing volatilization and biosorption/biodegradation by increasing the emission rates and the activity of sludge in the reactor, respectively.

Beside the influences of aeration and Henry's law coefficients affecting the transfer of a VOC between water and air as mentioned previously, biosorption and biodegradation depending on the K_{OW} value and biodegradability (i.e., due to the number of methylene groups in the chemical structure among benzene, toluene, and xylenes (Schwarzenbach *et al.,* 2003)) of the VOC are other important factors to determine the sludge-phase concentration of the substance. All these factors including aeration, biological treatment, the values of Henry's law coefficient and K_{OW} formed a complex system concurrently affecting the direction and potential of the transfer of a VOC amongst the phases of air, water and activated sludge. Table 3 was developed by dealing with the results and information acquired from this study to illustrate the relationship amongst these factors. Overall, according to the physicochemical properties of the VOC of concern, such as the Henry's law coefficients and K_{OW} values, the aeration effect on the concentrations of the VOC in air, water, and activated sludge may vary, eventually changing the fate of the VOC in the wastewater treatment processes.
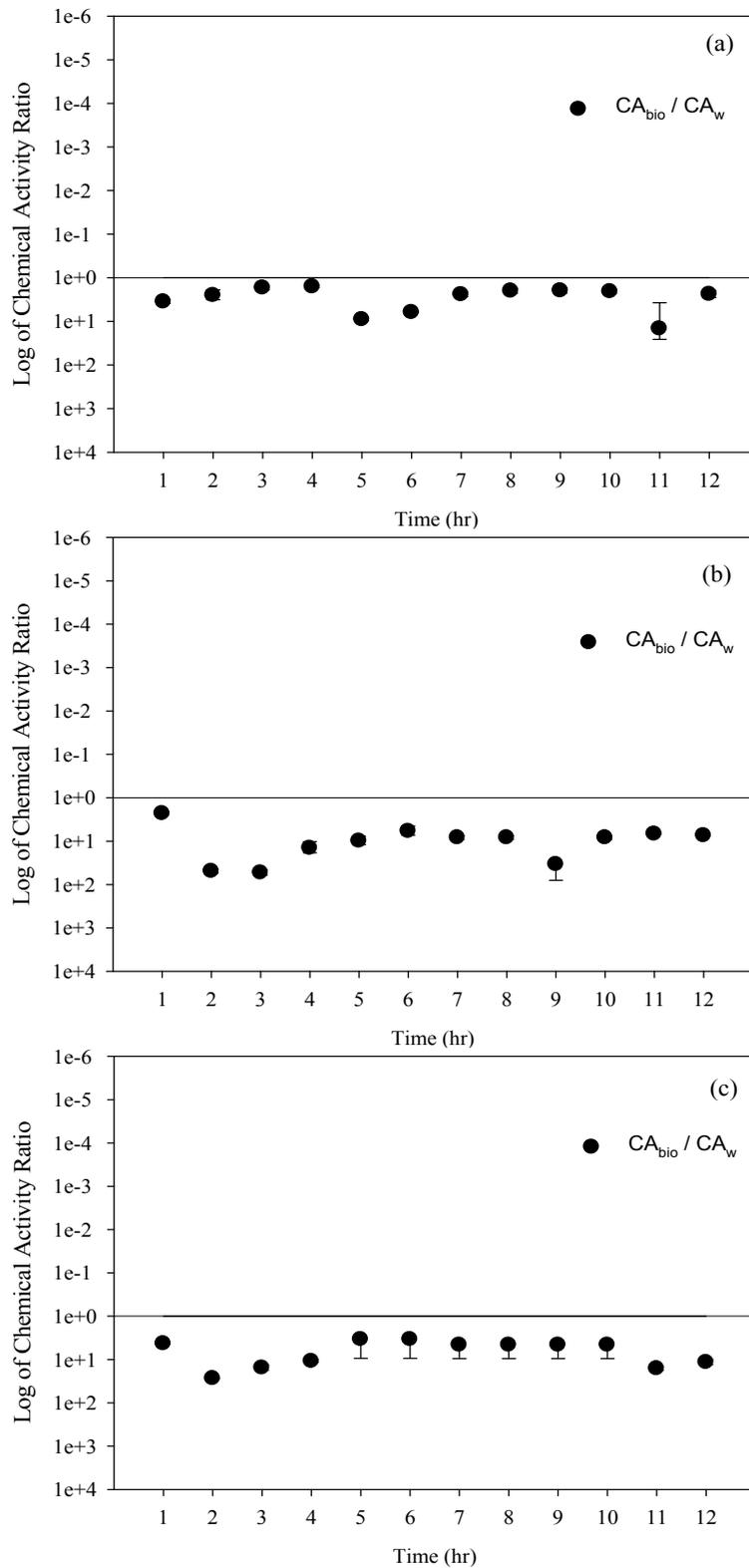
CONCLUSIONS

