บทที่ 5

Effect of Suspended Solid on Volatilization of MEK from Wastewater

Charun Bunyakan* Sansuk Seaoung, Junya Intamanee, and Jantima Chungsiriporn
Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University,
Hat Yai, Songkhla 90112
E-mail: charun.b@psu.ac.th*

Abstract

The volatilization of Methyl Ethyl Ketone (MEK) from wastewater was investigated in the pilot volatilization tank, (50 cm wide, 100 cm long and 20 cm deep). The experimental setup was used so that the volatilization of MEK could be examined as function of suspended solid in wastewater (SS), varied from 0 to 40 mg/L. The overall mass transfer coefficient ($K_{OL}a$) and the volatilization rate of MEK (R_{MEK}) were found to decrease significantly with increasing amount of SS. The reduction in $K_{OL}a$ and R_{MEK} were mainly attributed to the barrier effect to mass transfer and the liquid phase turbulence suppression due to the presence of organic mass in wastewater which reducing diffusion and eddy current (or the extent of turbulence) in bulk liquid phase, thus reducing the volatilization rate and $K_{OL}a$. The maximum in reduction of $K_{OL}a$ about 70% was observed at the SS of 40 mg/L. The relationship between $K_{OL}a$ and SS was proposed and the use of this correlation for predicting the R_{MEK} was discussed.

Keywords: MEK, Volatilization, Mass transfer coefficient, Suspended solid

1. Introduction

Volatilization has long been recognized as a mechanism whereby volatile organic compounds (VOCs) transfer across the water-air interface from wastewater to atmosphere. In the past, the volatilization of VOCs from wastewater has been viewed as a legitimate means for reducing the total organic load in wastewater. Today, the emissions of VOCs from wastewater are known as sources of exposure to hazardous substances and are increasingly subject to legislative controls by USEPA and other regulatory bodies. The method for estimating of VOC emission from wastewater to local airborne environment is needed to comply with the regulation. The VOC emissions can be determined by making experimental measurement which requires extensive sampling and analysis. The estimating of VOC emissions from wastewater 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 VOC from water. Moreover, most of the existing model included only the effect of the wind speed and water temperature [1,2,3]. The characteristic of water, particularly suspended solid (SS), is extremely different from that appears in actual wastewater. The presence of suspended solids in wastewater (inorganic flocculant, sand particles, organic sewage particles) may act as selective adsorbent sites for VOCs, reducing the solute partial pressure, and so reducing the volatilization rate. However, to our knowledge, there is no mass transfer model for predicting VOC volatilization rate from wastewater which actually related mass transfer coefficient to suspended solid. The objective of this study was to understand better the roles of suspended solid on mass transfer coefficient that allowed for the determination of the effects of SS on VOC volatilization process.

The experiments are conducted in a pilot volatilization tank where the SS can be varied and controlled at desired values. This type of setup is able to investigate the effect of the SS on mass transfer coefficients of MEK from wastewater.

2. Material and Methods

2.1 Materials

Wastewater was taken from wastewater treatment facility at the Prince of Songkla University Hat Yai Songkhla Thailand. The initial characteristic of wastewater is shown in Table 1. The desired amount of suspended solid (SS) in wastewater were obtained by concentrating wastewater via evaporation process or diluting with pure water to obtain higher and lower SS than that originally found in wastewater, respectively.

MEK wastewater solutions of required concentration were prepared by mixing predetermined amount of MEK (99.5 % Merck) with wastewater to a final volume of 100.

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 °C, a detector temperature of 200 °C and an oven temperature of 50 °C. The GC column was a HP-FAAP, Polyethylene glycol-TPA modified, Hewlett Packard, 30 m capillary glass column with an inside diameter of 0.32 mm. Helium was used as a carrier gas at a flow rate of 2 mL/min. This analytical system gave excellent resolution for MEK.

