Factors Effecting the Volatilization of Volatile Organic Compounds from Wastewater

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Abstract

This study was aim to understand the influence of the wind speed (U_{10cm}), the water depth (h) and the suspended solid (SS) on mass transfer coefficient ($K_{OL}a$) of volatile organic compounds (VOCs) which volatilized from wastewater. The novelty of this work is not the method used to determine $K_{OL}a$ but rather a use of actual wastewater instead of pure water as previous reported. The influence of U_{10cm}, h, and SS on $K_{OL}a$ was performed using volatilization tank with the volume of 100-350 L. Methyl Ethyl Ketone (MEK) is selected as a representative of VOCs investigated here in.

The results revealed that the relationship between $K_{OL}a$ and the wind speeds falls into two regimes with a break at the wind speed of 2.4 m/s. At $U_{10cm} \leq 2.4$ m/s, $K_{OL}a$ was slightly increased linearly with increasing U_{10cm}. For $U_{10cm} > 2.4$ m/s, $K_{OL}a$ increased more rapidly. The relationship between $K_{OL}a$ and U_{10cm} was also linear but has a distinctly higher slope. For the $K_{OL}a$ dependency on water depth, the $K_{OL}a$ were decreased significantly with increasing water depth up to certain water depth after that increasing in water depth has small effect on $K_{OL}a$. The suspended solid in wastewater also play an important role on $K_{OL}a$, increased SS resulting in a significant reduction of $K_{OL}a$ over investigated range of SS. Finally, the comparison between $K_{OL}a$ obtained from wastewater and that of pure water revealed that $K_{OL}a$ from wastewater were much lower than that of pure water which pronounces at high wind speed and at small water depth. This was due the presence of organic mass in wastewater which provided the barrier to mass transfer and reduced the degree of turbulence in water body resulting in low volatilization rate and thus $K_{OL}a$. From these results, the mass transfer model for predicting VOCs emission from wastewater is then recommended to develop from volatilization of VOCs from wastewater rather than those from pure water. The mass transfer coefficient models based on volatilization of VOCs from wastewater are being developed in our research group.

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บทคัดย่อ

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ปัจจัยที่มีผลต่อการระเหยของสารอินทรีย์ระเหยจากน้ำเสีย

การศึกษานี้มีวัตถุประสงค์เพื่อทำความเข้าใจถึงอิทธิพลของความเร็วลม (U_{10cm}) ความลึกของน้ำ (h) และของแข็งแขวนลอย (SS) ต่อสัมประสิทธิ์การถ่ายโอนมวลรวม ($K_{OL}a$) ของสารอินทรีย์ระเหย (VOCs) ที่ระเหยจากน้ำเสีย ความใหม่ของงานวิจัยนี้ไม่ได้อยู่ที่วิธีการหาค่า $K_{OL}a$ หรือการหาความสัมพันธ์ระหว่าง $K_{OL}a$ กับตัวแปรต่างๆข้างต้น แต่อยู่ที่การศึกษาโดยใช้น้ำเสียจริงแทนการใช้น้ำบริสุทธิ์ดังเช่นในงานวิจัยที่มีรายงานไว้ก่อนหน้านี้ การศึกษาอิทธิพลของ U_{10cm}, h, และ SS ต่อ $K_{OL}a$ ดำเนินการในถังระเหยขนาด100-350 L สารอินทรีย์ระเหยที่เลือกศึกษาคือ เมทิลเอทิล คีโตน (Methyl Ethyl Ketone, MEK)

ผลการศึกษาพบว่าความสัมพันธ์ระหว่าง $K_{OL}a$ กับ U_{10cm} แบ่งออกเป็นสองช่วงโดยมีจุดเปลี่ยนที่ U_{10cm} เท่ากับ 2.4 m s^{-1} ที่ $U_{10cm} \leq 2.4$ m s^{-1} $K_{OL}a$ เพิ่มขึ้นอย่างช้าๆแบบเชิงเส้นกับความเร็วลมที่เพิ่มขึ้น ที่ $U_{10cm} > 2.4$ m s^{-1} $K_{OL}a$ เพิ่มขึ้นอย่างรวดเร็ว ความสัมพันธ์ระหว่าง $K_{OL}a$ กับ U_{10cm} ยังคงเป็นแบบเชิงเส้นแต่มีความชันสูงกว่ามาก ผลการศึกษาอิทธิพลของความลึกของน้ำต่อ $K_{OL}a$ พบว่า $K_{OL}a$ ลดลงกับความลึกที่เพิ่มขึ้นจนถึงความลึกค่าหนึ่งจากนั้นพบว่าการเพิ่มขึ้นของความลึกมีผลต่อ $K_{OL}a$ น้อย ส่วนผลของ SS ต่อ $K_{OL}a$ พบว่าการเพิ่มของ SS มีผลทำให้ $K_{OL}a$ ลดลงอย่างมีนัยสำคัญตลอดช่วงของ SS ที่ศึกษา สุดท้ายจากการเปรียบเทียบระหว่าง $K_{OL}a$ ที่ได้จากการระเหยของ MEK จากน้ำเสียและจากน้ำบริสุทธิ์ พบว่า $K_{OL}a$ ที่ได้จากน้ำเสียมีค่าต่ำกว่าค่าที่ได้จากน้ำบริสุทธิ์มากโดยความแตกต่างนี้มีสาเหตุหลักมาจากสารอินทรีย์ที่แขวนลอยอยู่ในน้ำเสียซึ่งสามารถกีดกันการถ่ายโอนมวลและลดความปั่นป่วนในน้ำทำให้อัตราการระเหยและ $K_{OL}a$ ในกรณีของน้ำเสียต่ำกว่ากรณีของน้ำบริสุทธิ์มาก ดังนั้นแบบจำลองสำหรับทำนายการระเหยของ VOCs จากน้ำเสียควรพัฒนาจากข้อมูลการระเหยของVOCsจากน้ำเสียจริงมากกว่าการใช้ข้อมูลการระเหยของ VOCs จากน้ำบริสุทธิ์ แบบจำลองของสัมประสิทธิ์การถ่ายโอนมวลของ VOCs ที่ใช้ข้อมูลการระเหยของ VOCs จากน้ำเสียจริงกำลังดำเนินการพัฒนาในกลุ่มวิจัยนี้

