ABSTRACT

VOLATILIZATION OF CONTAMINANTS FROM WASTEWATERS

by
Shaoyan Wu

Emission of volatile organic compounds (VOCs) from many industrial wastewater treatment facilities are a major source of air pollution, and getting much attention from EPA. In order to determine "Best Available Control Technology" and "Lowest Achievable Emission Rate" for controlling emissions of VOCs from industrial wastewater, the accurate estimation of VOCs emission rate and realistic modeling of contaminant volatilization are required.

In this research, the volatilization of three compounds (Toluene, Xylene, and Aniline) were studied under varying aeration, stirring, and quiescent scenarios. The concentrations of contaminant were analyzed by HPLC. Experimental rate constants were obtained by using the first order reaction kinetics. Activity coefficients were calculated using UNIFAC program, then theoretical rate constants were evaluated from a model based on the Henry's Law.

For all three compounds, the experimental rate constants were less than the theoretical ones, and the difference between experimental rate constant and theoretical rate constant increases as the flowrate increases.

VOLATILIZATION OF CONTAMINANTS
FROM WASTEWATERS

by
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FROM WASTEWATERS

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This thesis is dedicated to
my parents and my husband

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TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

LIST OF TABLES
(Continued)

x

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Industrial wastewaters, such as contaminated groundwater, manufacturing plants effluent, and hazardous landfill leachate, often contain higher concentrations of volatile organic compounds (VOCs). Now the VOCs released from wastewater treatment operations (aeration, air stripping, and aerobic biodegradation) are considered a major source of air pollution [Ying et al, 1990; Kumar,et al, 1993; and Ruddy, et al 1993]. Emissions of VOCs from wastewater facilities may potentially cause odors, act as urban ozone and carcinogen precursors [Shen, et al, 1988] or exhibit toxicity to plant workers or downwind receptors.

Under the Clean Air Act of 1970 in the United States, the US. Environmental Protective Agency (EPA) has been controlling the discharge of emissions to the atmosphere from point sources through various regulations. In 1983 and 1984 the EPA promulgated a set of final regulations termed "Standards of Performance for New Stationary Sources Equipment Leaks of VOCs, Petroleum Refineries and Synthetic Organic Chemical Manufacturing Industry," which set the standard to control the emission of VOCs from process plant equipment or diffuse sources. Since the volatilization of VOCs run through the whole plant operation process, a net loss of material from the process could be found by estimating the VOCs in influents and effluents. These VOCs emissions are normally termed "fugitive emissions" [Lipton, et al, 1987].

Regulations on VOCs in wastewater are now emerging. VOC-containing aqueous waste streams used to be allowed to discharge to wastewater treatment plants regardless of whether these facilities treated the VOCs or simply vented them to the atmosphere. But new regulations have changed this situation. The first approach to VOCs control should

1

be to investigate the possibility of reducing source emissions through a change in process or materials to avoid the emissions from the wastewater treatment.

The Hazardous and Solid Waste Amendments of 1984 require in section 3004(n) that the EPA shall develop air emission standards for hazardous waste treatment, storage, and disposal facilities as necessary to protect human health and the environment. In 1988, EPA adopted a two-step process to develop these air-emission regulations and standards. In the first step, VOCs classified to reduce upper atmosphere ozone and to have toxic effects were evaluated and controlled. In the second step, the need for additional emission reductions of individual toxic pollutants was evaluated and potential emission control was evaluated for achieving any necessary emission reduction [Shen, 1988].

The EPA recently finalized its hazardous organic NESHAP (National Emission Standard for Hazardous Air Pollutants), or HON regulation. The HON regulates the emission of 112 hazardous air pollutants from the synthetic organic chemical manufacturing industry production processes and requires sources to apply the maximum achievable control technology [Shirley, 1994].

Right now, treatment at the generation point is preferred to avoid the "fugitive emission" from the transportation of wastewater. The EPA document EPA-450/3/90-004 entitled "Industrial Wastewater Volatile Organic Compounds---Background Information For BACT/LAER Determination" provides technical information to estimate emission of VOCs from the collection and treatment of industrial wastewater and to determine BACT (Best Available Control Technology) and LAER (Lowest Achievable Emission Rate) for controlling emissions of VOCs from industrial wastewater.

Many VOCs have a certain solubility in water. Thus a chemical process industry plant's wastewater streams frequently may contain VOCs in concentrations up to several thousand ppm (mg/L). For example, in the OCPSF (Organic Chemicals, Plastics, and Synthetic Fibers) industrial wastewater streams, the concentration of toluene can range from 1-25,000 (mg/L), benzene can range from 0.44-2800 (mg/L), hexane can range from

90-10,000 (mg/L) [Elliott, and Watkins, 1990]. There are some technologies to remove VOCs from wastewater such as air stripping, steam stripping, carbon and ion exchange adsorption, chemical oxidation, membrane separation, and liquid-liquid extraction. Air stripping to remove VOCs from wastewater is one of the proven technologies for many municipal wastewater treatment plants [Bell, Melcer, et al, 1993]. Air stripping is based on vapor-liquid equilibrium. By passing a certain volume of air through the wastewater, the air-water interface is increased. As a result, the transfer rate of the volatile organics into the vapor phase is increased. Air stripping can be cost-effectively applied to chemical process industries plants. A key advantage of air stripping is its low energy usage. In addition, the system can be easily upgraded to strip greater amount of VOCs with relatively small increases in capital cost. Preventive maintenance requirements are also low, provided careful consideration has been given to the fouling characteristics of the system [Okoniewski ,1992].

Since emissions of volatile organic chemicals from wastewater collection and treatment facilities are a potential concern to treatment plant operators, downwind receptors, and regulatory personnel, the accurate estimation of VOC emission rate and realistic modeling of contaminant transport into the atmosphere from wastewater become more important now. Because stripping and volatilization are the major removal mechanisms in the wastewater collection and treatment systems, some estimation models have been established for these situations.

Here, a mass transfer equation for air-water stripping system is given by Okoniewski [1992]:

$$KLa = \frac{L}{z} \times \frac{R}{R-1} \times \ln\left[\frac{\left(\frac{C_i}{C_o}\right)(R-1)+1}{R}\right] \tag{1.1}$$

Where $KLa =$ mass transfer coefficient, $L =$ liquid loading rate, $z =$ packing height, $C_i =$ influent concentration, $C_o =$ effluent concentration, $R =$ the stripping factor defined as

$R = HG/LP_l$, H = Henry's constant, G = gas loading rate, and P_l = operating pressure. This equation relates the packing height, liquid loading rate and other parameters. It can help to determine the key design parameters for a effective stripping system.

Another estimation of mass transfer coefficient is reported for stripping system during bubble aeration [Mihelcic, Baillod, et al 1993]:

$$K_L a = \frac{K_L a^*}{1 + \frac{K_L a^*}{2\phi_c}} \qquad (1.2)$$

Where $K_L a^*$ is the apparent mass transfer coefficient, ϕ_c is a correction term, and their expressions are given respectively:

$$K_L a^* = \frac{\alpha SOTR \theta^{T-20}}{V C_\infty^*} \qquad (1.3)$$

Where $SOTR$ is the standard oxygen transfer rate (1b/hour) [Whitmore, et al 1994], $\alpha = \frac{K_L a_{(wastewater)}}{K_L a_{(cleanwater)}}$, θ is a dimensionless temperature factor (usually assumed to be 1.024), V is the tank volume (L^3), C_∞^* is the dynamic saturation value for oxygen attained at infinite time in a clean water test (ML^{-3}).

$$\phi_c = \frac{\rho_a Q_G HRT}{M_a V (P_b + \gamma d_e)} \qquad (1.4)$$

In which ρ_a is the density of air (ML^{-3}), Q_G is the flow rate of air into the aeration basin ($L^3 T^{-1}$), M_a is the molecular weight of air, P_b is the barometric pressure during the test (atm), and d_e is the effective depth. Many common factors in stripping situation have been considered in this estimation.

Hsieh, Babcock, and Stenstrom [1994] developed a relationship by using the oxygen transfer coefficient to predict the emission rates of VOCs in diffused aeration system. They used a liquid-phase mass balance to describe the transfer of VOCs from the

liquid-phase into the gas-phase and derived an equation for the change of liquid-phase concentration from C_{Lo} to C_L during a period of time (Δt):

$$\ln\left(\frac{C_L}{C_{Lo}}\right) = -\frac{Q_G Hc}{V_L} S_d \Delta t \qquad (1.5)$$

A log-linear regression of the negative log of the concentration ratio versus time gives the slope (S_p):

$$S_p = \frac{Q_G Hc}{V_L} S_d \qquad (1.6)$$

where Q_G/V_L represents the air flowrate.

S_d is the degree of saturation of a VOC in the bubble, can be obtained by:

$$Sd = \frac{C_G}{C_L Hc} \qquad (1.7)$$

Where C_G is gas-phase concentration, mg/L; C_L is liquid-phase concentration, mg/L; Hc is Henry's constant (assume Henry's Law is valid in the system).

The mass transfer rate coefficient for VOCs can be estimated from experimental results as below:

$$K_L a = -\frac{Q_G Hc}{V_L} \ln\left[1 - (S_p)\frac{V_L}{Hc Q_G}\right] \qquad (1.8)$$

In this report, the equation to estimate emissions from surface aerated reactors is very complicated, but it described the mass transfer in a diffused aeration system in detail.

Bell, Melcer, et al, [1993] estimated air emission rates only multiplying the average VOC concentrations by the appropriate airflow rates.

Whether it is simple or complicated, all models for stripping and volatilization are based on Henry's law which describes the equilibrium between the liquid-vapor phases. In order to get reliable values of Henry's constants, QSARs (Quantitative Structure-Activity

Relationships) structure-based property models are required [Mihelcic, Baillod, et al 1993]. The most well known QSAR is the UNIFAC (UNIQUAC Functional Group Activity Coefficients) model. Using the UNIFAC model, accurate values of activity coefficients can be obtained. Under low pressure, Henry's constant may be equal to the product of activity coefficient at infinite dilution and pure component vapor pressure.

Although many models are available to estimate VOC emissions from wastewater collection and treatment facilities, it is still necessary to develop more and better models in order to provide better predictive tools.

In this thesis, the volatilization rates of three volatile organic compounds (Toluene, Xylene, and Aniline) are studied under stirring and aeration scenarios. The results obtained from the experiments are compared to calculations based on Henry's Law and general conclusions are drown.

CHAPTER 2

BACKGROUND

Volatilization of organic compounds involves the thermodynamic equilibrium. When the liquid phase (which contains the compound) is in thermodynamic equilibrium with the vapor phase (into which the compound is volatilizing), the compound reaches its maximum extent of volatilization.

Because of mass transfer limitations, the equilibrium between the liquid and vapor (gas) phases is not achieved in most cases. The phases are not in contact long enough for equilibrium to be established by diffusion of the compound from the liquid phase into the gas or vapor phase. The assumption of equilibrium may be approximately valid in some systems. The thermodynamic criteria for equilibrium between phases are expressed in some special properties; thermodynamics provides the equations which relate these properties to phase compositions, temperature, and pressure. Thus the connection between equilibrium criteria and physical reality is established primarily through the fugacity coefficient $\hat{\phi}_i$ for vapor phases and the activity coefficient γ_i for liquid phases. The vapor-liquid equilibrium (VLE) relationships starts at equation (2.1):

$$\hat{f}_i(liquid) = \hat{f}_i(vapor) \tag{2.1}$$

where $\hat{f}_i$ is the fugacity of compound i in the indicated phase.

In vapor phase:

$$\hat{f}_i(vapor) = \hat{\phi}_i y_i P \tag{2.2}$$

Where $\hat{\phi}_i$ is the fugacity coefficient, y_i is the vapor mole fraction. For most practical applications, the pressure is low enough to assume that the vapor behaves as an ideal gas. Therefor $\hat{\phi}_i = 1$, the equation (2.2) is replaced by:

$$\hat{f}_i(vapor) = y_i P = p_i \tag{2.3}$$

7

The partial pressure of a component in the vapor phase p_i is equal to the product of the mole fraction of the component in the vapor phase and its vapor pressure.

In liquid phase:

$$\hat{f}_i(liquid) = x_i\gamma_i f_i^{\circ} \tag{2.4}$$

Where x_i is the component mole fraction in the liquid phase, γ_i is the component activity coefficient in the liquid phase, and f_i° is the standard state fugacity for the component in the liquid phase.

In practice, the liquid phase is almost always a non-ideal mixture. This is especially true for mixtures containing water and organic compounds.

The activity coefficient is a measure of the non-ideality of the liquid mixture relative to the standard state that has been chosen for each component. For miscible mixtures, in which two or more components can be mixed together, the usual standard state is the Lewis-Randall (LR) standard state. At low pressures, the LR standard state fugacity is simply the pure component vapor pressure P_i°. Then, the f_i° in the above equation (2.4) would be replaced by P_i°.

$$\hat{f}_i(liquid) = x_i\gamma_i(LR)P_i^{\circ} \tag{2.5}$$

Where the "LR" is a reminder that the activity coefficient must be based on the Lewis-Randall standard state.

However, for solvent/solute mixtures and mixtures in which certain compounds are always dilute, the usual standard state is the Henry's Law standard state. In this case, either the f_i° in the equation (2 4) or the P_i° in the equation (2.5) is replaced by the Henry's Law constant $H_{i,j}$ which is defined by:

$$H_{i,j} = \lim_{x_i \to 0} \frac{\hat{f}_i}{x_i} \tag{2.6}$$

Note that whereas P_i° is characteristic of only component i, $H_{i,j}$ varies depending on whether component i is a liquid or gas under ambient conditions and on solubility of compound in solvent (in our case is water). Thus if the composition of the solvent

changes, the value of the Henry's Law constant for compound i will also change. Combining the above equations, the value of the Henry's constant at low pressures can be determined by:

$$H_{i,j} = \lim_{x_i \to 0} \frac{y_i P}{x_i} \tag{2.7}$$

Based on the definition, all mixture systems will become ideal according to Henry's Law when the composition of components approach zero. Thus, the activity coefficient for Henry's Law becomes equal to unity. In a range of composition in which the activity coefficient is close enough to one, Henry's law is considered to be valid for describing the thermodynamic equilibrium. But in a non-ideal system, an "effective" Henry's constant needs to be used:

$$H_{i,j}^{eff} = \frac{y_i P}{x_i} = \gamma_i H_{i,j} \tag{2.8}$$

Here this "effective" Henry's constant is not a constant at all.; it varies with composition as the activity coefficient varies. In most cases, the activity coefficient decreases as composition increases. Thus, the "effective" Henry's constant also decreases as composition increases. In addition, both the activity coefficient and the true Henry's constant are functions of temperature, so the "effective" Henry's constant should be as well.

As mentioned previously, Henry's constant $H_{i,j}$ can be measured at low pressures by taking the limiting value of the ratio of the vapor-phase partial pressure to the liquid-phase composition. Not all systems have had reliable Henry's constants reported, however. In some cases, experimental values are either missing or unreliable. There are several methods for estimation of these values. Perhaps the easiest to apply is based on methods for prediction of liquid-phase activity coefficients. These methods usually use the Lewis-Randall choice of standard states, as in equation (2.5)

Applying the definition of Henry's constant as given previously in equation (2.6), and using equation (2.5), we get:

$$H_{i,j} = \gamma_{i,j}^{\infty}(LR)P_i^{\circ} \tag{2.9}$$

The superscript on the activity coefficient indicates that we require the value at infinite dilution, and the additional subscript indicates the solvent. This activity coefficient can be evaluated by any of the standard methods for estimation of liquid-phase activity coefficients, such as the Margules equation, the van Laar equation, the Wilson equation, or the UNIFAC group-contribution method. When using these methods, we need to keep in mind their approximate nature.

We used the UNIFAC method to obtain the activity coefficients in this research. In the UNIFAC method, the size and shape contributions to the activity coefficient are called configurational (C), and the remaining group-group contributions residual (R):

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R \tag{2.10}$$

Both parts are based on the UNIQUAC equation. In addition to group interaction parameters, a_{mn} and a_{nm}, group volume parameters, R_k, and surface parameters, Q_k, are involved.

All parameters we used in this UNIFAC program are given in appendix A.

The absolute maximum volatilization rate for a contaminant can be determined by assuming that the gas phase is saturated with the contaminant. If so, then thermodynamic equilibrium exists between the gas and liquid phases. For a sufficiently dilute component, this equilibrium is described by Henry's Law. If the solution is more concentrated, Henry's law will be invalid. In this situation, the system can be described by an "effective" Henry's Law, as described earlier. In the general case, we would have:

$$\frac{y_i P}{x_i} = H_{i,j}^{eff} = \gamma_i(LR)P_i^{\circ} \tag{2.11}$$

Based on the definition, as the composition becomes ever more dilute, each of these quantities becomes the true Henry's Law constant. Written in this form, however,

the equation has general validity at low pressures, and the activity coefficient can be estimated by UNIFAC.

If we use experimental values for Henry's constant while not neglecting the composition dependence of the activity coefficient, then the following form can be used:

$$\frac{y_i P}{x_i} = H_{i,j}^{eff} = \frac{\gamma_i (LR)}{\gamma_i^{\infty}(LR)} H_{i,j} \tag{2.12}$$

Here, both the actual activity coefficient and its value at infinite dilution can be estimated by UNIFAC method, while still using a measured value for Henry's constant.

In either case, we write a material balance for our system:

$$-\frac{d(x_i \rho_L V)}{dt} = y_i \rho_V A \tag{2.13}$$

Where V is the volume of the liquid solution, A is the flow rate of the gas phases, and ρ_L and ρ_v are the molar densities of the two phases. Of course, the right-hand-side of this equation represents the volatilization rate of the contaminant. If we substitute by one of the previous expressions, and assume that the liquid density and volume are constant, we obtain:

$$-\frac{dx_i}{dt} = \frac{\rho_V A}{\rho_L V} x_i \frac{\gamma_i (LR) P_i^{\circ}}{P} = \frac{\rho_V A}{\rho_L V} x_i \frac{\gamma_i (LR) H_{i,j}}{\gamma_i^{\infty}(LR) P} \tag{2.14}$$

If we assume that over small time increments all of these variables (except xi) are constant, then we have an essentially first-order disappearance of the contaminant. Of course, this may be not strictly true. As mentioned above, the activity coefficient varies with composition, generally increasing as the composition decreases. Also, in practice, the volume of solution will also decrease with time as the solvent (water in our case) evaporates. Both of these factors will tend to cause contaminant volatilization slightly faster than the first-order "kinetics" would predict.

