Factors affecting the volatilization of volatile organic compounds from wastewater

Charun Bunyakan¹, Seansuk Seaoung², Junya Intamanee³ and Juntima Chungsiriporn⁴

Abstract
Bunyakan, C., Seaoung, S., Intamanee, J. and Chungsiriporn, J.
Factors affecting the volatilization of volatile organic compounds from wastewater

This study aimed to understand the influence of the wind speed (U₁₀cm), water depth (h) and suspended solids (SS) on mass transfer coefficient (K_a) of volatile organic compounds (VOCs) volatilized from wastewater. The novelty of this work is not the method used to determine K_a but rather the use of actual wastewater instead of pure water as previously reported. The influence of U₁₀cm, h, and SS on K_a was performed using a volatilization tank with the volume of 100-350 L. Methyl Ethyl Ketone (MEK) was selected as a representative of VOCs investigated here in.

The results revealed that the relationship between K_a and the wind speeds falls into two regimes with a break at the wind speed of 2.4 m/s. At U₁₀cm ≤ 2.4 m/s, K_a was slightly increased linearly with increasing U₁₀cm. For U₁₀cm > 2.4 m/s, K_a increased more rapidly. The relationship between K_a and U₁₀cm was also linear but has a distinctly higher slope. For the K_a dependency on water depth, the K_a decreased significantly with increasing water depth up to a certain water depth after that the increase in water depth

¹Ph.D.(Chemical Engineering), Assoc. Prof., ²M.Eng, Student in Chemical Engineering, ³B.Sc.(Chemistry), Senior Teacher, ⁴Ph.D.(Environmental Technology), Asst. Prof., Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkhla, 90112 Thailand.
Corresponding e-mail: charun.b@psu.ac.th
Received, 6 October 2005       Accepted, 20 April 2006
Factors affecting the volatilization of volatile organic compounds

Bunyakan, C., et al.

had small effect on $K_{oa}$. The suspended solids in wastewater also played an important role on $K_{oa}$. Increased SS resulted in a significant reduction of $K_{oa}$ over the investigated range of SS. Finally, the comparison between $K_{oa}$ obtained from wastewater and that of pure water revealed that $K_{oa}$ from wastewater were much lower than that of pure water which was pronounced at high wind speed and at small water depth. This was due the presence of organic mass in wastewater which provided a barrier to mass transfer and reduced the degree of turbulence in the water body resulting in low volatilization rate and thus $K_{oa}$. From these results, the mass transfer model for predicting VOCs emission from wastewater should be developed based on the volatilization of VOCs from wastewater rather than that from pure water.

Key words : VOCs, volatilization, mass transfer coefficient, MEK
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 models 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 was theoretically known to influence mass transfer rate in other systems (Cussler, 1984).

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).

Methods and Materials

1. Materials

Wastewater was taken from the wastewater treatment facility at Prince of Songkla University Hat Yai, Songkhla, Thailand. The characteristics of the wastewater are shown in Table 1.

MEK was selected as VOCs representative in this study since the volatilization of MEK from water is governed by both gas and liquid films. In other words, the volatilization rate of MEK from water is between that of VOCs whose the volatilization rates are controlled by gas film and liquid film, respectively. MEK (99.5%, Merck) was used in the experiments without any further purification.

2. Analysis

The liquid samples were analyzed using 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 180ºC, a detector temperature of 200ºC and an oven temperature of 50ºC. 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.

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 two main pieces of equipments; the volatilization tank (50 cm wide, 100 cm long, and 5-70 cm deep) and the wind generator system, as shown in Figure 1.

3.1 Solution preparation

Prior to starting an experiment, the wastewater and the pure water containing MEK was prepared by dissolving MEK in wastewater or water to the desired concentrations. The volumes of the wastewater and water were varied from 25 to 350 L depending on water depth, which varied from 5-70 cm.

3.2 Effect of the wind speed

The unsteady state volatilizations of MEK from wastewater and water were investigated at various wind speeds. 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 the water surface for 15 positions across the water surface.