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1. INTRODUCTION

Volatile organic compounds (VOCs) are present in municipal wastewater due to discharges from domestic, commercial and industrial source. Volatilization, biodegradation and sorption are main process affecting VOCs fate in wastewater treatment plants. VOCs volatilization has found to prevail in both primary and secondary clarifier in wastewater treatment plant (Corsi et al.,1991). Although, the VOCs emission fluxes from wastewater treatment plants can be measured using flux chamber, the estimating of VOC emissions using mass transfer model is prefer. Existing mass transfer models used for estimating VOC emissions from wastewater, however, are developed based on the volatilization of VOCs from pure water (Mackay and Yeun, 1983; Lunney et al., 1985; Bunyakan et al., 2001). Moreover, most of the existing model included only the effect of the wind speed above water surface and water temperature. These parameters did not relate to any dimension of wastewater basin such as length, width and depth of water basin which theoretically known to influence mass transfer rate in other systems.

The objective of this study was to understand the roles of the wind speed above water surface, the water depth and the suspended solid on mass transfer coefficient of MEK that allowed for the determination of these effects on VOCs volatilization rate from wastewater. The novelty of this work is not the method used to determine the mass transfer coefficient but rather a use of wastewater instead of pure water as previously investigated by other researchers (Mackay and Yeun, 1983; Lunney et al., 1985; Bunyakan et al., 2001). The comparison between the mass transfer coefficients obtained from VOCs volatilized from wastewater and those from pure water revealed that the mass transfer coefficients of VOCs from wastewater were significantly lower than that of pure water.

2. METHODS AND MATERIALS

2.1 Materials

Wastewater was taken from wastewater treatment facility at the Prince of Songkla University Hat Yai Songkhla Thailand. The characteristic of wastewater is shown in table

Table 1 Wastewater characteristic

Properties	mg/l
BOD$_5$	45-98
COD	2320-2960
Suspended solids (SS)	27-62

MEK is selected as VOCs representative in this study since the volatilization of MEK from water is governed by both gas and liquid film. Another word, the volatilization rate of MEK from water is between that of VOCs which the volatilization rate is controlled by gas film and liquid film, respectively. MEK (99.5%, Merck) is used in the experiments without any further purification.

2.2 Analysis

The liquid samples were analyzed using a gas chromatography (GC). The GC (Model HP9806, Hewlett Packard), equipped with a capillary column, a flame ionization detector and an integrator (Model 9860), was operated at an injection temperature of 180 $^\circ$C, a detector temperature of 200 $^\circ$C and an oven temperature of 50 $^\circ$C. The GC column was a (HP-FAAP, Polyethylene glycol-TPA modified, Hewlett Packard), 30 m capillary glass column with an inside diameter of 0.25 mm. Helium was used as a carrier gas at a flow rate of 0.2 mL/min. This analytical system gave excellent resolution for MEK.

2.3 Volatilization experiment

The experiments for unsteady state volatilization of MEK from wastewater were conducted in the pilot volatilization tank. The experimental set-up is comprised of two main pieces of equipments; the volatilization tank (50 cm wide, 100 cm long, and 5-70 cm deep) and the wind generated system, as shown in figure 1.

2.3.1 Solution preparation

Prior to starting an experiment, the wastewater and the pure water contained MEK was prepared by dissolving MEK in wastewater or water to the desired concentration. The volumes of the wastewater and water were varied from 25 to 350 L which depended on water depth, varying from 5-70 cm.
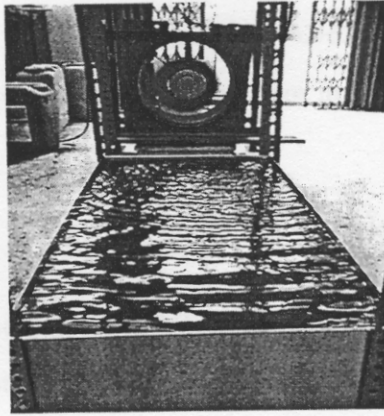
Figure 1. Pilot volatilization tank equipped with a wind generated system

2.3.2 Effect of the wind speed

The unsteady state volatilizations of MEK from wastewater and water were investigated at various wind speed. The wind speed was generated by a fan mounted just above water surface at the end of the volatilization tank (see figure 1). The speed of the fan was controlled by an inverter (Novem Inverters NSP series, Novem Engineering). The wind speeds were measured by using air velocity meter (Model TRI-Sense, Cole-Parmer Instrument Co.) at 10 cm above water surface for 15 positions across the water surface. The average value from 15 data points was then used as the average wind speeds at 10 cm (U_{10cm}) for each run. The U_{10cm} in the range of 0-4.42 m/s were used in this investigation. The water temperature, air temperature and relative humidity were monitored for all experiments using humidity/temperature meter (Model TRI-Sense, Cole-Parmer Instrument Co.) and they were 29±1 °C, 31±1 °C and 70-80%, respectively. The BOD$_5$, COD and SS of wastewater used in this study were 50-98 mg/L, 2320-2960 mg/L and 27-38 mg/L, respectively. The water depth of 20 cm, corresponding to the water volume of 100 L, was employed. The initial MEK concentrations in wastewater and in water were 600-759 mg/L and 659-756 mg/L, respectively.