The equation can be integrated, assuming these other variables are constant, to give:

$$\ln\left(\frac{x_{io}}{x_i}\right) = \left(\frac{\rho_V A}{\rho_L V}\right)\left(\frac{\gamma_i(LR)P_i^\circ}{P}\right)\Delta t = \left(\frac{\rho_V A}{\rho_L V}\right)\left(\frac{\gamma_i(LR)H_{i,j}}{\gamma_i^\infty(LR)P}\right)\Delta t \qquad (2.15)$$

where the factors multiplying the Δt represent the pseudo-first order rate constant for the volatilization of a contaminant,. assuming the establishment of a thermodynamic equilibrium between the phases, and it is also called "Theoretical" rate constant.

$$Rt = \frac{\rho_V A}{\rho_L V}\frac{\gamma_i(LR)H_{i,j}}{\gamma_i^\infty(LR)P} \qquad (2.16)$$

Thus these constants can be both calculated { using the expression (2.16) }and evaluated experimentally (the calculating equation will be given in Chapter 4). Note here, if calculated using Henry's constants, then these constants should be in units of pressure/mole fraction.

CHAPTER 3

EXPERIMENTAL METHOD

3.1 Sample Preparation

3.1.1 Toluene

The solubility of toluene in water is 0.051% (510 ppm). It is difficult to make a target concentration solution duplicately by just adding a certain content toluene in water. We made saturated toluene solution by adding an excess amount of toluene to water and stirring for 3 hours. Then the solution is transferred into a separated funnel and allowed to stand. The sample was taken from the bottom of the funnel.

3.1.2 Xylene

The solubility of xylene in water is 0.018% (180 ppm). The same method as 3.1.1. was used to make xylene sample.

3.1.3 Aniline

The solubility of aniline in water is 3.6%. We made approximate 100 ppm aniline solution by adding 100μl aniline to 1000 ml water.

3.2 Determination of the Volatilization Rates

In order to simulate the conditions possible in practice, different stirring rates and aeration rates were applied in these experiments.

3.2.1 Stirring Experiment

Having placed 200 ml of the target compound solution into an open 600 ml beaker, the solution was then stirred using a magnetic bar with a stirrer (Series 400HPS-Hot plate/Stirrer, VWR Scientific) while precisely controlling the stirring rate . Samples were

taken at various times from the beginning until the organic compound had completely volatilized (Except Aniline, see below).

The experiments were run at 250 rpm, 500 rpm, 750 rpm, 1000 rpm with Toluene, m-Xylene, and Aniline and 500 rpm only with p-Xylene and o-Xylene. The control experiments (without stirring) were carried out simultaneously for with each stirring experiment.

3.2.2 Aeration Experiment

200 ml of the target compound solution were placed into an open 600 ml beaker. The solution was aerated with a known flow rate of air introduced by a sparge. The flow rate of the air was measured using a calibrated rotameter. The samples were taken at various times from the beginning until the organic compound had completely volatilized (except Aniline, see below). The control experiments (without aeration) were conducted at the same conditions as the aeration experiments.

3.3 Analysis of Sample

3.3.1 Apparatus

The samples were analyzed by:

1) High performance liquid chromatography (HPLC) with a PDA Detector

2) Ultrasonic bath (FS-28, Fisher Scientific)

3) Membrane filter paper

●Millipore Cat No. HAMP 04700, type HA, pore size 0.45 μm.

●Millipore Cat No HVHP 04700, type HV, pore size 0.45μm.

3.3.2 Reagents

The reagents we used in this research were:

1) Acetonitrile(HPLC grade);

2)Methanol(HPLC grade);

3)Toluene(HPLC grade, Fisher Scientific);

4)m-Xylene(Certified grade, Fisher Scientific);

5)p-Xylene(Certified grade, Fisher Scientific);

6)0-Xylene(Reagent grade, Fisher Scientific);

7)Aniline(HPLC grade, Fisher Scientific).

3.3.3 Analytical Procedures

The experimental samples were analyzed by HPLC. Each analysis yielded the concentration of the organic compound remaining in the target solution, and a material balance gave the amount that had volatilized.

3.3.3.1 Toluene Acetonitrile and water were used as mobile phase and filtered though membrane filter paper, then degassed in a ultrasonic bath for 15 minutes.

Toluene samples were measured by a Waters 600E system controller with a RP-Select B C_{18} (5μm) column, Waters 994 programmable photodiode array detector and a Hewlett Packard series 1050 autosampler. The data were collected and calculated by Waters 5200 printer plotter and minichrom computer system.

The stock standard solution was made by weighing an accurate amount of pure toluene into a 10 ml volumetric flask which half filled with pure methanol. The resulting solution was diluted to the volume with methanol. The secondary dilution solution was prepared by adding an accurate volume of stock solution to a volumetric flask and diluted to volume with methanol. The calibration standards were made by taking the secondary dilution solution with different volume to obtain a proper calibration working range. For toluene the working range selected was 0-550 ppm (the saturated concentration of toluene is about 510 ppm). The HPLC operating conditions are listed in Table 3.1

Table 3.1 The HPLC Operating Conditions of Toluene

Mobile phase	acetonitrile 60%, water 40%
Flowrate	1 ml/min
Sparge rate	30 ml/min
Detector sensitivity	0.1 absorbance units full scale
Analytical wavelength	262 nm
Sample injection volume	20 μl

3.3.3.2 Xylene (m, p, and o-Xylene) A similar analytical procedure was employed for the three xylenes. The saturated concentration of xylenes are about 180 ppm. The calibration working range was set at 0-200 ppm. The HPLC operating conditions is listed in Table 3.2.

Table 3.2 The HPLC Operating Conditions of Xylenes

Mobile phase	acetonitrile 65%, water 35%
Flowrate	1 ml/min
Sparge rate	30 ml/min
Detector sensitivity	0.1 absorbance units full scale
Analytical wavelength	262 nm
Sample injection volume	20 μl

3.3.3.3 Aniline Because aniline is a more polar compound than either toluene or xylene, methanol and water were used to make the mobile phase in its HPLC analysis, a weaker mobile phase. The analysis procedure was similar to that for toluene (3.3.3.1). The maximum concentration of aniline used was about 100 ppm, so the calibration working range was set at 0-120 ppm. The HPLC operating conditions are listed in Table 3.3.

Table 3.3 The HPLC Operation Conditions of Aniline

Mobile phase	methanol 70 %, water 30%
Flowrate	1 ml/min
Sparge rate	30 ml/min
Detector sensitivity	0.1 absorbance units full scale
Analytical wavelength	254 nm
Sample injection volume	15µl

Note:

a) Mobile phase was freshly prepared each day.

b) The system was conditioned and cleaned before and after analysis with solvent.

c) The calibration curve was checked and corrected each day.

CHAPTER 4

RESULTS AND CALCULATIONS

4.1 Toluene

4.1.1 Stirring Experiments

Four stirring experiments were carried out with different stirring speeds. .Volatilization or stripping is a first order process as demonstrated experimentally for volatile organics by Rathbun and Tai [1984]. So experiments were assumed as the first-order reactions, then we get the equation:

$$\ln \frac{X_{io}}{X_i} = R_e \times \Delta t \tag{4.1}$$

Where X is the mole fraction of the compound, Re is experimental value of rate constant. All the stirring experiment data are given in Table 4.1, Table 4.2, Table 4.3 (appendix B), and Table 4.4 (appendix B).

Table 4.1 Volatilization of Toluene Stirring at 250 rpm (298K)

Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	445.39	100	86.8	0	
10	357.27	80.22	69.6	0.2200	0.02200
15	321.18	72.11	62.6	0.3266	0.02177
25	290.00	65.11	56.5	0.4287	0.01715
35	239.49	53.77	46.7	0.6201	0.01772
45	207.09	46.50	40.3	0.7655f	0.01701
60	168.13	37.75	32.8	0.9739	0.01623
75	135.23	30.36	26.3	1.1918	0.01589
90	102.90	23.10	20.0	1.4650	0.01628
105	57.62	12.94	11.2	2.0449	0.01948
125	52.64	11.82	10.3	2.1354	0.01708
175	24.03	5.40	4.7	2.9195	0.01668
205	11.05	2.48	2.2	3.6961	0.01802
235	6.64	1.49	1.3	4.2060	0.01798

Table 4.1(continued)

Control					
Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	459.60	100	89.8	0	
5	433.97	94.42	84.8	0.0574	0.01148
35	392.83	85.47	76.8	0.1570	0.00449
45	381.88	83.09	74.6	0.1853	0.00412
60	363.36	79.06	71.0	0.2350	0.00392
75	355.46	77.34	69.5	0.2570	0.00343
90	333.52	72.57	65.2	0.3208	0.00356
105	328.43	71.46	64.2	0.3361	0.00320
125	293.96	63.96	57.4	0.4470	0.00357
175	252.84	55.01	49.4	0.5978	0.00342
205	246.53	53.64	48.2	0.6230	0.00304
235	230.54	50.16	45.0	0.6901	0.00294

- X_i is mole fraction of contaminant

Table 4.2 Volatilization of Toluene Stirring at 500 rpm(295K)

Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	371.30	100	72.4	0	
5	332.40	89.52	64.8	0.1107	0.02214
10	281.45	75.80	54.8	0.2771	0.02771
15	242.27	65.26	47.2	0.4269	0.02846
25	180.79	48.69	35.2	0.7198	0.02923
35	133.50	35.95	26.0	1.0231	0.02940
45	99.35	26.74	19.3	1.3191	0.03002
55	73.67	19.85	14.4	1.6172	0.03034
70	45.45	12.23	8.8	2.1018	0.03098
90	24.25	6.52	4.7	2.7309	0.03173
110	12.29	3.31	2.4	3.4077	0.03309
130	6.02	1.62	1.2	4.1255	0.03755
155	2.18	0.59	0.4	5.1289	
175	0.52	0.14	0.1	6.5712	
Control					
Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	331.37	100	64.8	0	
5	321.55	97.04	62.2	0.03002	0.00600
15	299.86	90.49	58.6	0.09990	0.00666
35	293.50	88.56	57.4	0.12147	0.00347
45	278.98	84.19	54.5	0.17215	0.00383
55	268.84	81.11	52.5	0.20941	0.00381
70	257.15	77.58	50.2	0.25392	0.00363
90	249.62	75.32	48.8	0.28352	0.00315

Table 4.2 (continued)

110	228.04	68.80	44.5	0.37406	0.00340
130	207.88	62.73	40.6	0.50062	0.00359
155	200.92	60.62	39.3	0.67415	0.00323
205	168.87	50.97	32.9	0.85472	0.00364

4.1.2 Aeration Experiments

Aeration experiments were run at 11 ml/sec, 22 ml/sec, 33 ml/sec, and 44 ml/sec. The calculation of rate constant follows the equation(4.1) and (2.16).

As mentioned before, activity coefficient γ_i and γ^∞ (infinite dilution) can be obtained by using the UNIFAC FORTRAN computer program. All data are shown in Table 4.5, Table 4.6 (appendix B), Table 4.7 (appendix B), and Table 4.8 (appendix B).

Table 4.5 Volatilization of Toluene Aeration at 11 ml/sec(297K)

Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	477.40	100	93.3	0		12196	0.9301
1	278.48	58.33	54.4	0.5392	0.5392	12224	0.9323
2	175.73	36.81	34.3	0.9996	0.4998	12239	0.9334
3	102.34	21.44	19.9	1.5404	0.5135	12250	0.9343
4	55.72	11.67	10.9	2.1484	0.5371	12257	0.9348
5	30.97	6.49	6.1	2.7357	0.5471	12260	0.9350
6	12.38	2.59	2.4	3.6526	0.6088	12261	0.9352
8	6.98	1.46	1.4	4.2257	0.5282	12262	0.9353
10	2.37	0.50	0.5	5.3058	0.5316	12263	0.9354
12	0.64	0.13	0.1	6.6150	0.5513	12264	0.9354
14	0.059	0.012	0.0	8.9990	0.6427	12264	0.9354
Control							
Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	463.60	100	90.6	0			
2	391.33	84.41	76.5	0.1695	0.08476		
4	344.04	74.21	67.2	0.2984	0.07459		
6	340.70	73.49	66.6	0.3081	0.05135		
8	326.48	70.42	63.8	0.3576	0.04385		
10	321.17	69.28	62.8	0.3672	0.03672		
12	313.23	67.56	61.2	0.3268	0.03268		

<center>**4.2 Xylene**</center>

4.2.1 Stirring Experiments

4.2.1.1 m-Xylene The stirring experiments of m-Xylene were carried out with 250 rpm, 500 rpm, 750 rpm, and 1000 rpm. The results of the volatilization are given by Table 4.9, Table 4.10 (appendix B), Table 4.11 (appendix B), and Table 4.12 (appendix B).

Table 4.9 Volatilization of m-Xylene Stirring at 250 rpm (295K)

Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	191.93	100	32.5	0	
5	176.26	91.83	29.9	0.08512	0.01704
10	160.49	83.62	27.2	0.1790	0.01789
15	144.86	75.47	24.6	0.2814	0.01876
20	131.60	68.57	22.3	0.3774	0.01887
25	117.50	61.22	19.9	0.4908	0.01963
30	105.80	55.12	17.9	0.5957	0.01986
35	93.04	48.47	15.8	0.7242	0.02069
40	81.89	42.66	13.9	0.8519	0.02130
50	65.65	34.20	11.1	1.0730	0.02146
60	49.63	25.86	8.5	1.3528	0.02255
70	37.57	19.57	6.4	1.6311	0.02330
90	18,89	9.84	3.2	2.3189	0.02576
Control					
Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	177.67	100	30.1	0	
5	174.93	98.45	29.7	0.01558	0.00311
10	153.70	86.51	26.1	0.1449	0.01449
15	144.70	81.44	24.5	0.2053	0.01369
20	142.79	80.37	24.2	0.2186	0.01093
25	141.68	79.74	24.0	0.2263	0.00906
35	134.39	75.64	22.8	0.2791	0.00798
40	133.11	74.92	22.6	0.2888	0.00722
50	128.84	72.51	21.8	0.3214	0.00643
60	125.40	70.58	21.3	0.3485	0.00581
80	119.85	67.45	19.1	0.3938	0.00492
90	112.45	63.29	18.0	0.4575	0.00508

4.2.1.2 p-Xylene One stirring experiment was run with the speed 500 rpm. The result is shown in Table 4.13

Table **4.13** Volatilization of p-Xylene Stirring at 500 rpm(295K)

Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	153.49	100	26.0	0	
5	113.17	73.73	19.2	0.3048	0.06095
10	85.74	55.86	14.5	0.5824	0.05824
15	66.27	43.17	11.2	0.8400	0.05600
20	50.27	32.75	8.5	1.1164	0.05582
25	39.24	25.56	6.7	1.3642	0.05457
30	30.91	20.14	5.2	1.6027	0.05342
40	19.95	12.99	3.4	2.0408	0.05102
50	12.20	7.95	2.4	2.4013	0.04803
62	6.52	4.25	1.3	3.0279	0.04884
70	4.40	2.87	0.9		
80	2.73	1.55	0.5		
90	0.96	0.62	0.0		
Control					
Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	133.20	100	22.6	0	
5	94.09	70.63	15.9	0.3477	0.06954
10	78.46	58.90	13.3	0.5293	0.05293
15	74.83	56.17	12.7	0.5767	0.03845
20	67.80	50.90	11.5	0.6754	0.03377
25	58.96	44.26	9.0	0.8151	0.03260
40	50.88	38,20	8.6	0.9624	0.02406
62	38.50	28.90	6.5	1.2414	0.02002
70	34.79	26.12	5.9	1.3426	0.01918
90	30.90	23.20	5.2	1.4612	0.01624

4.2.1.3 o-Xylene One stirring experiment of o-Xylene was carried out with the speed 500 rpm. The result is given by Table 4.14

Table **4.14** Volatilization of o-Xylene Stirring at 500 rpm (298K)

Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	165.84	100	28.1	0	
5	83.16	50.15	14.1	0.6903	0.1381
10	47.76	28.80	8.1	1.2449	0.1245
15	26.07	15.72	4.4	1.8503	0.1236

Table 4.14 (continued)

20	15.18	9.15	2.6	2.3914	0.1196
25	8.86	5.34	1.5	2.9293	0.1172
30	5.39	3.25	0.9	3.4261	0.1142
40	2.59	1.56	0.4	4.1599	0.1040
50	1.53	0.92	0.3	4,6859	0.0937
60	1.28	0.77	0.2	4.8612	0.0810
80	1.14	0.68	0.1	4.9845	0.0623
Control					
Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	164.17	100	27.8	0	
5	126.52	77.07	21.4	0.2605	0.0494
10	102.26	62.29	17.3	0.4735	0.0473
20	75.41	45.93	12.8	0.7781	0.0389
30	64.00	38.98	10.9	0.9421	0.0314
50	49.11	29.91	8.3	1.2070	0.0241
60	44.18	26.91	7.5	1.3127	0.0219
80	35.32	21.52	5.9	1.5365	0.0192

4.2.2 Aeration Experiments

4.2.2.1 m-Xylene Four aeration experiments were run with flow rate 11 ml/sec, 22 ml/sec, 33 ml/sec, and 44 ml/sec. The results are shown in Table 4.15, Table 4.16 (appendix B), Table 4.17 (appendix B), and Table 4.18 (appendix B).

