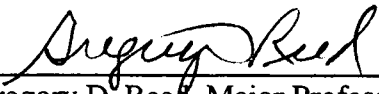


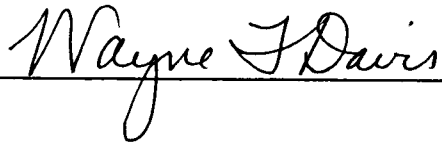
To the graduate council:

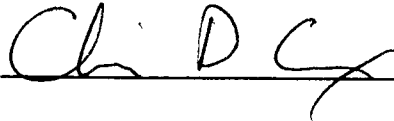
I am submitting herewith a thesis written by Ke Liu entitled " Feasibility study on a combined spray absorber - activated sludge process for volatile organic compound removal." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.



Gregory D. Reed, Major Professor

We have read this thesis
and recommend its acceptance:





Accepted for the Council:



Associate Vice Chancellor and Dean of
The Graduate School

**FEASIBILITY STUDY ON A COMBINED SPRAY
ABSORBER — ACTIVATED SLUDGE PROCESS
FOR VOLATILE ORGANIC
COMPOUND REMOVAL**

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Ke Liu

December 1997

ACKNOWLEDGMENTS

During the course of this research and my graduate study, I have been indebted to Dr. Gregory D. Reed for his constant encouragement and support, as well as his innovative spirit, broad knowledge and kindness. I sincerely appreciate Dr. Wayne T. Davis for his insightful ideas and suggestions, abundant experiences and great help. Special thanks to Dr. Chris D. Cox for his academic advice, encouragement, kindly help and serving on my committee.

I appreciate Carol H. Norman for her great contribution to some of the experiments. Our friendship made work easier. I also wish to thank Sharon F. Hale for her technical advice and patience.

I especially want to express gratitude to my friends Milton and Pat Russell. They have provided great encouragement and care during my graduate study in Knoxville, Tennessee.

ABSTRACT

The purpose of this study was to explore the feasibility of a combined spray absorber - activated sludge process for the removal of gas phase volatile organic compounds (VOCs). Three different solvents — water, bacteria slurry, and powdered activated carbon (PAC) slurry, were evaluated for this process. Methyl-ethyl-ketone (MEK) was studied as the target VOC. The rate of VOC removal in a spray absorber was the major concern for reactor volume reduction. Using PAC slurry as solvent, experimental results showed that the gas-to-liquid mass transfer rate was increased by a factor of 2. The effects of PAC to the subsequent activated sludge process were also explored. Experiments were conducted to evaluate the three major VOC fate mechanisms in the activated sludge unit: stripping, biodegradation, and adsorption on PAC. The results indicate that stripping is negligible if the VOC is readily biodegradable, and PAC can be biologically regenerated if the adsorption is reversible. PAC also serves as a reservoir to prevent stripping losses, especially at high concentration fluctuations. Therefore, PAC slurry is a promising solvent in this combined process. Experimental results and theoretical investigations indicate that a slurry of bacteria will not have significant enhancement to the efficiency of a spray absorber. Water is considered to be a feasible solvent for removal of relatively soluble and biodegradable VOCs. Gas retention time in a spray absorber can be within seconds. Design examples were given for MEK gas removal in this process. Further study on the mass transfer rate using PAC slurry as solvent and other aerobic bioreactor for volume reduction is recommended.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION	1
II. LITERATURE REVIEW	10
2.1. Gas-to-liquid Mass Transfer	10
2.1.1. Film Theory	10
2.1.2. Counter-current Packed Bed Scrubber	14
2.1.3. Spray Scrubber	18
2.2. Absorption with Chemical Reaction.	21
2.3. Fate of VOCs in Activated Sludge System	31
2.3.1. Adsorptions of VOCs on Biomass	31
2.3.2. Volatilization of VOCs in Aeration Tanks.	33
2.3.3. Biological Degradation of VOCs	34
2.4. Activated Carbon Added in Activated Sludge System	36
III. EXPERIMENTAL METHODOLOGY	39
3.1. Experiment Design	39
3.1.1. Adsorption Rate and Adsorption Isotherm	39
3.1.2. MEK Gas Scrubbing with Water and/or PAC Slurry	41
3.1.3. Stripping and Biodegradation	42
3.1.4. Desorption Rate	43
3.1.5. Effect of PAC on Biological Activity	44
3.2. Experimental Apparatus	44
3.3. Experimental Materials	47
3.4. Analytical Methods	48
IV. RESULTS AND DISCUSSIONS	50
4.1. Adsorption Isotherm and Adsorption Rate	50
4.2. MEK Gas Scrubbing	58
4.2.1. MEK Gas Scrubbing Using Water Only as Solvent.	61
4.2.2. MEK Gas Scrubbing Using PAC Slurry as Solvent	70
4.2.3. Prediction of Spray Chamber Operation	78
4.3. Stripping and Biodegradation	90
4.4. Desorption Rate	98
4.5. The Effect of PAC on MEK Biodegradation	101
4.5.1. Microbial Oxygen Consumption with and without PAC	101
4.5.2. Modeling of a PAC - Activated Sludge System for MEK removal.	107
V. CONCLUSSIONS AND SUGGESTIONS	114
LIST OF REFERENCES.	116
APPENDIXES	124
VITA	134

LIST OF TABLES

TABLES	PAGE
2.1 Listing of specific compounds that have been removed from waste gas with biofiltration	28
2.2 Biofilter operating parameters	29
3.1 Physical characters of size one Tellerette packing	45
3.2 Nutrients and buffer in synthetic acclimation solution.	48
4.1 MEK adsorption rate at different PAC concentrations.	55
4.2 MEK gas scrubbing in packed tower using water or PAC slurry as solvent	60
4.3 Packed tower operation using water as solvent	64
4.4 Packed tower operation using PAC slurry as solvent	65
4.5 Estimation of wetted surface area "a" and K_G	69
4.6 Estimation of K'_G and K'_L of MEK mass transfer from gas to droplets.	79
4.7 Liquid concentration (g/m^3) in equilibrium with cleaned gas at 25°C	83
4.8 Design parameters for a cocurrent-flow spray chamber	85
4.9 Design parameters for a horizontal cross-flow spray chamber.	87
4.10 Design example of a PAC - activated sludge system for MEK removal.	110

LIST OF FIGURES

FIGURES	PAGE
1.1 Schematic diagram of a combined spray absorber - bioreactor process	3
2.1 Concentration gradient near a gas-liquid interface	12
2.2 Nomenclature for mass balances in a packed-tower absorber	15
2.3 Design diagram for a co-current absorber	22
2.4 Gas-phase and liquid-phase solute-concentration profiles for an extremely fast irreversible reaction system $A + \nu B \rightarrow \text{product}$	24
3.1 Schematic diagram of the packed tower scrubber facility	46
4.1 Adsorption equilibria of MEK at 22°C	51
4.2 Relationship of logarithm equilibrium concentrations of aqueous MEK adsorption at 22°C	52
4.3 Adsorption rate of MEK on Calgon RB powdered activated carbon	54
4.4 Packed tower efficiency at different L/G and PAC slurry concentrations	59
4.5 Packed tower efficiency at different PAC loading	62
4.6 Relationship of K_{Ga} with $G^{0.7}L^{0.3}$	67
4.7 Comparison of modeling efficiency and real efficiency of MEK gas scrubbing with PAC slurry	75
4.8 Estimated mass transfer coefficient K'_G at different droplet diameters and falling distances	80
4.9 MEK concentration decay curve in stripping test	92
4.10 Biodegradation and stripping of MEK in batch aeration experiment	94
4.11 MEK stripping from water and PAC slurry	99
4.12 Desorption of MEK from PAC via stripping	102
4.13 Comparison of liquid-phase concentration C and solid-phase concentration C_s in stripping test	103
4.14 Comparison of microbial oxygen consumption for MEK biodegradation with and without PAC through Warburg respirometer test.	105
4.15 Illustration of the flow rate and concentration distribution in the PAC-activated sludge system	108

CHAPTER I

INTRODUCTION

The enactment of the Clean Air Act Amendments of 1990 motivated research on control technologies for volatile organic compound (VOC) emission. Current control technologies include physicochemical unit processes such as incineration, direct activated carbon adsorption, and absorption followed by ozonation or chlorination. Each of these options has undesirable characteristics, such as waste disposal issues because the compounds are not destroyed but only transferred to another media, or because of high capital and operation costs. Biochemical oxidation of VOCs by microorganisms is a potentially advantageous treatment technology in that it does not merely transfer an organic pollutant from one media to another like some physicochemical process, but it can destroy the pollutant while creating residual products that are relatively harmless. Therefore, biological options have the potential to be a low cost, high efficiency technology for removal of soluble, biodegradable VOCs.

Recently, biofilters and fixed bed bioscrubbers have been reported as VOC control devices in Europe and the United States. The biofiltration process utilizes moisturized microorganism films grown on the surface of media to absorb VOCs from gas and further biologically oxidize them into environmentally benign products, such as carbon dioxide and water. The fixed bed bioscrubbing process utilizes a fixed bed

scrubber for VOC absorption from gas and a separate water treatment bioreactor for further oxidation of the VOCs. However, several limitations of the two processes have been identified. First, fixed bed systems operate best at steady-state loading. Increased organic concentration or gas flow rate requires more bed depth, forcing the design decisions toward over sizing as a safety factor. Also, fixed bed reactors have problems with high head loss. A biofilter, by its very nature, has organisms which are at optimum activity only within a small temperature range. In addition, gas humidification is required for a biofilter to maintain an optimal moisture level, and is difficult to control (Swanson and Loehr, 1997). Furthermore, the overall efficiency of biofilters is usually limited by the biofilm's ability to capture and degrade the substrate (Ockeloen and Overcamp et al., 1996), thus reduction of bed volume is difficult. Therefore, biofilters or fixed bed bioscrubbers may not be satisfactorily cost-efficient in some applications. There is a need to develop other biological air pollution control devices to provide alternatives for industry.

Another approach with potential advantages was investigated in this research which includes an atomizer and atomized droplets for sorbing VOCs from the gas phase into water, and an activated sludge bioreactor for biodegradation of the VOCs in water. By separating the mass transfer and biodegradation processes into two reactors, both processes could be optimized and achieve more flexibility. A schematic diagram of a typical co-current spray scrubber is shown in Figure 1.1. Alternately, the process could utilize a counter-current atomizer section in the spray chamber. The later, however,

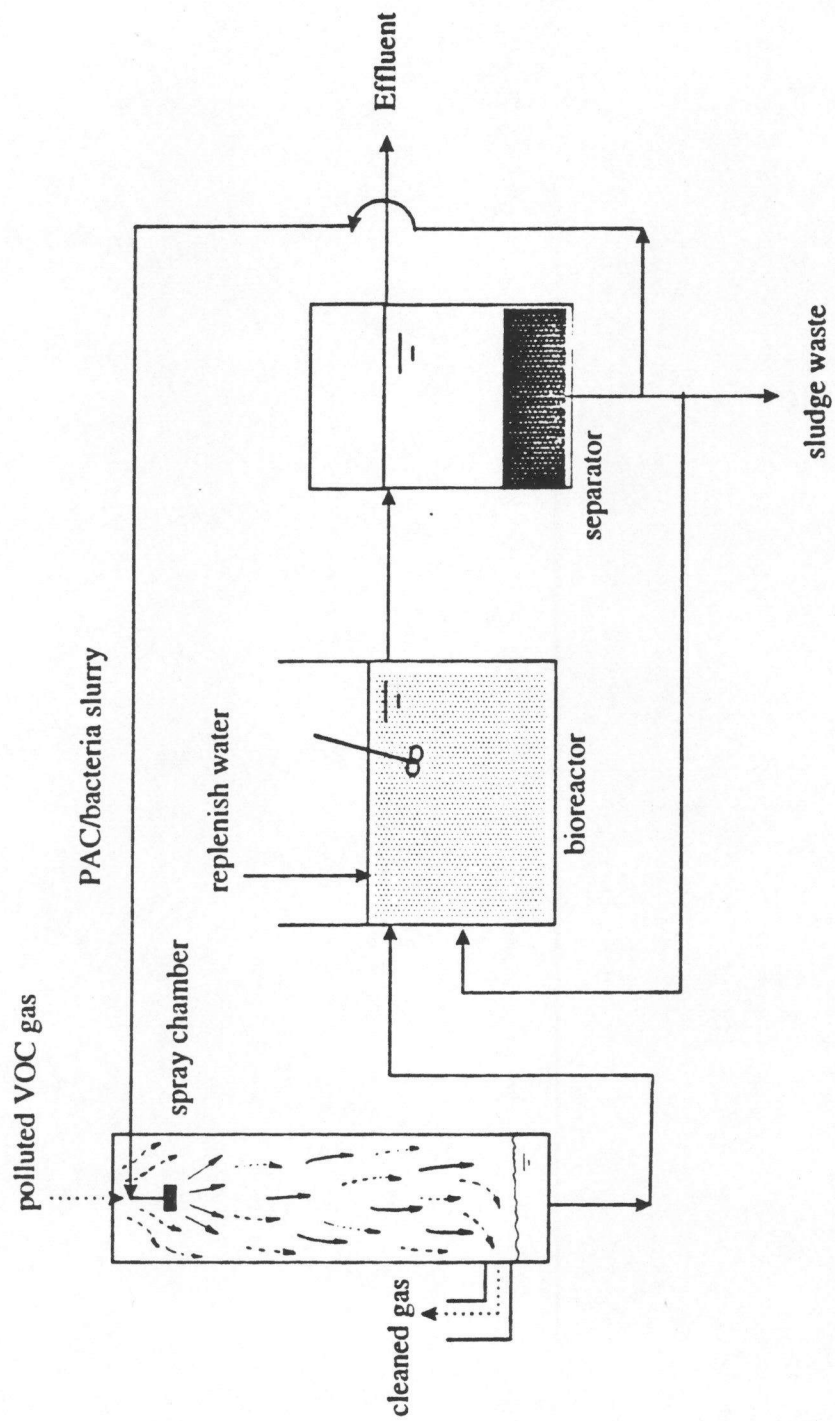


Figure 1.1 Schematic diagram of a combined spray absorber - bioreactor process.

would require larger droplets since droplets would fall due to gravity, thus reducing the surface area per unit volume and the subsequent mass transfer potential.

Spray chambers and spray dryers have been used in power generation facility flue gas desulfurization systems to maximize the reaction kinetics and effectiveness of chemical reactions. By producing small size droplets ($< 100 \mu\text{m}$) to provide a large surface to volume ratio and by placing chemicals in the droplets to obtain a chemical reaction, the short contact time in the spray chamber/dryer has achieved high efficiency performance. The operational characteristics of spray dryers for this purpose have been extensively researched (Buonicore and Davis 1992, Davis and Reed et al. 1985, Davis and Reed et al. 1984). The expected important advantages of this process over biofiltration or fixed bed bioscrubbing include: low head loss, which could reduce operation cost; unlike biofilters, there would be less concern about the VOC mass transfer rate being limited by the biodegradation rate in this system, making it possible to reduce the volume of the absorbing unit; and potential advantages in situations of high gas flow rate and/or high VOC concentration since the atomizer liquid injection rate could be altered to handle a fluctuation in the gas flow rate and/or VOC concentration.

Completely mixed activated sludge systems have been in wide application in industrial wastewater treatment. Bacteria can be acclimated to remove the target VOCs with reasonable efficiency if the VOCs are soluble and readily biodegradable (Swanson and Loehr, 1997). However, due to the volatile nature of VOCs, gas emission from the activated sludge reactor is of concern (Corsi and Card, 1992). This issue was studied in

this thesis by comparing the biodegradation rate and simultaneous VOC stripping rate through aeration.

The removal of VOC from the gas phase in the spray chamber is the key to obtaining a high process efficiency. Water can be used as a solvent to capture VOC from the gas phase. But water alone may not be capable of high efficiencies without the use of excessive water, dependent on the Henry's Law constant of the VOC. Other absorbents were reviewed in an effort to enhance the mass transfer efficiency. The first candidate considered was bacteria slurry since this would already be in the water from the recycle of the bioreactor. It was assumed that some biodegradation may occur in the spray chamber and hence increase VOC treatment efficiency. Bacteria slurries have been used as absorbents for deodorizing waste gas (Kohler, 1979), and treatment of volatile organic compounds (Burglund, 1983) and organic compounds (Awata, 1984) in waste gas. The second candidate was a water-based powdered activated carbon (PAC) slurry. It was assumed that the adsorption of VOC onto activated carbon within the droplets in the spray chamber would lower the dissolved VOC concentration, thus maintaining a high driving force for gas-to-liquid mass transfer. Calvert (1969) reported that the removal of benzene, toluene, trichloroethylene from air was greatly enhanced by adding activated carbon to the agitated bubbling scrubber. Kim and Pingel (1989) reported the same effect for toluene removal. Furthermore, processes of using combined activated carbon and bacteria slurry as absorbent for deodorization have been patented by Burant (1979) and Kanezashi (1980). PAC added to an activated sludge process has been widely researched in the past twenty years (DeWalle and Chian, 1976; Ying and Weber, 1979; Benedek,

1985; Zhang and Wang, 1990). An additional expected benefit of PAC slurries was to reduce stripping of the VOC from the bioreactor by keeping the dissolved VOC concentration at a low value. Ideally, PAC would be regenerated in the bioreactor and returned to the atomizer section, thus reducing the cost. Therefore, PAC slurries seemed to be a very promising absorbent. Most of the experiments were conducted to investigate the effects of PAC slurries in both the spray scrubber and bioreactor.

In the PAC-activated sludge bioreactor, substrate VOC may exist in three forms: dissolved in water, adsorbed on PAC and stripped out by aeration. In the optimal case, PAC serves as a buffer to keep a low dissolved VOC concentration, thus decreasing stripping. But bioregeneration of PAC would be limited if the desorption is slow. VOC biodegradation in the presence of PAC could be unaffected, enhanced, as predicted by some researchers (Rice et al. 1982), or even slowed down due to low VOC concentration. The relationship between the three processes, stripping, biodegradation and PAC adsorption/desorption, were studied in this research project to understand the removal rate of VOC and regeneration extent of PAC.

The objective of this study was to investigate the feasibility of utilizing spray chamber and bioreactor units to effectively remove and degrade VOCs. Primary considerations included: treatment efficiency of the spray chamber operating with different capture agents — water, bacteria slurries and PAC slurries; qualitative/quantitative relationship of biodegradation, stripping and adsorption in the activated sludge bioreactor. The following experiments were conducted:

- aqueous VOC adsorption isotherm and adsorption rate;
- VOC gas scrubbing with water and PAC slurry;
- stripping and biodegradation of VOC in water;
- desorption of VOC from PAC via stripping;
- microbial oxygen consumption with and without the presence of PAC.

In order to compare the treatment efficiency of the spray chamber with and without the presence of capture agents such as PAC or bacteria slurries, the same atomizer should be used in both studies. Although slurries with as high as 40% solid weight content can be atomized by a rotary atomizer at large flow rate (Spray Drying, 1976), no atomizer was available for spraying high concentration PAC slurries at low flow rate utilized in the laboratory scale. This problem was solved by using a packed bed scrubber to simulate the mass transfer within a spray chamber. If the surface areas and mass-transfer coefficients without chemical reaction are known in both sorption units, then the response of rate of sorption to chemical reactions in one unit can be used to predict that in the other unit. Danckwerts and Grillham (1966) showed that data taken in a small stirred-tank laboratory apparatus could be used to design a packed bed absorber when the chemical reactions were involved. Film theory has been commonly used for packed bed scrubber design. Under contract with EPA, Damle (1985) developed a computerized mathematical model called SPRAYMOD that simulates the spray dryer flue gas desulfurization system, based on film theory. Later, Partridge (1987) and Lackey (1992) further developed this model, still based on the film theory. If chemical reaction changes mass-transfer resistance in the liquid phase, as is expected to occur when PAC or

bacteria slurries are used, then the consequence on mass-transfer rate coefficients would be similar for both packed bed scrubbers and spray chambers. Therefore, the experimental results on a packed bed scrubber could be used to provide basic insight into the behavior of a spray chamber operating with the same capture agent. In the experiments conducted herein, a counter-current column packed with Tellerettes was used as the substitute to a spray chamber.

First, experiments were conducted with water only as the absorbent. The VOC treatment efficiency of the packed tower was measured at different water flow rates while maintaining constant gas flow rate. The gas-to-liquid mass transfer efficiency was calculated based on the results. Removal of the VOC from the activated sludge bioreactor was caused by both stripping and biodegradation. Batch tests of the concentration decrease as a result of aeration were conducted for both water and activated sludge solutions under the same conditions. The relationship of stripping versus concentration was obtained and utilized to estimate the amount of VOC stripped out during the bioreactor tests. VOC utilization by microorganisms was calculated by subtracting the amount of VOC stripped out from the total amount of decay that was observed.

Later, experiments were performed to study the effects of a PAC slurry as the capture agent. The first step was to measure the VOC adsorption rate in the liquid. If adsorption on PAC could not occur rapidly, PAC slurries would not improve the mass transfer efficiency. The experiments were conducted at the same initial VOC concentration, but at different PAC concentrations, in order to get the approximate PAC

concentration range of the slurries. The second step was to study the treatment efficiencies of the packed tower in response to PAC concentrations and slurry flow rates, while keeping the VOC concentration and the gas flow rate consistent for all these experiments. The results led to discussion on mass transfer mechanism at the presence of PAC and prediction of spray chamber performance. The third step was to study the desorption rate of VOCs from PAC by stripping tests with/without the presence of PAC at the same initial liquid phase VOC concentration. If the desorption was considerably fast, the loss of liquid phase VOC due to stripping would be compensated by desorption. By comparing the decay curves of gas phase concentration with and without PAC, the desorption rate was inferred. The last step was to study the effect of PAC on microbial activity through Warburg respirometer tests. The comparison tests on oxygen consumption of microorganisms with and without PAC were conducted, using several groups of initial VOC concentration. The rate of oxygen consumption represented the activity of microorganisms and VOC degradation rate. The observance of higher or lower oxygen consumption rate with PAC addition would indicate the effect of enhanced or retarded biological activity, respectively.

CHAPTER II

LITERATURE REVIEW

2.1. Gas-to-liquid Mass Transfer

The equipment used for gas-to-liquid mass transfer may be a packed tower filled with packing material, a plate-type unit containing a number of bubble-cap or sieved plates, an empty chamber into which liquid is sprayed, a wetted-wall column or a sparged vessel (Perry's, 1984). The gas and liquid can be made to flow at co-current, counter-current or cross-current direction, although counter-current flow is more commonly used to achieve higher absorption efficiency. Film theory, penetration theory, and surface-renewal theory are the most well-known theories to describe mass-transfer rate, with the former more easily and widely applied in industry.

2.1.1. Film Theory

Film theory has been widely used to describe the mechanism of gas-to-liquid interfacial mass transfer. Its basic hypotheses are: (1) a stable interface exists between liquid and gas flows such that both sides of the interface have a film of stagnant flow through which the absorbing species transfer by molecular diffusion; (2) the two phases are at thermodynamic equilibrium at the interface; and (3) chemical concentrations are uniform in the bulk flow of both phases. The concentration gradient near a gas-liquid

interface, as described by film theory, is shown in Figure 2.1. In cases of an operational system with a stable interface and low flow rates, the film theory corresponds well with reality. But in other cases with unstable interface or highly turbulent flows, the assumptions of this theory are invalidated and it fails to work well.

The absorption rate is an important concept. It is defined as the mass of absorbing species transferred through unit interface during unit time period. It can also be described as:

$$\text{mass transfer rate} = \frac{\text{driving force}}{\text{resistance}} \quad (2.1)$$

At steady-state, mass transfer rates are equal on both sides of the interface. Therefore, either of them can represent the absorption rate. In terms of the liquid mole fraction x , the absorption rate can be described by:

$$N = k_L(x_i - x) = \frac{x_i - x}{1/k_L} \quad (2.2)$$

where N is the mass transfer rate of solute per unit interfacial area, k_L is the liquid phase mass transfer coefficient, x_i is mole-fraction solute in the interfacial liquid. Similarly, in terms of the gas mole fraction y :

$$N = k_G(y - y_i) = \frac{y_i - y}{1/k_G} \quad (2.3)$$

where k_G is the gas-phase mass transfer coefficient and y_i is mole-fraction solute in the interfacial gas. Because the interfacial concentration can not be measured practically, a more useful relationship is:

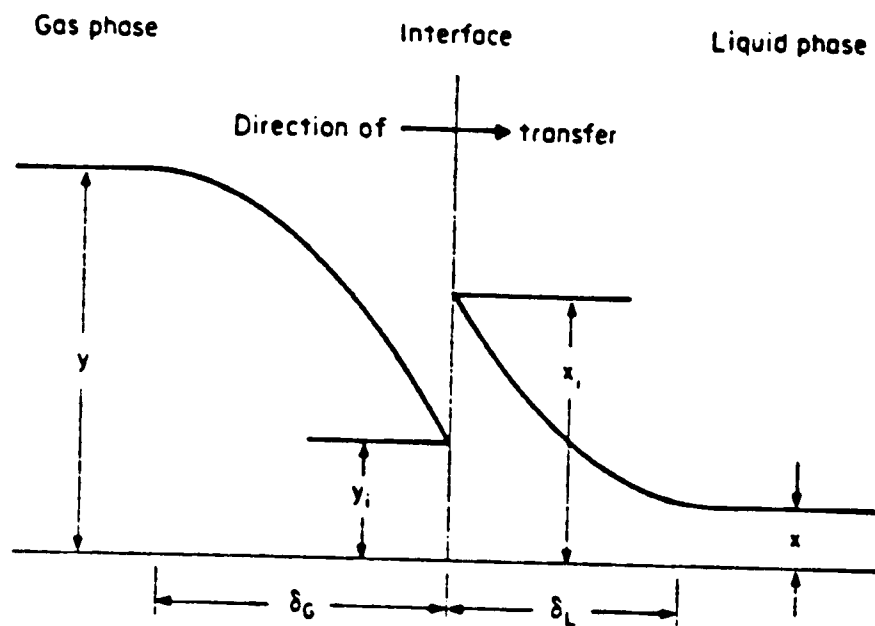


Figure 2.1 Concentration gradient near a gas-liquid interface.