Table 1. Wastewater characteristic

Properties	mg/l
BOD₅	45-98
COD	2320-2960
Suspended solids (SS)	27-62

2.3 Volatilization experiment

The experiments for unsteady state volatilization of MEK from wastewater and from pure water 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 20 cm deep) and the wind generated system, as shown in figure 1. The experiment conditions for all runs are summarized in Table 2.
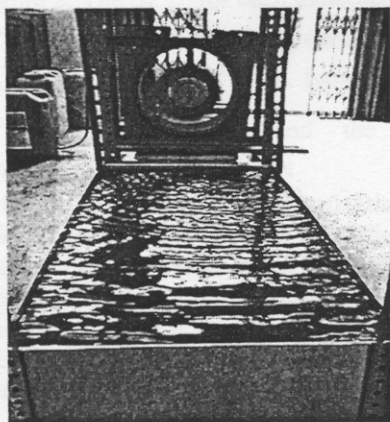

Figure 1. Pilot volatilization tank equipped with a wind generated system

Table 2.Experiment conditions

Run No.	SS (mg/l)	MEK Conc. (mg/l)	Air Temp. (K)	Water Temp. (K)
1	0	659	303	301
2	10	972	303	301
3	20	1136	304	301
4	30	1068	303	301
5	35	1185	303	301
6	40	1096	303	301

For each experimental run, one hundred liter of wastewater with predetermined SS, spiked with a known concentration of MEK, was placed in the volatilization tank. The wind speed above the water surface was control at 2.8 m/s in order to speed up the volatilization rate and make the experiment can be done in a suitable of time. The volatilization time was 5 hr. During experiment, liquid samples were collected periodically, at 10, 30 and 60 minute in the first hour and every hour for the rest of volatilization time, from the middle of the tank. 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 and the volatilization rate of MEK from wastewater.

2.4 Data Analysis

Overall mass transfer coefficient and volatilization rate of MEK were determine based on liquid concentration measured as function of volatilization time and volatilization tank operating parameters (i.e., SS)

Overall Mass Transfer Coefficients

Overall mass transfer coefficients ($K_{OL}a$) for MEK volatilization from wastewater are determined using two-film model, which is express as equation (1)

$$R_{MEK} = K_{OL}a\left(C_{MEK,L} - \frac{HC_{MEK,G}}{RT}\right) \quad (1)$$

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

a = surface area of wastewater, m²

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

$C_{MEK,G}$ = concentration of MEK in gas phase, mol/m³

H = Henry law constant, atm m³

R = universal gas constant =8.21x10⁻⁵ (atm m³/ mol K)

T = absolute temperature, K.

The air flow over the water surface removed MEK it volatile, maintaining the MEK concentration in gas phase above the wastewater surface at zero. Equation (1) reduces to

$$R_{MEK} = K_{OL}aC_{MEK,L} \quad (2)$$

The material balance around the volatilization tank, illustrated in Figure 1, can be expressed as equation (3)

$$R_{MEK} = -V\frac{dC_{MEK,L}}{dt} \quad (3)$$

where V = volume of volatilization tank, m³

t = volatilization time, s

Combining equation (2) and (3) gives

$$\frac{dC_{MEK,L}}{dt} = -\frac{K_{OL}a}{V}C_{MEK,L} \qquad (4)$$

The integration of equation (4) gives an unsteady state concentration profile

$$C_{MEK,L} = C_{MEK,Lo}\exp(-\frac{K_{OL}a}{V}t) \quad (5)$$

or $\quad \ln\dfrac{C_{MEK,L}}{C_{MEK,Lo}} = -\dfrac{K_{OL}a}{V}t \qquad (6)$

Providing that the concentration of MEK in volatilization tank is uniform, the overall mass transfer coefficient can be obtained from concentration-time data as shown by equation (6), using linear regression technique. Once the overall mass transfer coefficient is known, the volatilization rate of MEK at specific MEK concentration is readily estimated using equation (2).