In this study, a lab-scale bioreactor experiment was conducted to investigate the potential fates of three aromatic hydrocarbons (benzene, toluene, and xylenes) in wastewater treatment processes including primary sedimentation, aerobic biological treatment, and secondary sedimentation. The concentrations of the VOCs in the phases of air, water, and activated sludge were analyzed to determine the respective chemical activities and to predict the possible transfers of the VOCs among the three phases. The differences amongst the species, together with the effects of aeration and the presence of activated sludge were examined. The results suggested the following main conclusions. First, given appreciable levels of the VOCs being absorbed from the WWTPs and their volatility, the directions of the transfers of the VOCs were from activated sludge to water and from water to air, indicating the importance of volatilization for the fates of the VOCs in this reactor. Second, the presence of activated sludge in the bioreactor posed a positive effect on the transfers of the VOCs from air to water and from water to sludge, particularly for those VOCs with large K_{OW} values. Last, the effect of aeration on the fates of the VOCs was complex, simultaneously being affected by factors including the Henry's law coefficients and K_{OW} values of the VOCs and the presence of activated sludge in the system. For the VOCs with large Henry's law coefficients and small K_{OW} values, aeration might reduce the concentration of the VOCs in the air and water phases more significantly, resulting in positive and negative impacts on volatilization and biosorption/biodegradation of the VOCs in WWTPs, respectively, as unexpected for the design of the WWTPs for VOC removal.

Fig. 5. Estimated chemical activities (CAs) of (a) benzene, (b) toluene, and (c) xylenes in the phases of air and water under the scenario considering biological treatment without aeration, assuming the chemical activities was equal to 1 (the straight line).

Table 3. Summary of the effect of aeration on the fates of VOCs in the phases of air, water, and activated sludge given the Henry's law coefficient (K_H) and octanol-water partition coefficient (K_{OW}).

	Physicochemical properties of the substance			
	K_H		K_{OW}	
	Low[1,2]	High[1,3]	Low[1,4]	High[1,5]
Phase	Effect of aeration on reducing the selected-phase concentration of the substance			
Air	Weak	Strong	-	-
Water	Strong	Weak	Strong	Weak
Activated Sludge	-	-	Weak	Strong
	Positive effect of aeration on the direction of transferring potential			
	From air to water	From water to air	From activated sludge to water	From water to activated sludge

[1] With only three compounds being investigated in this study, the effect of aeration on the fates of the VOCs was described qualitatively rather than quantitatively. However, the numbers of these parameters of the VOCs investigated in this study were given here for readers' references.

[2] Such as benzene in this study, with a Henry's law coefficient of 5.5×10^{-3} atm-m^3/mol.

[3] Such as xylenes in this study, with a Henry's law coefficients ranging from 5.18×10^{-3} to 7.18×10^{-3} atm-m^3/mol.

[4] Such as benzene in this study, with an octanol-water partition coefficient of 2.13.

[5] Such as toluene and xylenes in this study, with octanol-water partition coefficients ranging from 2.72 to 3.2.

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