Table 4.15 Volatilization of m-Xylene Aeration at 11 ml/sec (298K)

Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	164.30	100	27.9	0		56375	0.9782
0.5	111.56	67.90	18.8	0.3872	0.7743	56418	0.9789
1	78.38	47.70	13.3	0.7402	0.7402	56442	0.9793
2	35.42	21.56	6.0	1.5346	0.7673	56476	0.9799
2.5	26.41	16.08	4.5	1.8280	0.7312	56485	0.9800
3	18.80	11.44	3.2	2.1678	0.7226	56490	0.9801
3.5	12.67	7.71	2.2	2.5622	0.7321	56495	0.9802
4	9.11	5.55	1.6	2.8920	0.7230	56499	0.9803
5	4.80	2.92	0.0	3.5328	0.7066	56504	0.9804
Control							
Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	186.33	100	31.6	0			
1	182.79	98.09	30.9	0.01921	0.01921		
2	175.77	94.33	29.8	0.05836	0.02918		

Table 4.15 (Continued)

3	175.41	94.14	29.7	0.06039	0.02013		
4	173.77	93.26	29.5	0.08167	0.01745		
5	171.72	92.16	29.1	0.1109	0.01633		

4.2.2.2 p-Xylene The aeration experiments of p-Xylene were carried out with flow rate 11 ml/sec., 22 ml/sec. Table 4.19, and Table 4.20 (appendix B) show the results .

Table 4.19 Volatilization of p-Xylene Aeration at 11 ml/sec.(295K)

Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	152.36	100	25.8	0		59208	0.8906
0.5	115.34	75.70	19.6	0.2784	0.5568	59328	0.8910
1	79.24	52.01	13.4	0.6538	0.6538	59268	0.8915
1.5	54.14	35.54	9.2	1.0347	0.6898	59289	0.8918
2	35.70	23.43	6.1	1.4511	0.7255	59304	0.8920
2.5	24.87	16.33	4.2	1.8125	0.7250	59314	0.8922
3	15.51	10.18	2.6	2.2850	0.7617	59324	0.8923
3.5	9.98	6.55	1.7	2.7256	0.7787	59329	0.8924
4	6.46	4.24	1.1	3.1603	0.7901	59330	0.8924
4.5	3.89	2.55	0.7	3.6685	0.8152	59332	0.8925
5	2.10	1.38	0.4	4.2844	0.8569	59332	0.8925
6	0.14	0.092	0.0	6.9925	1.1654	59333	0.8925
Control							
Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	151.96	100	25.8	0			
0.5	146.80	96.60	24.9	0.03453	0.06906		
1	139.15	91.57	23.6	0.08805	0.08805		
1.5	134.11	88.26	22.7	0.1249	0.08330		
2	126.19	83.04	21.4	0.1858	0.09292		
3	118.54	78.01	20.1	0.2484	0.08278		
4	110.38	72.64	18.7	0.3197	0.07992		
6	97.47	64.14	16.5	0.4441	0.07402		

4.2.2.3 o-Xylene Two aeration experiments were run with flow rate 11 ml/sec., and 22 ml/sec., the results are shown in Table 4.21, and Table 4.22 (appendix B).

Table 4.21 Volatilization of o-Xylene Aeration at 11 ml/sec.(300K)

Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	174.37	100	29.6	0		54588	0.6144

Table 4.21 (Continued)

0.5	126.27	72.41	21.4	0.3228	0.6456	54625	0.6148
1	93.44	53.59	15.8	0.6239	0.6239	54652	0.6151
1.5	66.73	38.27	11.3	0.9605	0.6404	54670	0.6153
2	48.81	27.99	8.3	1.2734	0.6367	54684	0.6154
2.5	33.66	19.31	5.7	1.6449	0.6580	54698	0.6156
3	23.77	13.63	4.0	1.9926	0.6642	54703	0.6156
4	11.90	6.82	2.0	2.6848	0.6712	54712	0.6158
5	5.78	3.31	1.0	3.4076	0.6815	54716	0.6159
6	3.19	1.83	0.50	4.0000	0.6667	54718	0.6159
7	2.15	1.24	0.4	4.3940	0.6277	54719	0.6159
8	1.51	0.87	0.3	4.7466	0.5933	54720	0.6159
9	1.24	0.71	0.2	4.9470	0.5497	54720	0.6159
10	1.16	0.66	0.1	5.0155	0.5015	54721	0.6159
Control							
Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	164.17	100	27.8	0			
1	153.78	93.67	26.1	0.0520	0.1041		
2	144.33	87.92	24.5	0.0654	0.0654		
3	136.67	83.25	23.2	0.1288	0.0611		
4	131.72	80.24	22.3	0.1833	0.0551		
5	126.52	77.07	21.5	0.2202	0.0522		
7	116.17	70.76	19.7	0.2605	0.0494		
10	102.26	62.29	17.3	0.3459	0.0473		

4.3 Aniline

4.3.1 Stirring Experiments

Three stirring experiments were carried out with speed 500 rpm, 750 rpm, and 1000 rpm.

Because the rate of volatilization of Aniline is slow, all the Aniline experiments were conducted for 5 hours.

The results are shown in Table 4.23, Table 4.24 (appendix B), and Table 4.25 (appendix B).

Table 4.23 Volatilization of Aniline Stirring at 500 rpm(296K)

Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	95.48	100	18.5	0	
10	95.31	99.82	18.4	0.00180	0.00018

Table 4.23 (Continued)

20	94.79	99.27	18.3	0.00734	0.00037
40	94.53	98.99	18.3	0.01007	0.00025
80	93.28	97.69	18.0	0.02339	0.00029
100	92,59	96.97	17.9	0.03074	0.00030
130	91.74	96.07	17.7	0.04006	0.00031
160	90.58	94.87	17.5	0.05271	0.00033
190	89.43	93.66	17.3	0.06547	0.00034
220	88.71	92.90	17.1	0.07361	0.00033
250	87.61	91.75	16.9	0.08610	0.00034
280	86.68	90.78	16.8	0.09679	0.00035
300	85.46	89.50	16.5	0.11094	0.00037
Control					
Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	85.50	100	16.5	0	
10	84.94	99.34	16.4	0.00661	0.00066
20	84.77	99.14	16.4	0.00865	0.00022
40	84.62	98.97	16.4	0.01037	0.00052
60	84.47	98.79	16.3	0.01213	0.00021
80	84.45	98.78	16.3	0.01229	0.00020
100	83.82	98.03	16.2	0.01983	0.00015
130	83.53	97.69	16.1	0.02331	0.00020
160	83.37	97.52	16.1	0.02516	0.00018
190	82.62	96.62	15.9	0.03434	0.00016
220	82.46	96.44	15.8	0.03620	0.00018
250	81.78	95.64	15.7	0.04457	0.00018
280	81.27	95.05	15.7	0.05078	0.00019
300	80.58	94.24	15.6	0.05932	0.00020

4.3.2 Aeration Experiments

Aeration experiments of Aniline were carried out with four flow rates. Each one ran for 5 hours. The results are shown in Table 4.26, Table 4.27 (appendix B), Table 4.28 (appendix B), and Table 4.29 (appendix B).

Table 4.26 Volatilization of Aniline Aeration at 22 ml/sec.(298K)

Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	91.37	100	17.7	0		90.37	0.00104
10	89.96	98.46	17.4	0.01555	0.00156	90.37	0.00104
20	89.64	98.11	17.3	0.01913	0.00096	90.37	0.00104

Table 4.26 (Continued)

40	88.49	96.85	17.1	0.03205	0.00080	90.38	0.00104
60	86.76	94.95	16.8	0.05182	0.00086	90.38	0.00104
90	84.79	92.80	16.4	0.07470	0.00083	90.38	0.00104
120	82.70	90.51	16.0	0.09967	0.00083	90.38	0.00104
150	80.25	87.83	15.5	0.12975	0.00087	90.38	0.00104
180	78.31	85.71	15.1	0.15421	0.00086	90.38	0.00104
210	76.64	83.88	14.8	0.17585	0.00084	90.38	0.00104
240	74.17	81.18	14.3	0.20855	0.00087	90.39	0.00104
270	72.44	79.28	14.0	0.23215	0.00086	90.39	0.00104
300	70.96	77.66	13.7	0.25283	0.00085	90.39	0.00104
Control							
Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	90.19	100	17.4	0			
10	90.03	99.82	17.4	0.00180	0.00018		
60	89.96	99.74	17.4	0.00262	0.00005		
90	89.47	99.20	17.3	0.00805	0.00009		
120	89.10	98.79	17.2	0.01216	0.00010		
150	88.14	97.72	17.0	0.02305	0.00015		
180	87.64	97.17	16.9	0.02871	0.00016		
210	86.55	95.96	16.7	0.04122	0.00020		
240	86.06	95.42	16.6	0.04685	0.00020		
270	85.33	94.61	16.5	0.05542	0.00021		
300	84.68	93.89	16.4	0.06302	0.00021		

CHAPTER 5

DISCUSSION

5.1 Stirring Experiment

In the stirring experiment, the solution is stirred by a magnetic stirrer from the bottom of beaker so that the intra-phase mass transfer is speeded up and the system reaches equilibrium faster than a quiescent one. Then volatilization rate of VOCs from the surface of the agitated solution is accelerated. For the nonpolar compounds, the toluene and xylenes, the stirring rate has a large effect on the evaporation rate. But the volatilization of the more polar compound, aniline, is affected much less by stirring rate . Following is a more detailed discussion of these experiment results.

5.1.1 Toluene

Figure 5.1 shows volatilization curves of toluene (based on the data of Table 4.1, Table 4.2, Table 4.3, Table 4.4).

From Figure 5.1, we can see that the curves go down very quickly at the beginning, then tend to become slow as the driving force (concentration) becomes small. Also, the higher the speed of stirring, the faster the contaminant volatilizes. The control experiment (without stirring) has a much slower rate of the volatilization.

Taking the average of the Re from the different stirring speed and comparing to each other, it can be found the rate constant of stirring at 250 rpm is 5 times as control one, 500 rpm is 10 times as control one, 750 rpm is 23 times as control one, and 1000 rpm is 53 times as control one.

The straight lines of kinetic curve of toluene with stirring treated as first order reaction (Figure 5.2) indicate the volatilization of toluene following the first-order kinetics.
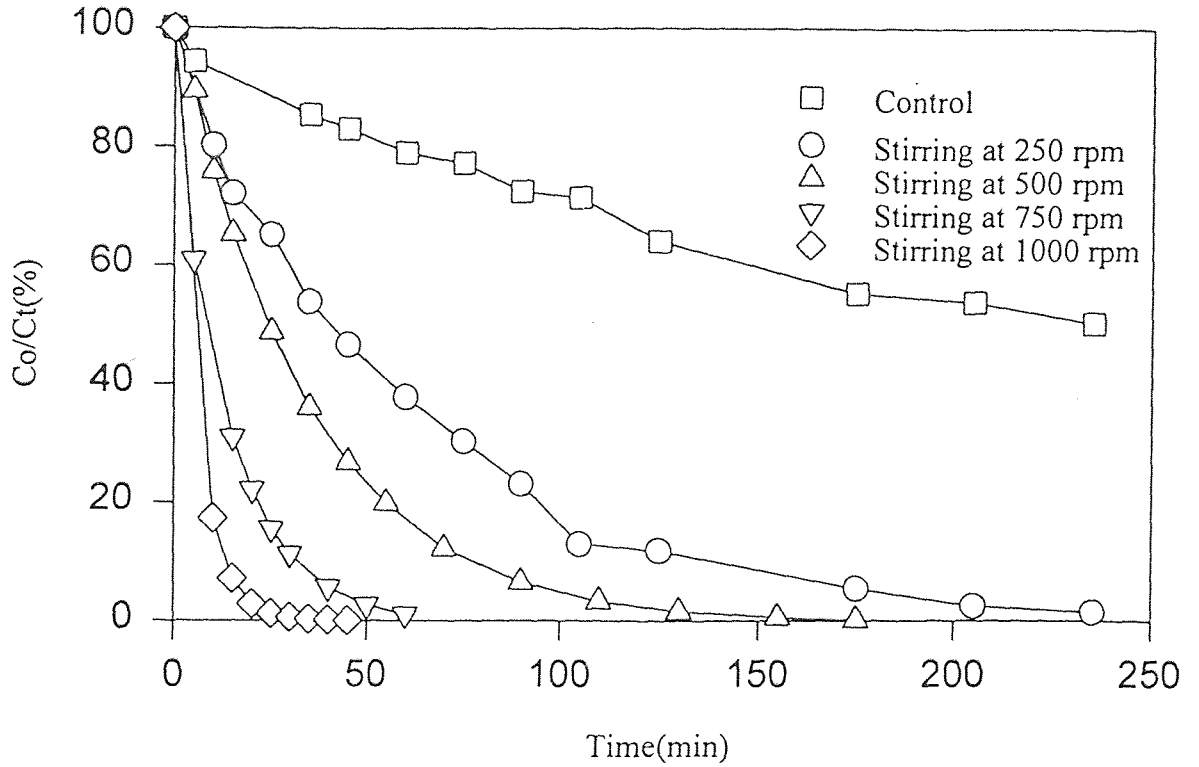
Figure 5.1 Volatilization Curve of Toluene with Stirring
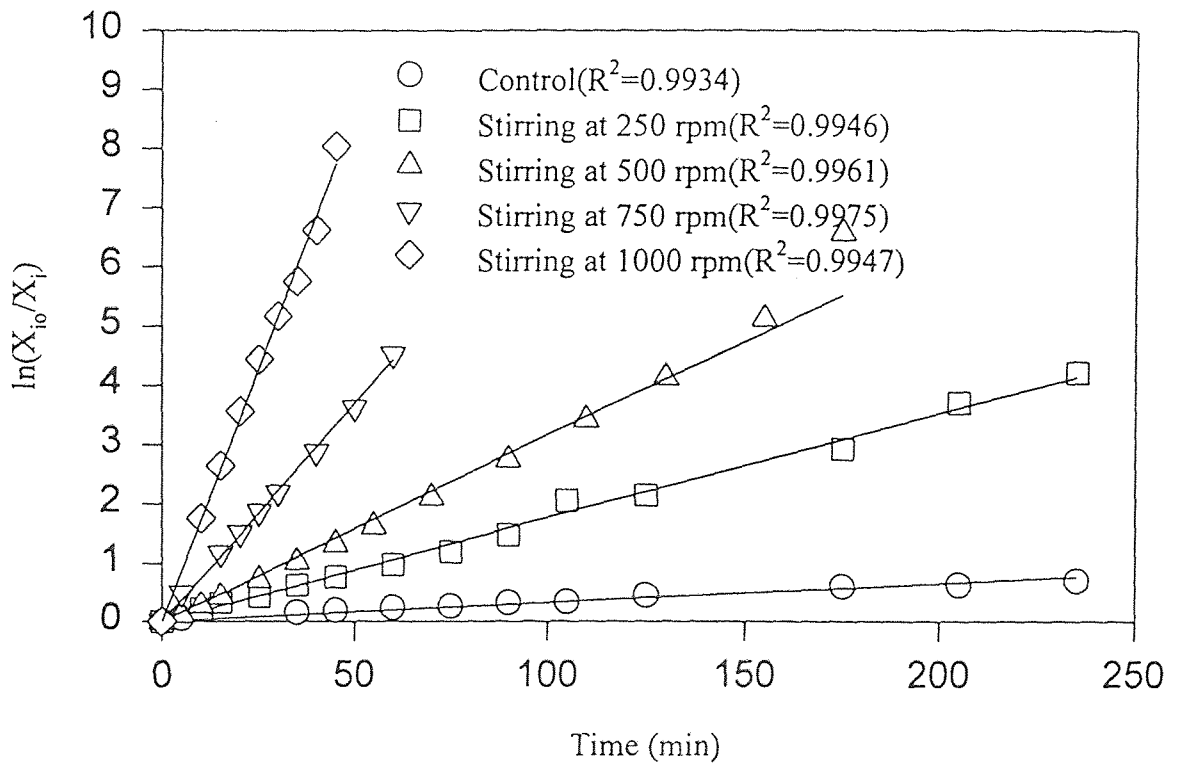
Figure 5.2 First Order Kinetic Curve of Toluene Volatilization with Stirring

5.1.2 Xylenes

Figure 5.3, Figure 5.4 (appendix C), Figure 5.5 (appendix C) (using data from Table 4.9, Table 4.10, Table 4.11, Table 4.12, Table 4.13, and Table 4.14) give the trend of volatilization of Xylenes.