3. Results and Discussion

3.1 Unsteady state concentration profiles

Typical concentration-time data of MEK during unsteady state volatilization from wastewater are shown in figure 2. The K_{OL} for each experiment was determined by performing a linear regression analysis of $\ln(C_{MEK,L}/C_{MEK,o})$ and t. A typical plot of $\ln(C_{MEK,L}/C_{MEK,o})$ versus t and the linear regression line is illustrated in figure 3.

From figure 3, the indexes of determination were above 0.98 indicating that the volatilization rate model, equation (2), described the experimental rate well. Another word, this indicates that the volatilization of MEK from wastewater is first order with respect to MEK concentration in liquid phase. The first order kinetics is the same as those found from MEK volatilization from pure water which has been previously reported [1].

3.2 Effect of suspended solid on $K_{OL}a$

Figure 4 illustrated the effect of SS on $K_{OL}a$. It clearly shown from this figure that the $K_{OL}a$ significantly decrease with increasing SS in wastewater. From figure 4, the relationship between $K_{OL}a$ and SS were linear, with R^2 of 0.98, and can be expressed by equation (7).

$$K_{OL,a} = 6.59x10^{-6} - 1.15x10^{-7}SS \qquad (7)$$

Equation (7) can be used to determine $K_{OL}a$ for MEK volatilization from wastewater contained SS up to 40 mg/L.
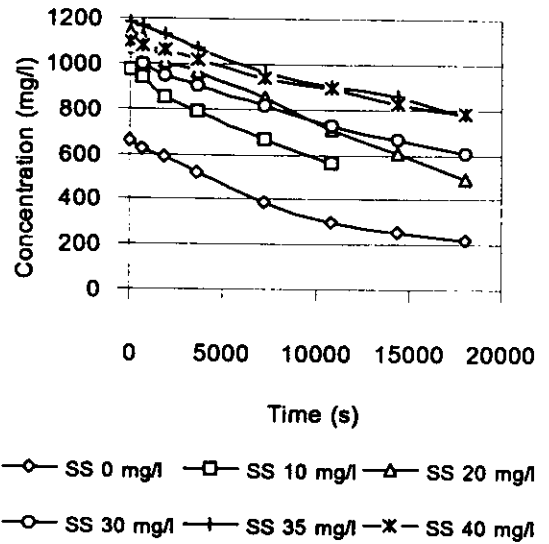

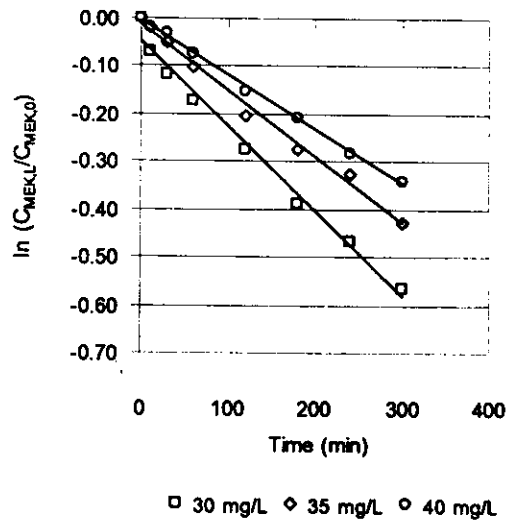Figure 2. Typical concentration-time data of MEK as function of time

Figure 3. Typical plot of $\ln(C_{MEK,L}/C_{MEK,o})$ vs. t for volatilization of MEK from wastewater

There are two mechanisms which may responsible for the decreasing of $K_{OL}a$ with increasing of SS. The suspended solid may act as an adsorption sink for MEK or act as a barrier to mass transfer. 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 [4]. Wakeham et al. [5] reported that only about 0.3% of VOC such as toluene and