2.3.3 Effect of water depth

The unsteady state volatilizations of MEK from wastewater and water were investigated at various water depths. The water depths were varied from 5 to 70 cm, corresponding to water volume varying from 25 to 350 L. To prevent the accumulation of MEK at near water surface, the wind speed over the water surface was kept constant at 2.81 m/s for all experiments. The water

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temperature was at room temperature (29±1 °C). The BOD_5, COD and SS of wastewater used in this study were 45-58 mg/L, 2868-3285 mg/L and 42-62 mg/L, respectively. The initial concentrations of MEK in wastewater and in water were in the same range as those for wind speed investigation.

2.3.4 Effect of Suspended solid

The unsteady state volatilizations of MEK from wastewater were investigated at various suspended solid. The water depths were at 20 cm, corresponding to water volume of 100 L. To prevent the accumulation of MEK at near water surface, the wind speed over the water surface was kept constant at 2.81 m/s for all experiments. The water temperature was at room temperature (29±1 °C). The SS of wastewater were varied from 0 to 40 mg/L. The initial concentrations of MEK in wastewater were between 659 and 1096 mg/L.

2.3.5 Volatilization time and liquid sampling

The volatilization time was 5 hr. During experiment, liquid samples were collected periodically, from the middle of the tank at predetermined depth from water surface depending on total water depth. The sampling periods were 30 and 60 minute in the first hour and every hour for the rest of volatilization time. Each liquid sample was collected in a 20 mL glass vial, capped immediately with a Teflon-lined septum, marked and placed in cooler. Each sample was filtrated and analyzed for MEK concentration. The concentration-time data of each run is used to determine the overall mass transfer coefficient of MEK.

2.3.6 Data analysis

The Overall mass transfer coefficients for MEK volatilization from wastewater and from pure water are determined from concentration-time data using two-film model and mass balance around the volatilization tank. Providing that the concentration of MEK in volatilization tank is uniform, the overall mass transfer coefficient can be obtained from the slope of a plot between $\ln[C_{MEK,L} / C_{MEK,o}]$ as shown by equation (1), which is detailed elsewhere (Bunyakan, et al. 2001)

$$\ln \frac{C_{MEK,L}}{C_{MEK,Lo}} = -\frac{K_{OL}a}{V}t \qquad (1)$$

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where $K_{OL}a$ = overall mass transfer coefficient of MEK, m³/s

$C_{MEK,L}$ = concentration of MEK in liquid phase at any time t , mol/m³

$C_{MEK,Lo}$ = concentration of MEK in liquid phase at t =0, mol/m³

V = volume of volatilization tank, m³

t = volatilization time, s

3. RESULTS AND DISCUSSION

3.1 The effect of the wind speed on $K_{OL}a$

The volatilization of MEK from wastewater and pure water were investigated at various wind speeds, varied from 0-4.42 m/s where the water depth was constant at 20 cm. In order to determine $K_{OL}a$ the concentration-time data were measured. The typical concentration-time data measured at difference depth from water surface, at the middle of the volatilization tank, for the volatilization of MEK from wastewater and pure water, at U_{10cm} of 2.81, are shown in figure 2. It clearly shown from figure 2 that the volatilization rate of MEK from wastewater was significantly lower than that of pure water as indicated by a lower in slope of concentration-time data. The concentrations of MEK were found uniform over the entire water body with a relative standard deviation (RSD%) less than 10%. Thus the equation (1) can be applied for $K_{OL}a$ determination.