Table 1. Wastewater characteristics analyzed from 27 water samples

<table>
<thead>
<tr>
<th>Properties</th>
<th>mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD₅</td>
<td>45-98</td>
</tr>
<tr>
<td>COD</td>
<td>2320-2960</td>
</tr>
<tr>
<td>Suspended solids (SS)</td>
<td>27-62</td>
</tr>
</tbody>
</table>
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\(\pm\)1\(^\circ\)C, 31\(\pm\)1\(^\circ\)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.

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 near the 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\(\pm\)1\(^\circ\)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 while the wind speed over the water surface was kept constant at 2.81 m/s for all experiments.

3.4 Effect of suspended solids

The unsteady state volatilizations of MEK from wastewater were investigated at various suspended solids. The water depths were at 20 cm, corresponding to water volume of 100 L. The water temperature was at room temperature (29\(\pm\)1\(^\circ\)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 while the wind speed over the water surface was kept constant at 2.81 m/s for all experiments.

3.5 Volatilization time and liquid sampling

The volatilization time was 5 hr. During the experiment, liquid samples were collected periodically from the middle of the tank at a 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 filtered and analyzed for MEK concentration. The concentration-time data of each run was used to determine the overall mass transfer coefficient of MEK.

3.6 Data analysis

The overall mass transfer coefficients for MEK volatilization from wastewater and from pure water were determined from concentration-time data using a two-film model and mass balance around the volatilization tank. Providing that the concentration of MEK in the volatilization tank is uniform, the overall mass transfer coefficient can be obtained from the slope of a plot between \(\ln\left[\frac{C_{MEK,L}}{C_{MEK,w}}\right]\) as shown by equation (1). The
Factors affecting the volatilization of volatile organic compounds

Bunyakan, C., et al.

1087

Results and Discussion

1. The effect of the wind speed on $K_{OLa}$

The volatilization of MEK from wastewater and pure water was 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 $K_{OLa}$ the concentration-time data were measured. The typical concentration-time data measured at different depth from water surface, at the middle of the volatilization tank, for the volatilization of MEK from wastewater and pure water, at $U_{10cm} = 2.81$, are shown in Figure 2. It is 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 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 equation (1) can be applied for $K_{OLa}$ determination.

The effect of the wind speed on $K_{OLa}$ for MEK volatilization from wastewater is shown in 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. $U_{10cm} = 2.81$ m/s.

$$\ln \frac{C_{MEK,L}}{C_{MEK,Lo}} = \frac{K_{OLa} V}{V} t$$

where $K_{OLa}$ = overall mass transfer coefficient of MEK, $m^2/s$

$C_{MEK,L}$ = concentration of MEK in liquid phase at any time $t$, $mol/m^3$

$C_{MEK,Lo}$ = concentration of MEK in liquid phase at $t = 0$, $mol/m^3$

$V$ = volume of volatilization tank, $m^3$

$t$ = volatilization time, $s$
Factors affecting the volatilization of volatile organic compounds

Bunyakan, C., et al.

Figure 3. From Figure 3, the data show that the relationship between $K_{ol,a}$ and $U_{10m}$ fell into two regimes with a break at the wind speed range of 2.4 m/s. At low wind speed regime, $U_{10m} < 2.40$ m/s, $K_{ol,a}$ of MEK slightly increased as the wind speed was increased. At the high wind speed regime, $U_{10m} > 2.40$ m/s, $K_{ol,a}$ of MEK was strongly influenced by the wind speed. The relationship between $K_{ol,a}$ and the wind speed was linear but had a distinctly higher slope compared with that of the low wind speed regime. The transition of $K_{ol,a}-U_{10m}$ relationship at 2.40 m/s agreed well with the results previously reported by a number of researchers, who mostly found the transition 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 was high enough to set the interface and liquid below in motion resulting in high turbulence and the appearance of waves. Consequently, $K_{ol,a}$ increased significantly with increasing wind speed in this regime.