52

tetrachloroethylene could be adsorbed onto particulates. These researches imply that the adsorption is a minor process to remove VOC from liquid. We then speculated 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 process, 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 $K_{OL}a$. Further confirmation or comparison of the experimental findings was made difficult by the apparent lack of data in literature concerning similar of this work, which may indicate that this topic remain a new.
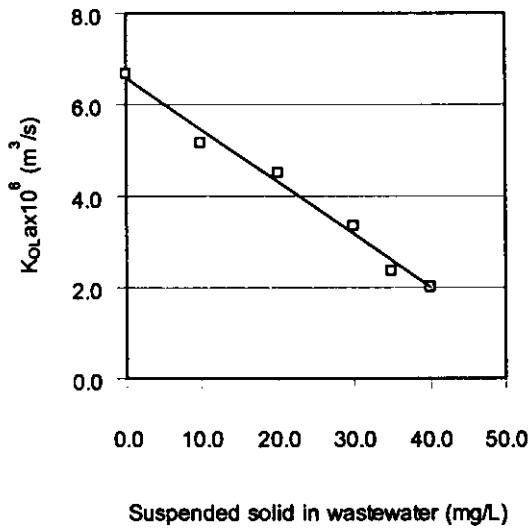
The calculated %R were listed in table 2 and plotted against the SS as illustrated in figure 5.

Table 2. The percent reduction in $K_{OL}a$ due to the presence of SS in wastewater

SS (mg/l)	$K_{OL}a$ X 10^6 (m^3/s)	%R
0	6.67	0
10	5.17	22
20	4.50	32
30	3.33	50
35	2.33	65
40	2.00	70

Figure 4 $K_{OL}a$ vs. SS for volatilization of MEK from wastewater at room temperature
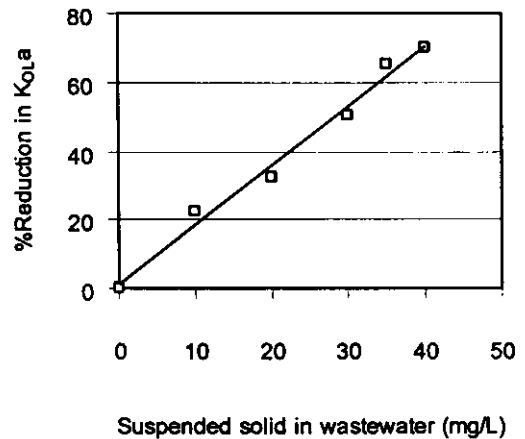
Figure 5. %Reduction in $K_{OL}a$ of MEK as function of suspended solid in wastewater

3.3 Effect of SS on the extent of $K_{OL}a$ reduction

The extent of a reduction in $K_{OL}a$ due to the presence of SS can be calculated by equation (8).

$$\%R = \frac{K_{OL}a,o - K_{OL}a}{K_{OL}a,o} x100 \qquad (8)$$

where %R = percent reduction in $K_{OL}a$ due to the presence of SS, %

$K_{OL}a,o$ = overall mass transfer coefficient at SS=0 mg/L,m^3/s

$K_{OL}a$ = overall mass transfer coefficient, of wastewater water at any SS, m^3/s

From figure 5, it clearly shown that the higher SS the more reduction in $K_{OL}a$ was observed. The relationship between %R and SS was linear, with R^2 of 0.98 and can be expressed by equation (9).

$$\%R = 1.73SS + 1.155 \qquad (9)$$

This equation can be used to estimate the reduction in $K_{OL}a$ and volatilization rate of MEK due to the presence of SS in wastewater for SS up to 40 mg/L.

3.4 Estimated MEK volatilization rate from wastewater

MEK volatilization rate from wastewater can be calculated from equation (2). Combining equation (7) with equation (2) we obtain.