Source: Perry's Chemical Engineers' Handbook, 1984, 6th edition, p14-8.

$$N = K_G(y - y^*) = k_G(y - y_i) = K_L(x^* - x) = k_L(x_i - x) \quad (2.4)$$

Here K_G and K_L are overall mass-transfer coefficient in terms of gas and liquid mole fraction, respectively; y^* is the gas-phase concentration in equilibrium with bulk liquid phase solute, and x^* is the liquid-phase concentration in equilibrium with gas phase solute.

If the equilibrium curve is a straight line with slope:

$$m = \frac{y_i - y^*}{x_i - x} \quad (2.5)$$

then equations (2.4) and (2.5) result in the following relationship between the local and overall mass-transfer coefficients:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{m}{k_L} \quad (2.6)$$

$$\text{and} \quad \frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{mk_G} \quad (2.7)$$

For a dilute system, the equilibrium concentration is related by Henry's Law:

$$p = Hx \quad (2.8)$$

where p is the solute gas pressure and H is the Henry's Law constant, and the following relationship exists:

$$m = H/P_T \quad (2.9)$$

where P_T is the total system pressure. For easily dissolved gases, the Henry's Law constant is very small. If k_G and k_L are close to each other, then equation (2.6) can be simplified as:

$$\frac{1}{K_G} \approx \frac{1}{k_G} \quad (2.10)$$

This case is called gas-phase controlled mass-transfer, which also applies when liquid phase resistance can be ignored, $mk_G \ll k_L$. Similarly, in cases of small values of H and closely k_G and k_L , or in cases of $mk_G \gg k_L$, mass-transfer is liquid-phase resistance controlled:

$$\frac{1}{K_L} \approx \frac{1}{k_L} \quad (2.11)$$

Units of the above mass-transfer coefficients are in terms of mole flux per mole-fraction driving force. These coefficients can also be defined in terms of the ratio of mole flux and solute pressure driving force or solute mole concentration, as described below:

$$N = k_G(y - y_i) = k_G'(p - p_i) \quad (2.12)$$

$$\text{and } N = k_L(x_i - x) = k_L'(c_i - c) \quad (2.13)$$

The conversion between the two sets of mass-transfer coefficients are:

$$k_G = k_G' p_T \quad (2.14)$$

$$\text{and } k_L = k_L' \bar{\rho}_L \quad (2.15)$$

Here p_T is the total system pressure and $\bar{\rho}_L$ is average mole concentration of solution.

2.1.2. Counter-current Packed Bed Scrubber

The countercurrent packed bed scrubber operates in a such a manner that the liquid and gas phases are in continuous contact with each other, therefore concentration change is also continuous along the tower height. The mass balance around the bottom and any cross section of the tower, as illustrated in Figure 2.2, gives:

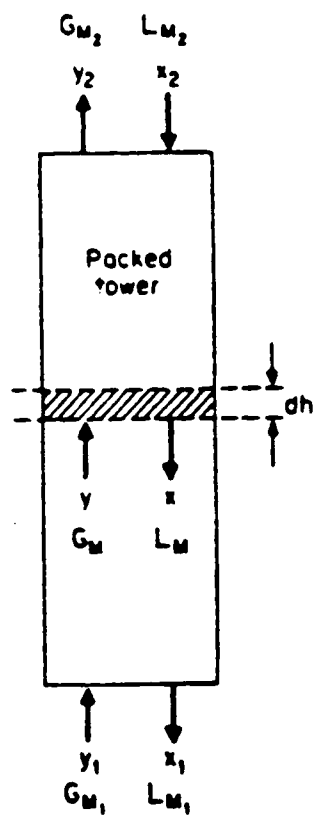


Figure 2.2 Nomenclature for mass balances in a packed-tower absorber.

Source: Perry's Chemical Engineers' Handbook, 1984, 6th edition, p14-18.

$$yG + xL = y_1G_1 + x_1L_1 \quad (2.16)$$

where L is the molar liquid flow rate and G is the molar gas flow rate. When the concentration of the solute is very small, and the change in flow rate of liquid and gas is negligible, the above equation can be simplified as:

$$y = \frac{L}{G} (x_1 - x) + y_1 \quad (2.17)$$

Based on mass balance equation (2.16), absorption rate equation (2.4) and phase equilibrium, mass transfer from gas to liquid at any section can be described by:

$$d(Gy) = K_G a (y - y^*) S (-dZ) \quad (2.18)$$

where “ a ” is the effective interfacial area per unit volume of reactor, S is the cross sectional area, and Z is the height from the bottom.

When the gas mixture is dilute and the equilibrium curve is linear over the range of composition x_1 to x_2 , integration of equation (2.18) gives:

$$G(y_1 - y_2) = K_G a S Z (y - y^*)_M \quad (2.19)$$

where $(y - y^*)_M$ is the logarithmic average of the concentration difference at the ends of the tower.

Defining the absorption factor, $A = \frac{L/G}{m}$, and integrating equation (2.17) with $x_2=0$ for pure solvent absorption, gives:

$$K_G a = \frac{L}{m Z S (1 + A)} \ln \frac{\frac{y_2}{H}}{\frac{y_2}{H} (1 - A) x_1} \quad (2.20)$$

This equation can be directly used to calculate K_{Ga} . Since the interfacial area is hard to measure and changes with operation conditions, K_{Ga} is normally used to define the absorption rate as a volumetric coefficient.

Onda et al. (1967, 1968) presented the following equations for estimating wetted surface area “a” and mass transfer coefficient k_L and k_G :

$$\frac{a}{a_t} = 1 - \exp[-1.45 \left(\frac{Sc}{S}\right)^{0.75} \left(\frac{L}{a_t \mu_L}\right)^{0.1} \left(\frac{L^2 a_t}{\rho_L^2 g}\right)^{-0.05} \left(\frac{L^2}{\rho_L S a_t}\right)^{0.2}] \quad (2.21)$$

$$k_L = 0.0051 \left(\frac{L}{a_t \mu_L}\right)^{2/3} (\mu_L / \rho_L D_L)^{-0.5} (a_t d_p)^{0.4} (\rho_L / \mu_L g)^{-1/3} \quad (2.22)$$

$$k_G = 5.23 [(G / a_t \mu_G)^{0.70} (\mu_G / \rho_G D_G)^{1/3} (a_t d_p)^{-2.0} (a_t D_G)] / RT \quad (2.23)$$

where,

Sc — critical surface tension of packing material

S — liquid surface tension, 0.073 N/m at 20°C

L (G) — liquid (gas) mass velocity, kg/(m²·s)

μ_L (μ_G) — liquid (gas) viscosity, kg/(m²·s)

D_L (D_G) — liquid (gas) phase diffusion coefficient, m²/s

ρ_L (ρ_G) — density of liquid (gas), kg/m³

D_p — equivalent diameter of packing, m

g — gravity, 9.8 m/s²,

a_t — total packing area, m²/m³.

These equations were correlations obtained from a number of liquid phase transfer data. Correlated packings include Raschig rings (1/4 ~ 2 inch), Berl Saddles (1/2 ~ 1.5 inch), Pall rings (1 inch) and rolls (1/2~1 inch). The liquid-phase correlations (2.21) and

(2.22) were found to be accurate within $\pm 20\%$ (Dvorak, 1996; Little 1997). But the gas-phase correlation (2.23) was found to have error as high as $\pm 50\%$ (Dvorak, 1996), especially at high gas flow rate and high gas-phase resistance.

2.1.3. Spray Scrubber

Spray absorbers currently are being applied on a large-scale commercial basis in systems for removing SO_2 from boiler flue gases. There are particularly advantageous when low pressure drop is essential and when the incoming gas contains particles. However, due to the short retention time of both droplets and gases in the chamber, on the order of 1 to 20 seconds, spray absorbers are especially applicable to systems in which the rate of transfer is gas-phase mass-transfer limited (Perry's, 1984).

There are fewer reports on mass-transfer models for spray absorbers than for packed bed scrubbers. Calvert (Wet Scrubber, 1972) presented some semi-theoretical equations for mass-transfer in spray absorbers. The gas-film coefficient given by Frössling was:

$$N_{sh} = \frac{k'_G R T d}{D_G} = 2 + 0.552 N_{Re}^{1/2} N_{Sc}^{1/3} \quad (2.24)$$

$$\text{where } N_{Re} = \frac{d u_t \rho_G}{D_G}, \text{ Reynolds number} \quad (2.25)$$

$$N_{Sc} = \frac{\mu_G}{\rho_G D_G}, \text{ Schmidt number} \quad (2.26)$$

The terminal velocity of droplet to gas, u_t , is a function of drop diameter. In the Stokes' Law region, $N_{Re} < 0.1$,

$$C = 24/Re \quad (2.27)$$

$$\text{and } u_t = \frac{g d^2 (\rho_L - \rho_G)}{18 \mu_L} \quad (2.28)$$

In the intermediate region, $0.1 < N_{Re} < 1000$,

$$C = (24/R_e)(1 + 0.14N_{Re}^{0.7}) \quad (2.29)$$

$$\text{and } u_t = \left[\frac{4gd(\rho_L - \rho_G)}{3\rho_G C} \right]^{0.5} \quad (2.30)$$

Depending on the residence time of droplets, θ , the liquid-film coefficient was modeled based on penetration theory or film theory. For short contact time, $(\frac{D_L \theta}{r_d^2})^{1/2} < 0.22$,

$$k'_L = 2 \left(\frac{D_L}{\pi \theta} \right)^{1/2} \quad (2.31)$$

for longer contact time, $(\frac{D_L \theta}{r_d^2})^{1/2} > 0.22$,

$$k'_L = \frac{10D_L}{d} \quad (2.32)$$

While developing a model for spray dryer desulfurization, Lackey(1992) used the mass-transfer coefficients as described by:

$$N_{sh} = \frac{k'_G R T d}{D_G} = 2 + 0.60 N_{Re}^{1/2} N_{Sc}^{1/3} \quad (2.33)$$

$$k'_L = \frac{4\pi^2 D_L}{3d} \quad (2.34)$$

Obviously, equation (2.33) and (2.34) are very close to equation (2.24) and (2.32), respectively. Lackey made an assumption in her model, that $N_{sh} = 2$. But this is not true for droplet sizes over 50 μm .

In counter-current or horizontal cross-flow spray chamber, the volumetric

interfacial area, a , is given by the following equation:

$$a = \frac{6Q_L}{dA_L u_d} \quad (2.35)$$

where Q_L is in terms of volumetric flow, $[L]^3/[T]$,

A_L is the cross sectional area perpendicular to the direction of liquid flow, $[L]^2$,

u_d is drop velocity relative to the wall, $[L]^3/[T]$,

d is Sauter mean droplet diameter, $[L]$.

In counter-current flow situation, the higher gas flow rate, the slower the droplet velocity relative to the wall, and the more droplet accumulation. According to Perry's (1984), counter-current operation of a spray absorber often requires low height-to-diameter ratio, in the order of 2:1, and the gas velocity often cannot exceed 2.3 m/s. The gas tends to be completely mixed axially. For a gas-phase mass-transfer limited system, the following equation can be used to predict treatment efficiency:

$$y_2/y_1 = 1/(1+N_G) \quad (2.36)$$

and

$$N_G = k_G a V / n_G \quad (2.37)$$

where N_G is number of gas-phase mass transfer units, k_G is gas-phase mass-transfer coefficient, a is surface to volume ratio, V is volume of spray section, and n_G is gas rate in terms of $\text{mol}/[T]$.

For horizontal cross-flow spray chambers, the gas is normally well mixed radially, instead of axially. Therefore, higher gas flow rate, around 7 m/s, is possible. The design equation for a gas-phase mass-transfer limited system is:

$$y_2/y_1 = \exp(-N_G) \quad (2.38)$$

Comparison of equation (2.36) and (2.38) indicates that a horizontal flow requires a lower number of mass-transfer units than does the counter-current flow, therefore it takes lower volume to achieve the same treatment efficiency.

Calvert (Wet Scrubber, 1972) proposed to design a co-current spray chamber as a Venturi scrubber. The co-current nature somewhat limits gas absorption. Figure 2.3 is a schematic diagram for a co-current absorber. The fractional solute removal for a dilute system is given by:

$$1 - y_2/y_1 = E (1 - mx_2/y_2)/(1 + mG_M/L_M) \quad (2.39)$$

where $E = (y_2 - y_1)/(y_2 - y_1^*) = 1 - \text{EXP}(-N_G)$ (2.40)

and $N_G = (K_{Ga}RT/P_T)t_c$ (2.41)

where N_G is number of overall mass transfer units, K_{Ga} is overall volumetric gas-phase mass-transfer coefficient for dilute systems, R is gas constant, T is gas temperature, P_T is total pressure, and t_c is effective gas-liquid contact time.

In a co-current spray chamber, the volumetric mass transfer surface area is given by:

$$a = (Q_w/Q_G)(6/d) \quad (2.42)$$

where Q_w and Q_G are volumetric flow, $[L]^3/[T]$,

d is the Sauter mean droplet diameter, $[L]$.

2.2. Absorption with Chemical Reaction

Chemical reaction in an absorber often takes place in the liquid phase. By reducing the liquid phase resistance, chemical reaction normally enhances the mass-

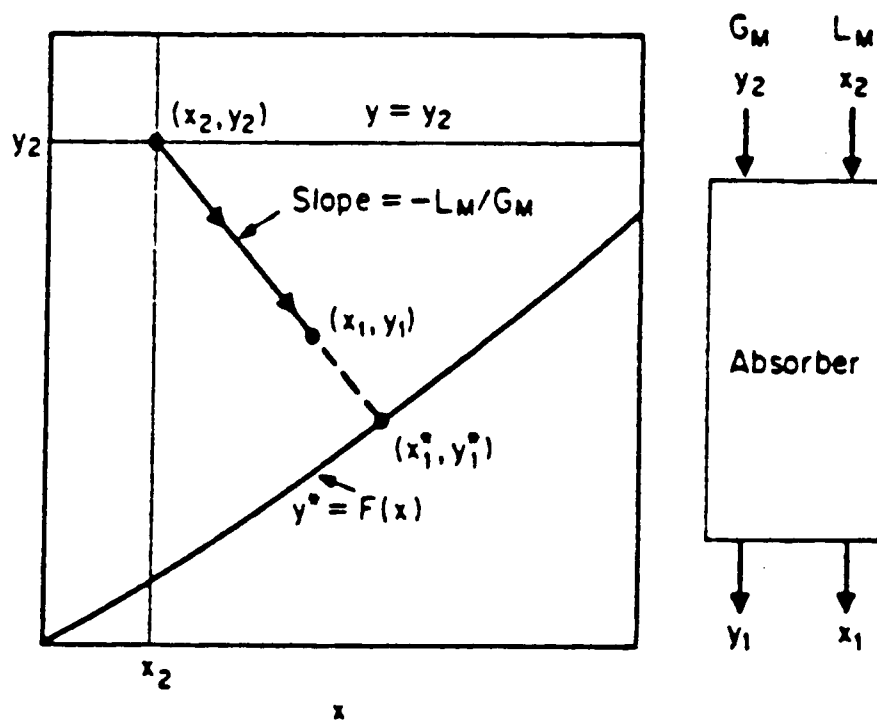


Figure 2.3 Design diagram for a co-current absorber.

Source: Perry's Chemical Engineers' Handbook, 1984, 6th edition, p14-39.

transfer process. Modeling of the rate of mass-transfer with chemical reaction is complex. Detailed literature review can be found in Perry's (1984). However, due to the fact that mass-transfer is a sequential process and is always controlled by the slowest step, the mass-transfer coefficient of k_{Ga} may be replaced with K_{Ga} in the following two cases: first, the system is gas-phase mass-transfer limited without chemical reaction; second, liquid-phase reaction, $A + \nu B \rightarrow \text{product}$, is extremely fast and irreversible such that the rate of absorption is governed by the gas-phase. Perry's proposed the criteria for such application: everywhere in the tower exists the following equation

$$y_i/y \leq 0.05 \quad (2.43)$$

$$\text{or} \quad mk_G/k_L = mk_G/(k_L^0 \phi) \leq 0.05 \quad (2.44)$$

where k_L^0 is the liquid phase mass transfer coefficient of physical adsorption; and ϕ is the reaction enhancement factor, estimated by:

$$\phi = 1 + B^0/\nu c_i \quad (2.45)$$

where B^0 is the bulk-liquid reactant concentration and c_i is the solute concentration at the gas-liquid interface. The concentration profile for an extremely fast irreversible reaction is shown in Figure 2.4.

For first-order or pseudo-first-order reactions, the Hatta number N_{Ha} usually is employed as the criteria for determining whether or not a reaction can be considered extremely slow. For extremely slow reactions, a reasonable criterion is:

$$N_{Ha} = (k_1 D_A)^{0.5}/k_L^0 = (k_2 B^0 D_A)^{0.5}/k_L^0 \leq 0.3 \quad (2.46)$$

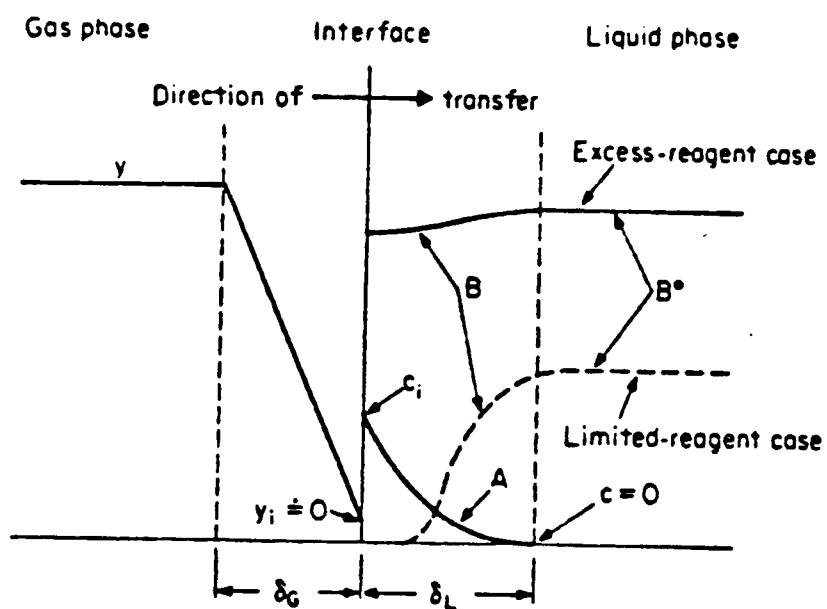


Figure 2.4 Gas-phase and liquid-phase solute-concentration profiles for an extremely fast irreversible reaction system $A + \nu B \rightarrow \text{product}$.

Source: Perry's Chemical Engineers' Handbook, 1984, 6th edition, p14-13.

where D_A is the liquid-phase diffusion coefficient of the solute in the solvent, k_1 is the first-order reaction rate coefficient and k_2B^0 is the pseudo-first-order reaction rate coefficient. When $N_{Ha} > 3$, the liquid-phase mass transfer coefficient k_L can be computed by:

$$k_L = (k_1 D_A)^{0.5} \quad (2.47)$$

Gas sorption capacity can be enhanced by suspending adsorption or reactive solids, such as activated carbon, activated sludge, and limestone. Since the 1970s', activated carbon slurry and bacteria slurry have been used as solvents in absorbers for odor removal (Burant, 1979; Kohler, 1979) and organic compounds removal (Burglund, 1983; Awata, 1984). But most of the applications were patented, therefore detailed knowledge is not validly available.

Mehta and Calvert (1967, 1969) studied gas sorption by suspensions of activated carbon in water in an agitated bubbler. They assumed the mass-transfer process to take place in the following manner: (1) the solute gas diffuses from the bulk of the gas phase to the gas-liquid interface; (2) the solute gas diffuses from the gas-liquid interface to the bulk of the liquid; (3) the diffused gas mixed in the bulk liquid; (4) The dissolved gas diffuses from the bulk of the liquid, through the liquid film surrounding the adsorbent particle, to the particle surface; and (5) the dissolved gas finally diffuses through the liquid, in the pore, to the pore internal surface. Their experimental results indicated a negligible resistance for step (4) and (5), and thus an instantaneous equilibrium between liquid-phase and solid-phase solute. Their experiments showed that high concentration

activated carbon particles (1.5%) could maintain a low concentration of the solute in the liquid and thus keep the efficiency close to the intrinsic efficiency of physical absorption. The intrinsic efficiency as defined by Calvert is the adsorption efficiency when liquid-phase solute concentration is zero. With 1% powdered activated carbon, the sorption of benzene, toluene and trichloroethylene were greatly improved. However, for highly soluble gases, such as acetone, the efficiency was already close to intrinsic efficiency in the absence of carbon, thus no improvement was observed.

Kim (1989) studied the removal of toluene from air, through absorption and subsequent adsorption onto powdered activated carbon (PAC) in a bubbler CSTR reactor. With PAC slurry concentration of 0.2 g/l, experiments showed great enhancement of the removal of toluene gas. He developed a mathematical model based on mass transfer at the gas-liquid interface, diffusion resistance in the boundary layer around activated carbon and diffusion resistance through activated carbon pores. In his study, PAC slurry concentration was very low, in the order of 10^2 mg/l, therefore a long residence time of 20 to 50 minutes was required and carbon pore diffusion was appreciable. The model predicted that diffusivity in the carbon pores and in the bulk liquid were on the same order of magnitude, approximately 10^{-3} cm²/min. The estimated gas-liquid mass transfer coefficient K_L was 0.6 cm/min. The diffusion resistance through the boundary layer was considered to be negligible because of high degree of mixing. And the mass-transfer coefficient inside carbon pore, k_s , was estimated to be approximately 10 cm/min.

The mass-transfer coefficient from bulk liquid to surface of particles, k_c , can be

described by the following equation for a particle of diameter " d_p " at rest in a large volume of stagnant fluid (Wet Scrubber, 1972):

$$k_c = \frac{N_A}{C_L - C_S} = \frac{2D_L}{d_p} \quad (2.48)$$

Any motion of the particle relative to the fluid will tend to make k_c larger. At high relative flow rates, $(N_{sh}) = k_c d_p / D_L$ was found to be proportional to $N_{Re}^{1/2} N_{Sc}^{1/3}$. Mass-transfer to particles in stirred vessels have been studied extensively. However, mass-transfer to particles inside a droplet has not been well reported.

Both biofiltration and bioscrubbing for VOC removal are absorption processes with biochemical reaction in the liquid phase. An important problem addressed by most of the literature was the effect of biochemical reaction on the mass-transfer process. The answer varies in different systems. Investigations on this issue mainly involve the following aspects: the chemical properties of the target VOC, such as Henry's Law coefficient and the diffusivity of the VOC in air and water; biodegradability of the target VOC, for which the kinetic coefficients were normally explored and expressed by the Monod equation; operational parameters of absorbers, such as height, specific surface area, gas and liquid flow rates, and counter-current versus cocurrent operation.

Swanson (1997) gave a listing of some specific compounds that have been removed from waste gas with biofiltration, as listed in Table 2.1. He also presented some typical operation parameters, as listed in Table 2.2. As addressed by most fixed-film models, the biofiltration process relies on the mechanism of liquid-phase diffusion and biological degradation of target chemicals, gas-phase mass-transfer is not the limiting

Table 2.1 Listing of specific compounds that have been removed from waste gas with biofiltration.

Ammonia	Butylaldehyde	nitrogen dioxide
carbon monoxide	acetate	nitrogen oxide
hydrogen sulfide	Scatole	pentane
acetone	Indole	Dimethyl sulfide
benzene	Methanol	triophene
butyl acetate	Methyl-ethyl-ketone	toluene
Diethyl amine	Styrene	trichloroethene
Dimethyl disulfide	Iso-propanol	tetrachloroethene
ethanol	methane	2-ethyl hexanol
hexane	methyl mercaptan	Xylene
Ethylbenzene	mono-, di, tri- chloromethane	

Source: Swanson, Warren J., and Loehr, Raymond C., 1997. Biofiltration: Fundamentals, Design and Operations Principles, and Applications. Journal of Environmental Engineering, June 1997, p539.

Table 2.2 Biofilter Operating Parameters.

Parameter name (1)	Description/comment (2)	Calculated as (3)	Typical units (4)	Typical range (5)	References (6)
Empty bed contact time (EBCT)	Measure of biofilter gas residence time	V/Q	seconds	15 - 60	Corsi and Seed (1994)
Surface loading	Volumetric gas loading	Q/A	$m^3/m^2/h$	50 - 200	Severin et al. (1993) Leson and Winer (1991) Mueller (1988)
Mass loading	Chemical mass loading rate per unit bed volume	QC/V	$g/m^3/h$	10 - 160	Sabo et al. (1993) Leson and Winer (1991) Medina et al. (1992)
Elimination capacity (EC)	Chemical mass removal rate per unit bed volume	$Q(C_i - C_e)/V$	$g/m^3/h$	10 - 160	Ottengraf and VanDenOever (1983) Severin et al. (1993) Devinny et al. (1993)
Removal efficiency	Performance measure	$(C_i - C_e)/C_i \times 100\%$	%	95 - 99	Ottengraf and VanDenOever (1983) Mueller (1988) Marsh (1992)

Note: V = biofilter volume, Q = gas flow rate, A = Area, C_i = influent concentration, and C_e = effluent concentration.