The rate of emission increases with the stirring speed increases in a similar way. In Figure 5.3, the two curves of stirring at 750 rpm, and 1000 rpm go down much more quickly than the others. Comparing the average rate constant of m-Xylene experiments, we find that the rate constant of stirring at 250 rpm is 7.7 times as the control (without stirring); stirring at 500 rpm is 11 times as control one; stirring at 750 rpm is 66 times as control one; and stirring at 1000 rpm is 146 times as control one. Though the quantitative relationship between stirring rate and volatilization rate constant is not established, the trend of volatilization is clear.
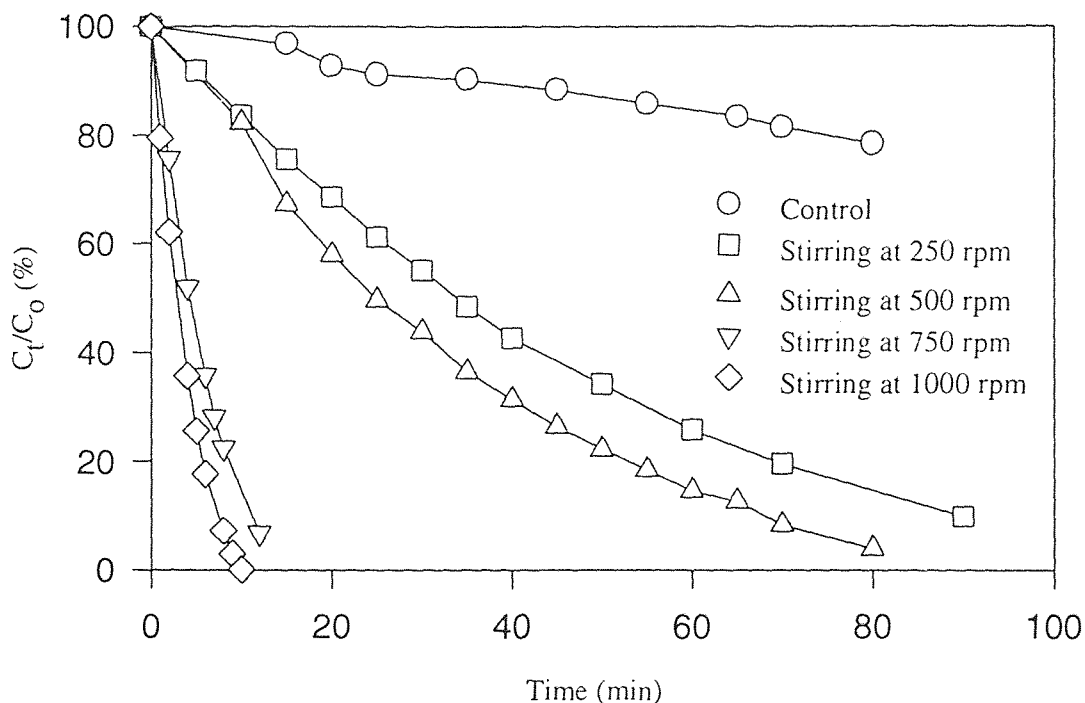
Figure 5.3 Volatilization Curve of m-Xylene with stirring

The kinetic curve of m-Xylene is given by Figure 5.6. It shows the volatilization of m-Xylene has very good agreement with the first order kinetics.
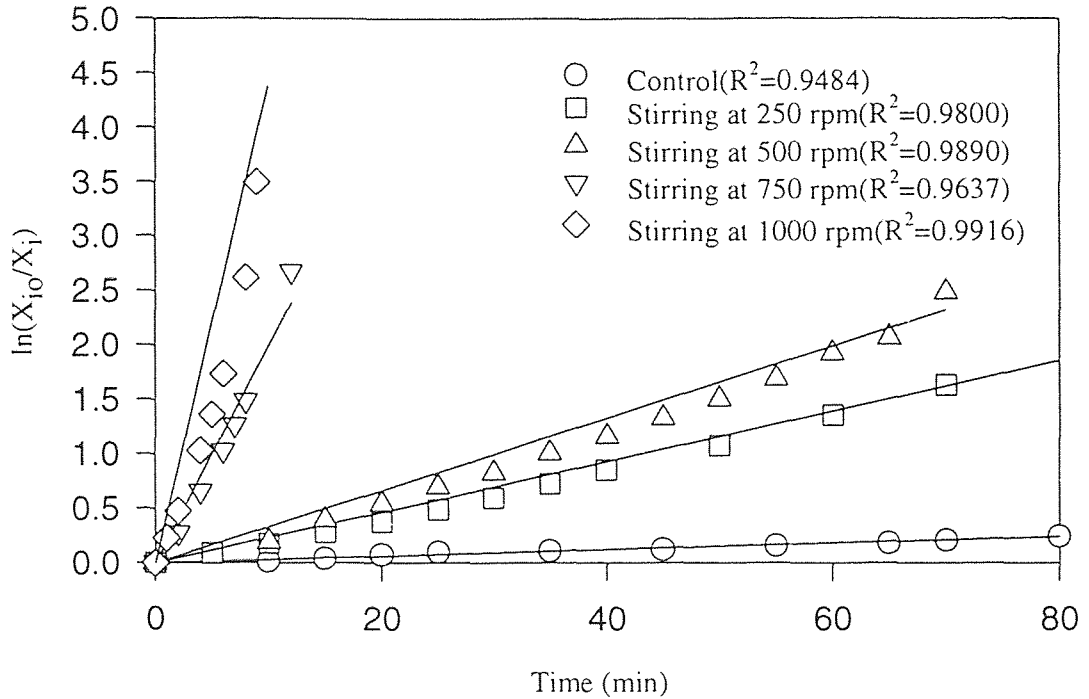
Figure 5.6 First Order Kinetic Curve of m-Xylene Volatilization with Stirring

5.1.3 Aniline

Figure 5.7. is drawn by using data of Table 4.23, Table 4.24, and Table 4.25.

It shows the volatilization trend of Aniline. From the figure, we can directly see that the curves go down very slowly. Within the 300 minute time range, the concentration of aniline only changed less than 25 percent. Because of a $-NH_2$ group is present in the structure, aniline is a polar compound and its solubility in water is as high as 3.5%.

In this case, the material balance can be written as :

$$\frac{d(x_i \rho_L V)}{dt} = -y_i \rho_v A \qquad (5.1)$$
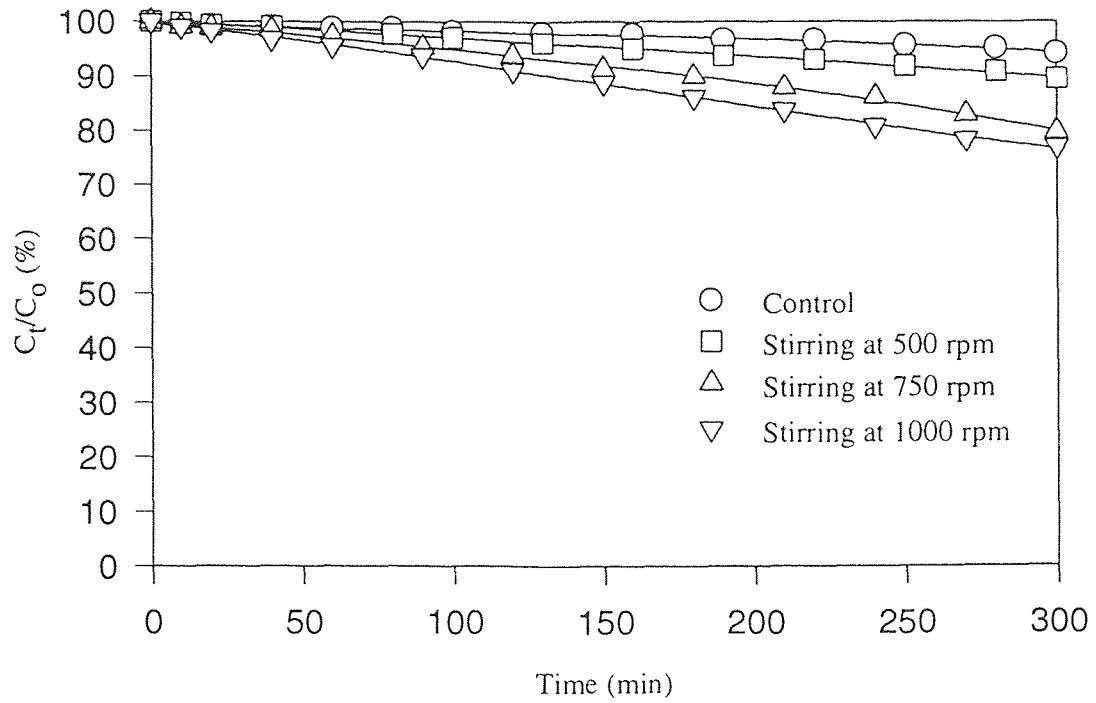
Figure 5.7 Volatilization Curve of Aniline with Stirring

The water also evaporates as it attempts to establish an equilibrium between the two phases. Since the water is nearly pure, if equilibrium were established, its partial pressure would equal its vapor pressure, which for water is 0.0312 atm at 25 °C. Thus the rate at which the water evaporates, assuming the entering air is dry and that the exiting air is saturated with water would be given by:

$$\frac{d(\rho_L V)}{dt} = -\left(\frac{P^{\circ}_{water}}{P}\right)\rho_v A \qquad (5.2)$$

We can divide the equation(5.1) and (5.2) to determine which substance volatilizes more quickly. Also, if we compare this ratio to the mole fraction of the contaminant, we can determine whether the solution will become more dilute or more concentrated with the passage of time. This ratio is:

$$\frac{\text{volatization rate of contaminant}}{\text{volatization rate of water}} = x_i \gamma_i (LR) \frac{P_i^{\circ}}{P_{water}^{\circ}} = x_i \frac{\gamma_i (LR)}{\gamma_i^{\infty} (LR)} \frac{H_{i,j}}{P_{water}^{\circ}} \qquad (5.3)$$

We can compare this ratio to the mole fraction of the contaminant by dividing by x_i. The quantity will be given by:

$$\gamma_i (LR) \frac{P_i^{\circ}}{P_{water}^{\circ}} = \frac{\gamma_i (LR)}{\gamma_i^{\infty} (LR)} \frac{H_{i,j}}{P_{water}^{\circ}} \qquad (5.4)$$

This quantity can be called the "volatilization susceptibility factor". If it is less than one, then the solution will become more concentrated (water evaporates faster than the contaminant). If it is approximately equal to one, then the concentration will not change. If the ratio is larger than one, then the solution will become more dilute. If it is much larger than one, then the water volatilization rate is not significant(at least compared to concentrated ones). Equation (5.4) can be used to evaluate volatilization susceptibility factor of toluene, xylene, and other contaminants.

For aniline, the volatilization susceptibility factor is about 6.3 (25°C), thus it will volatilize, but not much more quickly than water. As compared to toluene(the factor is 11310), xylenes (the factors are: 11860 for m-xylene, 10780 for p-xylene, and 7450 for o-xylene), the volatilization rate of aniline is much smaller.

Since water also volatilizes from the solution simultaneously as the aniline volatilizes, the volatilization of aniline deviates from the first order reaction kinetics. It can be demonstrated by comparing Figure 5.7 with Figure 5.1 or Figure 5.3. They are obviously different.

5.1.4 Comparison of Rate Constant with Different Contaminants

The solubility in water of xylene is 0.018%. It is smaller than Toluene (0.051%). Also, the activity coefficient of Xylene is 56500 in infinite dilute solution(at 25 °C), it is higher than 12270 of Toluene under the same condition. Aniline has the largest water solubility

(3.6%),and the smallest infinite dilution activity coefficient(90).The differences of these properties should be the main reason for the order of volatilization rate for three compounds.
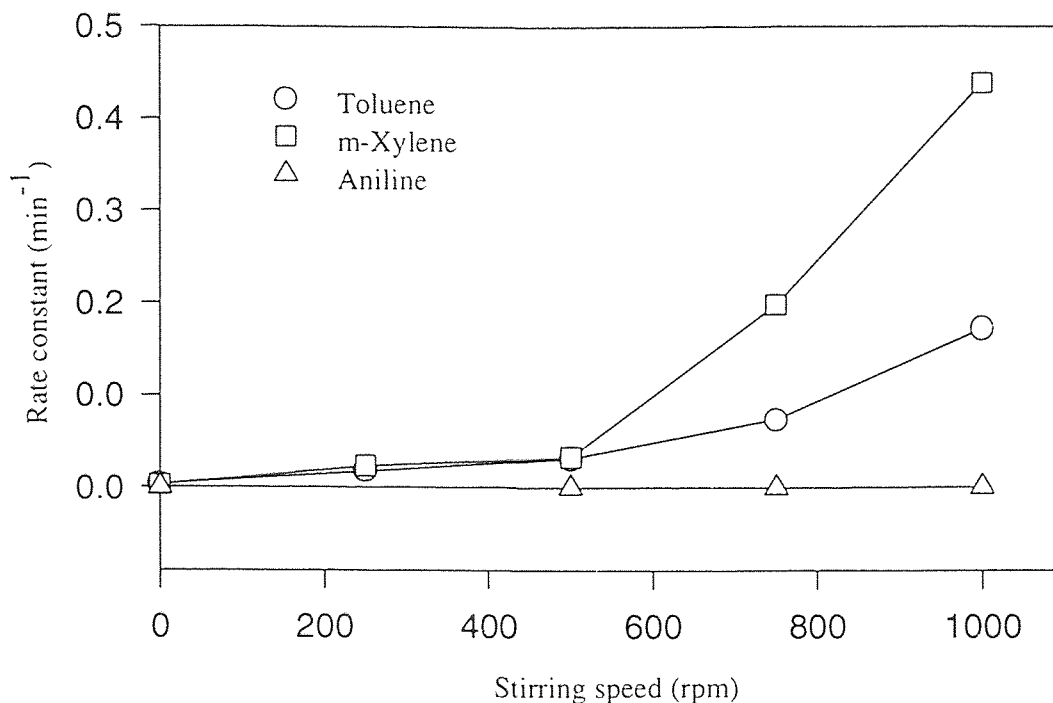
Figure 5.8 Comparison of Rate Constants with Stirring

Figure 5.8 gives the comparison of rate constant for toluene, m-xylene, and aniline. It shows that m-xylene volatilizes the fastest, toluene is slightly slower than m-xylene, aniline is the slowest.

5.2 Aeration Experiments

In aeration experiments, air flow is introduced into a solution which contains the contaminant by a sparge and produces many bubbles in the solution. The contaminant is brought out by the bubbles because both larger contact area between the solution and air is created by bubbles and solution is agitated by the air flow. Since the volatilization rate of the aeration experiment is larger than stirring ones for toluene and xylenes, it can be

inferred that air stripping is a much more efficient method to remove the nonpolar VOCs from water. For aniline the difference is not so great because the polar compounds are more difficult to remove from water due to their stronger hydrophilic property. The further discussion in the following several sections.

5.2.1 Toluene

Volatilization of m-xylene is presented in Figure 5.9 (using data of Table 4.5, Table 4.6, Table 4.7, and Table 4.8).
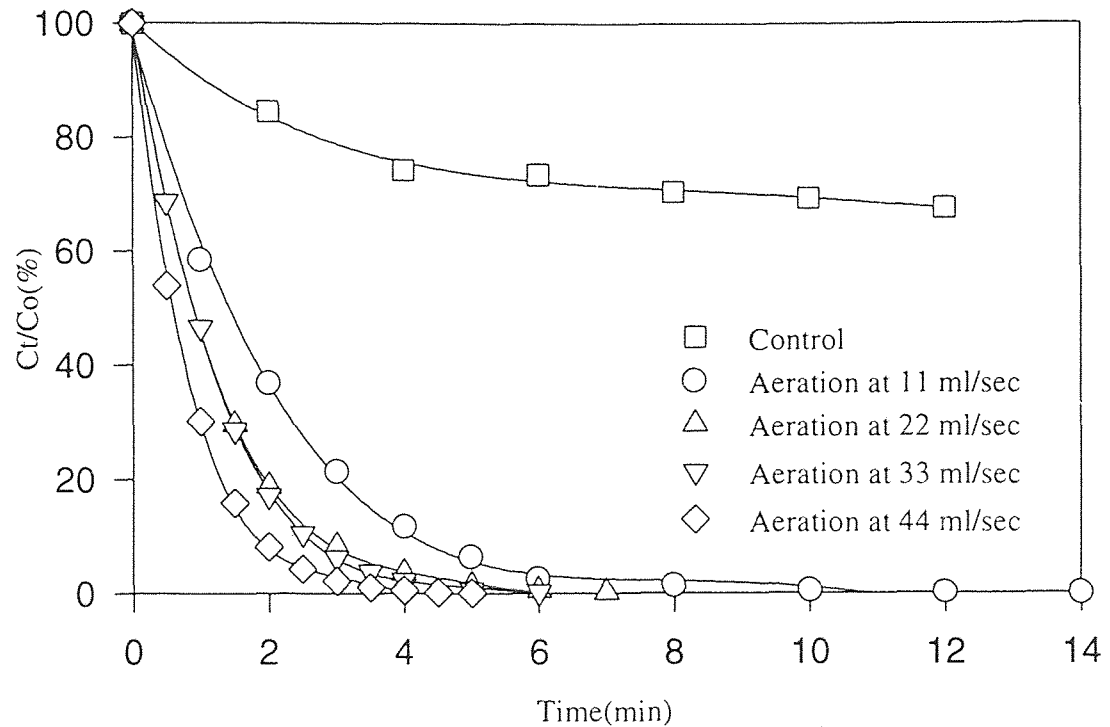
Figure 5.9 Volatilization Curve of Toluene with Aeration

It shows the concentration of toluene changed with the time at different aeration flowrates. From the figure, it is presented clearly that the rate of volatilization increases with the flowrate increases, and aeration experiments are much faster than the control (without aeration) one. That means efficiency of toluene removal by aeration is high.

That the straight lines of the kinetic curves when the evaporation process is treated as first order reaction indicates that the volatilization behavior of toluene obeys the first-order reaction kinetics (see Figure 5.10.).

As noted previously, rate constants can be evaluated experimentally by using the first order kinetics as equation (4.1) and determined theoretically by using calculation modal (2.16) based on Henry's Law in aeration experiments. The results of toluene evaporation are presented in Table 4.5, 4.6, 4.7, and 4.8. All the experimental values are smaller than theoretical ones. Taking the average of rate constants, and comparing them each other at different flowrates, we can get the relationship between theoretical rate constants and experimental ones (see Figure 5.11) the difference between Rt and Re increases with the flowrate increases. At flowrate of 11 ml/sec, Re is 62% of Rt; at 22 ml/sec, Re is 46% of Rt; at 33 ml/sec, Re is 36% of Rt; and at 44 ml/sec, Re is 35% of Rt.

The theoretical rate constant is calculated by assuming equilibrium occurs. The experimental value of rate constant is less than theoretical one, indicating that equilibrium is not achieved with aeration. As expected, the experimental rate constants for the stirring cases and control ones are much lower than for aeration. Since all experiments were conducted in the hood in the laboratory, thus providing a continuous overflow of air for all cases, we can confidently expect these to be the maximum possible rate constants for volatilization of compounds we test in these scenarios.