The effect of the wind speed on $K_{OL}a$ for MEK volatilization from wastewater is shown in figure 3. From figure 3, the data show that the relationship between $K_{OL}a$ and U_{10cm} falls into two regimes with a break at the wind speed range of 2.4 m/s. At low wind speed regime, U_{10cm} ≤2.40 m/s, the $K_{OL}a$ of MEK was slightly increased as the wind speed increased. At high wind speed regime, U_{10cm} > 2.40 m/s, the $K_{OL}a$ of MEK was strongly influenced by the wind speed. The relationship between $K_{OL}a$ and the wind speed is linear but has a distinctly higher slope as compared to that of low wind speed regime. The transition of $K_{OL}a$ -U_{10cm} relationship at 2.40 m/s are agree well with the results previously reported by a number of researchers, which usually found at 2-3 m/s (Bunyakan, et al., 2001; Wanninkhof, et al., 1991). The high wind speed, greater than 2.40 m/s, provided a shear stress at air-water surface that is high enough to set the interface and liquid below in motion resulting in high turbulence and the appearance of waves. Consequently, $K_{OL}a$ were increased significantly with increasing wind speed in this regime.
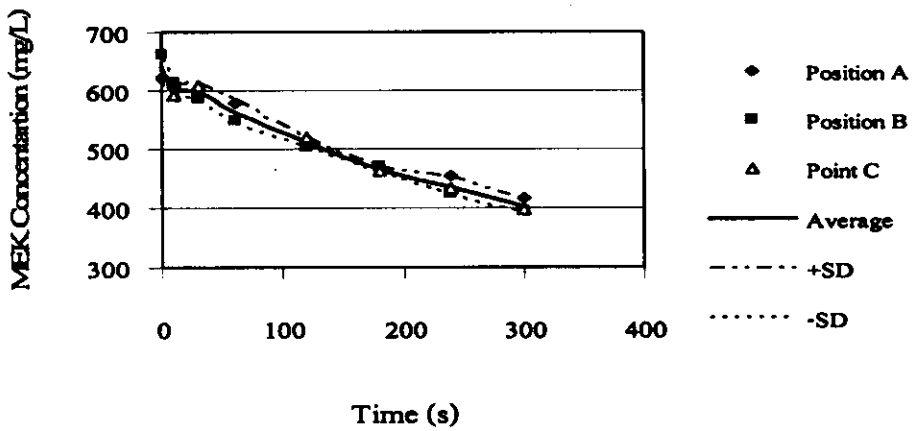
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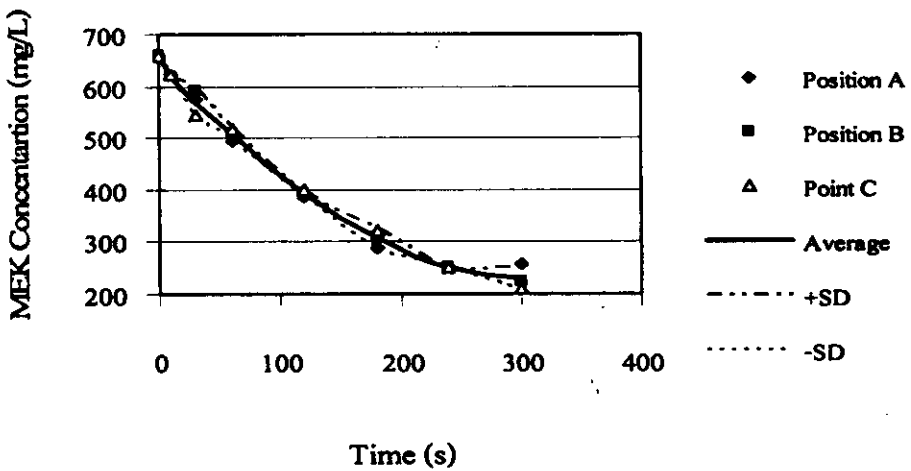
(b)

Figure 2. MEK concentrations as function of time measured at various water depths (Point A, B and C were 15, 10, and 5 cm below water surface, respectively); (a) wastewater and (b) pure water
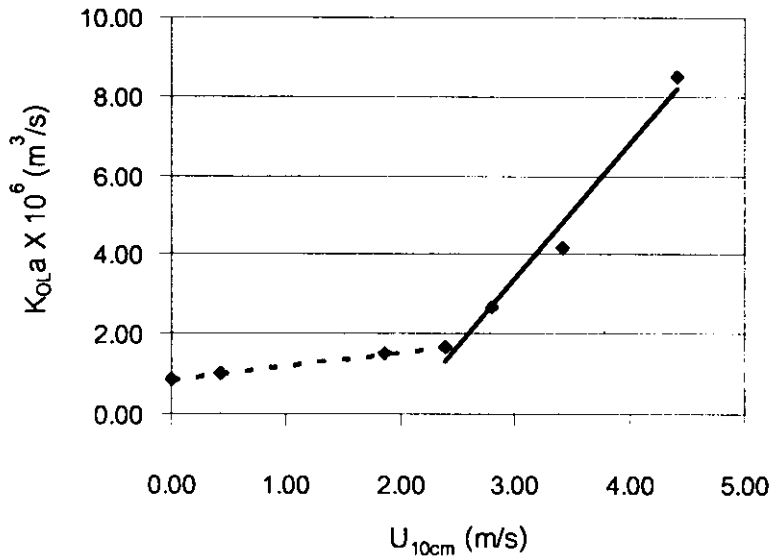
Figure 3. $K_{OL}a$ of MEK as a function of the wind speed ($T_{wastewater}= 29\pm1$ °C, Water depth = 20 cm and wastewater properties: BOD 50-98 mg/L, COD = 2320-2960 mg/L and SS = 27-38 mg/L)

The comparison between $K_{OL}a$ for MEK volatilization from wastewater and from pure water is shown in figure 4. It can be seen that the $K_{OL}a$ of wastewater were lower than those of pure water for all wind speeds. The ratios of $K_{OL}a$ (water) to $K_{OL}a$ (wastewater) are shown as function of U_{10cm} in figure 5. It can be seen from this figure 5 that the ratios of $K_{OL}a$ (water) to $K_{OL}a$ (wastewater) were roughly constant at 1.33 over the low wind speed regime ($U_{10cm} \le 2.40$ m/s). However, at high wind speed regime, $U_{10cm} > 2.40$ m/s, the ratio of $K_{OL}a$ (water) to $K_{OL}a$ (wastewater) were found to increase with increasing wind speed up to the wind speed of 3.4 m/s and then decreased slightly.