Source: Swanson, Warren J., and Loehr, Raymond C., 1997. Biofiltration: Fundamentals, Design and Operations Principles, and Applications. Journal of Environmental Engineering, June 1997, p538.

step. Parker (1996) studied tricking-filters for the treatment of several chlorinated compounds. The diffusive resistance in his experiment was negligible. Ockeloen (1996) developed a model for fixed-film bioscrubbers to investigate the design parameter for waste gas removal. The dimensionless Henry's Law constant ranged from 10^{-4} to 10^{-1} . A range of parameter values were tested for operational configuration, packing height, half-saturation coefficient, maximum substrate removal rate, superficial gas and liquid velocity, intermediate liquid treatment efficiency. He concluded that gas-phase mass-transfer coefficient had essentially no effect, and changes in the liquid-phase mass transfer coefficient had a small effect on the removal efficiency. The system was usually limited by the pollutant's Henry's Law constant and the biofilm's ability to degrade the substrate, and not by the gas-to-liquid mass transfer.

Overcamp (1993) developed an integrated model to describe the steady-state operation of a suspended growth bioscrubber for the control of biodegradable, volatile organic gases. The pollutant was absorbed and partially oxidized in the absorber, further oxidation was completed in the suspended bioreactor. The process parameters used were: volume of the absorber was 10 m^3 , gas flow rate was $3600 \text{ m}^3/\text{h}$, liquid flow rate was $18 \text{ m}^3/\text{h}$, mass transfer coefficients were $k_G = 360 \text{ m/h}$ and $k_L = 12.8 \text{ m/h}$. Biological kinetic parameters were: maximum substrate utilization rate $\mu = 0.3/\text{h}$, half-saturation coefficient $K_s = 1.0 \text{ gCOD/m}^3$, yield coefficient $Y = 0.3 \text{ gCOD/gCOD biomass}$, decay coefficient $b = 0.005/\text{h}$, and food loading $f = 0.2 \text{ gCOD/gCOD biomass}$. Dimensionless Henry's Law coefficient ranged from 0.05 to 0.0005. He discussed that the system was limited by the

rate of mass transfer in the absorber. Less than 10 to 20 percent of the biodegradation was expected to occur in the scrubber. Overall efficiency was a function of the absorption factor, the number of stages, and the Henry's Law coefficient of the pollutant. The system was predicted to perform well for soluble compounds like acetone, methyl ethyl ketone and methanol, with dimensionless Henry's Law constants of 0.0015, 0.0004 and 0.0002, respectively. The results were in support of Ottengraf's (1986) suggestion to design the system as a physical absorber using traditional chemical engineering procedures followed by a separate oxidation reactor using a biochemical design method. Overcamp also discussed that if a suspended-growth bioscrubber had a significantly different design than that envisioned in their paper, the performance could be completely different. For example, if the absorber was a bubble contactor sparged with the waste gas, a significant fraction of the substrate degradation could occur in the absorber.

2.3. Fate of VOCs in Activated Sludge System

As reviewed by Corsi (1991), the competing removal mechanism for VOCs in activated sludge system include: (1) sorption onto particle and biomass; (2) volatilization; (3) biodegradation. A brief description of each mechanism is provided below.

2.3.1. Adsorption of VOCs on Biomass

It is generally agreed upon that VOCs adsorbed on biomass are small compared to those go through volatilization or biodegradation in the aeration tank. Adsorption at low concentration and equilibrium can be described by:

$$q = K_p C_l \quad (2.49)$$

where q = mass VOCs sorbed to solids per mass of solids (mg/mg),

K_p = liquid-solid partition coefficient (m^3/mg solid),

C_l = liquid-phase VOC concentration (mg/m^3).

Karickhoff (1979) gave the following empirical relationship to describe K_p :

$$K_p = f_{oc} K_p' \quad (2.50)$$

$$K_p' = 6.3 \times 10^{-7} K_{ow} \quad (2.51)$$

where f_{oc} = fraction of mass of organic carbon in solids (g/g),

K_{ow} = octanol/water partition coefficient for a specific compound,

K_p' has units of m^3/g TSS and K_p has units of m^3/g VSS.

Namkung and Rittmann modified equation (2.50) and (2.51) by representing a biological cell of the structure $\text{C}_5\text{H}_7\text{O}_2\text{N}$, thus $f_{oc} = 0.531$. Their estimate of K_p is:

$$K_p = 3.345 \times 10^{-7} K_{ow} \quad (2.52)$$

Based on 6 VOCs and 6 semi- and non- volatile organic compounds, Dobbs (1989) developed the following equation to estimate organic contaminants sorbed to solids:

$$\log_{10} (K_p') = 0.58 \log_{10}(K_{ow}) + 1.14 \quad (2.53)$$

where K_p' has units of liters/kg. Equation (2.50) and (2.53) were observed to be consistent for adsorption to primary solids, mixed liquor solid and digested solids as long as the organic content of the solids was considered.

The adsorption removal rate from an aeration tank is proportional to the rate of sludge wasting, as described by:

$$R = qQ_w X \quad (2.54)$$

where Q_w is wasted sludge flow rate (m^3/s), and X is concentration of solid particles or biomass (mg/m^3).

2.3.2 Volatilization of VOCs in Aeration Tanks

Volatilization in aeration tanks involves two mechanisms: stripping by air bubbles and direct transfer from water surface. In a study of VOC emissions from sewer system, Corsi (1996) used the following equation to describe both mechanisms:

$$R = -K_L(C_l - C_g/H)A \quad (2.55)$$

where R = the rate of mass transfer (mg/s),

K_L = the overall mass transfer coefficient (m/s),

C_g = gaseous VOC concentration above a water surface, (mg/m^3),

C_l = aqueous VOC concentration, (mg/m^3),

H = the dimensionless Henry's law coefficient,

A = interfacial mass-transfer area (m^2).

A similar equation in terms of overall liquid phase mass-transfer coefficient were used by Kyosai (1991), in a study of water-surface desorption on volatile compound removal under bubble aeration. Kyosai predicted that 17 - 60% of the total transfer rate of chloroform, carbon tetrachloride, trichloroethylene, and tetrachloroethylene came from surface desorption in field conditions, although only 6% of O_2 transfer could be contributed to surface desorption.

For direct VOC transfer across a water surface adjacent to open atmosphere, C_g can be assumed to be small and negligible. Therefore equation (2.55) can be

approximated by

$$R = -K_L C_L A. \quad (2.56)$$

For covered system or the release of highly saturated air bubbles to the water surface, equation (2.56) will overestimate the transfer.

For rising air bubbles saturated with VOC, stripping loss can be described by

$$R = -GC_L H \quad (2.57)$$

where G = gas flow rate (m^3/s).

Normally, rising air bubbles reach only partial saturation with VOC, equation (2.57) can be modified as following to account for degree of saturation (Roberts, 1983):

$$R = -GC_L H \{ 1 - \exp[\psi k_o A / HG] \} \quad (2.58)$$

and
$$\psi = (D_{\text{VOC}} / D_{\text{O}_2})^{0.6} \quad (2.59)$$

where k_o is a system specific oxygen transfer coefficient ($1/\text{s}$), D_{VOC} and D_{O_2} are diffusivity of VOC and O_2 in water, respectively, and all other variables are as defined previously. Equation (2.58) is system specific. The underlying assumptions are: (1) isothermal system, (2) well mixing in water, (3) ideal vapor behavior, (4) equilibrium obeys Henry's Law, (5) constant liquid volume and hydraulic conditions, and (6) constant bubble size and aeration rate.

2.3.3. Biological Degradation of VOCs

The predominant microorganisms degrading VOCs are heterotrophs. Bacteria and fungi are the most common. Compounds to be treated must be readily biodegradable and nontoxic. Alcohol, ethers, aldehydes, ketones, monocyclic aromatics, organic amines and

sulfide have been reported to be easily biodegradable (Swanson, 1997). More artificial compounds, such as chlorinated compounds, have low degradation rate or even require cometabolites. For instance, trichloroethylene removal by methanotrophs requires the presence of toluene. But some genetically engineered strains can utilize chlorinated compounds as primary substrates.

The Monod kinetic model was commonly used to describe biological degradation of VOCs:

$$dC_1/dt = -q_{\max} X C_1 / (K_s + C_1) \quad (2.60)$$

where C_1 = aqueous VOC concentration (mg/m^3),

$q_{\max}$ = maximum specific substrate utilization rate ($\text{mg}/\text{mgVSS}\cdot\text{S}$),

K_s = half velocity constant (mg/m^3),

X = active cell concentration (mgVSS/m^3).

Overcamp (1993) proposed a representative value of $K_s=1\text{mg}/\text{l}$ for easily biodegradable VOCs.

In cases of high aqueous VOC concentration or low half-saturation coefficient, $C_1 \gg K_s$ and equation (2.60) can be approximated by

$$dC_1 / dt = -q_{\max} X \quad (2.61)$$

where biodegradation was in zero order and the maximum rate is reached. In cases of low aqueous VOC concentration or hardly degradable VOCs, $K_s \gg C_1$, the substrate utilization is in first order with respect to C_1 , as described by

$$dC_1 / dt = -(q_{\max}/K_s) X C_1. \quad (2.62)$$

Namkung (1987) reported that typical values of $q_{\max}/K_s$ ranged from 0.1 to 100 $\text{m}^3/\text{gVSS/d}$, with very degradable compounds having $q_{\max}/K_s$ in excess of $10^3 \text{ m}^3/\text{gVSS/d}$. The values of $q_{\max}/K_s$ for chlorobenzene, ethylbenzene, benzene and toluene were 0.21, 0.23, 0.32 and $0.40 \text{ m}^3/\text{gVSS/d}$, respectively. These rate constants lead to prediction of greater than 94% biodegradation of the above VOCs in municipal activated sludge system in Chicago.

2.4. Activated Carbon Added in Activated Sludge System

The applications of activated carbon in biological water and wastewater treatment process were developed in the 1970's. Two major application fields are: powdered activated carbon added into activated sludge units, and granular activated carbon bed in biological fixed-film process. As addressed by DeWalle (1976), some of the benefits of powdered activated carbon (PAC) added into activated sludge units are: removal of adsorbable inorganics and refrigerant organics; reduction of toxicity; resistance to shock loading; and improved floc formation, sludge settling and dewatering. However, the mechanisms of the biological activated carbon process have not been well understood. Different theories and experimental results have been presented on the relationship between biodegradation and carbon adsorption, which provide fundamentals for two big concerns: the effect of activated carbon on substrate biodegradation and biological regeneration of activated carbon.

According to Rice and Robinson (1982), although the micropores of activated carbon are too small for bacteria to migrate into them, desorption can take place through

the reaction of exoenzymes with adsorbate in micropores. Ying and Weber (1979) suggested that biological reaction rates became higher on activated carbon due to an enrichment of the organics by carbon adsorption. Zhang (1991) brought up a different hypothesis: the simple combination of biodegradation and carbon adsorption. Through Warburg tests and fixed-film column tests on phenol degradation, he concluded that: the biodegradation rates of microorganisms attached to carbon and suspended in liquid were almost the same so long as the substrate concentration around the microorganisms was the same. In other words, the bioreaction rate had little relation with the adsorbed phenol; a decrease in bioreaction rate could occur if the phenol concentration in liquid phase was lowered by carbon adsorption. Physical desorption due to concentration difference and subsequent biological degradation of solute were recognized by all reporters.

Biological regeneration of activated carbon has been reported by Kim (1989), Hutchinson (1990) and other researchers. The reported concentrations of PAC in activated sludge system are normally between 500 - 3000 mg/l. DeWalle et. al. (1976) studied the biological regeneration of powdered activated carbon added to plug flow activated sludge units maintained at the sludge age of 3, 5, 10, and 15 days, with carbon concentrations ranging from 0 to 1000 mg/l. They observed that the apparent adsorption capacity gradually increased with increased solids retention time, and suggested that the regeneration was determined by the ratio of biological solids to carbon solids. Daily regenerated adsorptive capacity was reported to be in the order of magnitude of 0.01mgCOD/mgPAC/day in their system. Schultz (1984) studied the mechanism of

bioregeneration of phenol-contaminated PAC by activated sludge through ^{14}C batch experiments, and concluded that: PAC did not enhance the biodegradation of phenol, but bioregeneration of the carbon was essentially complete for this substrate; the controlling mechanism for bioregeneration is desorption by a lowering of the liquid phase concentration and not directly by bacterial or enzymatic attack; the major advantage of PAC addition is the ability of the PAC to act as a reservoir and dampen the effects of shock loads of adsorbable organics. Schultz stated that several authors suggested bioregeneration of activated carbon is controlled by the reversibility of adsorption, and a reversibly adsorbed substrate can be removed from the carbon.

Based on some US and European models, Benedek (1982) developed a model for a carbon-activated sludge system. In his model, the relationship for the utilization of the soluble biodegradable substrate was described by Monod kinetics. The addition of PAC was assumed to have no effect on the half saturation coefficient k_s for the soluble degradable substrate. However, the maximum substrate utilization rate constant $q_{\max}$ for the soluble biodegradable substrate increases as a result of attachment of bacteria to the carbon surface. Lee and Johnson (1979) reported a $q_{\max}$ increment of 14% with non-adapted organisms and 79% with adapted organisms. Benedek experimentally proved that this model has a high reliability for both the batch and continuous operation.

CHAPTER III

EXPERIMENTAL METHODOLOGY

Methyl-ethyl-ketone (2-butanone, MEK) was chosen to be the target VOC. It is widely used as a solvent for paint, printing ink, and synthetic leather manufacturing. It is listed as a hazardous air pollutant (HAP) in the 1990 Clean Air Act Amendments. The OSHA limit for MEK is 200 ppm in air. Removal of MEK gas by biofiltration has been reported by Deshusses (1995) and Chou (1997).

3.1. Experiment Design

3.1.1. Adsorption Rate And Adsorption Isotherm

Two solvent additions were studied to determine their effectiveness in enhancing the mass transfer in a spray chamber. They were powered activated carbon and bacteria. In order for either to be effective in reducing the VOC concentration, it would be necessary for the solvent to adsorb a substantial amount of the target VOC in the short retention time of the droplets in the spray chamber (normally 10-20 seconds). The adsorption rate was tested by measuring the decay of liquid phase VOC concentration after short contact with PAC or bacteria. Glass bottles (120 ml) with Teflon-lined silicone septa caps were used as containers. PAC was dried in a 100°C oven for 2 hours and kept in a dessicator prior to its use. Bacteria slurry with concentration around

3 g MLSS/L had been aerated for 12 hours without substrate addition prior to its use. At the beginning of each test, the container was filled with 130 ml of bacteria slurry or PAC slurry of known concentration and capped, leaving almost no head space. A PTF magnetic stir bar was used to suspend the slurry at a constant stirring speed. Then 50 μ l pure liquid MEK was injected into the bottle through a stainless steel precision syringe. Liquid samples were taken with disposable syringes and filtered into 2 ml sampling vials. In experiments with bacteria, in order to observe the instantaneous cell-surface uptake, liquid samples were taken only after 30 seconds contact time. In experiments with PAC, liquid samples were taken after 0.5, 1.5, 3.5, 7.5, and 14.5 minutes. Since the sampling process usually took about 30 seconds, the real contact times of MEK and carbon were recorded as the times when the samples were filtered into the sampling vials. Blank samples (water only, no slurry) showed the initial concentration of MEK averaged 351 mg/l, with less than 2% deviation. Since no significant difference was observed for blank sample concentrations taken at 30 seconds and 30 minutes, the container was considered to be gas tight.

The liquid phase equilibrium isotherm was important to decide the distribution of VOCs in liquid and solid PAC. Glass bottles (120 ml) were filled with different concentrations of 130 ml PAC slurry, about 10 glass beads, and capped. Then the bottles were injected with 100 μ l pure liquid MEK and placed on a roller at 22.5°C for one day. Liquid samples were taken to measure the equilibrium liquid concentration. Blank samples showed only 2% loss of MEK during the process.

3.1.2. MEK Gas Scrubbing with Water and/or PAC Slurry

As stated in Chapter I, due to the potential clogging problem of slurry atomization at low flow rates, a packed tower was used to simulate the spray chamber mass transfer characteristics. The tower was designed to have 40-50% removal efficiency with water only as absorbent. This would allow PAC enhancement to be easily measured. The sorption efficiency with and without the presence of PAC in the water would provide a direct test of the hypothesis of using PAC as an enhancement. No experiments were conducted with bacteria slurry as the solvent in the packed tower. Therefore, the packing had no biomass film. Eight tests were conducted in each case, with and without PAC. Relatively constant gas flow rate (about 40 acfm) and MEK gas concentration (500 - 550 ppm) were used in all the tests to keep the gas phase resistance constant and to make the experimental results more comparable. In order to observe the effect of different liquid flow rates and PAC concentrations, the liquid flow rates were varied from 0.29 gpm to 0.92 gpm, and three PAC concentration were used: 10 g/l, 20 g/l, and 40 g/l.

The gas flow rate was calibrated by conducting standard pitot traverses in the inlet air flow line going to the packed tower. The pitot tube was then placed at the location which represented the average velocity in order to observe the fluctuation on a continuous basis. The liquid flow rate was controlled by the pump pressure setting. Liquid effluents were collected for one minute and the volume was measured to determine the flow rate. The flow rates were continuously monitored throughout each test to ensure constant flow rates. The inlet gas concentration was continuously measured for 15 minutes and at the end of the test. Outlet gas concentration was continuously measured at the second 15

minutes of each experiment. Normally a steady-state condition was achieved at 15 minutes after operation conditions were held constant. Each test was completed within 35 minutes.

3.1.3. Stripping and Biodegradation

The kinetics of VOC biodegradation are critical for the performance of a biological treatment system. Aeration experiments in a bench scale completely mixed batch (CMB) reactor were conducted to obtain the substrate utilization rate. According to Benfield and Randall (1987), mixed liquor suspended solids have little effect on oxygen transfer and can be neglected in gas-to-liquid mass transfer. Based on equations (2.57) and (2.58), the gas-liquid mass transfer characteristics of a laboratory apparatus should be constant regardless of the presence of activated sludge. In order to distinguish the effect of VOC stripping and biodegradation, comparison tests with and without the presence of activated sludge were conducted with the following procedure.

Liquid MEK was first dissolved into water in a glass bottle (120 ml), then transferred into the reactor to prevent instant loss by evaporation of MEK from the surface. After one minute of aeration, a liquid sample was taken to measure the initial MEK concentration. Later, a 3 ml sample was taken every 20 to 30 minutes. Sample volume was so small that it can be ignored. In the experiments with activated sludge, activated sludge had been aerated for 12 hours without any substrate addition before tests, and 50 ml solutions were taken for MLSS measurement at the beginning and end of the experiment.

The above method did not give concern to the effect of surface-active material produced by bacteria on the stripping of VOCs. A more proper way may be to use the supernatant of activated sludge solution in the stripping tests without bacteria. But the effect of biological surface-active material can be ignored if liquid mixing in the aeration tank is turbulent (Benefield and Randall, 1987). Since the aeration rate used in this experiment was much higher than that in an aeration tank, the results of this study are still valid.

3.1.4. Desorption Rate

If PAC slurry is used as the capture agent, it is important to have reversible adsorption so that VOCs could be effectively removed by biodegradation in the aeration tank. A comparison of stripping experiments with and without the presence of PAC were conducted to study the desorption rate of MEK from PAC. Due to the same reason stated earlier, the effect of low concentration PAC (2%) on bubble sizes and thus stripping characteristics of a laboratory apparatus should be negligible. MEK liquid and 10 g/l PAC slurry were mixed in polypropylene plastic bottles, and rolled with glass beads for 24 hours to reach equilibrium. After allowing settling for several hours, the upper half volume of supernatant was dumped into the bench scale CMB reactor for stripping test. After the supernatant test, the PAC slurry remaining in the bottles was also used to conduct stripping test in the same CMB reactor. In both experiments, the gas phase MEK concentration was analyzed every 10 to 20 minutes by a Miran-1A spectrometer. At the beginning of both stripping tests, liquid samples from the reactor were taken for the measurement of initial MEK concentrations.

3.1.5. Effect of PAC on Biological Activity

The metabolism activity of aerobic microorganisms can be represented by the oxygen consumption rate. The microbial oxygen consumption rate with and without the presence of PAC provides a direct indication of the effect of PAC on microbial activity. Warburg respirometer tests were conducted for this purpose. The experimental matrix included 81, 269, and 1885 mg/l MEK in buffer solutions with and without the addition of 5 g/l PAC. Duplicate samples were analyzed. A blank pair without MEK was used to indicate endogenous respiration. Ten ml samples were added into 125 ml flasks. Activated sludge had been aerated for 12 hours without any substrate before the experiment. Bacteria were placed into a small flask and stirred to provide an even distribution. Three ml of well mixed activated sludge was taken by a 1000 μ l precision pipette and added into each of the 125 ml flask. One ml 20% KOH solution was added into the central well of each flask for CO₂ absorption. Then the flasks and manometers were attached together and started shaking in the water bath. Ten minutes later, the recording of manometer reading began. The manometer heights were recorded every 30 to 60 minutes. Changes of manometer heights indicated changes of pressure in the flasks due to microbial oxygen consumption.

3.2. Experimental Apparatus

An illustration of the experimental packed tower scrubber system is provided in Figure 3.1. This system consisted of the following components: (1) liquid supply; (2) gas supply; (3) packed tower; (4) liquid and gas discharge; and (5) sampling ports. A 55 gallon iron barrel fitted with a motor stirrer was used as a water or PAC slurry supply

tank. Liquid was pumped from the bottom of the tank and sprayed into the packed tower through a 2 mm ID nozzle to provide an even distribution to the top of the packing. The tower was constructed from stainless steel and had an inner diameter of 8 inches. It contained a depth of 2.0 ft of Size One polypropylene Tellerette packing (Ceilcote Corp.), supported by a stainless steel screen. The characteristics of the Tellerette packing are shown in Table 3.1. Inlet air was pumped by a fan into a PVC gas pipe of 3 feet length and 2 inch ID. MEK vapor of high concentration was generated by placing MEK liquid in a glass impinger kept in a room-temperature water bath. Nitrogen gas was passed through the impinger and used as the carrier gas to prevent explosion. The impinger was able to generate MEK of constant concentration for up to 40 minutes. The MEK vapor was injected into the mainstream air at the head of the inlet PVC pipe to allow complete mixing before entering the tower. The inlet gas distribution portion at the bottom of the tower was capped as shown in Figure 3.1 to prevent the gas line from being wetted by liquid flow. Outlet gas was discharged into a fume hood through an aluminum hose of 4 inch ID. Liquid effluent from the tower was collected in a barrel and disposed after each test. The packed tower had two sampling ports, one on the PVC inlet pipe 2 inch below the tower, the other on the outlet gas hose 1.5 feet above the tower packing. The inlet PVC pipe also had a 0.25 inch hole for flow rate sampling by a pitot tube.

Table 3.1. Physical Characters of Size One Tellerette Packing (Ceilcote Inc.)

O.D.	loop height	number/ft ³	free volume	surface	packing factor	temperature
1.81"	0.75"	1000	87%	55 ft ² /ft ³	36	200°F

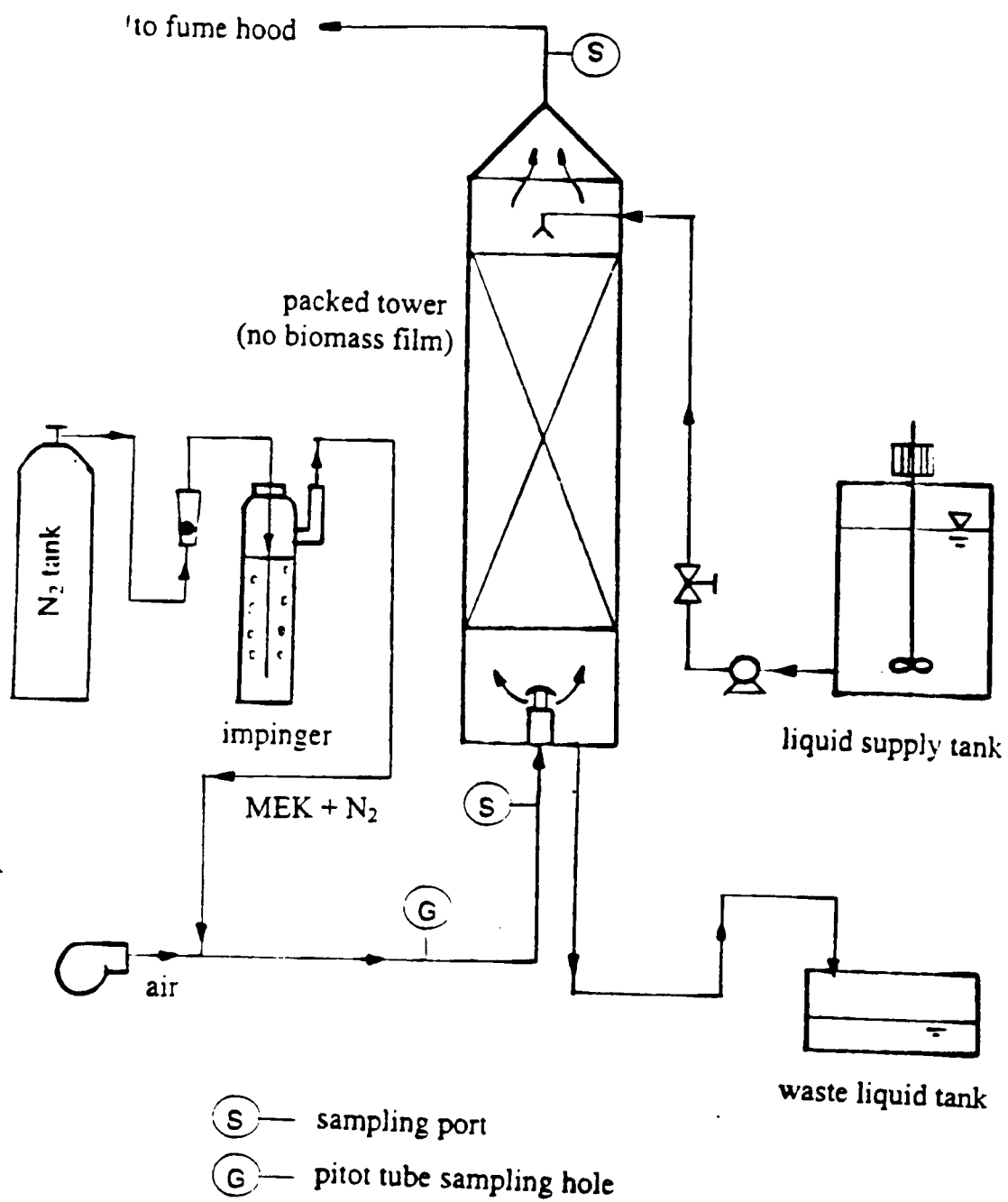


Figure 3.1 Schematic diagram of the packed tower scrubber facility.