5.2.2 Xylenes

Figure 5.12, Figure 5.13 (appendix C), and Figure 5.14 (appendix C) present the volatilization of xylenes for aeration cases. Compare to 10 minutes for stirring at 1000 rpm experiment of m-xylene, all aeration process just take less than 6 minutes(see Table 4.10, and all tables in Chap 4.2.2.). It clearly indicates that the volatilization rate of xylenes is speeded up by aeration with the flowrate increases.
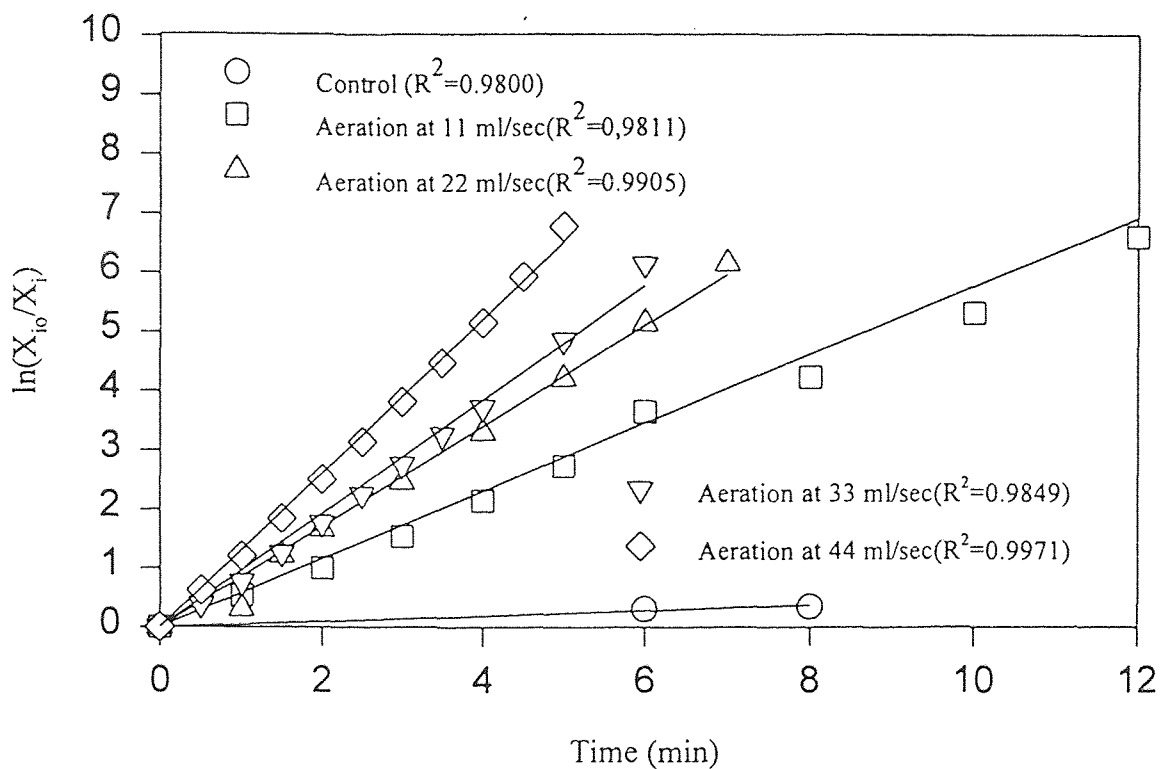
Figure 5.10 First Order Kinetic Curve of Toluene Volatilization with Aeration
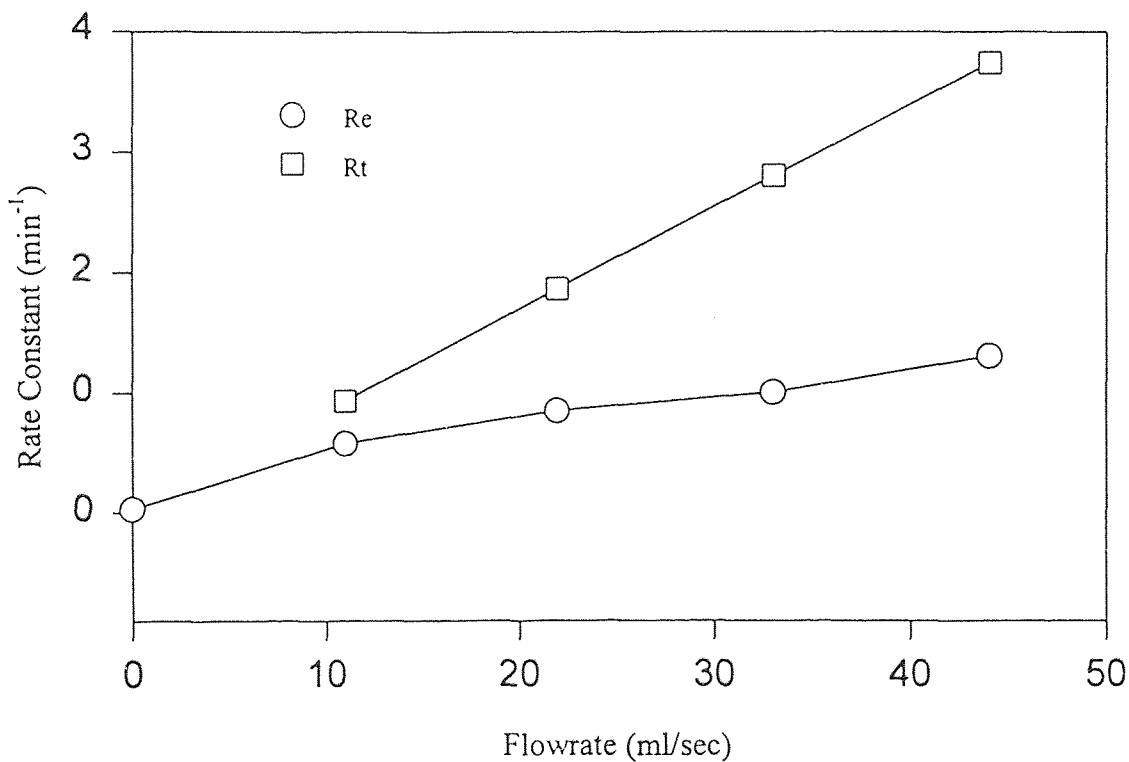
Figure 5.11 Comparison of Rate Constants of Toluene
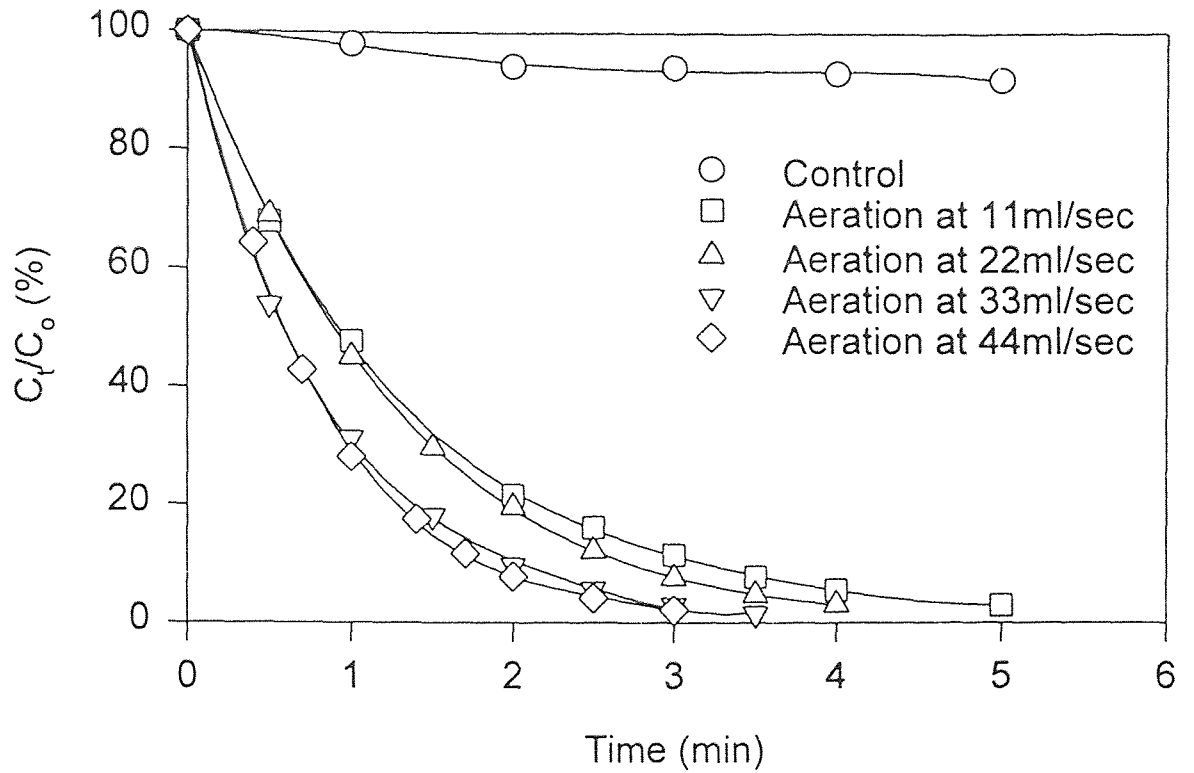
Figure 5.12 Volatilization Curve of m-Xylene with Aeration
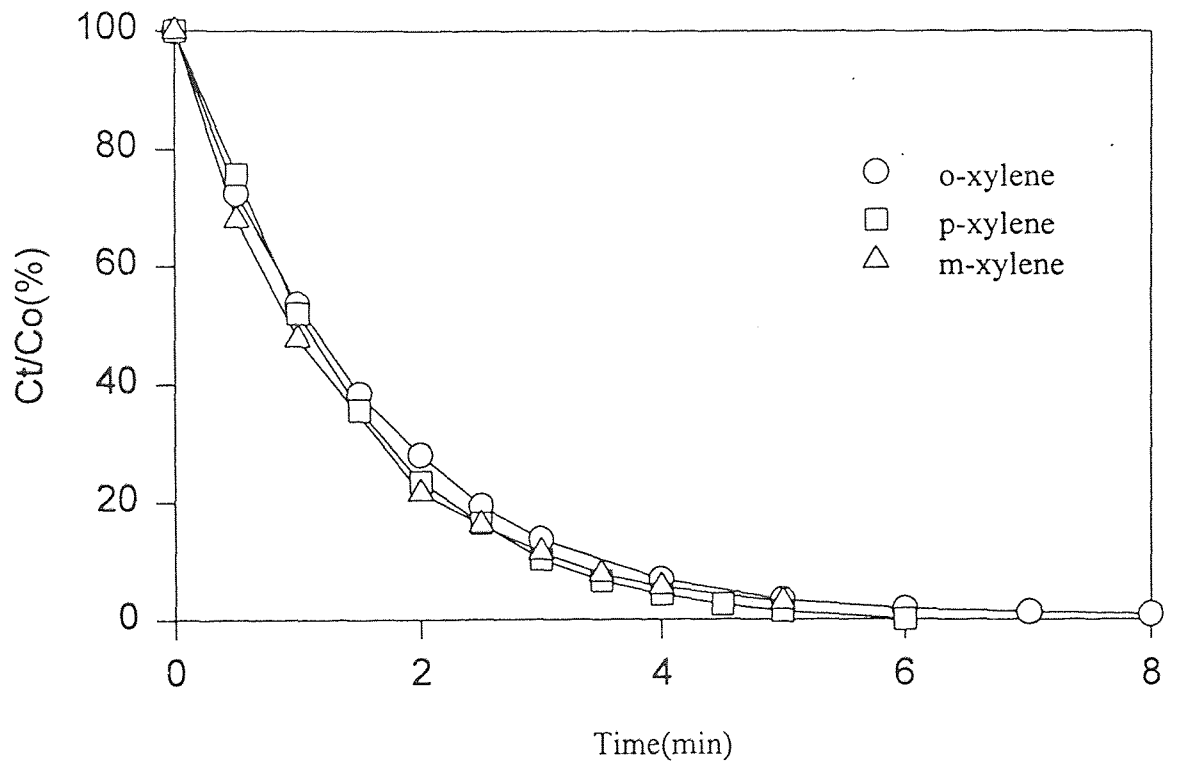
Figure 5.15 Comparison of Volatilization of Xylenes

Figure 5.15 compares the volatilization of the three xylenes. The three curves are only slightly different, but still can be separated by increasing sequence: o-xylene, p-xylene, and m-xylene. The result may be caused by the difference in Henry's constant values. Their Henry's constants are: 370.1 (atm/mol.frac.) for m-xylene; 336.9 (atm/mol.frac.) for p-xylene; 232.5 (atm/mol.frac.) for o-xylene [Carl, et al, 1991].

Figure 5.16 presents the difference between experimental and theoretical values for rate constants of m-xylene volatilization at different aeration flowrates. The difference between Re and Rt increases as the aeration flowrate increases. At flowrate 11 ml/sec, Re is 74% of Rt; at 22 ml/sec, Re is 70% of Rt; at 33 ml/sec, Re is 40% of Rt; and at 44 ml/sec, Re is 33% of Rt. Thus the higher the speed of aeration, the further the system is from the equilibrium.

In addition, Figure 5.17, Figure 5.18 (appendix C), and Figure 5.19 (appendix C) are the kinetic curves of the xylenes. Figures show that the volatilization of xylenes follows first order reaction kinetics.

5.2.3 Aniline

The trend of volatilization of aniline is shown in Figure 5.20 (appendix C). It clearly shows that the rate of volatilization is very slow. Despite increases in the flowrate of aeration , the rate is still not accelerated much.

Figure 5.21 (appendix C) presents the comparison of the both theoretical and experimental rate constants. Like other contaminants we mentioned above, aniline also has the smaller Re than Rt. It indicates the equilibrium is not achieved. At flowrate 22 ml/sec, Re is 63% of Rt; at 44 ml/sec, Re is 46% of Rt; at 66 ml/sec, Re is 39% of Rt; and at 88 ml/sec, Re is 26% of Rt.
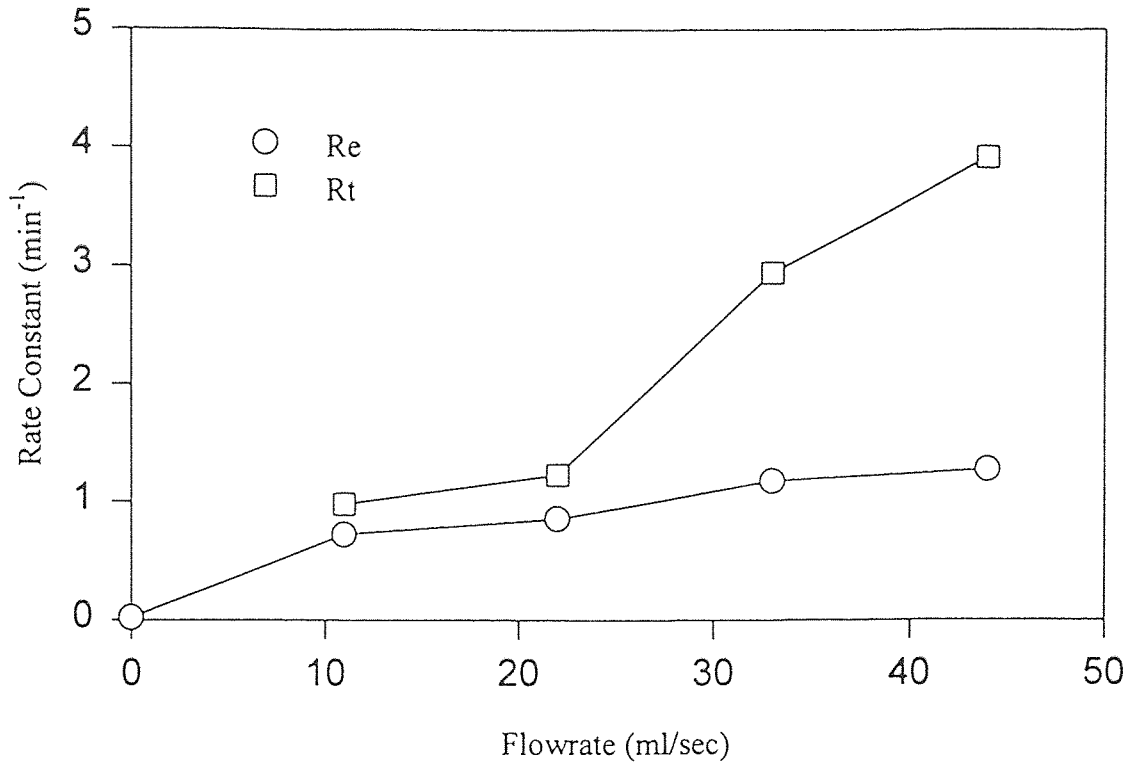
Figure 5.16 Comparison of Rate Constants of m-Xylene

Time (min)
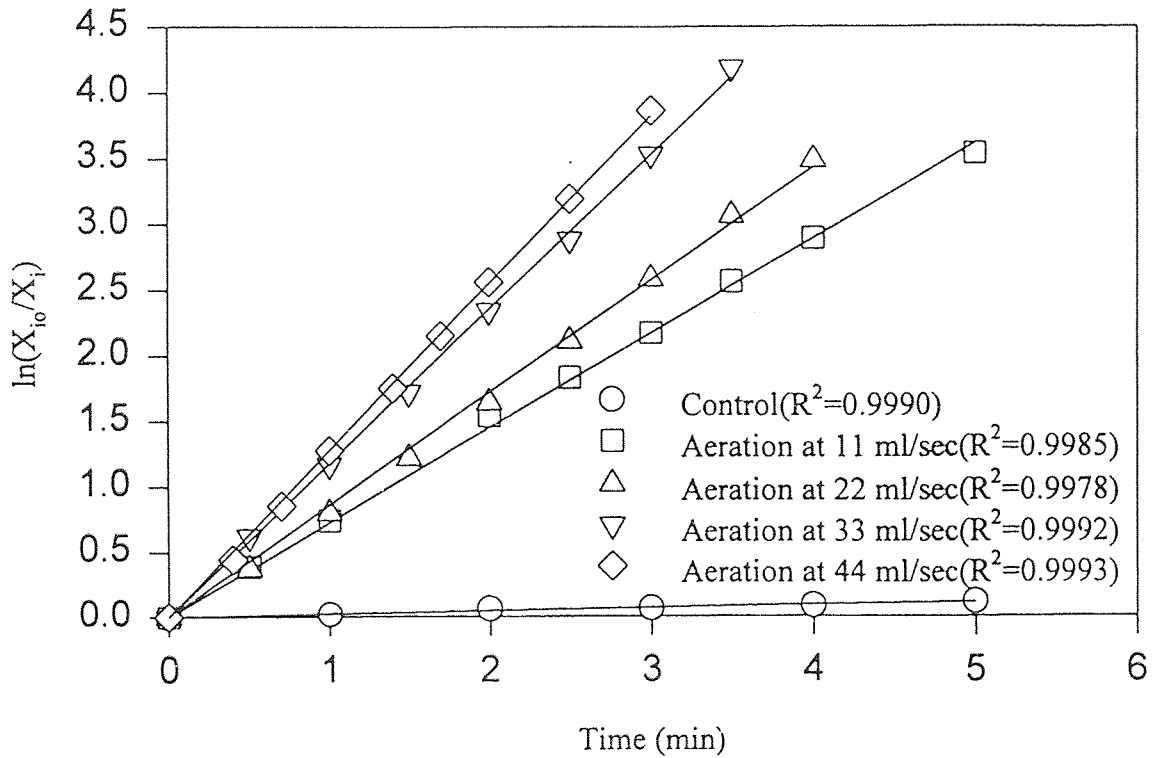
Figure 5.17 First Order Kinetic Curve of m-Xylene Volatilization with Aeration

5.2.4 Evaluating Mass Transfer Coefficient

Mass transfer coefficients in aeration system can be evaluated by relationships we mentioned in Chapter 1. These relationships were developed by Hsieh, Babcock, and Stenatrom[1994].