The comparison between $K_{ol,a}$ of 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 $U_{10m}$ in Figure 5. It can be seen from this figure 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 \( U_{10} < 2.40 \text{ m/s} \). However, at the high wind speed regime, \( U_{10} > 2.40 \text{ m/s} \), 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 decrease slightly. This may attributed to the fact that the turbulence in the water body increased with increasing wind speed. The organic masses suspended in wastewater 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) then increased with increasing wind speed up to a wind speed of 3.4 m/s. When the wind speed was higher than 3.4 m/s, the wind speed is high enough to overcome both the turbulence suppression and barrier effects. Thus the \( K_{ol,a} \) (wastewater) increased and the ratio of \( K_{ol,a} \) (water) to \( K_{ol,a} \) (wastewater) decreased as shown in Figure 5.

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. It is clearly shown from this figure 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 was lower than that at the lower depth, the mass transfer coefficient was then decreased with increasing water depth. The organic masses presented in wastewater suppressed the turbulence and provided a barrier to mass transfer, thus \( K_{ol,a} \) of wastewater was significantly lower than that of

Figure 5. The ratio \( K_{ol,a} \) (in water) / \( K_{ol,a} \) (in wastewater) of MEK as function of the wind speed at \( T_{water} = 29\pm1^\circ\text{C} \) and a water depth of 20 cm.
pure water, particularly at shallow water as shown in Figure 8. However, at water depth greater than the certain value of 30 cm, the degree of turbulence in water body was dominated by the water depth, the $K_{ol,a}$ of wastewater and of pure water were then approximately the same as evidenced in Figure 8.

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 believe that the suspended solid present in wastewater played an important role on the reduction of $K_{ol,a}$ in wastewater as compared to pure water. The effect of suspended solids (SS) on $K_{ol,a}$ was then investigated. $K_{ol,a}$ were measured as function of SS presented in wastewater which was 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/s and 20 cm, respectively. The influence of SS on $K_{ol,a}$ is illustrated in Figure 9.

It is clearly shown from Figure 9 that the $K_{ol,a}$ significantly decreased with increasing SS in wastewater. There are three possible mechanisms which may be responsible for the decrease of $K_{ol,a}$ with increasing 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 investigated adsorption of VOCs on suspended solid particles. Most of the previous research reported that the removal of VOCs due to adsorption onto suspended solid was considerably low and strongly depended on water temperature, the low temperature was preferred (Bianchi and Varney, 1998). Wakeham et al. (1983) reported...
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)

Figure 8. The comparison between $K_{vol}$ of MEK from wastewater and from pure water at various water depth.
that only about 0.3% of VOCs such as toluene and tetrachloroethylene were adsorbed on to particulates. From these previous works we can see that the adsorption is a minor process for removal of VOCs from liquid. We then believed that the significantly decreased of $K_{ol}a$ in the presence 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 $K_{ol}a$.

**Conclusion**

The volatile emissions of MEK from wastewater and from pure water were investigated in a 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 fell into two regimes with a break at the wind speed of 2.4 m/s. At $U_{10}\text{m} \leq 2.4$ m/s, $K_{ol}a$ was slightly increased with increasing $U_{10}\text{m}$ and a linear relationship between $K_{ol}a$ and $U_{10}\text{m}$ was observed. For $U_{10}\text{m} > 2.4$, $K_{ol}a$ increased more rapidly. The relationship between $K_{ol}a$ and $U_{10}\text{m}$ was also linear but had a distinctly higher slope. The $K_{ol}a$ of MEK volatilized from wastewater decreased significantly with increasing water depth and the suspended solid in wastewater. The $K_{ol}a$ of MEK volatilized from wastewater were lower than those of pure water. These were pronounced 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 a 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 was then recommended to be developed from volatilization of VOCs from wastewater rather than those from pure water.

**Acknowledgements**

This research is sponsored by PSU and NRTC (annual budget year 2003). The authors are also thankful to the Graduate School for financial support to the second author. Other supports from the Faculty of Engineering and the Department of Chemical Engineering at Prince of Songkla University are gratefully acknowledged.

**References**