A 2 liter glass flask fitted with a coarse air dispersion stone was used as the bench scale CMB reactor. The compressed air supply to the air dispersion stone was measure using a rotameter and kept constant during each experiment. The flask was placed in the fume hood. No cap was used while conducting experiments of aeration from water and activated sludge. In the experiments with PAC slurries and their comparison experiments with water only, a Teflon coated magnetic stirrer was used to keep PAC suspended and tokeep consistent conditions for comparison tests. The flask was capped by a rubber stopper covered by aluminum. Gas inlet and outlet glass tubes were fitted in the stopper.

3.3. Experimental Materials

The liquid MEK used in this study was HPLC grade, with 99.9% purity (Baxter Science). It had a density of 0.80 g/ml at 25°C, a boiling point of 80°C, and a water content of 0.032%.

Four types of powered activated carbon were tested for their initial adsorption of MEK from water after one minute of contact: Norit SX2 (Norit America Inc.), Calgon RB, BL and RC (Calgon Corporation). Calgon RB showed the highest initial adsorption for MEK and was chosen to be used in all experiments with PAC. This Calgon RB PAC as supplied has the following characters: minimum Molasses number of 400, minimum Iodine number (mg/g) of 1070, 60-75% through 325 US mesh (44 μm), and maximum moisture content of 2%.

The microbial seed was taken from the aeration tank of the Knoxville Kuwahee Wastewater Treatment Plant. The acclimation was conducted in a batch mode, using the phosphate buffer and nutrients as listed in Table 3.2. The solution was added on a daily

basis, about 1.5 L/d. Glucose was initially used as carbon source, then progressively replaced by MEK. Final MEK dosage was 350 mg/l/day, which was added as 0.5 ml twice a day. Low concentrations of yeast, bactopectone and beef were used to maintain good growth of bacteria. These substrates were not present when conducting the experiment of MEK biodegradation. MLSS was maintained at 4-6 g/l. Daily sludge waste was about 5% volume.

Table 3.2 Nutrients and Buffer in Synthetic Acclimation Solution.

Components	(mg/l)	Components	(mg/l)
(NH ₄) ₂ SO ₄	250	CuCl ₂ ·2H ₂ O	0.15
KH ₂ PO ₄	750	CoCl ₂ ·6H ₂ O	0.2
K ₂ HPO ₄	1600	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	0.2
Na ₂ HPO ₄	750	Na ₂ B ₄ O ₇ ·10H ₂ O	0.1
CaCl ₂ ·2H ₂ O	30	Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	40
MgCl ₂ ·6H ₂ O	30	yeast	50
FeCl ₃ ·6H ₂ O	5	bactopectone	100
MnSO ₄ ·7H ₂ O	0.4	beef	100
ZnCl ₂	0.5		

3.4. Analytical Methods

The liquid concentration of MEK was measured by a HP 5890 Series II gas chromatography, equipped with a flame ionization detector (FID), HP 7673A auto sampler and HP3396B integrator. A HP-1 chromatography column (15m×0.32mmID) was used. The temperatures of the inlet and the FID were 240°C and 250°C, respectively. The oven temperature was programmed from 30°C to 200°C at the rate of 15°C/min, with a 3 minutes hold at 30°C and a 12 minutes hold at 200°C. The column carrier gas (He)

flow rate was set at 2.0 ml/min. The inlet split ratio was 50:1. The FID was operated at an H₂ flow rate of 35 ml/min, an air flow rate of 425 ml/min and a make-up gas (He) flow rate of 30 ml/min. Standard solutions were made from 100 µg/ml (Chem. Service) and 1000 µg/ml (Hewlett Packard) certified MEK standards. Analysis deviation was within 2%. The detection limit for MEK was 1 mg/l. Liquid samples were taken with 5 ml sterile syringes and immediately filtered through 45 µm PVDF membrane filters (Acrodisc LC, Welton Com.), into 1.5 ml GC auto sampler vials covered with Teflon-lined silicone septa. Sampling time was less than 30 seconds in most cases. Samples were stored at 4°C for less than 48 hours before analysis.

Gas phase MEK concentrations were analyzed with a Miran-1A Portable Gas Analyzer. Teflon tubing was used to connect sampling ports with the analyzer. Sampling gas and dry dilution air at the ratio of 1:4 were pumped through the 5.6 L gas cell by the self-contained pump of the analyzer. The response time of the infrared energy absorption to the change of sample concentration was about 3 minutes, allowing a large number of analyses in a relatively short time. The detection limit for MEK was 0.4 ppm. Certified nitrogen gas with 1003 ppm MEK (National Specialty Gases) was used as the calibration gas.

CHAPTER IV

RESULTS AND DISCUSSIONS

The following experiments were conducted in this study:

- aqueous MEK adsorption isotherm and adsorption rate;
- MEK gas scrubbing using water and/or PAC slurry;
- stripping and biodegradation of MEK in water;
- desorption of MEK from PAC via stripping;
- microbial oxygen consumption with and without the presence of PAC.

4.1. Adsorption Isotherm And Adsorption Rate

The adsorption isotherm of MEK onto PAC in water at 22°C is shown in Figure 4.1. This is obviously a Type I adsorption, which is most commonly seen for nonelectrolyte adsorption from aqueous solution, as discussed by Mattson (1971). Since Langmuir and Freundlich isotherm equations are the two most widely used models for description of adsorption equilibria, both models were fit to the data. The Freundlich isotherm was found to fit the data better. As shown in Figure 4.2, the regression of logarithm of the solid-phase concentration q (mg/g), versus the logarithm of the concentration C (mg/l), is a straight line. The Freundlich isotherm is:

$$q = KC^{1/n} = 6.56C^{0.491} \quad (R^2 = 0.9584) \quad (4.1)$$

The adsorption capacity of MEK on PAC type RB is in the same order of

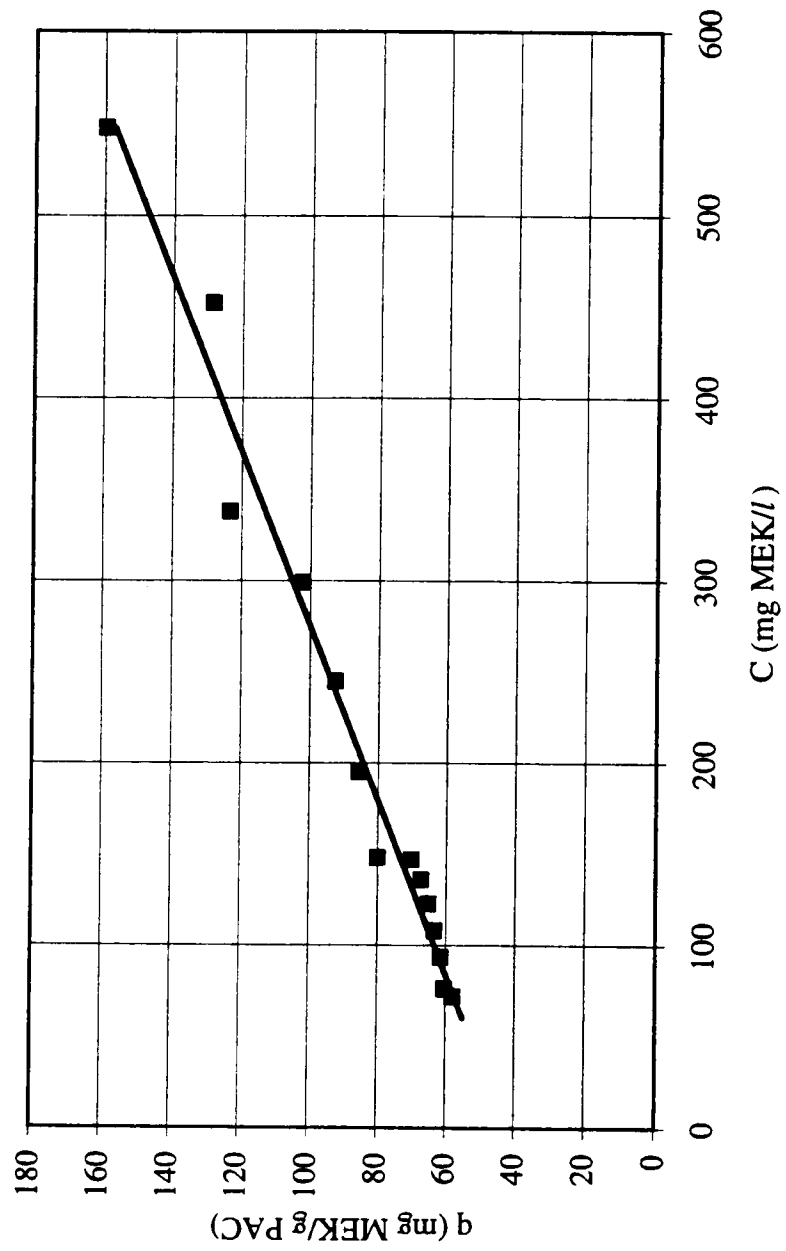


Figure 4.1 Adsorption equilibria of MEK at 22°C.

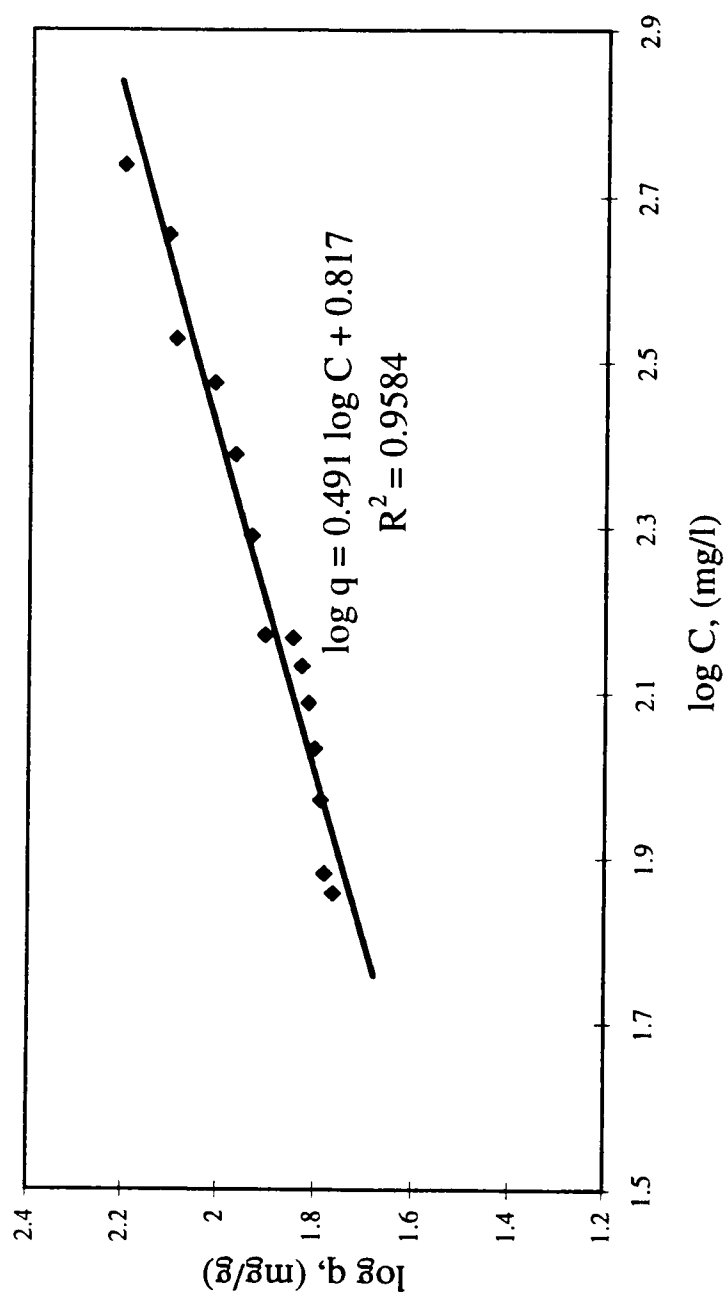


Figure 4.2 Relationship of logarithm equilibrium concentrations of aqueous MEK adsorption at 22°C.

magnitude as that of toluene on Filtrasorb 200 (Furasawa, 1973) and an order of magnitude lower than that of benzene on PAC type BL (Kim and Pingel, 1989). In equation (4.1), the exponent index $1/n$ represents the strength of adsorption. A smaller $1/n$ indicates a stronger adsorption. A higher K indicates a higher adsorption capacity. Comparing the coefficients of MEK with other organics, as reported in Table 13.2 of Water Quality and Treatment (1990), the adsorption of MEK is found to be weak and reversible, typical of a low molecular weight ketones. The capacity is comparable with those of low molecular weight organics, such as 1,1-dichloroethane and benzene.

The results of the adsorption rate experiment, as shown in Figure 4.3, indicates a very rapid adsorption rate. After 1 minute of adsorption, the dissolved MEK concentration was reduced from 351 mg/l to 92.5, 64 and 53 mg/l at PAC concentrations of 7.0, 9.0 and 10.0 g/l, respectively.

In order to study the adsorption rate, a meaningful concept is defined as "saturation coefficient", q/q^* , where q^* is the equilibrium concentration of the aqueous MEK. " q/q^* " indicates the extent to reach equilibrium and also relates to the driving force of adsorption. From Table 4.1, an interesting fact was found: in all the experiments, q/q^* reached about 60% at 1 minute after adsorption started, ranging from 60% to 65%, with a slightly increased value at lower aqueous concentration. The saturation coefficient increased gradually toward 100% later on. This fact gives an indication of the adsorption kinetics. Generally, the adsorption of solutes by activated carbon has three steps. First, external diffusion, transport of solute from bulk liquid to the exterior surface of carbon.

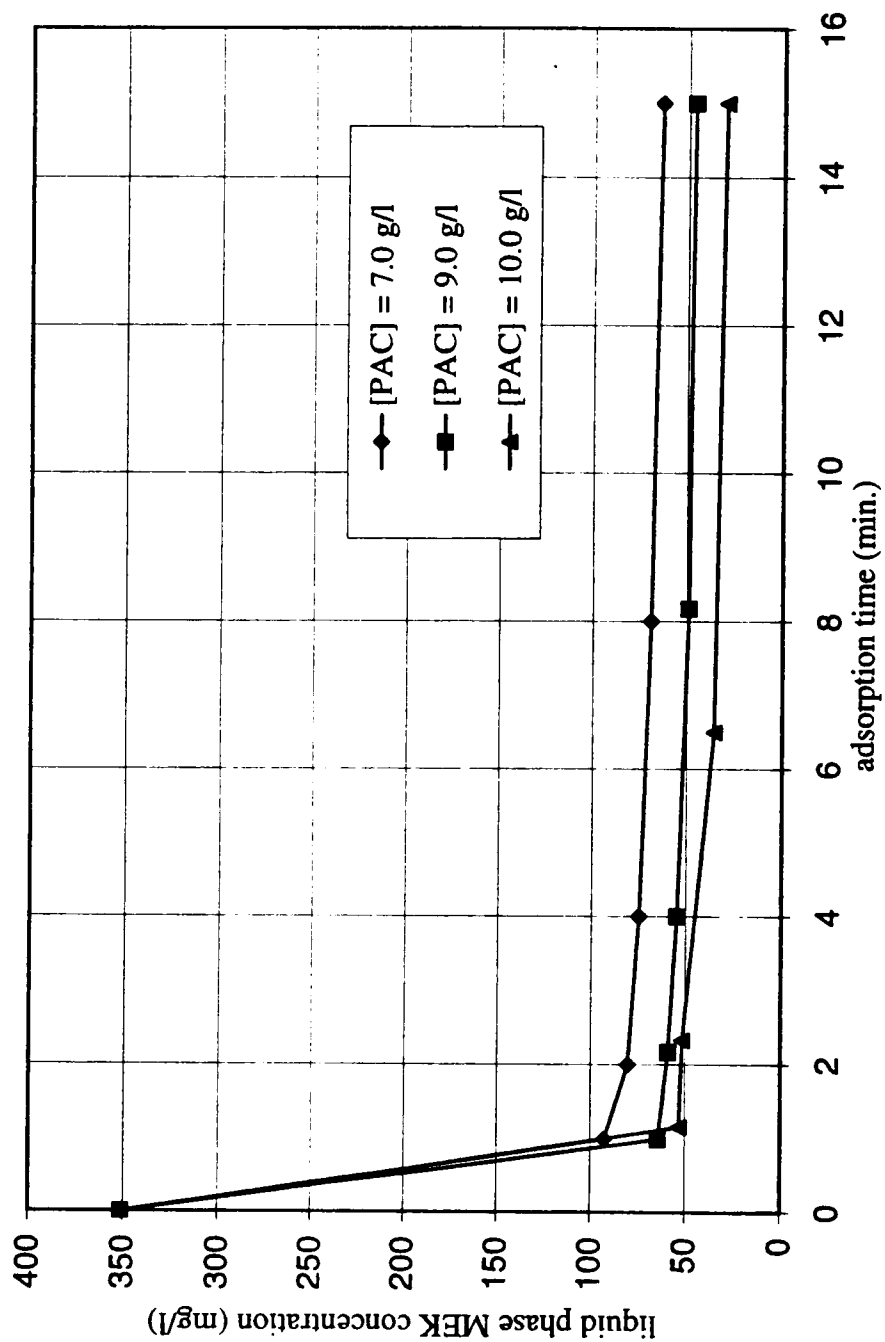


Figure 4.3 Adsorption rate of MEK on Calgon RB powdered activated carbon.
(liquid volume = 130 ml, $[MEK]_0 = 351 \text{ mg/l}$)

Table 4.1 MEK adsorption rate at different PAC concentrations.

PAC concentration (mg/l)	contact time (min)	aqueous MEK concentration C (mg/l)	solid-phase MEK concentration q (mg/g)	equilibrium MEK concentration q* (mg/g)	saturation coefficient q/q* (%)
7.0	0	351	0	117	0
	1	92.5	36.9	60.6	60.1
	2	80.1	38.7	56.4	68.6
	4	74.5	39.5	54.5	72.5
	8	68.9	40.3	52.4	76.9
	15	63.6	41.1	50.4	81.5
9.0	0	351	0	117	0
	1	64.0	31.9	50.6	63.0
	2.2	58.8	32.5	48.5	67.0
	4	54.4	33.0	46.7	70.7
	8.2	49.0	33.6	44.3	75.8
	15	46.4	33.8	43.2	78.2
10.0	0	351	0	117	0
	1.2	53.0	29.8	46.1	64.6
	2.3	51.4	30.0	45.4	66.0
	6.5	35.4	31.6	37.8	83.6
	15	30.0	32.1	34.8	92.2

Second, intraparticle diffusion. Except for small amount of adsorption on the exterior surface of carbon, solute must diffuse within the pores of carbon, including surface diffusion. Third, adsorption at the surface. Step three is very fast compared with the first two steps (Mattson, 1971), and the first two diffusion steps are normally the limiting steps. The adsorption kinetics depends on the pore size of the carbon relate to the molecular size of the solute in cases of intraparticle diffusion-controlled adsorption (Cini, 1980). The time to reach equilibrium can be seconds or days. Furusawa (1973) reported an equilibrium time of less than 25 minutes for adsorption and desorption of benzene onto GAC Filtrasorb 200 at the concentration range of 10^{-6} mol/cm³. Water Quality (1990) reported that 15 minutes is sufficient time for molecules such as dimethylphenol (molecular weight = 122, C_0 = 90 mg/l, carbon dose = 250 mg/l) to equilibrate with 325 mesh (44 μ m) particles if mixing is good. Calvert(1969) showed experimentally that intraparticle diffusion could be a non-limiting process if pore size of carbon is large relative to the molecular, as studied in their experiment, the adsorption of propane, ethylene, butane, and benzene by a kind of PAC with particle size less than 20 μ m and pore size bigger than 20 $\text{\AA}$. Considering the small molecular weight of MEK, large Iodine number (400mg/g) and small particle size (70% particles are smaller than 44 μ m) of Calgon RB carbon, it is very possible that equilibrium time could be within several minutes. The rapid adsorption of MEK indicates most adsorption sites are easy to reach, the exterior diffusion and the initial intraparticle diffusion are both fast. The slowed-down adsorption later on is controlled by further intraparticle diffusion. Although

the experiment was unable to measure the adsorption within the first several seconds, it is quite possible that substantial amount of adsorption (q/q^* close to 60%) already occurred within this short period of time. The rapid adsorption is quite favorable for enhancing the sorption of gas in a packed tower or spray chamber, where liquid retention times in both apparatus are in the order of 1 to 10 seconds.

However, as discussed in the above paragraph, depending on the relative motion of the particles to the liquid fluid surrounding them, the adsorption could be controlled by exterior diffusion or intraparticle diffusion. Because the apparatus used in the adsorption rate experiment is similar to a small agitator, where liquid turbulence may be stronger than that in sprayed droplets or liquids flowing through packing, a slower diffusion could occur in spray chambers or packed towers, therefore less adsorption at the same retention time. More research needs to be conducted in this area to determine the adsorption rate in liquid flow of a spray chamber.

It has been well known that the absorption/adsorption of nonionized chemicals is not affected by pH. pH was not controlled in this experiment. However, the relationship of absorption/adsorption capacity/rate with pH should be considered if the target VOC is ionized.

The instantaneous cell-surface uptake of MEK by 3 g MLSS/l activated sludge were tested to be negligible. After 30 seconds of mixing, the measured liquid MEK concentration were close to the initial concentration of 351 mg/l; the differences were within the analysis error of 2%. The octanol/water partition coefficient of MEK is 1.82

(Hazardous Waste, 1983). At a sludge concentration of $MLVSS = 20,000 \text{ g/m}^3$, the amount of MEK adsorbed on biomass is estimated to be about 1.2 % of the total amount in water, based on equations (2.49) and (2.53). Therefore, cell adsorption will not be an effective mechanism for enhancing mass-transfer of MEK in spray chambers. Assume that the Monod kinetics of biodegradation is in first order; maximum substrate utilization rate $q_{\max} = 1 \text{ gVOC/MLVSS/hr}$, half saturation coefficient $k_s = 1 \text{ mg/l}$; sludge concentration $MLVSS = 10,000 \text{ g/m}^3$; diffusivity of VOC $= 10^{-9} \text{ m}^2/\text{s}$; and physical absorption rate coefficient $k_L^0 = 5 \times 10^{-5} \text{ m/s}$; the Hatta number N_{Ha} in equation (2.46) is calculated to be 1.05; and the ratio of k_L/k_L^0 is 1.2 according to Figure 14-17 in Perry's (1984). This could be the optimal case of possible enhancement by biodegradation, but it is not magic yet. When VOC concentration in the liquid is higher, Monod kinetics could be in zero order, the enhancement could be smaller. Therefore, the bacteria concentration has to be very high to achieve a high liquid phase reaction rate to enhance the mass transfer process. Based on the above discussions and the suggestion of Overcamp (1993), bacteria slurry was, a slurry of bacteria is expected to have little enhancement to the gas-to-liquid mass-transfer of MEK in the spray chamber, and is not used as solvent in the packed tower scrubbing experiment.

4.2. MEK Gas Scrubbing

At a relatively constant inlet gas phase concentration of 500 ppm and gas flow rate of 40 acfm, treatment efficiencies of the packed bed scrubber were recorded as a response to changes of PAC concentrations and L/G values, as shown in Figure 4.4 and Table 4.2.