Mass transfer coefficients can be calculated by equations (1.5,1.6,1.7, and 1.8) using data we obtained from aeration experiments.

Figure 5.22 shows mass transfer coefficients of the three compounds (toluene, m-xylene, and aniline) with different aeration flowrates.

From Figure 5.22, we can clearly observe that the mass transfer coefficient of aniline is very low and almost does not change as aeration flowrate increases. For toluene and m-xylene , the mass transfer coefficients increase as aeration flowrate increases.
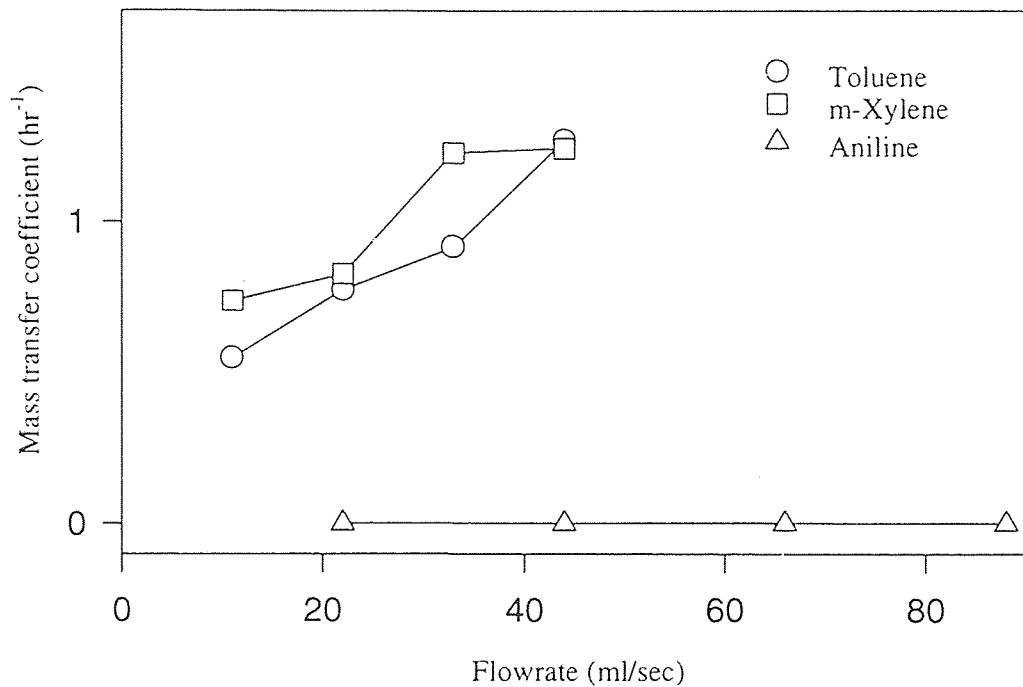
Figure 5.22 Relationship of mass transfer coefficient and aeration flowrate

CHAPTER 6

CONCLUSIONS AND SUGGESTIONS

Three volatile compounds, Toluene, Xylenes, and Aniline , were studied in the thesis under varying aeration and stirring conditions to simulate the process of VOCs treatment in wastewater. These three compounds were chosen because toluene is one of major compound found in wastewater influent samples [Michael, Pellizzai, et al, 1991] and Xylenes and Aniline (one kind of amines) are also usually found in wastewater as a main contaminant [Shen, Sewell, et al, 1988].

As the results we discussed in Chapter 5, Aniline volatilizes the slowest in three compounds because of its high polarity and solubility and low Henry's constant in water. Stirring and aeration only change its emission very slightly. Hence, aniline can not be removed by simple air stripping. Because the volume of solution decreases with the time as the solvent evaporates, the result is obviously away from the normal first order kinetics.

Stirring and aeration can affect the volatilization rate both of xylene and toluene. Although xylene volatilizes slowly in quiescent solution because of its higher boiling point (around 140°C), its volatilization can be accelerated with stirring and raised significantly by aeration.

The kinetic treatment of the results is showed these evaporation processes obey the first order kinetics for xylenes and toluene. The rate constants are used to compare the rate of evaporation.

The Henry's constant of toluene is 353.1 atm/mol.frac, which is not much different from m-xylene (370.1 atm/mol.frac). From the results of stirring, though toluene has a lower boiling point, toluene volatilizes slower than m-xylene because xylene has a lower polarity than toluene. Under the aeration condition, the difference of theoretical rate constants between toluene and m-xylene is less than 5%. The difference of experimental

42

rate constants has no evident regularity, but it is obvious in the results that toluene volatilizes with a similar rate to m-xylene with aeration. That means the aeration speeds up the volatilization of toluene more than for xylene.

For all three compounds, the experimental rate constants are less than theoretical rate constants, and the difference between Rt and Re increases as the flowrate increases. If air flows through faster, the bubbles are larger, have less surface area for equilibration and less time to equilibrate. So the gas coming out is less saturated at higher flowrates. The quantitative relationship between difference of rate constants and aeration flowrate needs to be studied in further work.

In addition, only three compounds can not make the general conclusion of the study. More compounds need to be investigated in the same and other different conditions. The effects of polarity of compounds on volatilization rate could be another parameter which should be considered.

As mentioned above, aniline and other compounds with high water solubility are difficult to remove from water by air stripping. For removing these compounds, steam stripping is becoming more and more popular recently[Bravo, 1994]. Since the high temperatures inherent in steam stripping allow for the removal of heavier, more soluble organics, the next attempt might be focused on temperature effect.

APPENDIX A

PARAMETERS USED IN UNIFAC PROGRAM

Group Volume Parameters R_k and Surface Parameters Q_k

group	R_k	Q_k
ACH	0.5313	0.400
$ACCH_3$	1.2663	0.968
$ACNH_2$	1.0600	0.816
H_2O	0.92	1.40

Interaction Parameters of Toluene

m\n	ACH,1	$ACCH_3$,2	H_2O,3
ACH,1	0.0	167.0	903.8
$ACCH_3$,2	-146.8	0.0	5695.0
H_2O,3	362.3	377.6	0.0

Interaction Parameters of Aniline

m\n	ACH,1	$ACNH_2$	H_2O
ACH,1	0.0	668.2	903.8
$ACNH_2$	650.4	0.0	-339.5
H_2O	362.3	213.0	0.0

APPENDIX B

TABLES OF RESULTS AND CALCULATIONS

Table 4.3 Volatilization of Toluene Stirring at 750 rpm (297K)

Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	405.15	100	78.9	0	
5	246.79	60.91	48.1	0.4958	0.09917
15	125.47	30.97	24.4	1.1724	0.07816
20	89.73	22.15	17.5	1.5077	0.07539
25	62.93	15.53	12.3	1.8625	0.07450
30	45.46	11.22	8.8	2.1877	0.07292
40	22.86	5.64	4.5	2.8752	0.07188
50	10.83	2.67	2.1	3.6222	0.07245
60	4.39	1.08	0.8	4.5253	0.07542
Control					
Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	458.72	100	89.6	0	
5	449.43	97.97	87.8	0.02047	0.00409
15	443.62	96.71	86.7	0.03348	0.00223
20	441.89	96.33	86.4	0.03739	0.00187
25	431.00	93.96	84.2	0.06235	0.00249
30	404.87	88.26	79.1	0.1249	0.00416
40	400.44	87.30	78.3	0.1359	0.00340
50	391.94	85.44	76.6	0.1573	0.00315
60	380.73	83.00	74.4	0.1864	0.00311

Table 4.4 Volatilization of Toluene Stirring at 1000 rpm (298K)

Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	433.72	100	84.5	0	
10	75.09	17.31	14.6	1.7540	0.1754
15	30.81	7.10	6.0	2.6449	0.1763
20	12.31	2.84	2.4	3.5623	0.1781
25	5.12	1.18	1.0	4.4396	0.1775
30	2.46	0.57	0.5	5.1726	0.1724
35	1.37	0.32	0.3	5.7579	0.1645
40	0.58	0.13	0.1	6.6175	0.1654
45	0.14	0.03	0.0	8.0388	0.1786

45

Table 4.4 (continued)

Control					
Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	414.81	100	81.1	0	
10	291.88	70.36	57.0	0.3516	0.03516
20	265.77	64.07	51.9	0.4453	0.02227
25	263.25	63.46	51.4	0.4548	0.01819
30	262.54	63.29	51.3	0.4575	0.01525
35	249.65	60.18	48.8	0.5079	0.01451
45	245.81	59.25	48.0	0.5234	0.01163

Table 4.6 Volatilization of Toluene Aeration at 22 ml/sec(297K)

Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	485.74	100	94.7	0		12195	1.8602
1	353.98	72.87	68.9	0.3165	0.3165	12214	1.8631
1.5	143.94	29.63	28.0	1.2166	0.8110	12243	1.8676
2	91.71	18.88	17.9	1.6674	0.8337	12251	1.8688
3	40.99	8.44	8.0	2.4727	0.8242	12259	1.8699
4	17.82	3.67	3.5	3.3057	0.8264	12261	1.8704
5	7.14	1.47	1.4	4.2203	0.8441	12263	1.8706
6	2.82	0.58	0.6	5.1493	0.8582	12263	1.8706
7	1.03	0.21	0.0	6.1565	0.8795	12264	1.8707
Control							
Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	463.60	100	90.6	0			
2	391.33	84.41	76.5	0.1695	0.0848		
4	344.04	74.21	67.2	0.2984	0.0746		
6	340.70	73.49	66.6	0.3081	0.0514		

Table 4.7 Volatilization of Toluene Aeration at 33 ml/sec (296K)

Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	585.99	100	114.0	0		12350	2.7868
0.5	402.02	68.61	78.3	0.3769	0.7539	12377	2.7929
1	273.02	46.59	53.2	0.7640	0.7640	12395	2.7971
1.5	167.73	28.62	32.7	1.2513	0.8341	12411	2.8007
2	100.24	17.11	19.5	1.7661	0.8830	12421	2.8029
2.5	61.66	10.52	12.0	2.2521	0.9008	12426	2.8041
3	36.92	6.30	7.2	2.7650	0.9217	12430	2.8049
3.5	22.36	3.82	4.4	3.2665	0.9333	12432	2.8055
4	14.	2.39	2.7	3.7347	0.9337	12433	2.8058
5	4.51	0.77	0.9	4.8675	0.9735	12434	2.8060

Table 4.7 (continued)

6	1.26	0.21	0.3	6.1450	1.0241	12435	2.8061
7	0.27	0.046	0.0	7.6868	1.0981	12435	2.8061
Control							
Time(min)	Conc(ppm)	%(C_t/C_o)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	463.60	100	90.6	0			
2	391.33	84.41	76.5	0.1695	0.0848		
4	344.04	74.21	67.2	0.2984	0.0746		
8	326.48	70.42	63.8	0.3508	0.0439		

Table 4.8 Volatilization of Toluene Aeration at 44 ml/sec(296K)

Time(min)	Conc(ppm)	%(C_t/C_o)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	510.29	100	99.4	0		12361	3.7192
0.5	275.12	53.91	53.6	0.6180	1.2359	12396	3.7295
1	153.71	30.12	29.9	1.2002	1.2002	12414	3.7349
1.5	80.87	15.85	15.8	1.8425	1.2283	12424	3.7381
2	41.52	8.14	8.1	2.5092	1.2546	12429	3.7397
2.5	22	4.31	4.3	3.1443	1.2577	12432	3.7406
3	11.11	2.18	2.2	3.8275	1.2758	12433	3.7411
3.5	5.73	1.12	1.1	4.4897	1.2828	12434	3.7413
4	2.93	0.57	0.6	5.1604	1.2901	12435	3.7415
4.5	1.34	0.26	0.3	5.9427	1.3206	12435	3.7415
5	0.575	0.11	0.0	6.7888	1.3578	12435	3.7415
Control							
Time(min)	Conc(ppm)	%(C_t/C_o)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	463.60	100	90.6	0			
2	391.33	84.41	76.5	0.1695	0.0848		
4	344.04	74.21	67.2	0.2984	0.0746		
8	326.48	70.42	63.8	0.3508	0.0439		

Table 4.10 Volatilization of m-Xylene Stirring at 500 rpm (295K)

Time(min)	Conc.(ppm)	%(C_t/C_o)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	191.43	100	32.3	0	
10	157.39	82.22	26.6	0.1958	0.01958
15	128.82	67.29	21.7	0.3962	0.02641
20	111.09	58.03	18.7	0.5443	0.02721
25	95.09	49.67	16.0	0.6998	0.02799
30	83.91	43.83	14.2	0.8249	0.02750
35	69.82	36.47	11.8	1.0088	0.02882
40	60.09	31.39	10.1	1.1587	0.02897
45	50.68	26.48	8.6	1.3290	0.02953

Table 4.10 (continued)

50	42.70	22.30	7.2	1.5006	0.03001
55	35.37	18.48	6.0	1.6887	0.03070
60	28.02	14.63	4.7	1.9219	0.03203
65	24.23	12.65	4.1	2.0673	0.03180
70	15.93	8.32	2.7	2.4863	0.03552
80	7.58	3.96	1.3	3.2288	0.04036
Control					
Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	174.65	100	29.6	0	
10	172.58	98.81	29.3	0.01192	0.00119
15	168.90	96.71	28.6	0.03349	0.00223
20	161.98	92.75	27.5	0.07531	0.00376
25	159.18	91.14	26.7	0.09274	0.00371
35	157.61	90.24	26.5	0.1026	0.00293
45	154.19	88.28	26.1	0.1246	0.00277
55	149.74	85.73	25.4	0.1539	0.00280
65	145.61	83.37	24.7	0.1819	0.00280
70	142.11	81.36	24.1	0.2062	0.00295
80	136.84	78.35	23.2	0.2440	0.00305

Table 4.11 Volatilization of m-Xylene Stirring at 750 rpm (295K)

Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	180.16	100	30.3	0	
2	136.40	75.71	23.1	0.2783	0.1391
4	93.76	52.04	15.9	0.6532	0.1633
6	64.60	35.86	10.9	1.0258	0.1709
7	50.79	28.19	8.6	1.2663	0.1809
8	40.62	22.55	6.9	1.4897	0.1862
12	12.43	6.90	2.1	2.6743	0.2228
Control					
Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	186.33	100	31.6	0	
2	175.77	94.33	29.8	0.01922	0.01922
4	173.77	93.26	29.5	0.05836	0.02918
6	166.76	89.50	28.3	0.06039	0.02013
8	166.19	89.12	28.2	0.08167	0.01745
10	158.99	85.33	26.9	0.1109	0.01633
12	158.17	84.88	26.8	0.1144	0.01849

Table 4.12 Volatilization of m-Xylene Stirring at 1000 rpm (295K)

Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	180.78	100	30.7	0	
1	143.71	79.49	24.4	0.2295	0.2295
2	112.30	62.12	19.0	0.4761	0.2381
4	64.55	35.71	10.9	1.0298	0.2574
5	46.47	25.70	7.9	1.3586	0.2717
6	32.01	17.71	5.4	1.7313	0.2886
8	13.20	7.30	2.2	2.6172	0.3271
9	5.47	3.03	0.9	3.4983	0.3887
10	0.19	0.11	0.3	6.8425	0.6842
Control					
Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	176.30	100	29.9	0	
2	164.32	93.20	27.9	0.0704	0.03520
4	150.23	85.21	25.5	0.1600	0.04000
6	148.68	84.33	25.2	0.1705	0.02841
8	143.79	81.56	24.4	0.2038	0.02548
10	141.98	80.53	24.1	0.2165	0.02165

Table 4.16 Volatilization of m-Xylene Aeration at 22 ml/sec (295K)

Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	158.60	100	26.9	0		59203	1.2288
0.5	109.39	68.97	13.9	0.3715	0.7431	59243	1.2300
1	71.47	45.06	8.1	0.7972	0.7971	59273	1.2307
1.5	47.02	29.64	4.6	1.2159	0.8106	59299	1.2311
2	30.93	19.50	2.5	1.6349	0.8174	59309	1.2314
2.5	19.27	12.15	1.4	2.1082	0.8432	59319	1.2315
3	12.04	7.59	0.8	2.5787	0.8595	59324	1.2317
3.5	7.42	4.68	0.4	3.0618	0.8748	59329	1.2317
4	4.87	3.07	0.0	3.4836	0.8709	59334	1.2318
Control							
Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	163.63	100	31.9	0			
2	163.20	99.74	31.8	0.00263	0.0013		
4	162.97	99.59	31.8	0.00404	0.0010		
6	161.59	98.75	31.5	0.01255	0.0021		

Table 4.17 Volatilization of m-Xylene Aeration at 33 ml/sec. (295K)

Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	151.82	100	25.7	0		59208	2.9350
0.5	81.77	53.86	13.9	0.6188	1.2377	59268	2.9380
1	47.46	31.26	8.1	1.1629	1.1629	59294	2.9392
1.5	27.33	18.00	4.6	1.7149	1.1433	59314	2.9402
2	14.63	9.63	2.5	2.3400	1.1700	59324	2.9407
2.5	8.52	5.61	1.4	2.8800	1.1520	59329	2.9410
3	4.47	2.94	0.8	3.5257	1.1752	59330	2.9411
3.5	2.31	1.52	0.0	4.1873	1.1963	59333	2.9412
Control							
Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	163.63	100	31.9	0			
2	163.20	99.74	31.8	0.00263	0.0013		
4	162.97	99.59	31.8	0.00404	0.0010		
6	161.59	98.75	31.5	0.01255	0.0021		

Table 4.18 Volatilization of m-Xylene Aeration at 44 ml/sec.(296K)

Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	166.88	100	28.3	0		58231	3.9123
0.4	107.28	64.28	18.2	0.4419	1.1047	58280	3.9157
0.7	71.41	42.79	12.1	0.8490	1.2129	58310	3.9177
1	46.78	28.03	7.9	1.2720	1.2720	58335	3.9193
1.4	29.12	17.45	4.9	1.7462	1.2477	58349	3.9203
1.7	19.45	11.65	3.3	2.1497	1.2645	58354	3.9206
2	12.95	7.76	2.2	2.5562	1.2781	58359	3.9209
2.5	6.88	4.12	1.2	3.1890	1.2756	58364	3.9213
3	3.51	2.11	0.0	3.8610	1.2870	58369	3.9216
Control							
Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	167.35	100	32.7	0			
2	167.08	99.84	32.6	0.00162	0.00081		
4	165.76	99.05	32.4	0.00955	0.00238		
6	162.72	97.23	31.8	0.02806	0.00467		

Table 4.20 Volatilization of p-Xylene Aeration at 22 ml/sec.(295K)

Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	156.81	100	26.6	0		59203	1.7810
0.5	108.35	69.10	18.4	0.3697	0.7394	59243	1.7822
1	65.70	41.90	11.1	0.8700	0.8700	59278	1.7833
1.5	40.05	25.54	6.8	1.3650	0.9100	59303	1.7840
2	23.66	15.09	4.0	1.8912	0.9456	59313	1.7843
2.5	12.02	7.67	2.0	2.5686	1.0274	59324	1.7846
3	5.30	3.38	0.9	3.3878	1.1292	59329	1.7847
3.5	1.93	1.23	0.3	4.4002	1.2572	59332	1.7848
4	0.056	0.036	0.0	7.9375	1.9844 ·	59334	1.7849
Control							
Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	151.96	100	25.8	0			
0.5	146.80	96.60	24.9	0.03453	0.0691		
1	139.15	91.57	23.6	0.08805	0.0881		
1.5	134.11	88.26	22.7	0.1249	0.0833		
2	126.19	83.04	21.4	0.1858	0.0929		
3	118.54	78.01	20.1	0.2484	0.0828		
4	110.38	72.64	18.7	0.3197	0.0799		

Table 4.22 Volatilization of o-Xylene Aeration at 22 ml/sec.(298K)

Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	173.87	100	29.5	0		56366	1.2288
0.5	103.10	59.30	17.5	0.5227	1.0454	56423	1.2300
1	64.44	37.06	10.9	0.9927	0.9927	56456	1.2307
1.5	40.90	23.52	6.9	1.4472	0.9648	56476	1.2311
2	26.53	15.26	4.5	1.8800	0.9400	56485	1.2314
2.5 ·	17.79	10.23	3.0	2.2798	0.9119	56489	1.2315
3	11.58	6.66	1.0	2.7080	0.9030	56498	1.2317
3.5	7.70	4.43	0.5	3.1168	0.8905	56499	1.2317
4	5.49	3.15	0.3	3.4555	0.8639	56501	1.2317
5	2.89	1.66	0.1	4.0972	0.8194	56502	1.2318
6	1.77	1,02	0.0	4.5858	0.7643	56503	1.2318
Control							
Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	164.17	100	27.8	0			
0.5	155.85	94.93	26.4	0.0520	0.1041		
1	153.78	93.67	26.1	0.0654	0.0654		
2	144.33	87.92	24.5	0.1288	0.0611		
3	136.67	83.25	23.2	0.1833	0.0551		
4	131.72	80.24	22.3	0.2202	0.0522		

Table4.22 (continued)

5	126.52	77.07	21.5	0.2605	0.0494		
7	116.17	70.76	19.7	0.3459	0.0473		

Table 4.24 Volatilization of Aniline Stirring at 750 rpm (298K)

Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	90.87	100	17.6	0	
10	89.93	98.97	17.4	0.01040	0.00104
20	98.86	98.89	17.4	0.01117	0.00056
40	89.42	98.41	17.3	0.01604	0.00040
60	88.43	97.32	17.1	0.02720	0.00045
90	86.55	95.25	16.7	0.04868	0.00054
120	85.24	93.81	16.5	0.06390	0.00053
150	82.93	91.27	16.0	0.09137	0.00060
180	81.68	89.89	15.8	0.10660	0.00059
210	79.75	87.77	15.4	0.13047	0.00062
240	78.18	86.04	15.1	0.15041	0.00063
270	75.29	82.85	14.6	0.18809	0.00069
300	72.44	79.72	14.0	0.22663	0.00075
Control					
Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	90.19	100	17.4	0	
10	90.03	99.82	17.4	0.00180	0.00018
60	89.96	99.74	17.4	0.00262	0.00005
90	89.47	99.20	17.3	0.00805	0.00009
120	89.10	98.79	17.2	0.01216	0.00010
150	88.14	97.72	17.0	0.02305	0.00015
180	87.64	97.17	16.9	0.02871	0.00016
210	86.55	95.96	16.7	0.04122	0.00020
240	86.06	95.42	16.6	0.04685	0.00020
270	85.33	94.61	16.5	0.05542	0.00021
300	84.68	93.89	16.4	0.06302	0.00021

Table 4.25 Volatilization of Aniline Stirring at 1000 rpm (300K)

Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	103.45	100	20.0	0	
10	102.48	99.07	19.8	0.00094	0.00094
20	101.67	98.28	19.7	0.01732	0.00087
40	100.15	96.81	19.4	0.03238	0.00081
60	98.82	95.53	19.1	0.04571	0.00076
90	96.94	93.72	18.7	0.06491	0.00072
120	94.26	91.12	18.2	0.09303	0.00078
150	91.90	88.84	17.8	0.11840	0.00079
180	89.00	86.03	17.2	0.15046	0.00084
210	86.52	83.64	16.7	0.17871	0.00085
240	83.64	80.79	16.2	0.21327	0.00081
270	80.99	78.29	15.7	0.24473	0.00091
300	79.62	76.97	15.4	0.26174	0.00087
Control					
Time(min)	Conc.(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re
0	103.06	100	19.9	0	
10	102.97	99.91	19.9	0.00091	0.00009
20	102.93	99.87	19.9	0.00131	0.00007
40	102.93	99.87	19.9	0.00132	0.00003
60	102.78	99.73	19.9	0.00271	0.00005
90	102.32	99.28	19.8	0.00724	0.00008
120	101.69	98.67	19.7	0.01334	0.00011
150	101.43	98.42	19.6	0.01591	0.00011
180	100.83	97.84	19.5	0.02188	0.00012
210	100.50	97.52	19.4	0.02515	0.00012
240	100.21	97.23	19.4	0.02810	0.00012
270	99.50	96.54	19.2	0.03522	0.00013
300	98.24	95.33	18.9	0.04788	0.00015

Table 4.27 Volatilization of Aniline Aeration at 44 ml/sec.(296K)

Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	85.92	100	16.6	0		90.27	0.00177
10	84.52	98.37	16.3	0.01639	0.00164	90.27	0.00177
20	84.04	97.82	16.2	0.02207	0.00110	90.27	0.00177
40	82.92	96.51	16.0	0.03554	0.00089	90.27	0.00177
60	81.74	95.14	15.8	0.04986	0.00083	90.27	0.00177
80	80.00	93.11	15.5	0.07136	0.00089	90.27	0.00177
100	79.11	92.07	15.3	0.08260	0/00083	90.27	0.00177
130	77.75	90.50	15.0	0.09985	0.00077	90.27	0.00177
190	73.99	86.11	14.3	0.1495	0.00078	90.27	0.00177
220	71.92	83.71	13.9	0.1778	0.00081	90.27	0.00177
250	70.24	81.75	13.6	0.2015	0.00081	90.28	0.00177
280	68.05	79.20	13.2	0.2332	0.00083	90.28	0.00177
300	67.52	78.59	13.1	0.2409	0.00080	90.28	0.00177
Control							
Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	85.50	100	16.5	0			
10	84.94	99.34	16.4	0.00661	0.00066		
20	84.77	99.14	16.4	0.00865	0.00022		
40	84.62	98.97	16.4	0.01037	0.00052		
60	84.47	98.79	16.3	0.01213	0.00021		
80	84.45	98.78	16.3	0.01229	0.00020		
100	83.82	98.03	16.2	0.01983	0.00015		
130	83.53	97.69	16.1	0.02331	0.00020		
160	83.37	97.52	16.1	0.02516	0.00018		
190	82.62	96.62	15.9	0.03434	0.00016		
220	82.46	96.44	15.8	0.03620	0.00018		
250	81.78	95.64	15.7	0.04457	0.00018		
280	81.27	95.05	15.7	0.05078	0.00019		
300	80.58	94.24	15.6	0.05932	0.00020		

Table 4.28 Volatilization of Aniline Aeration at 66 ml/sec.(295K)

Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	98.97	100	19.1	0		90.20	0.00247
5	98.57	99.60	19.1	0.00396	0.00079	90.20	0.00247
10	98.13	99.16	19.0	0.00847	0.00085	90.20	0.00247
20	98.03	99.06	18.9	0.00945	0.00047	90.20	0.00247
30	96.75	97.76	18.7	0.02260	0.00075	90.20	0.00247
45	95.72	96.72	18.5	0.03339	0.00074	90.21	0.00247
65	94.28	95.26	18.2	0.04851	0.00075	90.21	0.00247
85	92.45	93.42	17.9	0.06808	0.00080	90.21	0.00247
100	91.26	92.21	17.6	0.08107	0.00081	90.21	0.00247
130	88.60	89.53	17.1	0.11063	0.00085	90.21	0.00247
150	86.71	87.61	16.8	0.13223	0.00088	90.21	0.00247
180	83.92	84.80	16.2	0.16494	0.00091	90.21	0.00247
220	80.17	81.00	15.5	0.21065	0.00095	90.22	0.00247
260	76.07	76.87	14.7	0.26313	0.00101	90.22	0.00247
300	72.50	73.26	14.0	0.31124	0.00103	90.22	0.00247
Control							
Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	99.55	100	19.2	0			
10	99.20	99.64	19.2	0.00360	0.00036		
20	99.15	99.60	19.2	0.00465	0.00020		
30	98.90	99.34	19.1	0.00664	0.00022		
45	98.64	99.08	19.1	0.00920	0.00020		
65	97.91	98.35	18.9	0.01665	0.00025		
85	97.90	98.34	18.9	0.01677	0.00020		
130	97.07	97.51	18.8	0.02524	0.00019		
150	96.86	97.29	18.7	0.02748	0.00018		
180	96.09	96.52	18.6	0.03542	0.00020		
220	95.08	95.50	18.4	0.04603	0.00021		
260	93.97	94.39	18.2	0.05773	0.00022		
300	92.78	93.19	17.9	0.07048	0.00023		

Table 4.29 Volatilization of Aniline Aeration at 88 ml/sec.(300K)

Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re	γ_i	Rt
0	103.29	100	20.0	0		90.46	0.00477
10	101.58	98.34	19.6	0.01674	0.00167	90.46	0.00477
20	100.26	97.07	19.4	0.02978	0.00149	90.46	0.00477
40	97.52	94.41	18.8	0.05749	0.00144	90.47	0.00477
60	95.44	92.40	18.4	0.07901	0.00132	90.47	0.00477
90	92.23	89.29	17.8	0.11324	0.00126	90.47	0.00477
120	89.38	86.53	17.3	0.14463	0.00121	90.47	0.00477
150	86.09	83.35	16.6	0.18217	0.00121	90.47	0.00477
180	82.75	80.11	16.0	0.22179	0.00123	90.48	0.00477
210	80.17	77.61	15.5	0.25346	0.00121	90.48	0.00477
240	76.27	73.84	14.7	0.30327	0.00125	90.48	0.00477
270	73.81	71.46	14.3	0.33608	0.00124	90.48	0.00477
300	70.94	68.68	13.7	0.37579	0.00125	90.49	0.00477

Control

| Time(min)	Conc(ppm)	%(Ct/Co)	$X_i \times 10^{-6}$	$\ln X_{io}/X_i$	Re		
0	103.06	100	19.9	0			
10	102.97	99.91	19.9	0.00091	0.00009		
20	102.93	99.87	19.9	0.00131	0.00007		
40	102.93	99.87	19.9	0.00132	0.00003		
60	102.78	99.73	19.9	0.00271	0.00005		
90	102.32	99.28	19.8	0.00724	0.00008		
120	101.69	98.67	19.7	0.01334	0.00011		
150	101.43	98.42	19.6	0.01591	0.00011		
180	100.83	97.84	19.5	0.02188	0.00012		
210	100.50	97.52	19.4	0.02515	0.00012		
240	100.21	97.23	19.4	0.02810	0.00012		
270	99.50	96.54	19.2	0.03522	0.00013		
300	98.24	95.33	18.9	0.04788	0.00015		

APPENDIX C

SUPPLEMENT OF FIGURES
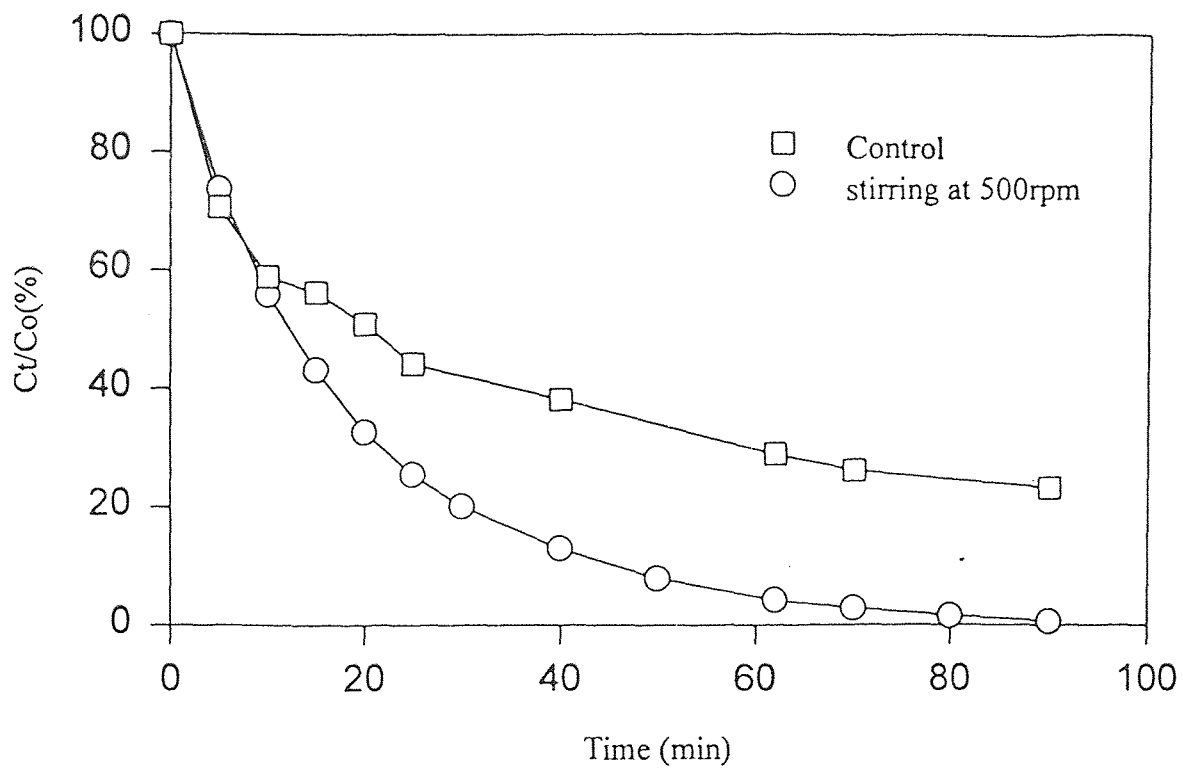
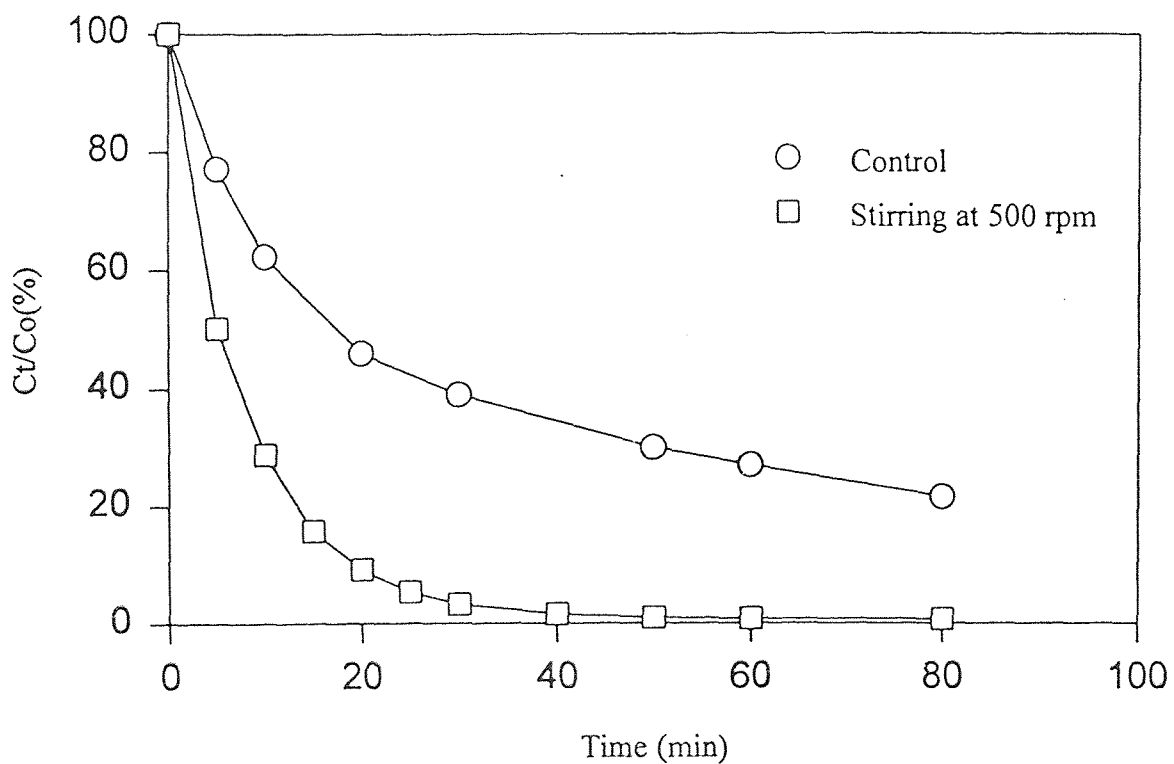Figure 5.4 Volatilization Curve of p-Xylene with Stirring