This may attributed to the fact that the turbulence in the water body was increased with increasing wind speed. The organic masses suspended in wastewater were acted as both the turbulence suppression medium and as a barrier to mass transfer through diffusion process resulting in a significant reduction of mass transfer as compared to that in pure water. Thus the ratios of $K_{OL}a$ (water) to $K_{OL}a$ (wastewater) were then increased with increasing the wind speed up to the certain wind speed which high enough to overcome the turbulence suppression and barrier effects due to the suspended organic masses then the ratio of $K_{OL}a$ (water) to $K_{OL}a$ (wastewater) were decreased as shown in figure 5.
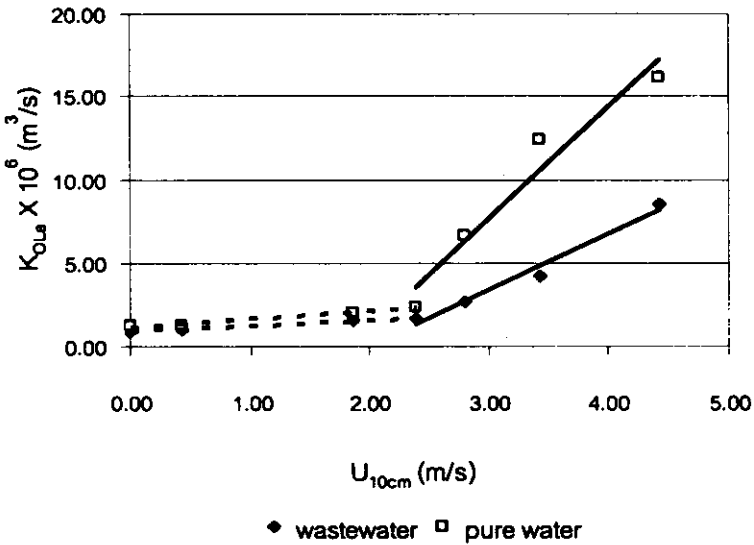
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Figure 4. The comparison between $K_{OL}a$ of MEK volatilization from wastewater (BOD 50-98 mg/L, COD = 2320-2960 mg/L and SS = 27-38 mg/L) and that from pure water at T_{water}= 29±1 °C and a water depth of 20 cm.
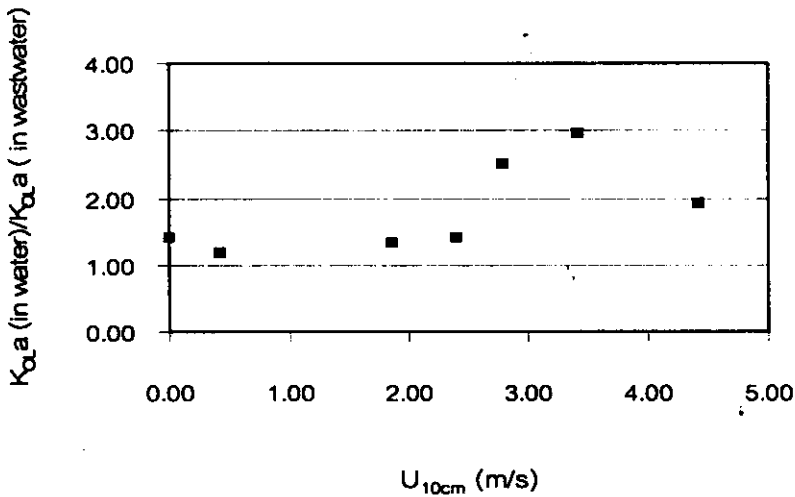

Figure 5. The ratio $K_{OL}a$ (in water)/ $K_{OL}a$ (in wastewater) of MEK as function of the wind speed at T_{water}= 29±1 °C and a water depth of 20 cm.

3.2 The effect of the water depth on volatilization rate of MEK

In the case where the water is fairly deep, the volatilization of VOCs from wastewater due to surface wind speed may depend on the water depth. In this research we have investigated the volatilization of MEK from pure water and wastewater for various water depth varied from 5-