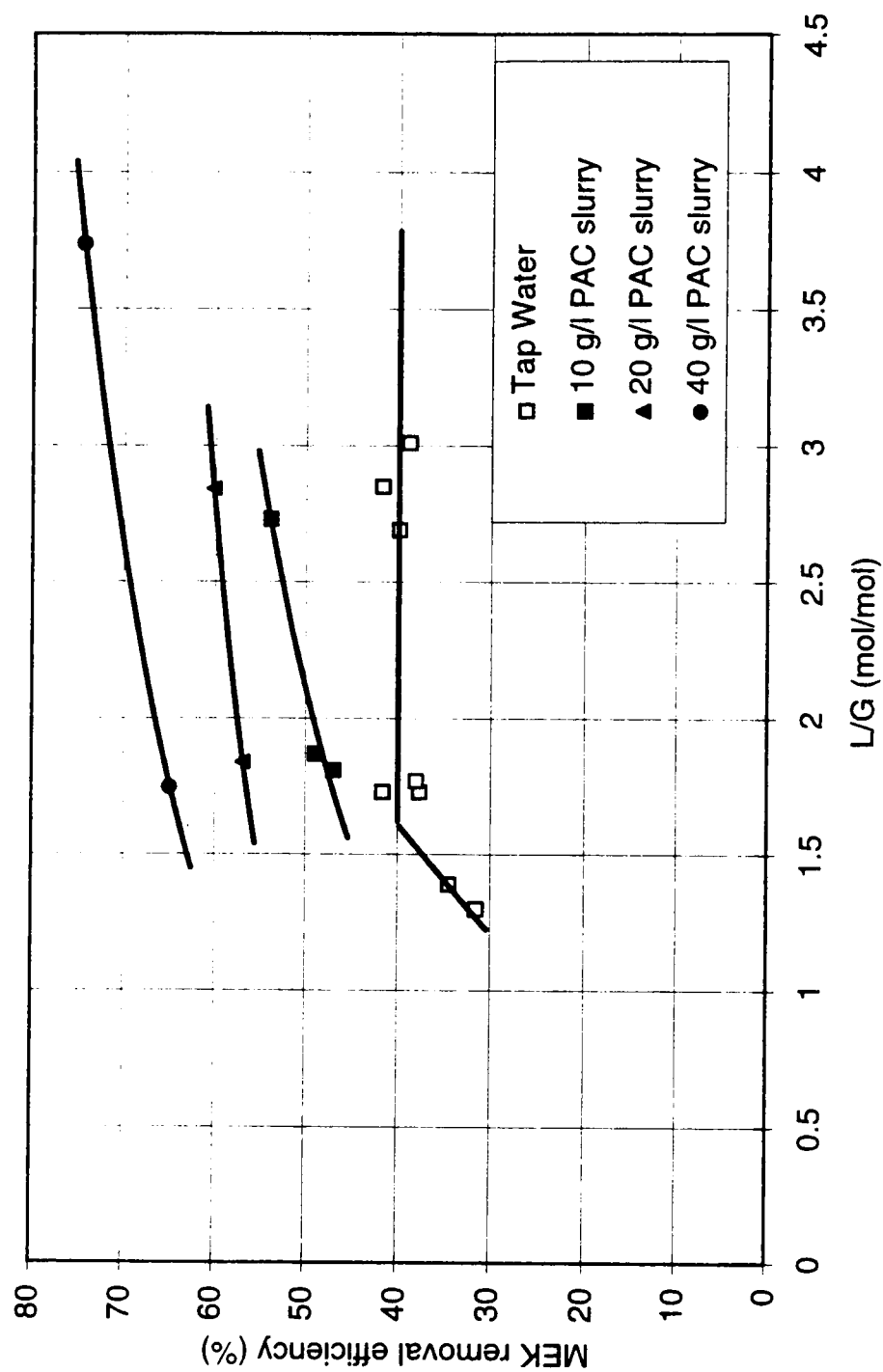


Figure 4.4 Packed tower efficiency at different L/G and PAC slurry concentrations.

Table 4.2. MEK gas scrubbing in packed tower using water or PAC slurry as solvent.

test number	liquid	liquid flow rate (gpm)	gas flow rate (acfm)	L/G (mol/mol)	inlet concentration y_{inf} (ppm)	outlet concentration y_{eff} (ppm)	efficiency (%)
1	tap water	0.290	41	1.30	532	364	31.5
2	tap water	0.350	41	1.39	543	356	34.4
3	tap water	0.425	40	1.73	529	309	41.6
4	tap water	0.463	44	1.73	524	327	37.6
5	tap water	0.466	43	1.77	527	327	38.0
6	tap water	0.676	41	2.69	506	304	39.9
7	tap water	0.690	39	2.85	515	300	41.7
8	tap water	0.720	39	3.01	520	318	38.8
9	10g/l PAC	0.686	41	2.73	479	221	53.9
10	10g/l PAC	0.460	41	1.81	501	266	46.9
11	10g/l PAC	0.462	40	1.87	493	252	48.9
12	20g/l PAC	0.454	40	1.84	508	219	56.9
13	20g/l PAC	0.697	40	2.84	504	201	60.2
14	20g/l PAC	0.626	41	2.49	534	186	65.2
15	40g/l PAC	0.439	41	1.75	524	184	64.9
16	40g/l PAC	0.919	40	3.74	519	133	74.4

Since both the PAC concentration and L/G value affect efficiency, efficiencies versus [PAC]•L/G were plotted in Figure 4.5. The treatment efficiencies were relatively constant with water only as absorbent, approximately 40% at L/G ranging from 1.7 to 2.9 mol/mol. Using PAC slurry, the treatment efficiencies increased from 47% to 74% as a response of the increment of PAC mass loading.

4.2.1. MEK Gas Scrubbing Using Water Only As Solvent

In order to calculate the mass-transfer coefficients, the equilibrium coefficient must be known. At the low inlet concentration of about 500 ppm, gas-liquid equilibrium obeys Henry's Law. According to Handbook of Environmental Fate and Exposure Data (1990), Henry's Law constant of MEK is 1.05×10^{-5} atm·m³/mol or 0.584 atm·(mole gas/mol air)/(mole gas/mole water) at 25°C. Since pressure drop of this short tower is less than 0.5 inch of water, the total pressure in the packed tower is very close to 1 atm. In most cases, Henry's Law constant, H, is very sensitive to temperature change. In general, increasing temperature will decrease gas solubility in water and increase H. The change in H with temperature can be determined from the following semi-empirical equation:

$$H_1/H_2 = \exp (B/T_1 - B/T_2) \quad (4.2)$$

For MEK, $B = -4012.16$, correlation coefficient $r = 0.983$, at temperature range of 20°C to 100°C (Zierold, 1996). In this study, the gas temperatures were mostly 25°C, and the water temperatures were mostly between 19°C and 20°C. Considering water has much higher heat capacity than air, the temperatures of the gas-to-liquid interfaces were

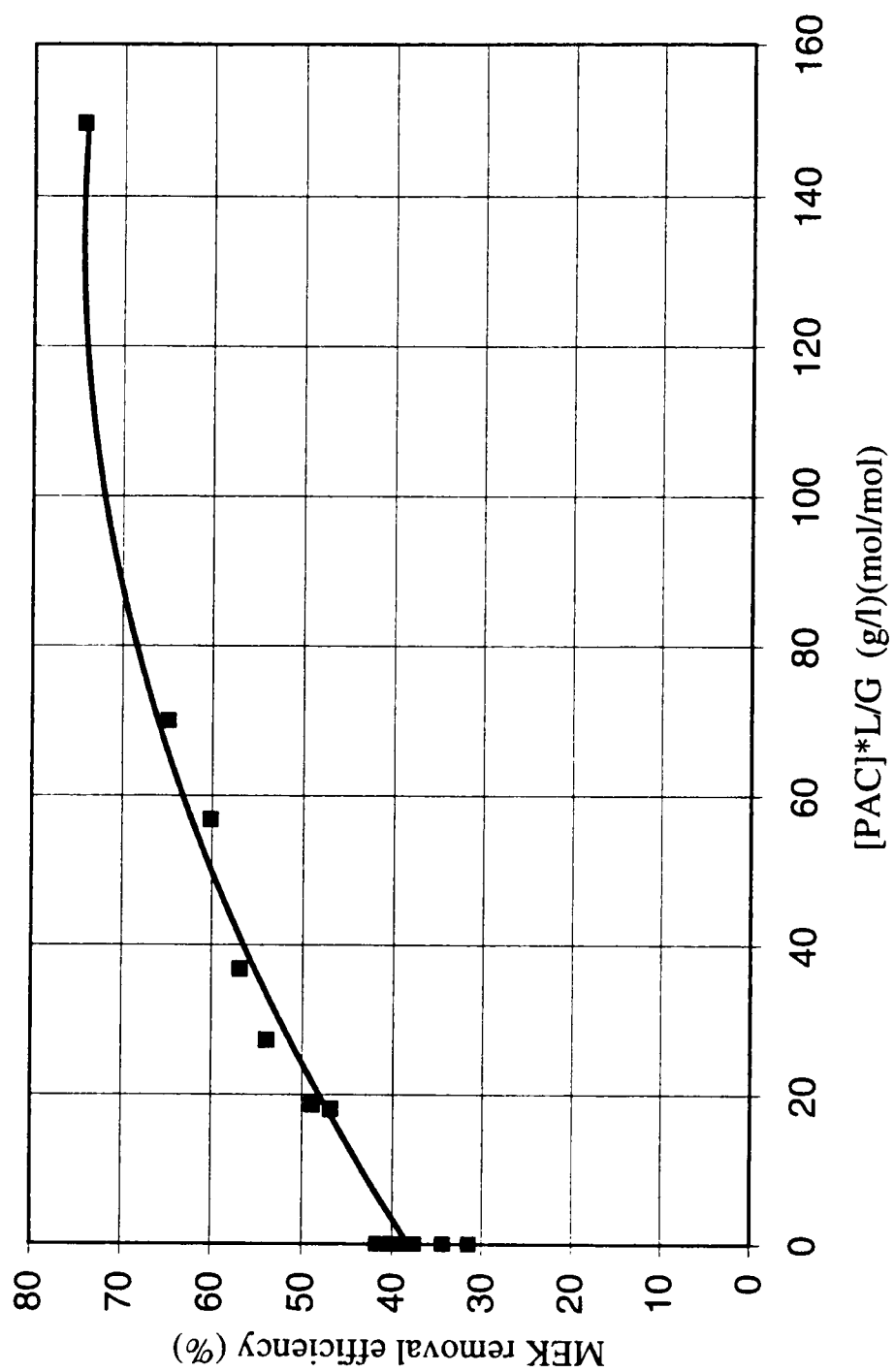


Figure 4.5 Packed tower efficiency at different PAC loading.

assumed to be close to water temperature. Therefore a mean temperature of 19.5 °C was used for calculating Henry's constant, and the equilibrium coefficient, "m", was modified to :

$$m_{19.5^{\circ}\text{C}} = m_{25^{\circ}\text{C}} \exp(-4012.16/292.65 + 4012.16/298.15) \quad (4.3)$$

$$= 0.453 \text{ (mol gas/mol air)/(mol gas/mol water).}$$

The following equations were used to calculate the overall mass-transfer coefficient:

$$x_1 = \frac{G(y_1 - y_2)}{L} \quad (4.4)$$

$$(y - y^*)_M = \frac{(y_1 - y_1^*) - (y_2 - y_2^*)}{\ln[(y_1 - y_1^*)/(y_2 - y_2^*)]} \quad (4.5)$$

$$K_{Ga} = \frac{G(y_1 - y_2)}{ZS(y - y^*)_M} \quad (4.6)$$

For PAC slurry operation, the driving force is calculated as if there was no chemical reaction (adsorption) in the liquid phase (Perry's, 1984). The results are shown in Table 4.3 and Table 4.4.

As seen from Table 4.3, with water only as absorbent, treatment efficiency increased from 30% to 40% when the liquid flow rate increased from 60 mol/min to 90 mol/min. However, a further increment of liquid flow rate did not improve the efficiency. The efficiency remained constant while liquid flow rate changed from 90 mol/min to 150 mol/min. The calculated K_{Ga} values do not show an obvious increment with higher liquid flow rates. It was speculated that this transfer process was gas-phase resistance

Table 4.3 Packed tower operation using water as solvent.

Test number	L (gpm)	L (mol/min)	G (acfm)	G (mol/min)	y ₁ (ppm)	y ₂ (ppm)	(y-y*) _M (ppm)	K _{Ga} (mol/ft ³ /min)	Efficiency (%)	G ^{0.7} L ^{0.3} (mol/min)	K _{Ga} /G ^{0.7} L ^{0.3} (1/ft ³)
1	0.29	61.6	41	47.4	532	364	417	27.4	31.5%	34.0	0.807
2	0.35	73.6	41	47.4	543	356	419	30.3	34.4%	35.2	0.861
3	0.425	89.4	40	46.2	529	309	387	37.6	41.6%	35.9	1.046
4	0.463	97.4	44	50.8	524	327	398	36.0	37.6%	39.1	0.923
5	0.466	98.0	43	49.7	527	327	399	35.7	38.0%	38.5	0.926
6	0.676	142	41	47.4	506	304	384	35.8	39.9%	40.1	0.891
7	0.69	145	39	45.0	515	300	385	36.0	41.7%	38.9	0.926
8	0.72	151	39	45.0	520	318	399	32.6	38.8%	39.2	0.832

Note: packing height Z = 2.0 ft, tower I.D. = 8 inch, packing volume = 0.698 ft³.

Table 4.4 Packed tower operation using PAC slurry as solvent.

Test number	PAC (g/L)	L (gpm)	L (mol/min)	G (acfm)	G (mol/min)	y ₁ (ppm)	y ₂ (ppm)	Efficiency	(y-y*) _M (ppm)	K _{Ga} (mol/ft ³ /min)
9	10	0.686	144	41	47.4	479	221	53.9%	318	55.0
10	10	0.46	96.7	41	47.4	501	266	46.9%	350	45.6
11	10	0.462	97.1	40	46.2	493	252	48.9%	338	47.2
12	20	0.454	95.5	40	46.2	508	219	56.9%	319	60.0
13	20	0.697	147	40	46.2	504	201	60.1%	313	64.1
14	20	0.626	132	41	47.4	534	186	65.2%	309	76.4
15	40	0.439	92.3	41	47.4	524	184	64.9%	296	77.9
16	40	0.919	193	40	46.2	519	133	74.4%	270	94.6

Note: packing height Z = 2.0 ft, tower I.D. = 8 inch, packing volume = 0.698 ft³.

controlled. Therefore, increasing the water flow rate could not effectively improve mass transfer. In order to prove that gas-phase resistance was controlling in this absorption process, the following calculation were conducted based on literature information.

According to Perry's (1984), as a rule of thumb, k_G increases roughly as the 0.7 power of gas flow rate G , while k_L increases roughly as the 0.5 power of liquid flow rate L . G has little effect on k_L , and L has little effect on k_G . The interfacial area increases roughly in the 0.3 power of L . Combining these rules, the following approximate relationships exist:

$$k_G \propto G^{0.7} L^{0.3} \quad (4.7)$$

$$k_L \propto L^{0.8} \quad (4.8)$$

These equations provide a means to prove the hypothesis that $\frac{1}{K_G a} = \frac{1}{k_G a}$ for MEK transfer into water. Dividing $K_G a$ values by $G^{0.7} L^{0.3}$, a relatively constant value was obtained, with less than 10% deviation, as shown in Table 4.3 and Figure 4.6. Since $\frac{1}{K_G a}$ is comprised of $\frac{1}{k_G a}$ and $\frac{m}{k_L a}$, very possibly $\frac{1}{K_G a}$ is dominated by $\frac{1}{k_G a}$. In other words, $K_G a$ showed the same relationship with G and L as $k_G a$ should do. On the other hand, since $\frac{m}{k_L a} \propto L^{-0.8}$, a two fold increase in L in our experiments could decrease

$\frac{m}{k_L a}$ by a factor of 0.4. If $\frac{m}{k_L a}$ is bigger than 15% of $\frac{m}{k_L a}$, then a 10% increment of $K_G a$ would have been observed. Therefore, $\frac{m}{k_L a}$ must be less than 1/5 - 1/6 of $\frac{1}{k_G a}$. This is

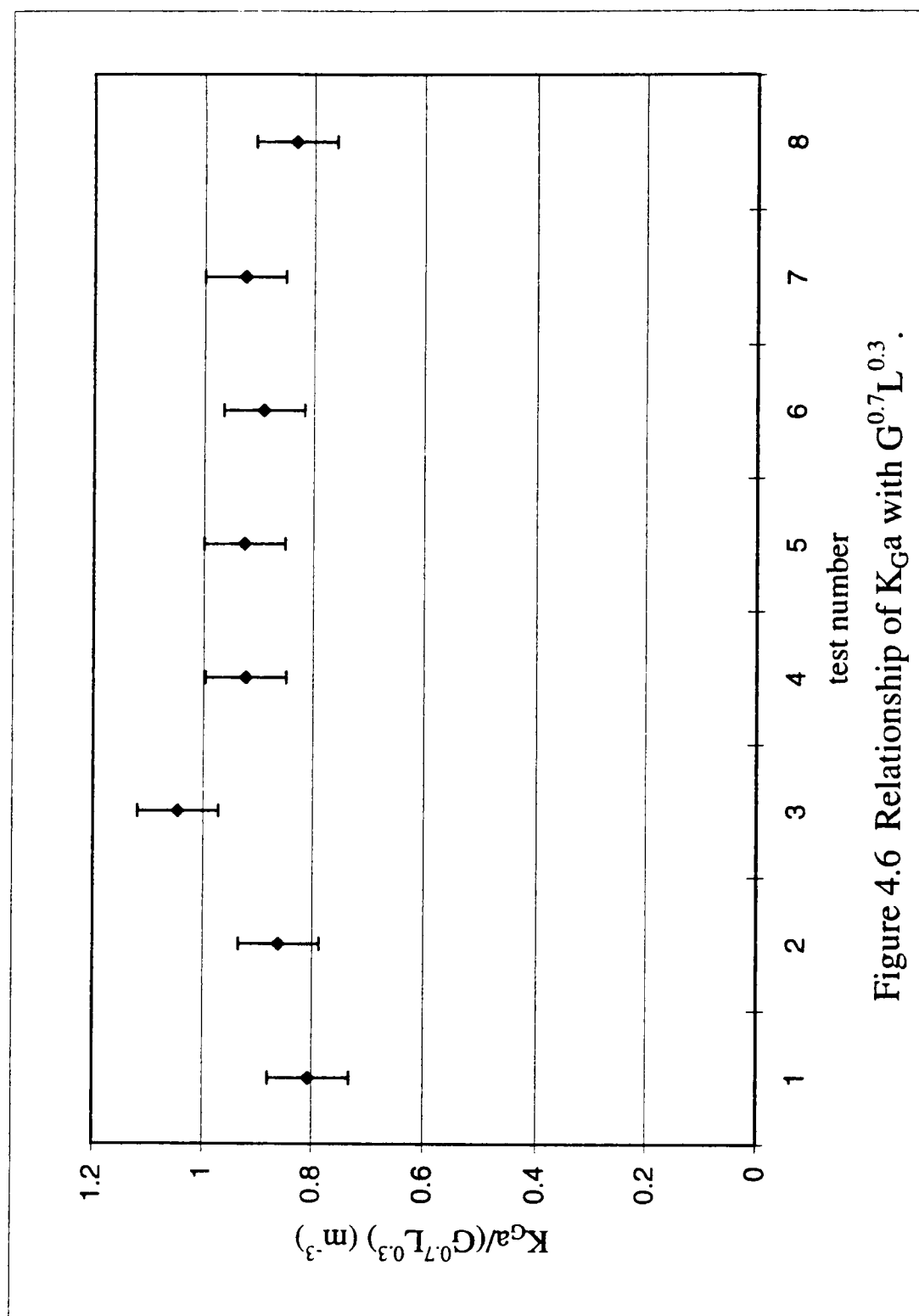


Figure 4.6 Relationship of K_{Ga} with $G^{0.7}L^{0.3}$.

reasonable, considering MEK has a high solubility. Onda's correlation (equations (2.21), (2.22) and (2.23)) were used for an estimation of wetted surface area and mass-transfer coefficients in this study. The total interfacial area for Size one Tellerettes is $55 \text{ ft}^2/\text{ft}^3$ ($180 \text{ m}^2/\text{m}^3$). The estimated interfacial area is about 18 - 25% of the total area, as shown in Table 4.5. Normally, wetted area should be 30 - 70% in packed tower operation. However, higher liquid flow rates were unable to be achieved in the experiments because the pump was already operating at its highest pressure range.

Although the liquid flow rates were low, the mass transfers were not limited by equilibrium. In all the experiments, the calculated gas phase concentration in equilibrium with bulk-liquid MEK, " m_x ", was only about 0.1-0.2 times " y_1 " at the bottom of the tower.

At the operational condition of test number 5, the estimated values of k_L and k_G were $6.93 \times 10^{-5} \text{ m/s}$ and $1.57 \text{ mol/ft}^2/\text{min}$ ($6.88 \times 10^{-3} \text{ m/s}$), respectively, as shown in Appendix B. As seen from Table 4.5, the experimental results lead to a k_G value of $3.09 \text{ mol/ft}^2/\text{min}$ for test number 5, based on the calculated wetted surface area. Therefore, Onda's prediction is about 49% lower than the experimental value. The estimated ratio of liquid resistance to gas resistance is about 1:29, which also indicates that MEK adsorption in the packed tower is gas-phase resistance controlled.

Based on the above discussions, the mass transfer process in this study was considered to be gas-phase resistance controlled. Therefore, values of overall mass transfer coefficient K_G were very close to those of gas phase mass transfer coefficient k_G .

Table 4.5 Estimation of wetted surface area "a" and K_G .

Test number	L (gpm)	L (kg/m ² /s)	a/a _i	a (ft ² /ft ³)	K _G a (mol/ft ³ /min)	K _G (mol/ft ² /min)	K _G (mol/m ² /s)
1	0.29	0.565	0.177	9.76	27.4	2.81	0.504
2	0.35	0.681	0.190	10.45	30.3	2.90	0.520
3	0.425	0.827	0.204	11.20	37.6	3.36	0.602
4	0.463	0.901	0.210	11.54	36.1	3.13	0.561
5	0.466	0.907	0.210	11.57	35.7	3.09	0.554
6	0.676	1.316	0.240	13.19	35.8	2.72	0.487
7	0.69	1.343	0.241	13.28	36	2.71	0.486
8	0.72	1.402	0.245	13.48	32.6	2.42	0.434
9	0.686	1.336	0.241	13.25	55.0	4.15	0.745
10	0.46	0.896	0.209	11.52	45.6	3.96	0.710
11	0.462	0.900	0.210	11.54	47.2	4.09	0.734
12	0.454	0.884	0.208	11.46	60.0	5.23	0.939
13	0.697	1.357	0.242	13.33	64.0	4.80	0.862
14	0.626	1.219	0.233	12.84	76.4	5.95	1.068
15	0.439	0.855	0.206	11.33	78.0	6.89	1.235
16	0.919	1.789	0.266	14.66	94.8	6.47	1.160

Note: $a_i = 55 \text{ ft}^2/\text{ft}^3 = 180 \text{ m}^2/\text{m}^3$.

Later discussion will be based on the assumption that $k_G = K_G$ in physical absorption situation.

4.2.2. MEK Gas Scrubbing Using PAC Slurry As Solvent

As seen from Table 4.4, the mass-transfer coefficient K_{Ga} increased from 46 mol/ft³/min to 95 mol/ft³/min as a response of increased PAC mass loading. While K_{Ga} was only about 36 mol/ft³/min with water only as solvent. By using PAC slurry as capture agent, the mass transfer rates were increased by a factor of 1.3 to 2.6. The following discussion were conducted to investigate the mass transfer mechanism at the presence of PAC.

First, the mass transfer process was considered to be from gas to liquid, then to PAC, in which PAC acting like a chemical reagent to reduce the liquid phase resistance. As stated in Chapter II, if physical absorption is gas-phase resistance controlled, the overall mass-transfer coefficient K_G can be substituted by the physical absorption mass-transfer coefficient k_G . As discussed earlier, MEK scrubbing with water only in the packed tower is gas-phase controlled, therefore the mass transfer coefficient K_G at the presence of PAC slurry should be equal to physical gas phase mass transfer coefficient k_G . Since the gas flow rates and packing porosity in both experiments with water only and PAC slurry were kept relatively constant, around 40 acfm, the values of gas phase resistance k_G in experiments with PAC slurry can be assumed to be close to those in experiments with water. Also, since the range of liquid flow rates used in both experiments with water and PAC slurry were about the same, except for test number 16,

the range of wetted surface area were considered to be close, as seen from Table 4.5. Therefore, the K_{Ga} values in most experiments with PAC slurry should be close to those in experiments with water. A representative value of $K_{Ga} = 36 \text{ mol/ft}^3/\text{min}$ in physical absorption experiments should apply to the experiments with PAC slurry, except test number 16, which had a higher liquid flow rate. If liquid adsorption onto PAC was efficient enough to bring the liquid phase MEK concentration to nearly zero at anywhere in the packing, a maximum efficiency of the packing tower could be achieved, as calculated from the following equations:

$$Gdy = -K_{Ga}(y-m \times 0)Sdh \quad (4.9)$$

$$y_2/y_1 = \exp(-K_{Ga}SZ/G) \quad (4.10)$$

$$\text{efficiency} = (1-y_2/y_1) \times 100\% \quad (4.11)$$

Using the higher range of K_{Ga} value from experimental results of physical absorption, $37 \text{ mol/ft}^3/\text{min}$, and the constant gas flow rate of 46.2 mol/min , the maximum efficiency was calculated to be 43%. Therefore, PAC slurry could not increase the efficiency to higher than 43% simply by increasing liquid phase mass transfer coefficient k_L , or to say decreasing liquid phase MEK concentration.