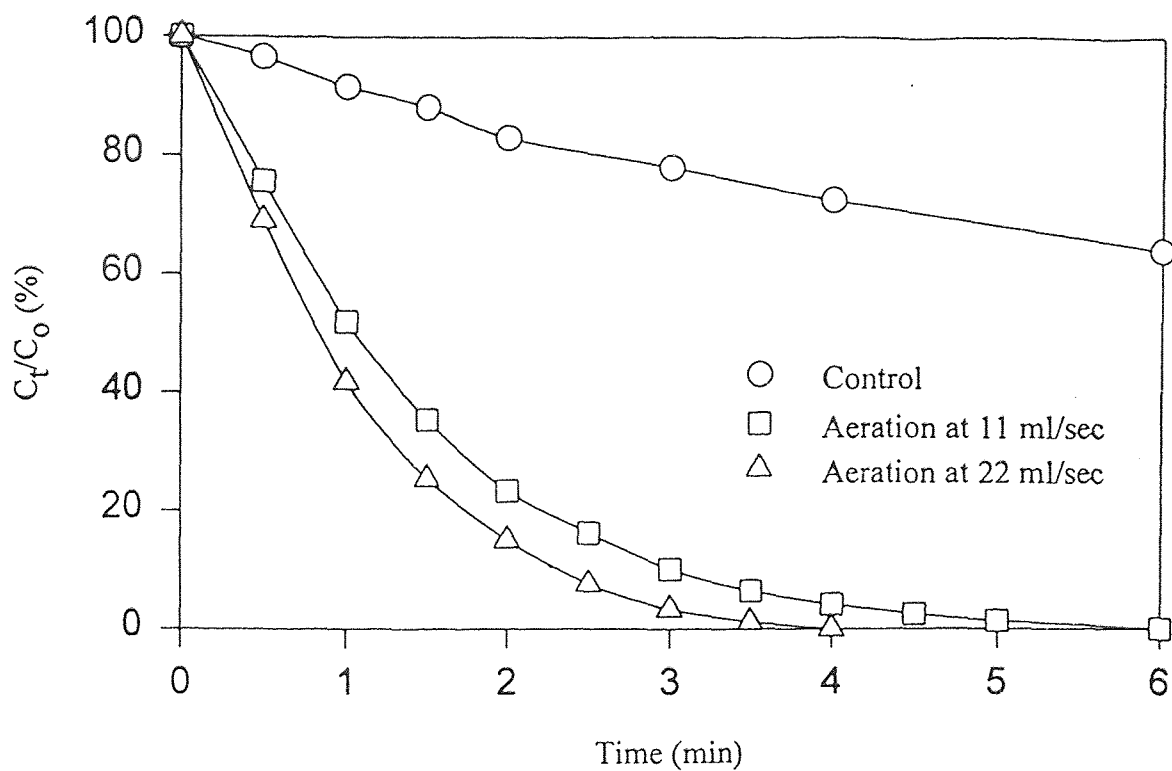Figure 5.5 Volatilization Curve of o-Xylene with Stirring

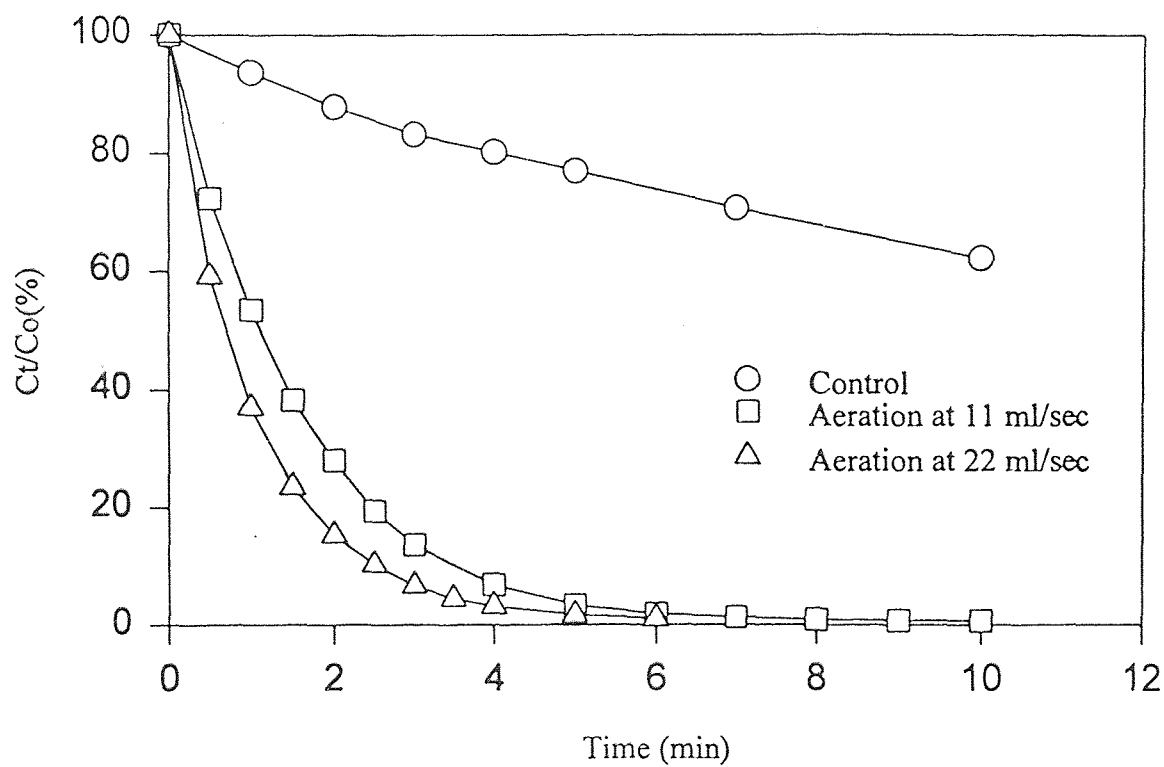**Figure 5.13** Volatilization Curve of p-Xylene with Aeration

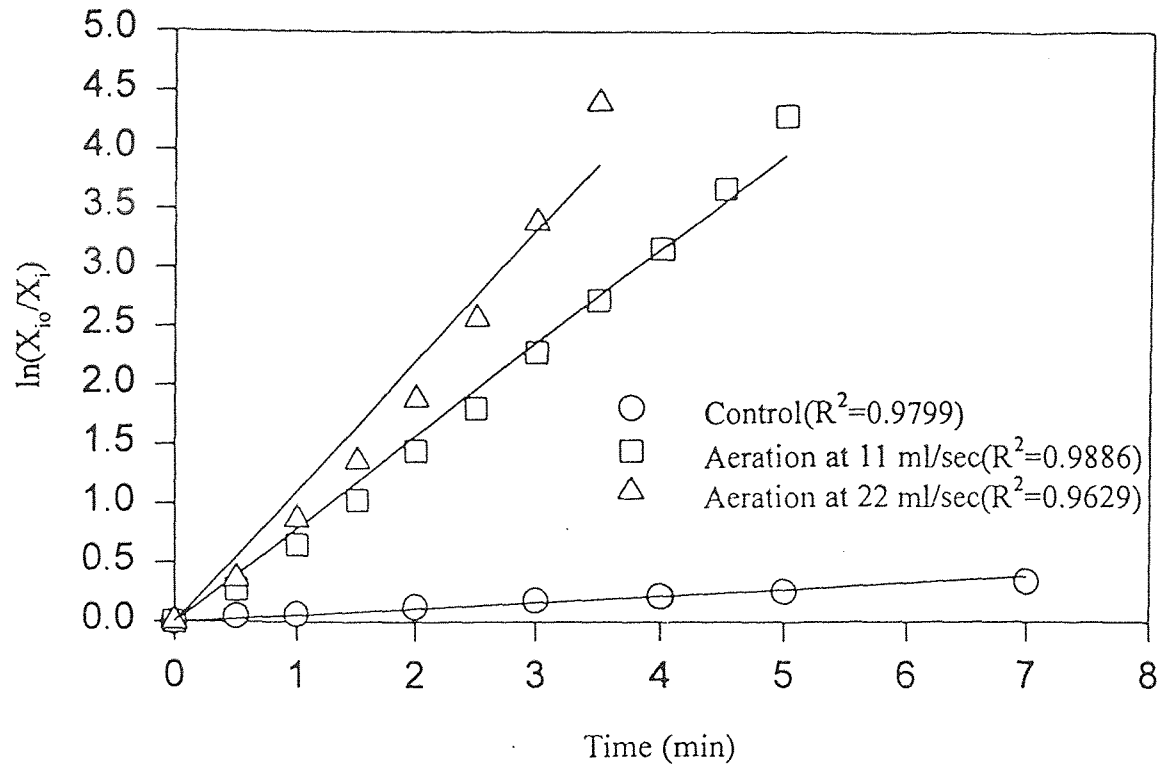**Figure 5.14** Volatilization Curve of o-Xylene with Aeration

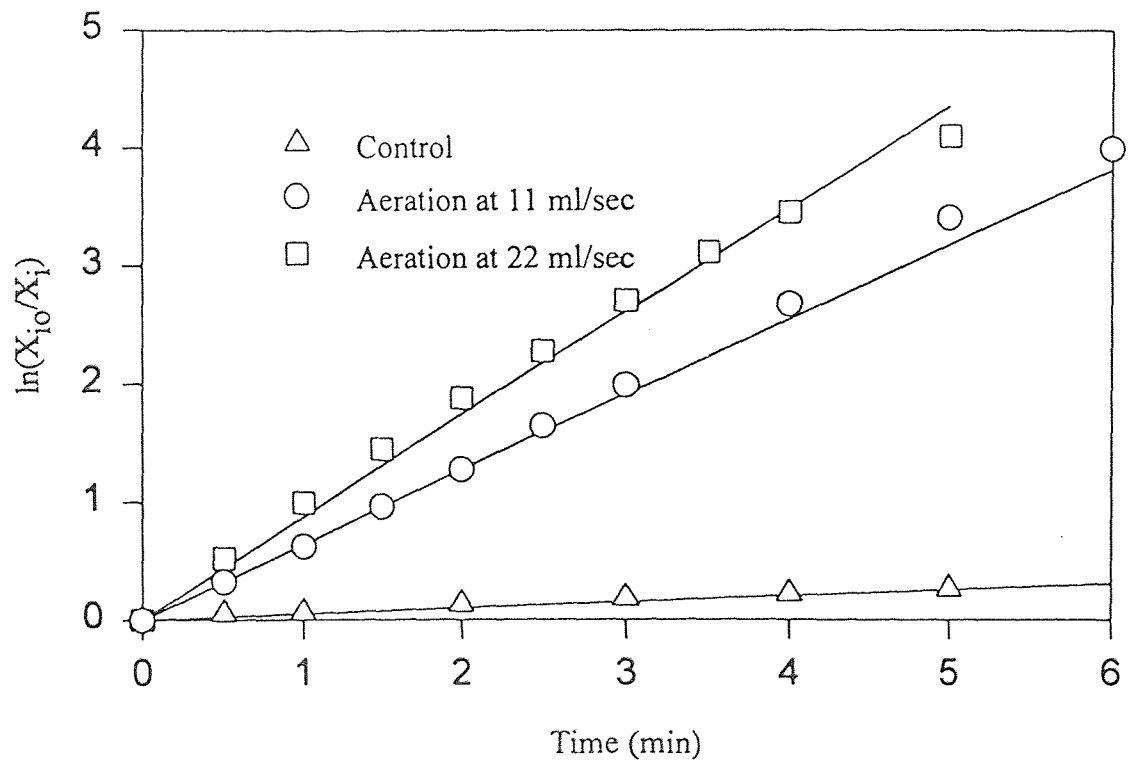**Figure 5.18** First Order Kinetic Curve of p-Xylene Volatilization with Aeration

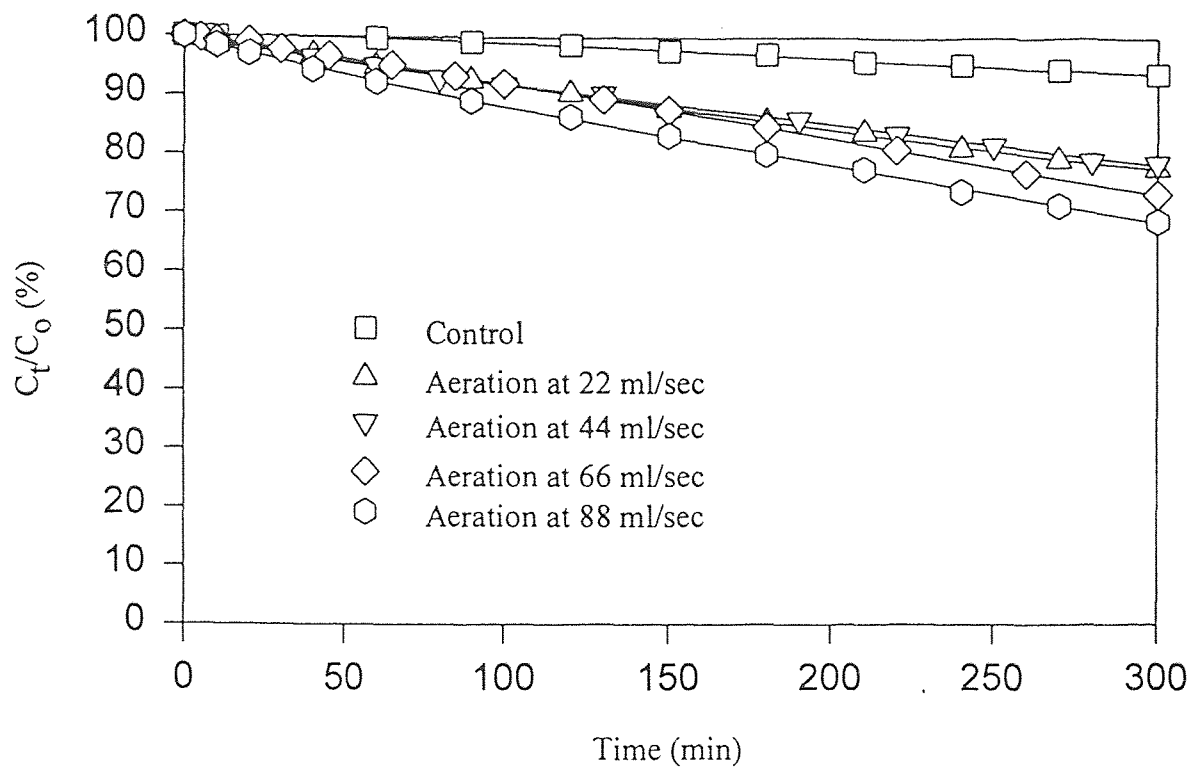**Figure 5.19** First Order Kinetic Curve of o-Xylene Volatilization with Aeration

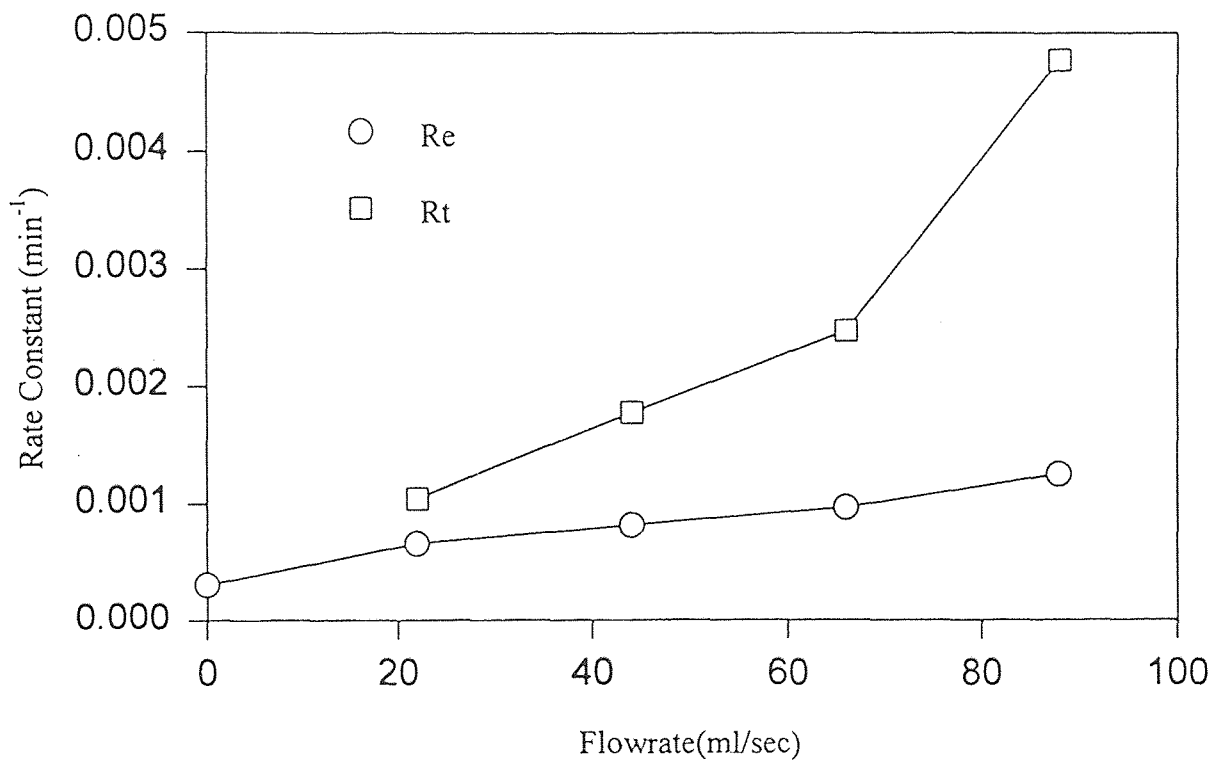**Figure 5.20** Volatilization Curve of Aniline with Aeration

Figure 5.21 Comparison of Rate Constants of Aniline

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