$$R_{MEK} = (6.59x10^{-6} - 1.15x10^{-7}SS)C_{MEK,L} \quad (10)$$

Application of equations (10) is demonstrated through an example. Consider the wastewater contains MEK with a concentration in the range of 400 to 600 mg/L. The effect of SS on volatilization rate of MEK, calculated from equation (10) is depicted in figure 6.
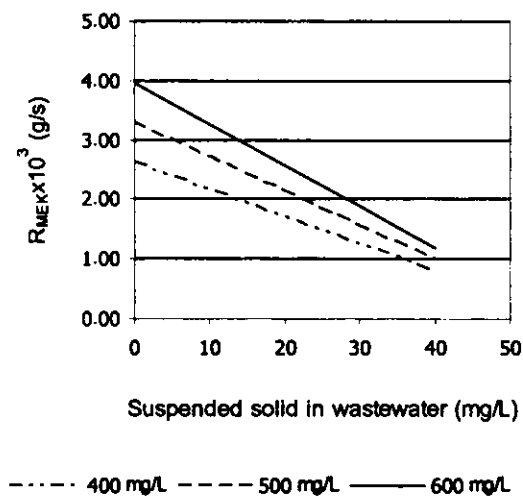

--·--· 400 mg/L ----- 500 mg/L ——— 600 mg/L

Figure 6. Predicted volatilization rate of MEK from wastewater as function of SS, MEK concentrations varied from 400-600 mg/L.

It can be seen from figure 6 that the MEK removal from wastewater was decreased significantly with increasing SS content in wastewater. Although, the wind speed over the surface, used in this study, is considerably high, 2.81 m/s, the reduction of volatilization rate was still significant, up to 70% at the SS of 40 mg/L. This implies that SS provide the strong barrier to MEK diffusion and the strong turbulence suppression in bulk liquid and at air-liquid inter phase. The barrier effect and the turbulence suppression due to the presence of SS may be the same as those due to the presence of a surfactant film which can reduce MEK volatilization up to 80% [6,7].

5. Conclusion

A study of the volatilization of MEK from wastewater was conducted to understand the role of suspended solid on MEK volatilization process. The study reveals that the suspended solid is an important parameter, which significantly affects the volatilization rate. The overall mass transfer coefficient ($K_{OL}a$) and the volatilization rate of MEK (R_{MEK}) were found to decrease significantly with increasing amount of SS. The reduction in $K_{OL}a$ and R_{MEK} were mainly attributed to the barrier effect to mass transfer and the liquid phase turbulence suppression due to the presence of organic mass in wastewater, which reducing diffusion and eddy current (or the extent of turbulence) in bulk liquid phase, thus reducing the volatilization rate and

$K_{OL}a$. Moreover, the relationship between the $K_{OL}a$ and the SS was proposed and the use of this correlation to predict the R_{MEK} from wastewater was discussed.

References

[1] Bunyakan, C., Tongsoi, P. and Tongurai, C. 2001. Film Mass Transfer Coefficient for the Prediction of Volatile Organic Compound Evaporation Rate from Open Water Basin. Songklanakrin J. Sci. Technol. 23(4), 563-577.

[2] Mackay, D., and Yeun, A.T.K. (1983). Mass Transfer Coefficient Correlations for Volatilization of Organic Solutes from Water. Environ. Sci. Technol. 17, 211-217.

[3] Wanninkhof, R., and Bliven, L.F. 1991. Relationship Between Gas Exchange, Wind Speed, and Radar Bacjscatter in Large Wind-Wave Tank. J. Geophys. Res. 96(C2), 2785-2796.

[4] Bianchi, A., and Varney, M.S. 1998. Volatile Organics in the Surface Waters of a British Estuary. Part 2. Fate Process. Water. Res. 32(2), 371-379

[5] Wakeham, S.G., Goodwin, J.T., and Davis, A.C. 1983. Distributions and Fate of Volatile Organic Compounds in Narragnseet Bay, Rhode Island. Can. J. Fish Aquat. Sci. 40(Suppl. 2), 304-321

[6] Bunyakan, C., Malakam, S.,and Tongurai, C. 2002. Effect of Surfactant on Mass Transfer Coeficient for Volatilization of Volatile Organic Compounds from Water Basin. Songklanakrin J. Sci. Technol. 23(4), 563-577.

[7] Broecker, H.C., Petermann, J., and Siems, W. 1978. The Influence of Wind on CO$_2$-exchange in a Wind-wave tunnel Including the Effect of Monolayers. Journal of Marine Research. 36(4), 595-610.