Another possible mechanism was direct gas adsorption onto PAC particles protruding from the surface of a liquid film. No mathematical model was found for this situation. An adjustment to a GAC fixed bed adsorption model (Jonas, 1979) was able to explain the results reasonably.

The original Jonas' model gave GAC weight for mass transfer zone of a fixed

GAC bed as following:

$$W_c = \rho_B Q_g \ln(C_0/C_x) / k_v \quad (4.12)$$

where, W_c — weight of carbon mass in the transfer zone, M

ρ_B — bulk density of carbon, ML^{-3}

Q_g — gas flow rate, L^3T^{-1}

C_0 — influent gas concentration

C_x — effluent gas concentration

k_v — adsorption rate, T^{-1}

The above equation is equivalent to the differential equation of mass transfer along the bed height:

$$Q_g dC = - (k_v C) S dH \quad (4.13)$$

where, S is the cross-sectional area of the fixed bed, in units of M^{-2} . The definition of volumetric adsorption rate k_v is based on the assumption of pseudo first order kinetics of surface adsorption. In other words, the concentration of the solid reactant, reactive activated carbon surfaces, does not change. This assumption is valid when carbon surfaces are only sparsely occupied by organics, as in the mass transfer zone of GAC bed. The value of k_v is proportional to adsorption surface per unit volume. In Jonas's experiments (Jonas, 1978), at constant operational conditions of GAC bed, k_v values ranged from 12.3 min^{-1} to 18.2 min^{-1} for seven organic vapors, including CCl_4 , $ChCl_3$, benzene, p-dioxane, sec-Butylamine, 1,2-dichloroethane and Pyridine. Therefore, k_v is not quite chemical specific. To explain the experimental data in this study, the gas was

assumed to be always in contact with fresh carbons protruding on the film surfaces. Meanwhile, since both the slurry flow rate and the PAC concentration contribute to the amount of carbon on the surface, and they were constant during each test, the amount of carbon on the film surface was assumed to be constant everywhere in the tower. In order to model the direct gas adsorption, the packed tower was visualized as a plug flow, fixed carbon bed reactor with high porosity. The concept of volumetric adsorption rate k_v is used herein, except that it is much smaller than that in a real fixed GAC bed.

Combining Jonas' model for vapor phase adsorption and equation (2.18) for gas-to-liquid absorption, the following equation can be used to describe the mass-transfer process using PAC slurry as solvent in the packed tower:

$$G dy = - [k_v(yP_T/RT)Sdh + K_{Ga}(y-mx)Sdh] \quad (4.14)$$

where G is the gas flow rate, in units of mol/min; y is MEK gas concentration in units of mol/mol; k_v is in units of min^{-1} ; P_T is the total system pressure, in units of kPa; R is Gas constant, $8.314 \text{ m}^3 \text{ kPa}/(\text{kmol}\cdot\text{K})$; T is the temperature, in units of K. The two items on the right side of equation (4.14) represent gas-phase adsorption and gas-to-liquid mass-transfer, respectively. As discussed earlier, the gas phase concentration in equilibrium with bulk-liquid MEK was only 0.1-0.2 times y_1 using water as solvent. And if the liquid concentration is zero, the efficiency can only reach 43%, which is close to experimental efficiency. The PAC slurry is expected to reduce the liquid phase concentration in the packed tower. Therefore, assuming $mx = 0$ in equation (4.14) is reasonable and will not bring about big error. By making this approximation, equation (4.14) was simplified and

integrated to be:

$$y_2/y_1 = \exp[- (k_v p_T/RT + K_{Ga})SZ/G] \quad (4.15)$$

A K_{Ga} value of $36 \text{ mol/m}^3/\text{min}$ was used. Regression of experimental data gives an estimation of k_v (see Appendix C):

$$k_v = 0.486 [\text{PAC}]L \quad (4.16)$$

where k_v is in units of min^{-1} ; $[\text{PAC}]$ is the concentration of PAC slurry, in units of g/l ; and L is the liquid flow rate, in units of min^{-1} . The comparison of experimental efficiencies and the estimated efficiencies based on equation (4.15) and (4.16) is shown in Figure 4.7. This model fits the data well except that it over estimates the efficiency for Test number 16, which had a higher liquid flow rate than the rest of the tests. Possibly because of big fluctuation of liquid flow rate, the steady state was not maintained in test 16.

The estimated k_v values vary from 8.45 min^{-1} (0.14 sec^{-1}) to 67.5 min^{-1} (1.12 sec^{-1}), as seen from Appendix C. The k_v value given by Jonas(1978) was 2600 sec^{-1} for a gas-adsorption bed filled with $190 \mu\text{m}$ GAC and operated at a gas flow rate of 2 ft/sec . In our experiments, the gas flow rate was 2 ft/s and about 60-70% of the PAC particles are smaller than $44 \mu\text{m}$. Based on the fact that k_v is proportional to $d_p^{-1.5}$ (Jonas, 1978), k_v value is predicted to be at least 23300 sec^{-1} for a tower filled with $40 \mu\text{m}$ PAC and having the same bulk density of the GAC bed, 0.468 g/cm^3 . Comparing the ratio of the estimated k_v values (0.14 to 1.12 sec^{-1}) to 23300 sec^{-1} , bulk PAC density of this visualized vapor-phase adsorption tower only needs to be $((0.14 \text{ to } 1.12 \text{ sec}^{-1}) / 23000 \text{ sec}^{-1} \times 0.468 \text{ g/m}^3 =)$ 4.2 to 22.6 g/m^3 , or $((4.2 \text{ to } 22.6 \text{ g/m}^3) \times 0.698 \text{ ft}^3 \times 0.0283 \text{ m}^3/\text{ft}^3 =)$

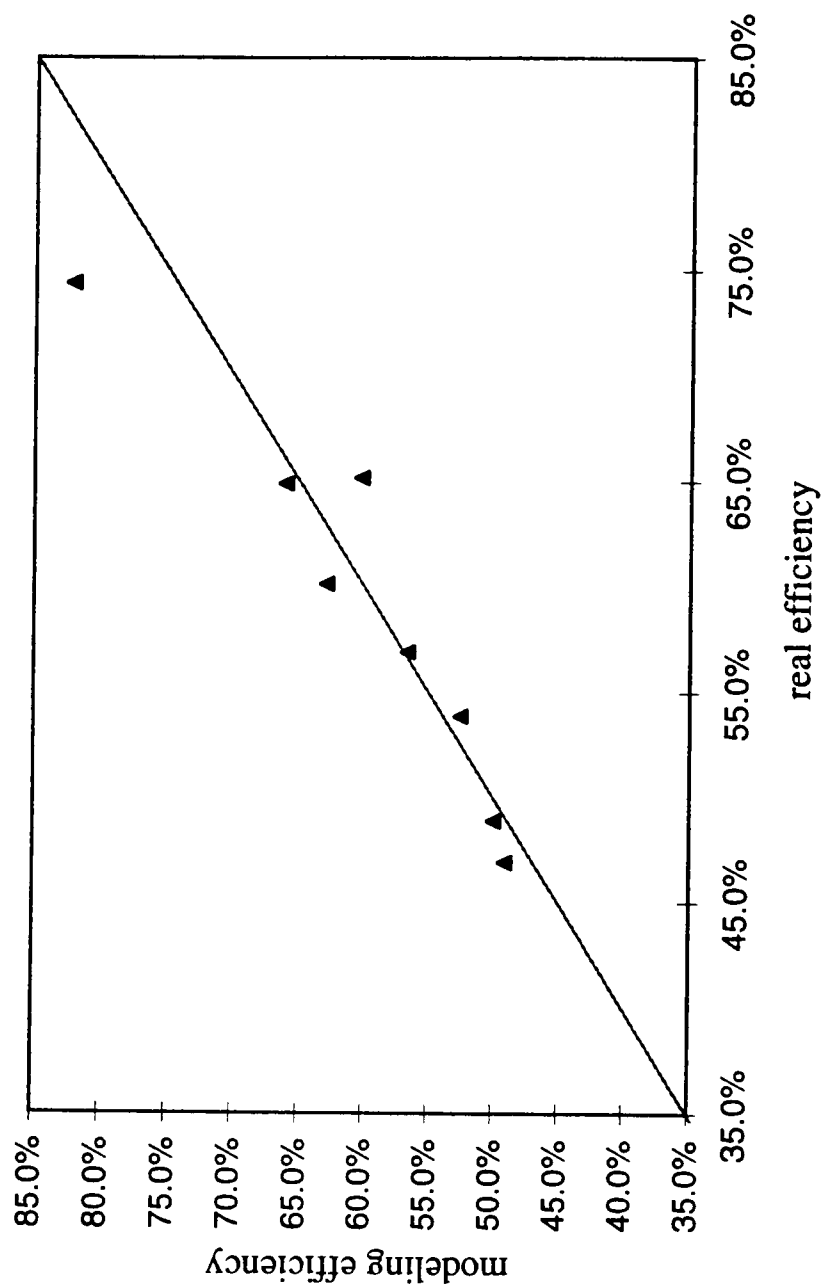


Figure 4.7 Comparison of modeling efficiency and real efficiency of MEK gas scrubbing with PAC slurry.

0.083 to 0.45 gram in the total packing tower.

In the following discussion, Test number 10 is taken as an example to see how much PAC needs to be on the surface of liquid film. Liquid holdup in the tower was tested to be about 1 liter, resulting a mean retention time of 34.5 seconds for the slurry. Assuming utilized PAC has the same retention time as the rest of the liquid slurry, the flow rate of active PAC was calculated to be $(0.083\text{g}/34.5\text{sec}) = 0.0024\text{ g/sec}$. Since total PAC flow rate was $(0.029\text{ l/sec} \times 10\text{ g/l}) = 0.29\text{ g/sec}$, the utilized PAC only accounts for $(0.0024/0.29 =) 0.83\%$ of the total carbon. The mass transfer rate ratio k_{vpT}/RT to K_{Ga} is 0.23:1, therefore gas phase adsorption accounts for 19% $(= 0.23/1.23)$ of the overall removal. Gas-phase adsorption capacity was $[(46.2\text{mole gas/min} \times (493-252)\text{ppmMEK/gas} \times 10^{-6}/\text{ppm} \times 72\text{g MEK/mole MEK} \times 19\%] / (0.504\text{ g PAC/min}) =) 0.30\text{ g MEK/g PAC}$, which was reasonable and close to the value given by Jonas(1978), around 0.35 (g organic vapor) / (g GAC).

It is also possible that PAC slurry increased the gas-phase mass-transfer coefficient by providing a rougher gas-to-liquid interface. But the importance of this mechanism was assumed to be minor, since this has not been reported in the numerous articles relevant to absorption containing particle slurries.

The experimental tower height was only 2 ft. To achieve 95% removal using water as solvent, at the operation condition of Test number 5, a height of 14.2 ft is required. Without considering the gas-phase adsorption mechanism, if the presence of PAC slurry can reduce the liquid phase MEK concentration to nearly zero in the packed

tower, then the required tower height to achieve 95% removal will be 12.0 ft using PAC slurry as solvent. If the gas-phase adsorption mechanism is considered, then only 7.8 ft of packing is needed, as calculated from equation (4.15) and (4.16). Therefore, direct gas-phase adsorption could be quite beneficial if it does exist.

Based on the literature review in Chapter II and the experimental results, liquid-phase adsorption onto PAC was assumed to have different importance at different processes, depending on the physical absorption characteristics. If the physical absorption is gas-phase resistance controlled, such as in this study, then at the abundance of PAC, solute adsorption onto PAC can keep the equilibrium gas-phase concentration of the bulk-liquid solute small and maximize the driving force. While without PAC, liquid concentration may build up and reduce the driving force. Therefore, PAC addition can help reduce the liquid flow rate or absorber volume. But in most cases the improvement of overall mass transfer rate will be in the same order of magnitude as the physical adsorption rate. If the liquid-phase resistance is significant in physical-absorption process, then the presence of enough PAC can greatly increase the liquid phase mass transfer coefficient k_L , and the overall mass-transfer coefficient K_G can approach k_G . For less soluble VOCs, liquid-phase resistance control is more likely to occur in the physical absorption process; in these cases, the mass-transfer rate could be increased by orders of magnitude.

Direct gas-phase adsorption is only a hypothesis and needs further investigation. However, if this mechanism does exist, mass-transfer could be greatly enhanced for

droplets with high PAC content and low water content, since gas phase adsorption is much more effective than liquid phase adsorption. In a spray chamber operation, smaller droplet diameters are expected to provide more chance for carbon particles to be exposed at the surface of droplets, therefore more vapor phase adsorption and higher sorption efficiency. The size of PAC is mostly in the range of 10 - 60 μm , which is close to droplet size ($<100 \mu\text{m}$) in cocurrent spray chambers. Therefore, some of the droplets will contain PAC while others do not. Meanwhile, due to droplet size distribution, it is highly possible that some droplets will contain a single PAC particle with a very thin film around it. Mass-transfer to these droplets would be the fastest among all the droplets. Since the vapor phase adsorption rate constant k_v is proportional to 0.5 power of relative gas-PAC velocity, as presented by Jonas(1978), significant amount of vapor phase adsorption is expected to occur near the atomizer, where particles have high velocities relative to the gas. It is speculated that PAC slurry can better improve mass-transfer in a spray chamber than in other absorbers because of this phenomenon.

4.2.3. Prediction Of Spray Chamber Operation

Using the semi-theoretical equations presented in Chapter II (section 2.1.3), for droplets in the size range of 100 - 800 μm , k'_G and k'_L values for MEK transferring from gas to droplets falling freely for different lengths are calculated and illustrated in Table 4.6 and Figure 4.8. The estimated liquid phase resistance $\frac{H}{k'_L}$ and gas phase resistance

$\frac{1}{k'_G}$ are close to each other, which is different from the results of the packed tower

Table 4.6 Estimation of k_G' and k_L' of MEK mass-transfer from gas to droplets.

D_p (10^{-6} m)	U_i (m/s)	R_e	Sh	k_G' (mol/m ² .s.atm)	t (sec)	$(D_L U_i^2)^{0.5}$	k_L' (m/s)	$1/k_G'$ (atm.m ² .s/mol)	H/k_L'	$1/K_G'$	K_G' (mol/m ² .s.atm)
10	3.14E-03	2.18E-03	2.03	79.40							
20	1.26E-02	1.74E-02	2.084	40.76							
50	7.46E-02	2.59E-01	2.322	18.17							
100	2.59E-01	1.80E+00	2.849	11.15	3.86	1.285	1.07E-04	0.090	0.076	0.166	6.03
200	7.35E-01	1.02E+01	4.021	7.86	1.36	0.382	5.35E-05	0.127	0.152	0.279	3.58
300	1.21E+00	2.52E+01	5.175	6.75	0.83	0.198	4.07E-05	0.148	0.200	0.349	2.87
400	1.66E+00	4.60E+01	6.29	6.15	0.60	0.127	4.76E-05	0.163	0.171	0.334	3.00
500	2.07E+00	7.19E+01	7.366	5.76	0.48	0.091	5.32E-05	0.173	0.153	0.327	3.06
600	2.47E+00	1.03E+02	8.416	5.49	0.41	0.069	5.81E-05	0.182	0.140	0.323	3.10
700	2.85E+00	1.38E+02	9.442	5.28	0.35	0.055	6.24E-05	0.190	0.131	0.320	3.12
800	3.21E+00	1.78E+02	10.45	5.11	0.31	0.046	6.62E-05	0.196	0.123	0.319	3.14

Note: drop falling distance = 1 meter, $H = 8.152E-6$ atm.m³/mol, $D_L = 1.07E-5$ cm²/s, $D_G = 9.56E-2$ cm²/s, $Sc = 1.508$.

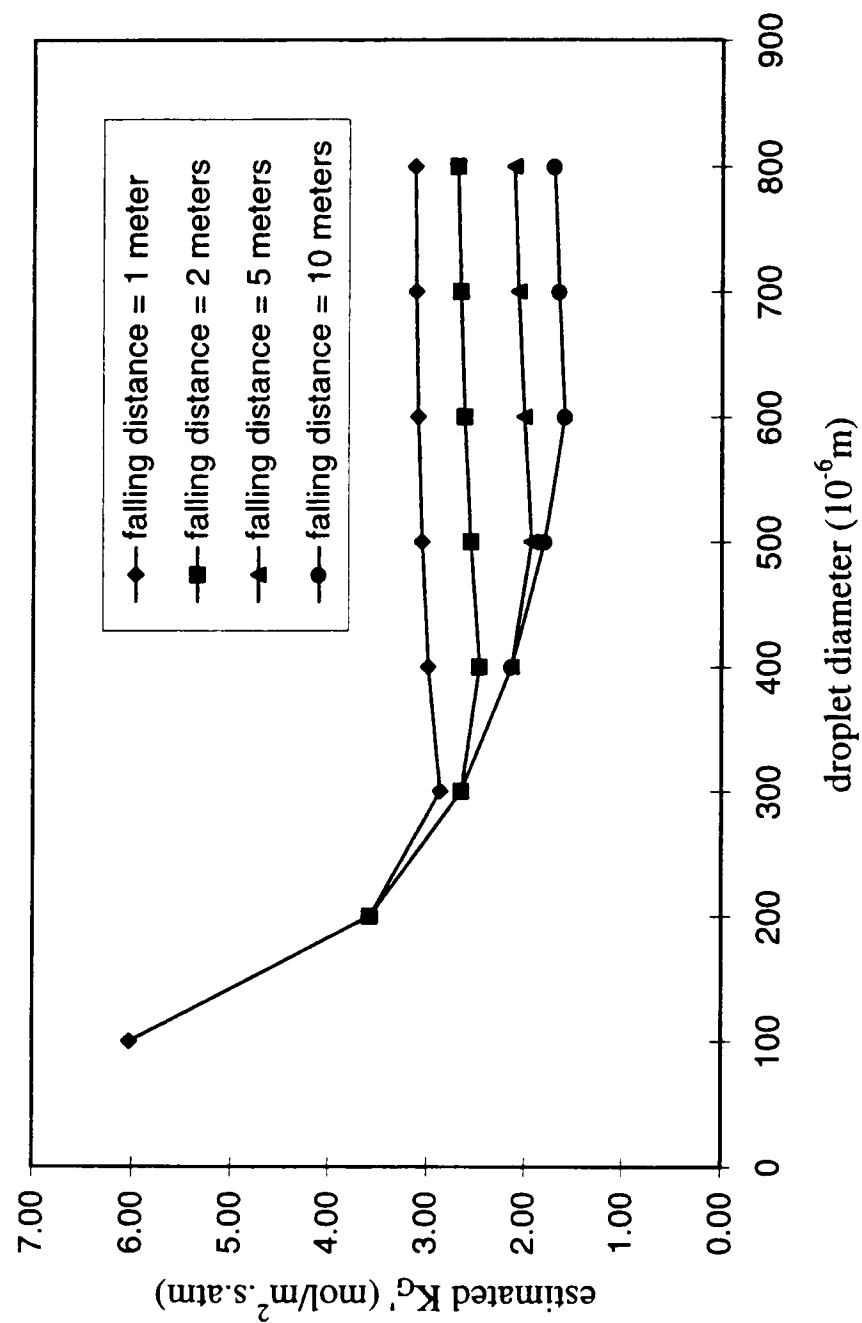


Figure 4.8 Estimated mass-transfer coefficient K_G' at different droplet diameters and falling distances.

experiment conducted herein. Because experimental measurements of mass transfer coefficients in spray chambers are not available, predicted performance will be based upon the mass transfer coefficients presented in Table 4.6.

Since the calculated gas-phase resistance and liquid-phase resistance are close, using PAC slurry for MEK gas scrubbing in spray chambers could be more beneficial than in a gas-phase resistance controlled process, as discussed earlier. With the abundance of PAC, the liquid phase resistance can be greatly reduced and the process could become gas-phase resistance controlled. Therefore the overall mass transfer coefficient K_G' can be increased to be close to K_G' . As seen from Table 4.6, $\frac{1}{k_G'}$ is about 40 - 60% of $\frac{1}{K_G'}$, therefore the mass transfer rate of MEK in a spray chamber can be increased to 1.6 - 2.5 times by using PAC slurry as solvent.

As seen from Figure 4.8, for a certain droplet diameter, longer falling/contacting distance results in lower average mass-transfer coefficient K_G' in the chamber. This is caused by saturation of the contaminant in the droplet, which is reflected by a lower k_L' value. k_G' values are not affected by the falling distance. This fact gives an indication that compared with using water only as absorbent, using PAC slurry could be even more beneficial in cases of long contact time, since aqueous adsorption can keep a low liquid-phase concentration and prevent the droplets from being saturated with MEK.

Figure 4.8 also shows that the mass-transfer coefficient K_G' is much higher at

droplet diameters smaller than 300 μm . Meanwhile, smaller droplets have bigger specific surface area. Therefore, smaller droplet diameter is preferred in spray absorbers.

Compared with other operational configurations, a co-current spray chamber can have smaller droplets, higher mass transfer area, and lower gas pressure drop. But due to equilibrium limitations, single stage cocurrent spray chamber scrubbing will result in a low liquid effluent concentration. Table 4.7 shows the liquid concentration in equilibrium with cleaned gas for different VOCs. In cases of Henry's Law constant greater than $10^{-3} \text{ atm}\cdot\text{m}^3/\text{mol}$, the possible liquid VOC concentration of the effluent from the spray chamber could be too low for biodegradation in the activated sludge system to be efficient. The activated sludge unit has to have a big volume to effectively remove VOCs from such low concentration, high flow rate liquid. Using PAC slurry as solvent, the liquid flow rate can be reduced, but the liquid phase VOC concentration still can not exceed the equilibrium concentration. If the effluent from the aeration tank is not reused as the liquid feeding to the spray chamber, the designed liquid VOC concentration in the aeration tank must be much lower than the equilibrium concentration to be able to effectively remove the target VOC. Otherwise, high percentage of VOC will be discharged from this treatment process. If the effluent from the aeration tank is reused as the liquid feeding to the spray chamber, then the designed liquid VOC concentration in the aeration tank should also be much lower than the equilibrium concentration listed in Table 4.7 to have efficient gas scrubbing in the spray chamber. Otherwise the liquid feeding rate has to increase. In either case, the aeration tank has to operate at

Table 4.7 Liquid concentration (g/m^3) in equilibrium with cleaned gas at 25°C.

	Henry's Law constant ($\text{atm}\cdot\text{m}^3/\text{mol}$)	cleaned gas concentration			
		1 ppm	10 ppm	25 ppm	50 ppm
benzene	4.6×10^{-3}	0.017	0.17	0.43	0.85
toluene	5.7×10^{-3}	0.016	0.16	0.40	0.81
chlorobenzene	1.1×10^{-3}	0.102	1.02	2.05	4.09
acetone	3.75×10^{-5}	1.55	15.5	38.7	77.5
MEK	1.05×10^{-5}	6.86	68.8	171	342

concentrations about one order of magnitude lower than the equilibrium concentrations. Depending on Monod kinetics, slow biodegradation and a big required bioreactor volume could occur. Therefore, it is concluded that a single stage cocurrent spray chamber may not be suitable for removing VOCs with Henry's Law coefficient higher than 10^{-3} atm·m³/mol in this combined process. However, using PAC slurry as solvent, multiple stage cocurrent-flow spray chamber operation may be feasible. Because the effluent liquid from a latter stage can be used as the influent liquid of its former stage, thus the whole system can operate in a semi-counter-current flow situation. Further study is needed.

For VOCs with smaller Henry's Law constants, such as MEK, the effluent liquid concentration from a single stage spray chamber is still high enough for the bioreactor to perform well. An example is given herein to illustrate the possible operational parameters. The designed operational conditions are: temperature = 19.5°C, inlet MEK concentration $y_2 = 500$ ppm, outlet MEK concentration $y_1 = 25$ ppm. Sauter mean diameter of droplets = 100 µm. As seen from Figure 4.8, the estimated K_G value is about 6 mol/m²/s for 3.9 second contact time. To be conservative, a K_G value of 0.55 mol/m²/s (see Table 4.5) as a result of the packed tower operation with water is also used for the design. The design results based on equations (2.39) - (2.42) are shown in Table 4.8. If operating at $L/G = 15$ mol/mol, to clean 10³ m³ MEK gas, 11 m³ waste liquid will be generated and the effluent MEK concentration will be 127 mg/l. In total, 1396 g MEK will be cleaned from the gas. The disadvantage of cocurrent operation is: droplets are

Table 4.8 Design parameters for a cocurrent-flow spray chamber.

L/G (mol/mol)	specific surface area (m ² /m ³)	N _G	E equation (2.39)	K _G = 6 mol/m ² /s		K _G = 0.55 mol/m ² /s	
				K _{Ga} (mol/m ³ /s)	contact time (sec)	K _{Ga} (mol/m ³ /s)	contact time (sec)
15	662	3.84	0.9785	3972	0.039	364	0.43
20	882	3.55	0.9714	5292	0.027	485	0.30
40	1764	3.24	0.9607	10584	0.012	972	0.14

L_M/G_M (mol/mol) > $m \left[\frac{1}{y_1/y_2} - 1 \right]$. Sauter mean droplet diameter = 100 μm .

mixed with the gas and have to be removed by another device such as a wet cyclone. But cyclones normally have low cost and high efficiencies.

As seen from Table 4.8, the required gas-liquid contact time is less than one second, which means a high efficiency and low volume requirement of the spray scrubber. Compared with the empty bed contact time of a biofilter (typically 15 - 60 seconds), the gas retention time in a cocurrent spray chamber can be 15 to 60 times smaller than that of a biofilter. Therefore, the volume of a cocurrent spray chamber can be 15 to 60 times smaller than that of a biofilter.