70 cm where the wind speed at water surface was fixed at 2.81 m/s. The MEK concentrations in bulk liquid were measured at various positions along the water depth. The typical concentration-time data for volatilization of MEK from wastewater and pure water at high water depth are illustrated in figure 6 and 7.
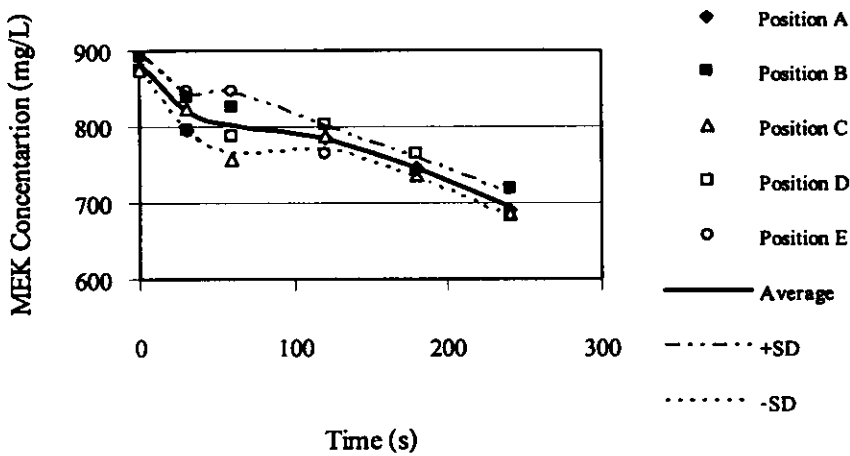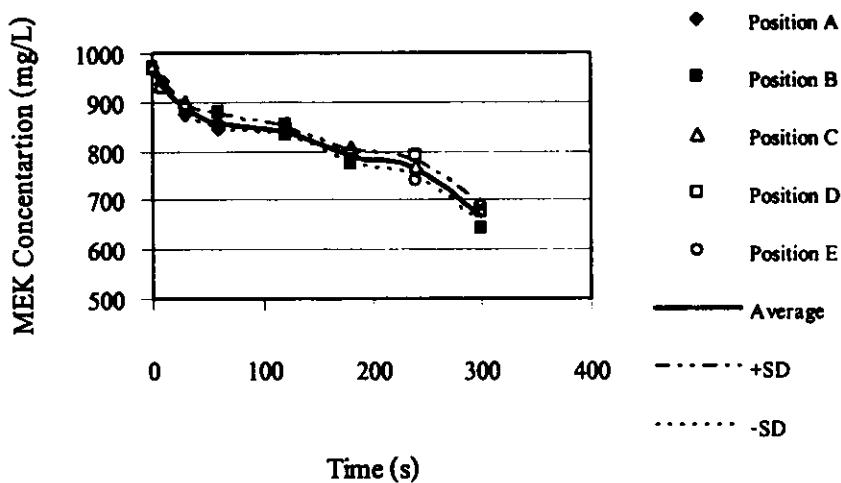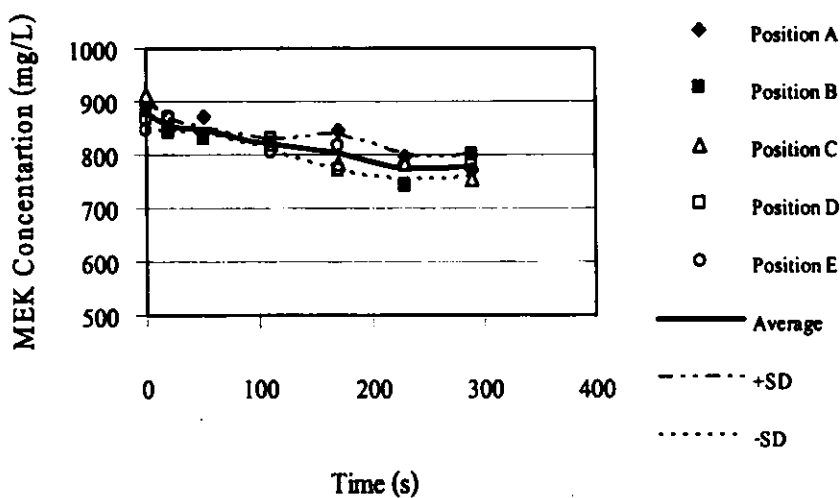

(a)
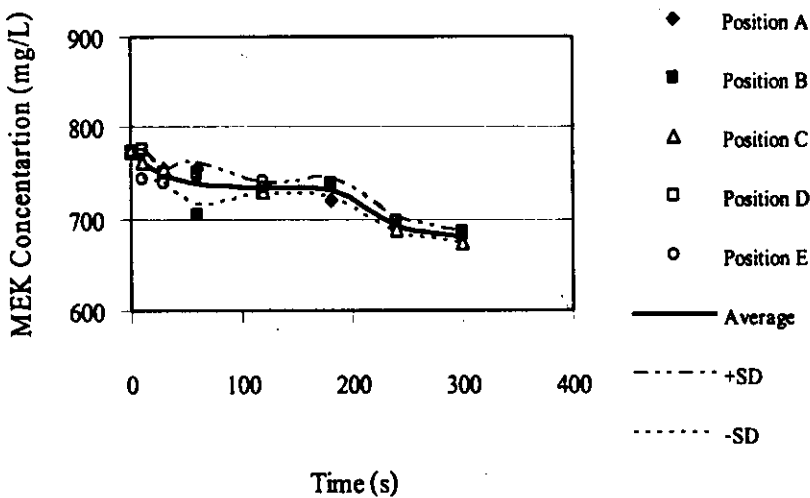
(b)

Figure 6. Typical concentration-time data for volatilization of MEK from wastewater at high water depth

a) Total depth of 40 cm (A = 35 cm ,B = 30 cm, C = 20 cm, D = 10 cm and E = 5 cm below water surface)

b) Total depth of 60 cm (A = 55 cm ,B = 40 cm, C = 30 cm, D = 20 cm and E = 5 cm below water surface)

(a)

(b)

Figure 7. Typical concentration-time data for volatilization of MEK from pure water at high water depth. a).Total depth of 40 cm (A = 35 cm ,B = 30 cm, C = 20 cm, D = 10 cm and E = 5 cm below water surface) b). Total depth of 65 cm (A = 60 cm ,B = 50 cm, C = 35 cm, D = 20 cm and E = 5 cm below water surface)

From figure 6 and figure 7 we can see that the volatilization rate, which is proportional to a slope of concentration-time data, of MEK volatized from wastewater and pure water were found to depend on the water depth. The larger the water depth the smaller the volatilization rate was observed. However, the concentration of MEK even at the largest water depth still can be

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assumed as uniform concentration with a relative standard deviation (RSD%) less than 10% as evidenced in figure 6 and figure 7. Thus the equation (1) can still be applied to determine the $K_{OL}a$ at various water depth that investigated in this work.