As stated in Chapter 2, a horizontal cross-flow spray chamber is superior to a counter-current flow spray chamber. The designed droplet diameter has to be at least 600 - 800 μm to prevent the droplets from being carried out by the gas. As seen from Figure 4.8, the estimated K_G value is about 2 $\text{mol}/\text{m}^2/\text{s}$ for droplets with Sauter mean diameter of 800 μm . As a comparison, a K_G value of 0.55 $\text{mol}/\text{m}^2/\text{s}$ is also used for the design. The design results for the above example problem with a horizontal cross-flow spray chamber are shown in Table 4.9. The required contact times are also within several seconds. Using a K_G value of 2 $\text{mol}/\text{m}^2/\text{s}$, at gas-liquid contact time of 5.23 seconds, droplet diameter of 800 μm , chamber height of 2 meter, spray density of $5 \times 10^{-3} \text{ m}^3/\text{m}^2/\text{s}$, the required liquid to gas flow ratio is calculated to be $(5.23 \text{ sec} \times 5 \times 10^{-3} \text{ m}^3/\text{m}^2/\text{s} / 2\text{m}) = 0.013$. To clean 1000 m^3 gas, 13 m^3 waste liquid will be generated, with 107 mg/l MEK. Using a K_G value of 0.55 $\text{mol}/\text{m}^2/\text{s}$, at a gas retention time of 4.76 seconds, the required liquid flow ratio Q_L/Q_G is 0.052 m^3/m^3 , and the effluent MEK concentration is

Table 4.9 Design parameters for a horizontal cross-flow spray chamber.

Q_L/A_L $m^3/m^2/s$	liquid hold up	a m^2/m^3	$K_G = 2 \text{ mol}/m^2/s$		$K_G = 0.55 \text{ mol}/m^2/s$	
			K_{Ga} $mol/m^3/s$	contact time (sec)	K_{Ga} $mol/m^3/s$	contact time (sec)
5×10^{-3}	0.16%	11.7	23.4	5.23	6.43	19.0
2×10^{-2}	0.6%	46.7	93.5	1.31	25.7	4.76

Sauter mean droplet diameter = 800 μm .

27 mg/l. The liquid hold up in the chamber is smaller than 1% in both designs, and gas pressure drops are low. Again, comparing the required gas retention time, the volume of a horizontal cross-flow spray chamber can be 10 to 15 times smaller than that of a biofilter.

Similar liquid effluent concentration will be obtained for other VOCs scrubbed at the similar operation conditions and mass-transfer rates. For those VOCs not suitable for cocurrent spray chamber, a horizontal cross-flow spray chamber using PAC slurry as solvent may be feasible, considering that liquid-phase concentration may not be too low to limit the efficiency of the activated sludge process.

The semi-theoretical equations for estimation of mass-transfer coefficients of droplets show great sensitivity to Henry's Law constant. The diffusivities of VOCs are normally in the same order of magnitude, with representative values of $2 \times 10^{-5} \text{ cm}^2/\text{sec}$ in water and $0.1 \text{ cm}^2/\text{sec}$ in air. At the same Schmidt number, gas phase mass transfer coefficients k'_g do not have wide variation, a liquid phase mass transfer coefficients k'_L should also be relatively constant as long as the gas-liquid contacting time is constant. The differences in overall mass transfer coefficient K'_g are mainly caused by Henry's Law constant H . H can have several orders of variance for different VOCs. The physical absorption of VOCs with Henry's Law constant higher than $10^{-3} \text{ atm} \cdot \text{m}^3/\text{mol}$ by sprayed droplets is considered to be liquid-phase controlled. Henry's Law constant of MEK is in the order of $10^{-5} \text{ atm} \cdot \text{m}^3/\text{mol}$. The liquid and gas phase mass transfer resistance of MEK transferring from gas into droplets are close to each other, as stated earlier. Therefore, for

those VOCs with Henry's Law constant higher than 10^{-3} atm·m³/mol, although the gas-phase mass transfer resistance could be close to that of MEK, the liquid-phase mass transfer resistance could be two orders of magnitude higher than that of MEK; thus the overall mass transfer coefficient could be two orders of magnitude lower than that of MEK. Therefore, the required specific surface area for physical absorption of these VOCs could be two orders of magnitude higher than those presented in Table 4.8 and Table 4.9. A Sauter mean diameter of 800 µm as presented in Table 4.9 is already the lowest possible value, the multiple of liquid flow rate and gas retention time has to be two orders of magnitude higher than those presented in Table 4.9. Therefore, physical absorption in a spray chamber will not be of high efficiency for scrubbing these VOCs with high Henry's Law constant. Capture agents such as PAC slurry have to be used to increase mass transfer and to reduce liquid consumption. Further work on spray chamber scrubbing of VOCs with high Henry's Law constants using PAC slurry will be meaningful, in terms of widening the application of this combined spray absorber - bioreactor process.

Comparing the above two configurations, it is obvious that cocurrent-flow has shorter gas retention time and lower liquid consumption for MEK removal. This is reasonable considering that a smaller Sauter mean diameter results in a higher specific surface area and thus a lower liquid consumption. In both cocurrent and cross-flow designs, the effluent liquid MEK concentration from the spray chamber are high enough to maintain a good subsequent bioreactor operation.

As seen from equations (2.37) and (2.41), the number of mass-transfer units N_G is proportional to mass transfer coefficient K_G , specific surface area and gas-liquid contact time. Since the specific surface area in a spray chamber can be varied by adjusting the liquid flow rate or the wheel speed, the treatment efficiency could be maintained when gas flow rate or concentration fluctuates.

If PAC slurry is used as solvent, the mass-transfer rate of the spray chamber is expected to be improved, as discussed earlier. Assuming a K_G increase of a factor of 2, as the experimental result of packed tower operation (see Table 4.5), then the liquid flow can be cut to one half, or the volume of spray chamber can be reduced to one half.

If bacteria present in the droplets at $MLVSS = 10,000 \text{ g/m}^3$, assuming all the $MLVSS$ are comprised of living cells and cell water content is 90%, then 10% weight/volume of the droplets will be living cells. Solute concentration distribution in the droplet and mass-transfer process may be affected. If the bacteria concentration is too high, the adsorption capacity of PAC could be reduced since PAC particles could be partially covered by bacteria slurries in the droplets. Therefore, it is speculated that The ratio of PAC concentration to sludge concentration in the aeration tank should not be too low. With the presence of bacteria slurry, a spray chamber could have clogging problem. Further quantitative investigation is needed.

4.3. Stripping and Biodegradation

The batch experiments of stripping of MEK solution were conducted at 19°C room temperature and an aeration rate of 2 l air/l water/min. As discussed in Chapter II,

the first order kinetics equation

$$dC/dt = -kC \quad (4.17)$$

is most appropriate to describe the bubble stripping process. The basic assumptions of this equation are valid in this experiment: (1) isothermal system, (2) well mixed system, (3) ideal vapor behavior, (4) concentration of solute obeys Henry's law, (5) constant liquid volume, (6) total pressure is large compared to the solute vapor pressure. Here k is the observed mass transfer constant from liquid to gas phase, which is related to the Henry's Law constant, gas flow rate, liquid volume, temperature and overall liquid-gas mass transfer coefficient. Exponential regression of C/C_0 versus time results in a constant of $k = 0.0044 \text{ min}^{-1}$, as shown in Figure 4.9. Since the surface turbulence was very strong in this 2 liter flask aerated with 4 liter air per minute, it is speculated that the surface desorption was quite significant in this test.

Since the stripping rate is first order with respect to liquid phase concentration, depending on Monod kinetics, reducing the liquid phase concentration by adding PAC in the bioreactor could be favorable for VOC treatment. If the Monod kinetics is in zero order, then decreased concentration will results in lower stripping rate, and the ratio of stripping to biodegradation will be lower. If the Monod kinetics is in first order, then the ratio of stripping to biodegradation will be constant. In cases of fluctuation of concentration, PAC can serve as a reservoir to prevent stripping. Also, a CSTR aeration tank generates less VOC volatilization than a plug flow aeration tank. Normally, diffused aeration provide air flow of 20 - 30 scfm per 1000 ft³ tank volume (Benefield

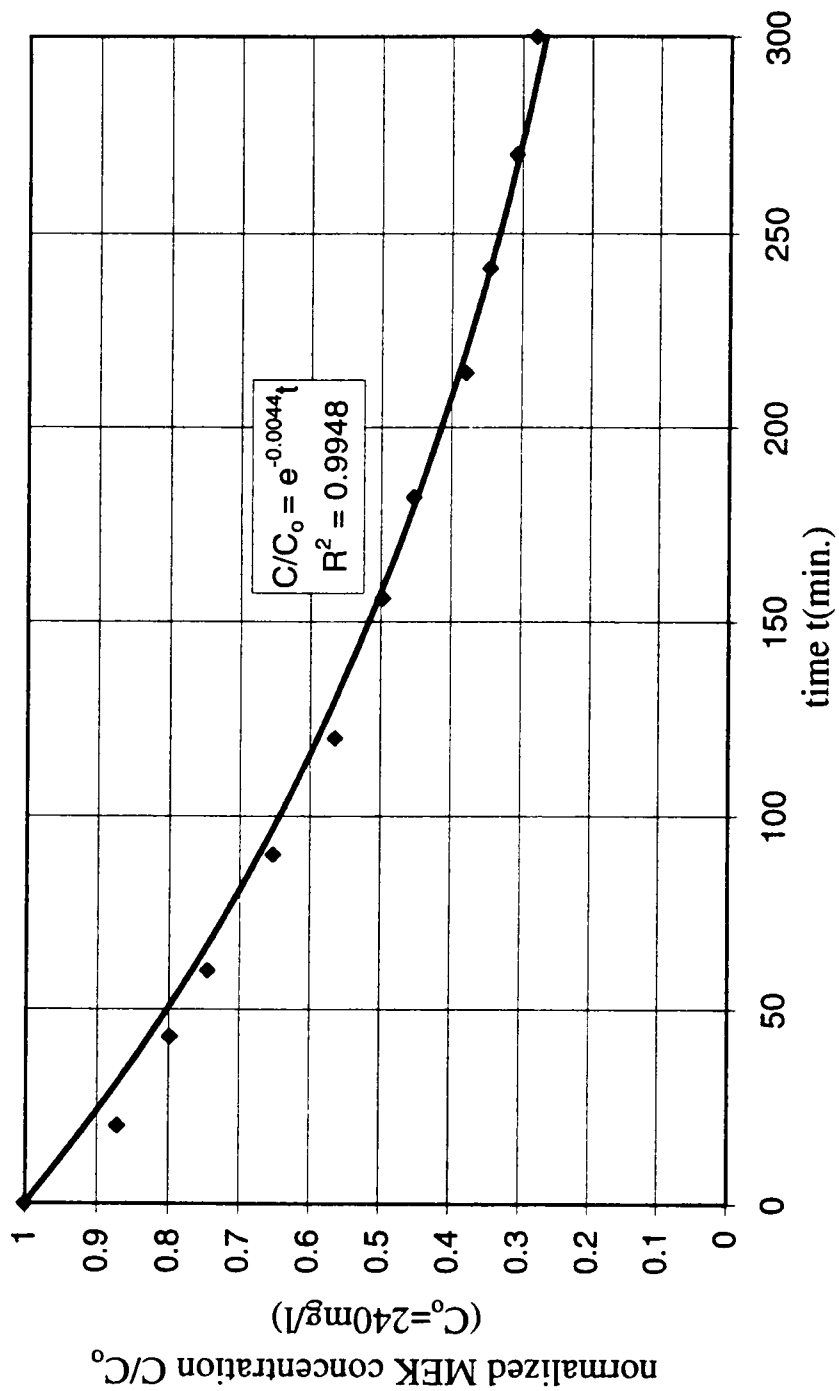


Figure 4.9 MEK concentration decay curve in stripping test.
 ($T=19^\circ\text{C}$, water volume=2030ml, air stripping rate = 2l
 air/l water/min.)

and Randall, 1987), or 0.02 - 0.03 m³ air/m³ volume/min. Namkung and Rittman (1987) reported a typical gas supply of 5 - 10 (m³ air)/(m³ water) in the aeration tank of most public owned treatment plants. Assuming a hydraulic retention time of 4 hours, this value converts to 0.02 - 0.04 (m³ air)/(m³ volume)/min. The worst case of volatilization occurs when the air bubbles are saturated with VOC during transport through water. Stripping lost can be estimated by equation (2.57). At 20°C and the aeration rate of 0.03 (m³ air)/(m³ volume)/min, the bubbling stripping loss of MEK from an aeration tank are estimated to be 6.26×10⁻⁵, 6.26×10⁻⁴, and 6.26×10⁻³ g/(m³ volume)/hour, at MEK concentrations of 0.1, 1.0, 10 mg/l, respectively. If direct surface volatilization is significant, then the loss could be higher than the above values, as stated in Chapter II. The stripping loss for more volatile VOCs with Henry's Law constants in the range of 10⁻³ atm·m³/mol is estimated to be two order of magnitude higher than the above values. The aeration rate of this experiment was 50 times stronger than that in the aeration tank. The experimental condition could lead to a MEK stripping losses of 0.0264, 0.264, and 2.64 g/(m³ volume)/hour at MEK concentrations of 0.1, 1.0, 10 mg/l, respectively. Results of the stripping experiment should not be used as an estimation to field data.

The activated sludge biodegradation experiment was conducted at 19°C room temperature, and aeration rate of 2 l air/l water/min. The decay curve is shown in Figure 4.10. Linear regression fitted the data well:

$$C(\text{mg/l}) = 215 - 2.2896 t(\text{min.}) \quad (R^2 = 0.9991) \quad (4.18)$$

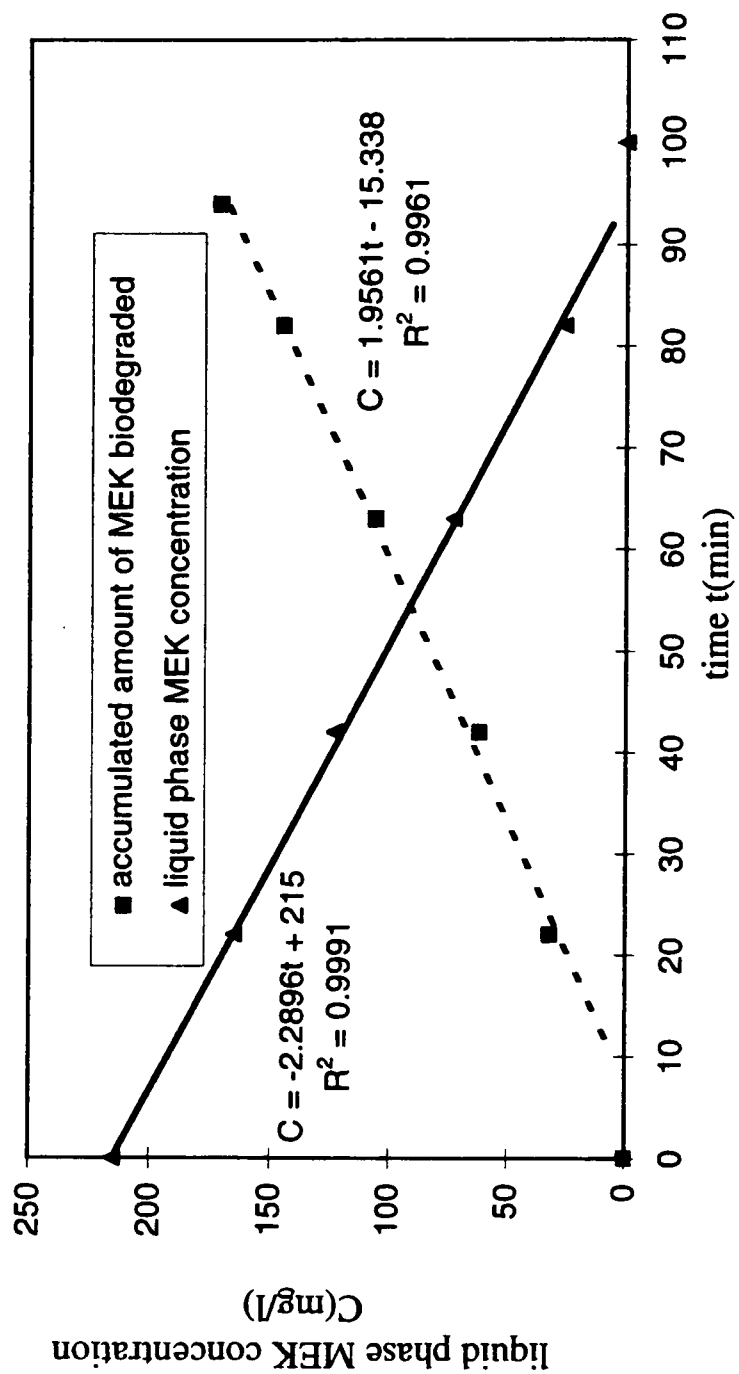


Figure 4.10. Biodegradation and stripping of MEK in batch aeration experiment. ($T=19.1^{\circ}\text{C}$, $\text{MLSS}=5.30\text{g/L}$, $\text{volume}=2030\text{ml}$, $\text{aeration rate} = 2 \text{ l air/l water/min.}$)

The overall decay of MEK was caused by both stripping and biodegradation. Since the stripping rate under the same condition has been described by equation (4.17). Subtracting stripping from the total removal gives the amount of MEK biodegraded (see Appendix A). The amount stripped is about 20% of the total decay. This batch test was similar to a plug-flow tank with strong aeration and surface turbulence, therefore it was the worst case. Field operation of a CSTR reactor will not result in such strong stripping loss, as stated earlier.

In this experiment, MLSS was measured to be 5.18 g/l before reaction and 5.42 g/l after reaction. An average of 5.30g/l was used in calculation, since the change of MLSS (X) was within 5%. Because the accumulative MEK biodegradation curve was a straight line, indicating a zero order biodegradation, the maximum substrate utilization rate $q_{\max}$ in the Monod equation is calculated as :

$$q_{\max} = (-dS/dt)/X = 0.022 \text{ mg MEK/mg MLSS}\cdot\text{hr.} \quad (4.19)$$

Assuming a conversion factor of 2.2 g COD/g MEK (COD/ThOD = 0.9), $q_{\max}$ is converted to 1.16 mg COD/mg MLSS·d, which is smaller than the $q_{\max}$ value for municipal wastewater at 20°C, 6 - 8 mgCOD/mgMLVSS/d (Benefield and Randall,1987). This batch experiment was unable to provide the value of half saturation coefficient k_s , because MEK concentration reached zero very quickly, without time period of slowed reaction rate, and the detection limit for dissolved MEK was around 1 mg/l for MEK. But since the degradation was in zero order at the MEK concentration as low as 26 mg/l, as seen from Figure (4.10), it is inferred that k_s value should be less than 5 mg/l.

Deshusses(1995) reported a k_s value of 1.37 mg/l. Assuming $VSS/SS = 0.8$ and $k_s = 1.37$ mg/l, the q_{max}/k_s value was calculated to be 0.48 gVSS/m³/d, which is comparable to other biodegradable VOCs, such as benzene and toluene, as stated in Chapter II.

At a sludge concentration of 4,000 gVSS/m³, given the above kinetics, the biodegradation rates are calculated to be 7.48, 46.4 and 96.7 g/m³ volume/hour at MEK concentrations of 0.1, 1.0, 10 mg/l, respectively. In field condition, the bubbling stripping loss of MEK could be just $6.5 \times 10^{-3}\%$ ($= 6.26 \times 10^{-3}$ g/m³/hr / 96.7 g/m³/hr). If an aeration tank operates at MEK concentration of 10 mg/l, with the aeration and surface turbulence as strong as this batch experiment, then the ratio of stripping to biodegradation could be 2.7% ($= 2.64$ g/m³/hr / 96.7 g/m³/hr). The Monod kinetics is close to zero order at MEK concentration of 10 mg/l. Therefore the percentage of stripping is higher than that in a first order Monod kinetics senario. But the stripping loss is still small compared with biodegradation. This result is consistent with Corsi (1991) and Namkung's (1987) conclusion that biodegradation is the major removal mechanism for biodegradable VOCs with a q_{max}/k_s value higher than 0.1 m³/gVSS/d, when the Monod kinetics is in first order.

Based on earlier discussion, the concentration of MEK in the liquid effluent from a cocurrent spray chamber is approximately in the range of 100 mg/l, which is equivalent to 220 mg COD/l. Therefore, a conventional activated sludge aeration tank will be able to remove MEK from the scrubbing water with good treatment efficiency. This combined spray chamber - bioreactor process is assumed to be able to feasible for removing MEK from waste gas.

For a rough estimation of biodegradation in spray chamber, the following operation condition is assumed: Sauter mean droplet diameter = 100 μm , specific surface area = 1000 m^2/m^3 , bacteria concentration = 40,000 gVSS/m^3 . The liquid hold up in the spray chamber is calculated to be ($\frac{ad}{6} =$) 0.0167 m^3 liquid/ m^3 volume. Assuming zero order (maximum) biodegradation in the droplets, $q_{\text{max}} = 0.0275$ g MEK/g MLVSS $\cdot$ hr, the rate of MEK removal by biodegradation in the spray chamber is calculated to be (0.0275 g MEK/g MLVSS $\cdot$ hr $\times$ 40,000 gVSS/m^3 liquid $\times$ 0.0167 m^3 liquid/ m^3 volume =) 18.4 gMEK/ m^3 volume/hr. Assuming a mass transfer coefficient of $K_G = 0.55$ mol/ m^2 /s, the physical adsorption inside a spray chamber has the mass transfer rate of 550 mol/ m^3 volume/s. The biodegradation in an activated sludge unit with MLVSS = 4 kg/m^3 is 110 g/ m^3 volume/hr. Therefore, the volumetric rate of biodegradation in the spray chamber could account for 16.7 % of biodegradation. A separate biological reactor is still necessary for removal of VOCs. But the above calculations are based on the possible highest parameters. Gas pressure drop increases when droplet hold up increases. Sludge concentration of 40,000 gVSS/m^3 means 40% of liquid volume is made up of living cells. The absorption of MEK by droplets would be reduced. For practical purposes, it is not economic to spray such high concentration bacteria slurries. Meanwhile, during the short retention time inside a spray chamber, the concentrations of VOCs in droplets have great changes, the dynamic response of microbial activity to changes of substrate concentration needs further investigation.

4.4. Desorption Rate

Results of the stripping tests with and without PAC are shown in Figure 4.11. The initial MEK concentration of supernatant and PAC/water slurry was 174 mg/l, 172 mg/l in the liquid phase and 229 ppm, 228 ppm in the air stripped out, respectively. Comparing the two curves, it is obvious that the slope of the decay curve of stripping from PAC is much lower than that of stripping from water, which means a slower total mass decay. Therefore, the presence of PAC serves as a reservoir to prevent MEK from being stripped out.

Due to the higher initial total amount of MEK mass in the aqueous phase, in the experiment of MEK stripping from PAC/water slurry, more MEK was stripped out and the dissolved MEK concentration was higher at the same period of time. The difference of the curves was caused by desorption of MEK from PAC. If the adsorption is completely irreversible, then the stripping curve with PAC would have been the same as that without PAC.

The following equations were used to calculate the desorption rate during the process. The mass balance equation for MEK transferring from liquid phase to gas phase is:

$$Gy = -LdC/dt \quad (4.20)$$

where, G — air flow rate, 2 $l_{air}/min.$ (1 $l_{air}/l_{water}/min.$);

L — liquid volume, 2 l ;

y — gas phase concentration, g/m^3 ;

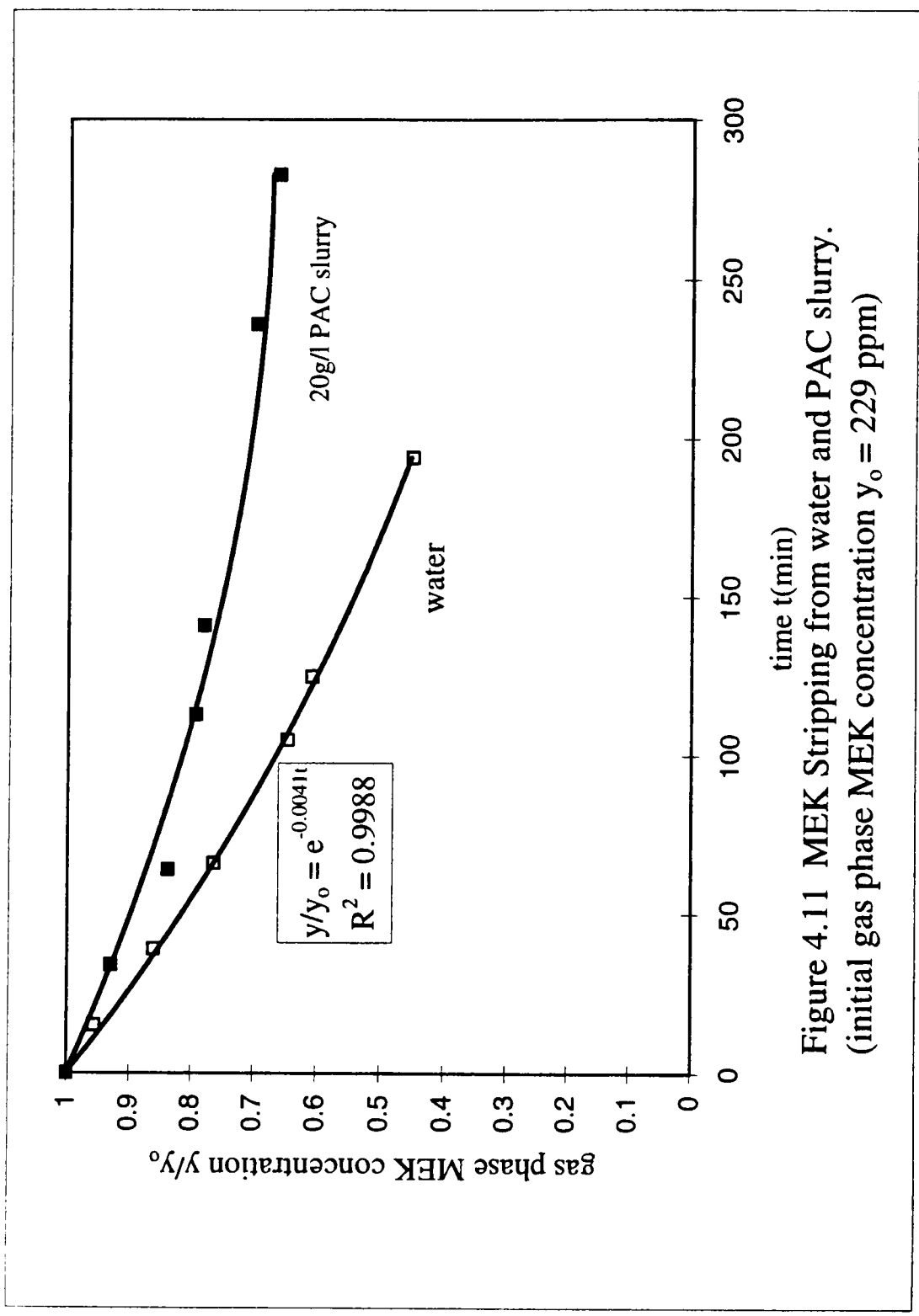


Figure 4.11 MEK Stripping from water and PAC slurry.
(initial gas phase MEK concentration $y_0 = 229$ ppm)

C — liquid phase concentration, mg/l.