3.3 The effect of the water depth on $K_{OL}a$

The effect of the water depth on $K_{OL}a$ for volatilization of MEK from wastewater and from water is shown in figure 8 and figure 9, respectively. It clearly shown from these figures that the $K_{OL}a$ decreased significantly with increasing water depth. Since, at high water depth, the degree of turbulence due to the surface wind is lower than that in lower one, the mass transfer coefficient is then decreased with increasing water depth. The organic masses presented in wastewater suppresses the turbulence and provide a barrier to mass transfer thus $K_{OL}a$ of wastewater is significantly lower than that of pure water, particularly at shallow water as shown in figure 10. However, at water depth greater than the certain value of 30 cm, the degree of turbulence in water body is dominated by the water depth, the $K_{OL}a$ of wastewater and of pure water are then approximately the same as evidenced in figure 10.
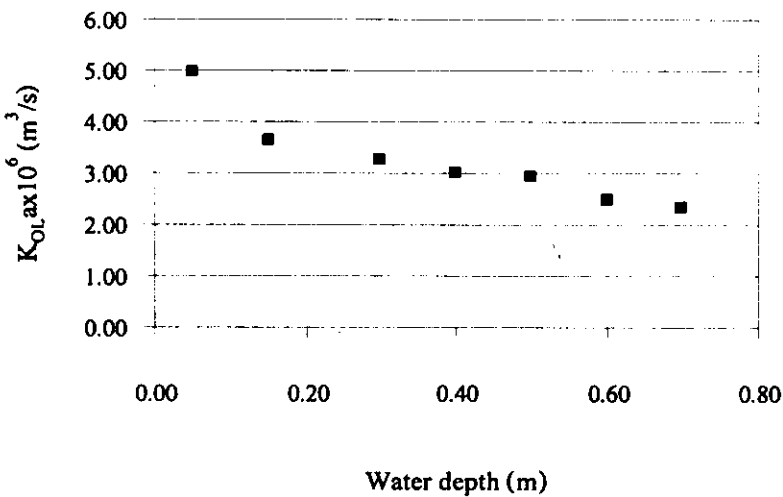

Figure 8. $K_{OL}a$ of MEK as a function of water depth for volatilization of MEK from wastewater at U_{10cm} = 2.81 m/s and $T_{wastewater}$= 29±1 °C. (wastewater properties: BOD 50-98 mg/L, COD = 2320-2960 mg/L and SS = 27-38 mg/L)
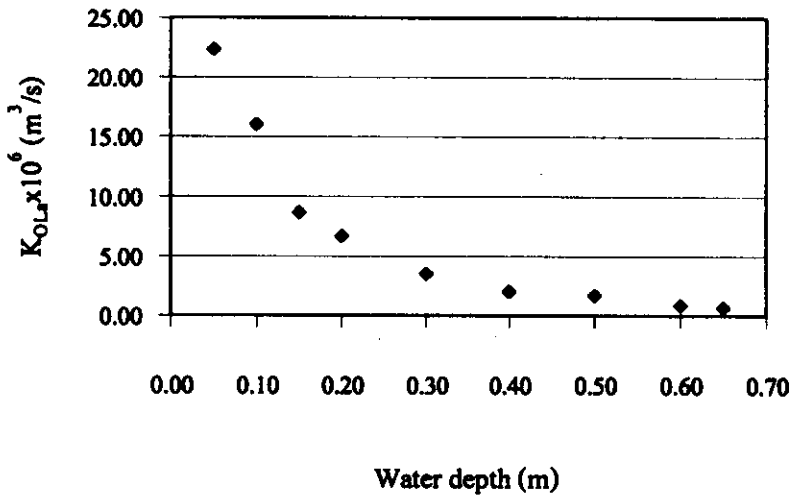
Figure 9. $K_{OL}a$ of MEK as a function of water depth for volatilization of MEK from pure water at $U_{10cm} = 2.81$ m/s and $T_{water} = 29 \pm 1$ °C.
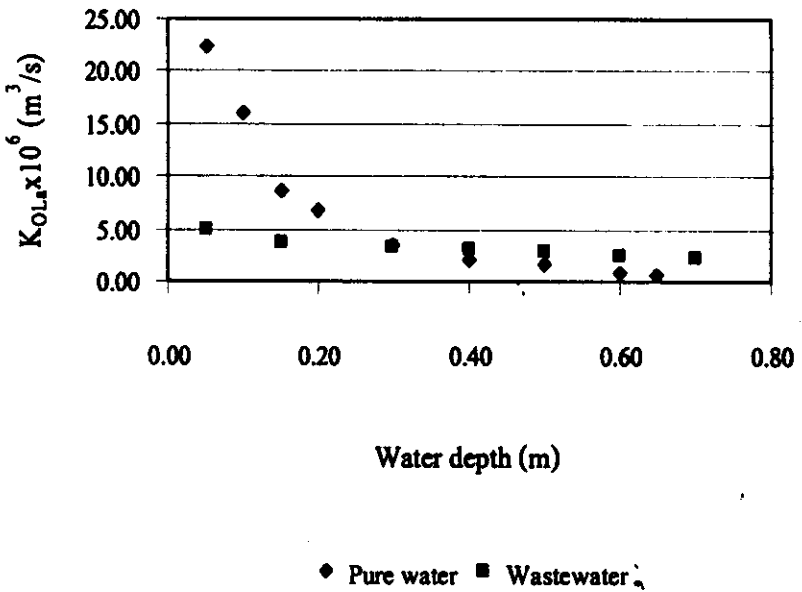

♦ Pure water ■ Wastewater

Figure 10. The comparison between $K_{OL}a$ of MEK from wastewater and from pure water at various water depth.

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3.4 The effect of the suspended solid on $K_{OL}a$

From the previous results of the effect of the wind speed and the water depth on $K_{OL}a$, we have speculated that the suspended solid presented in wastewater played an important role on the reduction of $K_{OL}a$ in wastewater as compared to pure water. The effect of suspended solid (SS) on $K_{OL}a$ is then investigated. The $K_{OL}a$ were measured as function of SS presented wastewater which varied from 0-40 mg/L. The wind speed over the water surface and the water depth of wastewater were controlled at 2.81 m and 20 cm, respectively. The influence of SS on $K_{OL}a$ is illustrated in figure 11.
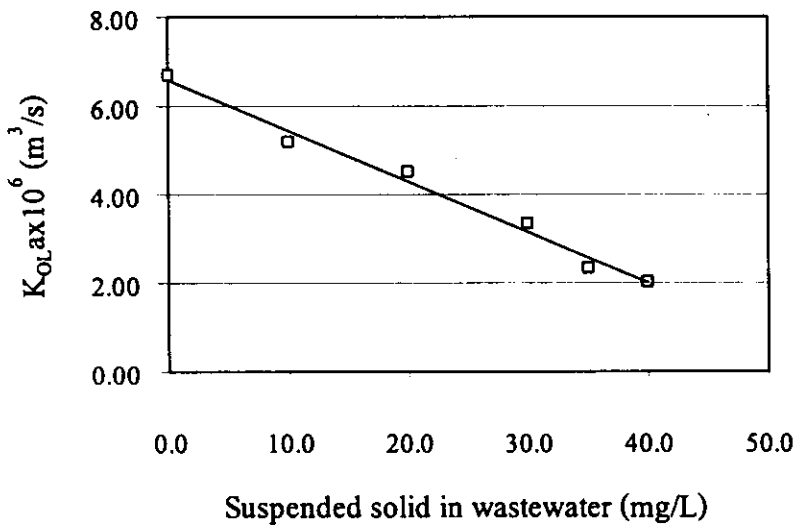

Figure 11. The effect of SS on $K_{OL}a$ of MEK at wind speed of 2.81 m/s, water depth of 20 cm and water temperature of 29 ± 1 $^{\circ}$C.

It clearly shown from figure 11 that the $K_{OL}a$ significantly decrease with increasing SS in wastewater. There are three possible mechanisms which may responsible for the decreasing of $K_{OL}a$ with increasing of SS. These are the adsorption of MEK on solid particles, the barrier to mass transfer and the suppression of turbulence in water by suspended solid particles. A number of researches have been investigated on adsorption of VOCs on suspended solid particle. Most of the previous research reported that the removal of VOC due to adsorption process into suspended solid were considerably low and strongly depend on water temperature, the low temperature is prefer (Bianchi and Varney,1998). Wakeham et al. (1983) reported that only about 0.3% of VOC such as toluene and tetrachloroethylene could be adsorbed onto particulates. From this review we

can see that the adsorption is a minor process to remove VOCs from liquid. We then speculated that the significantly decreased of $K_{OL}a$ in the presented of SS found in our investigation may be attributed mostly to the barrier effect and the turbulence suppression due to the presence of the organic solid in wastewater. In this case, the suspended solid in wastewater acts as a barrier for MEK transfer, reducing diffusion ability and eddy current (or the extent of turbulence) in bulk liquid phase, and thus reducing the volatilization rate and $K_{OL}a$.

4. CONCLUSION

The volatilizations of MEK from wastewater and from pure water were investigated in pilot scale volatilization tank. The influence of the surface wind speed, the water depth and the suspended solid on $K_{OL}a$ were determined. The results revealed that the relationship between $K_{OL}a$ and the wind speeds falls into two regimes with a break at the wind speed of 2.4 m/s. At $U_{10cm} \leq 2.4$ m/s, $K_{OL}a$ was slightly increased with increasing U_{10cm} and the linear relationship between $K_{OL}a$ and U_{10cm} was observed. For $U_{10cm} >2.4$, $K_{OL}a$ increased more rapidly. The relationship between $K_{OL}a$ and U_{10cm} was also linear but has a distinctly higher slope. The $K_{OL}a$ of MEK volatilized from wastewater were decreased significantly with increasing water depth and the suspended solid in wastewater. The $K_{OL}a$ of MEK volatilized from wastewater were lower than that of pure water. These pronounce at high wind speed and shallow water conditions. The lower $K_{OL}a$ found in wastewater as compared to pure water was due to the difference in water body characteristics. The presence of organics masses in wastewater provided the barrier to mass transfer and reduced the degree of turbulence in wastewater resulting in low volatilization rate and thus $K_{OL}a$. The mass transfer model for predicting VOCs emission from wastewater is then recommended to develop from volatilization of VOCs from wastewater rather than those from pure water.

5. ACKNOWLEDEMENTS

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