The kinetics of stripping is described by equation (4.17). Combining equation (4.17) and equation (4.20) gives the following equation:

$$Gy = LkC \quad (4.21)$$

$$dy/dt = (L/G)k dC/dt = ky \quad (4.22)$$

Therefore, decay of gas phase concentration has the same mathematical expression as the liquid phase concentration decay, which can be described as:

$$y/y_0 = e^{-kt} \quad (4.23)$$

Exponential regression of data of supernatant stripping test gave a “k” value of 0.0041 min⁻¹, as shown in Figure 4.11.

The initial liquid concentration C_0 was calculated to be 164 mg/l based on equation (4.21), which is slightly lower than the measured value. Because only gas phase concentrations were measured during the stripping process, C_0 of 164 mg/l was used, so that mass balance calculation of MEK is consistent.

In the process of stripping from PAC/water slurry, the mass balance of MEK from time zero to time t is described by the following equation:

$$m(q_0 - q) + (Gy_0/kL - Gy/kL) = G/L \int_0^t y dt \quad (4.24)$$

in which m is the PAC dosage (g/l) and q is the adsorption capacity (mg MEK/g PAC). The second item represents the decrease of dissolved MEK concentration, expressed by equation (4.21). The right side item represents the amount of MEK stripped out, which can be calculated from the area below the stripping curve. The $(q_0 - q)$ values at any time t

were calculated from equation (4.24) and plotted in Figure 4.12. Since initial concentration q_0 was in equilibrium with C_0 , q_0 was calculated to be 80.2 mg/g based on the isotherm equation (4.1). Thus the solid phase concentration q at time t is obtained by subtracting the desorbed amount from q_0 . The liquid-phase concentration C_s in equilibrium with solid-phase q is calculated from the equilibrium isotherm curve. Also, liquid-phase concentration C at time t was calculated from equation (4.21). The value of $(C-C_s)$ provided the desorption driving force. The values of C_s and C were very close to each other, as seen from Figure 4.13. Due to experimental error and the not exactly repetitive adsorption isotherm, C_s values were slightly (less than 9%) higher than C . Although not very precise, the result still gave an indication that desorption required a very small driving force in this experiment. The solid and liquid phases were almost in equilibrium during the stripping process.

Because desorption is the reverse process of adsorption for reversible adsorption, fast desorption is consistent with fast adsorption, as shown earlier. The desorption rate depends on the character of PAC and VOC, and solid-liquid mixing. It is possible to choose a proper PAC so that desorption is not a limiting step in the PAC - activated sludge system. The same conclusion was inferred from the work of Benedek (1985) and Sigurdson(1978).

4.5. The Effect Of PAC On MEK Biodegradation

4.5.1. Microbial Oxygen Consumption With And Without PAC

The microbial oxygen consumption during batch biodegradation tests with and

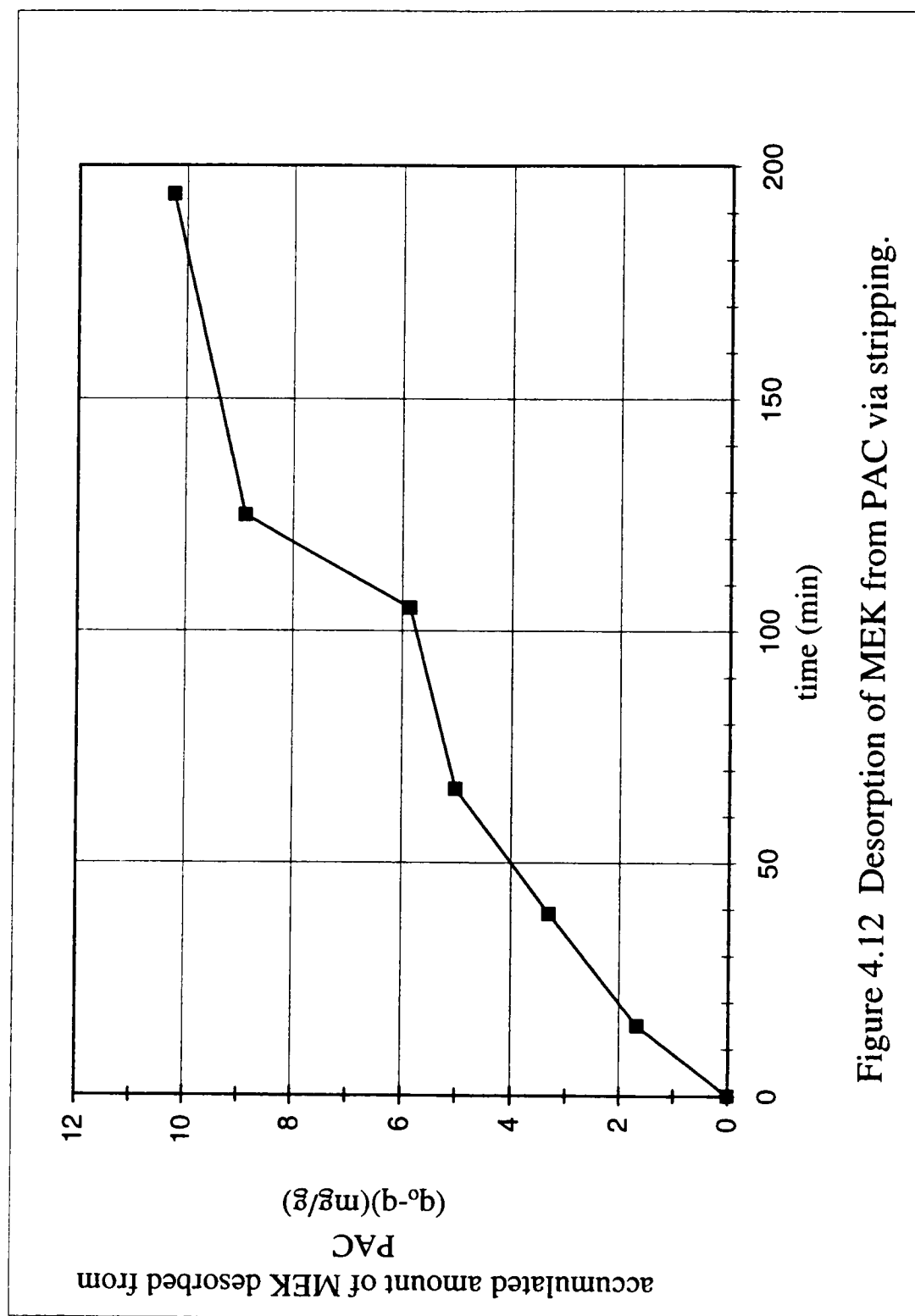


Figure 4.12 Desorption of MEK from PAC via stripping.

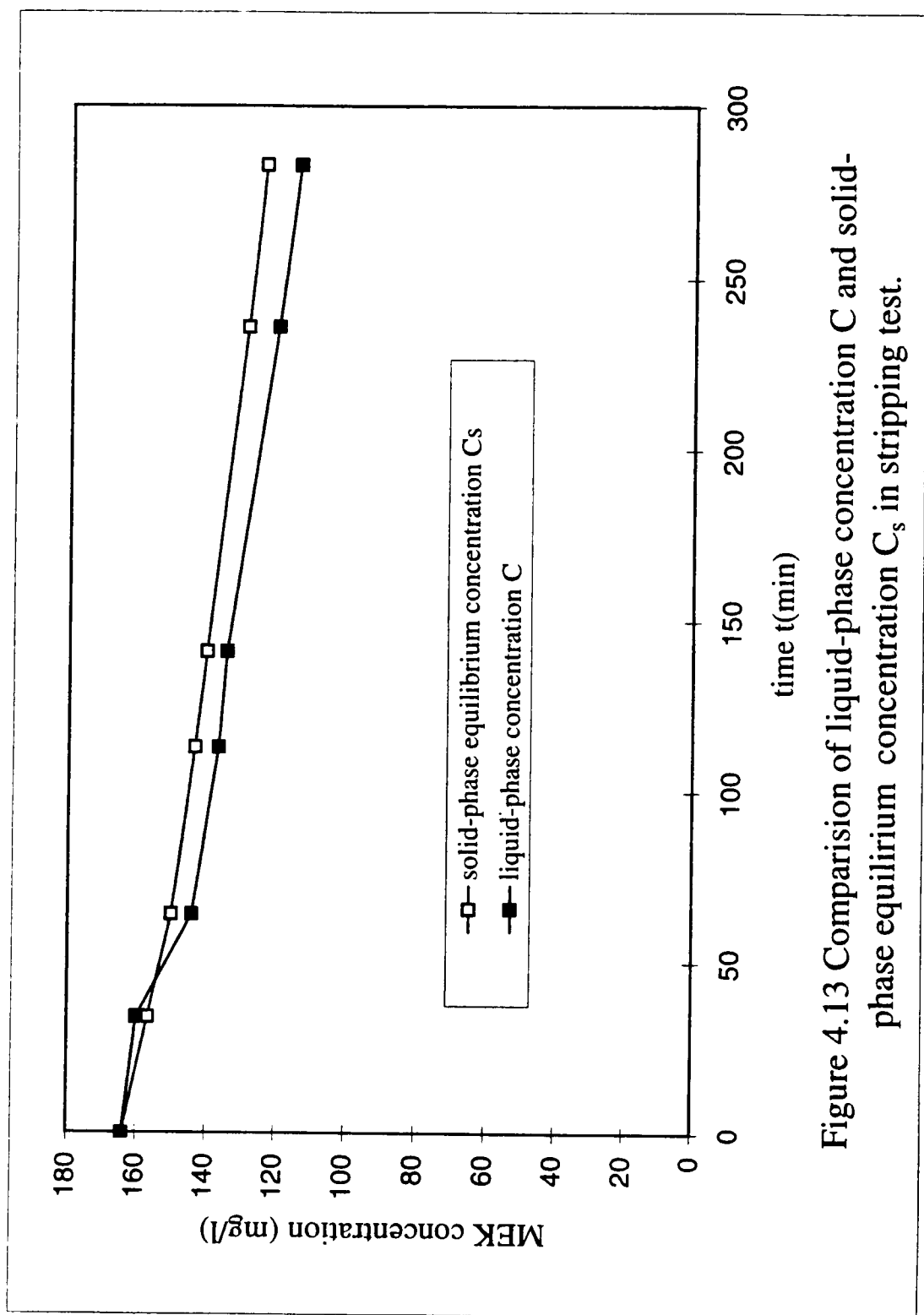


Figure 4.13 Comparison of liquid-phase concentration C and solid-phase equilibrium concentration C_s in stripping test.

without the presence of PAC were studied through the Warburg respirometer tests. Initial MEK concentration were 81, 269, 1885 mg/l. PAC dosage of 5 g/l was chosen to immediately reduce the liquid phase concentration to the magnitude of 1 mg/l, 10 mg/l and 100 mg/l based on the results of the adsorption rate experiment that the adsorption can reach 60% equilibrium after one minute. The results of accumulated oxygen consumption versus time are shown in Figure 4.14. Slopes of the curves indicate the oxygen consumption rates. It was observed that the oxygen consumption for endogenous respiration was constant throughout the test. At the same MEK dosage, no significant difference of accumulated oxygen consumption rates occurred between samples with and without PAC. Oxygen transfer limitation was excluded, since higher oxygen consumption rates had been observed while the bacteria population increased, as in the sample case of 1885 mg/l MEK. Sample pairs with and without PAC went to endogenous respiration at the same time, 1 hour or 6 hours later at MEK concentration of 81 mg/l and 269 mg/l, respectively. In other words, no enhancement or dampening of bioactivity was observed. Therefore, the result is in conflict with the hypothesis of enhanced biodegradation due to higher substrate concentration on PAC surface (Rice, 1982). The result is consistent with the conclusion of Zhang (1990) and Schultz (1984), as presented in Chapter II. Considering that MEK degradation does not require extracellular hydrolysis prior to cell uptake, the result is reasonable.

The results can be explained by two factors: rapid desorption and low half-saturation coefficient k_s . Although part of the MEK was adsorbed onto PAC at the

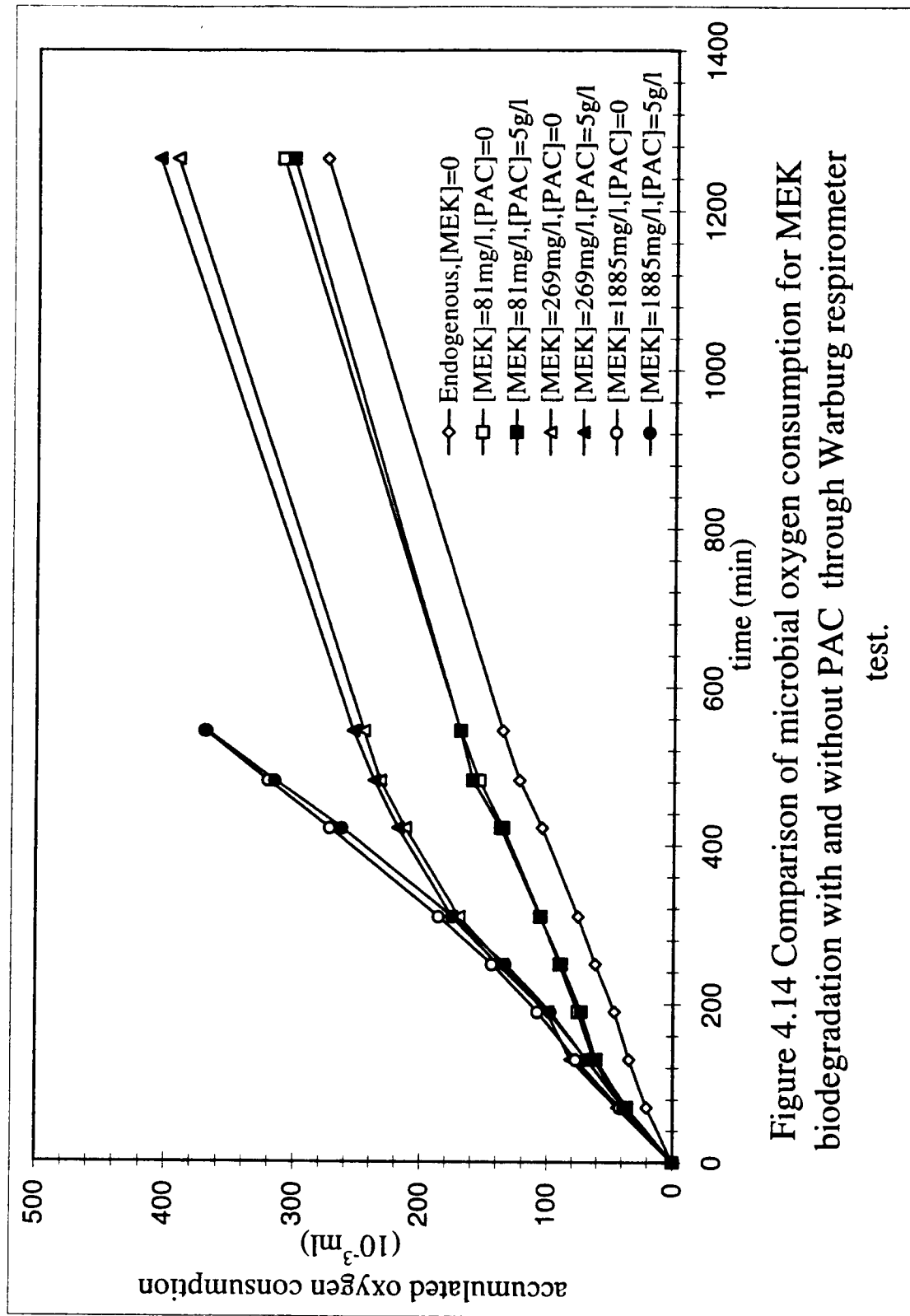


Figure 4.14 Comparison of microbial oxygen consumption for MEK biodegradation with and without PAC through Warburg respirometer test.

beginning of the test, it was desorbed after the bacteria have reduced the liquid phase concentration. If the adsorption was so strong as to be irreversible, then the samples with PAC should go to endogenous respiration much earlier than those without PAC, due to the exhaustion of dissolved MEK. However, this was not the case observed, which meant adsorption was weak and at least readily reversible. This was consistent with the result of the stripping test on PAC/water slurry. Second, according to the Monod equation, if the half-saturation coefficient k_s for the substrate is high, PAC can retard the substrate utilization rate due to decreased liquid phase concentration. The biodegradation batch test had proved that k_s value was less than 5 mg/l, and equals 1.37 mg/l as given by Deshusses(1995). Therefore, it is reasonable that the MEK concentration difference due to different initial MEK concentrations did not result in different oxygen uptake rates. It also helps to explain why no obvious period of reduced oxygen uptake rate was observed before endogenous respiration.

The reversibility of adsorption and k_s value are considered to be the controlling factor of PAC regeneration and substrate removal. As pointed out by Water Quality (1990), adsorption of many kinds of VOCs is weak and reversible. For some complex substrates which are either strongly adsorbed or hardly biodegradable, the application of a PAC -activated sludge system is not suitable (Schultz,1984).

For the samples with initial MEK concentration of 1885 mg/l, at the beginning of the test, the oxygen uptake rate was equal to that of samples with initial MEK concentration of 269 mg/l at first. However, it kept on increasing later on. The increment

of oxygen uptake rate was a result of cell growth. The result indicates that 1885 mg/l MEK is not toxic to the microorganisms tested. Adding PAC in the bioreactor can reduce the toxicity by decreasing substrate concentration, if the bioactivity is inhibited at high substrate concentration.

The results indicated that the PAC - activated sludge process can be a simply combination of physical adsorption and suspended cell growth, if the target VOC is easily biodegradable and the adsorption is readily reversible, then regeneration of the VOC contaminated PAC is feasible and fast, depending on the kinetics of biodegradation. This is consistent with the model of PAC -activated sludge system given by Bebedek (1985).

4.5.2. Modeling Of A PAC - Activated Sludge System For MEK Removal

Based on the experimental results, the following assumptions are made to develop a mathematical model for VOC removal in PAC - activated sludge system: (1) cell adsorption and volatilization of VOCs are ignored; (2) overall equilibrium prevailed between the aqueous and adsorbed VOC in the aeration tank; (3) biodegradation in the spray chamber is ignored. A schematic diagram is shown in Figure 4.15.

To simplify the mathematical relationship, the amount of VOC scrubbed and fresh PAC feeding can be assumed to be added in the make-up fresh water. The spray chamber liquid flow and supernatant from the separator simply constitute the recirculation flow which has no concentration change. Since the amount of biomass in the spray chamber is much smaller than in the aeration tank, sludge retention time can be approximated by:

$$\theta_c = \frac{VX}{Q_w X_w} \quad (4.25)$$

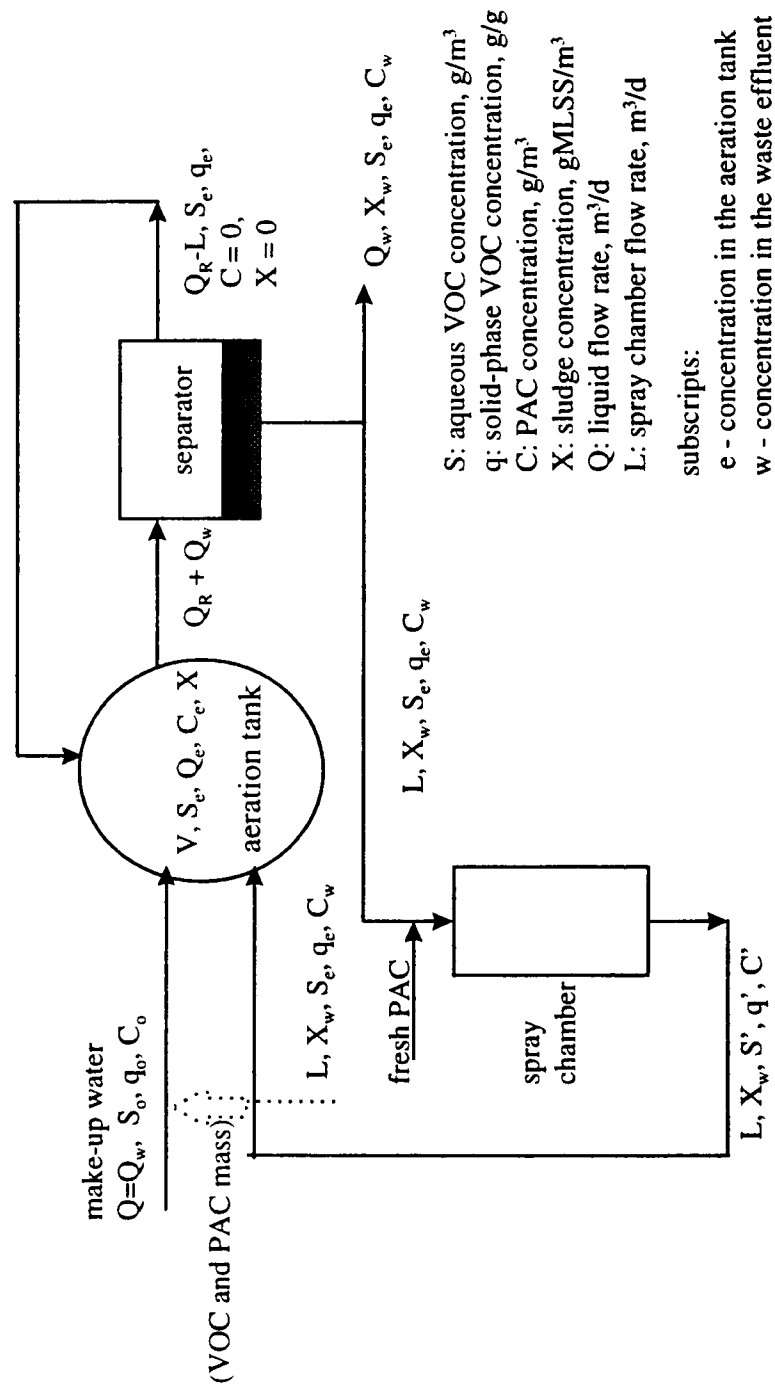


Figure 4.15 Illustration of the flow rate and concentration distribution in the PAC-activated sludge system.

The mass balance for PAC is:

$$\text{PAC dosage (g/d)} = Q_w C_w \quad (4.26)$$

Assuming complete mixing of PAC and bacteria, the following relationship exists:

$$\frac{C}{C_w} = \frac{X}{X_w} \quad (4.27)$$

Ignoring the liquid loss in the spray chamber, fresh water supply Q is equal to waste water flow rate Q_w . Kinetics of biodegradation in the aeration tank can be described by:

$$V y q X = K_d X V + Q_w X_w \quad (4.28)$$

$$q = \frac{q_{\max} S_e}{k_s + S_e} \quad (4.29)$$

Therefore, the following equations can be deduced:

$$1/\theta_c = y q - K_d \quad (4.30)$$

$$S_e = \frac{k_s (1 + K_d \theta_c)}{\theta_c (y q_{\max} - K_d)} \quad (4.31)$$

The mass balance for the biomass is:

$$y[\text{total scrubbed VOC (g/d)} - Q_w (S_e + C_w q_e)] = K_d X V + Q_w X_w \quad (4.32)$$

Combining equation (4.25) and (4.32), gives:

$$Q_w = \text{scrubbed VOC(g/d)} / [X_w (1 + \theta_c K_d)/y + S_e + C_w q_e] \quad (4.33)$$

$$V = Q_w \theta_c (X_w/X) \quad (4.34)$$

A design example for an MEK loading of 1000 g/d is shown in Table 4.10. The mass loading of the aeration tank is 21 g/m³/h and 64 g/m³/h at sludge retention times of 10 days and 2.5 days, respectively. This is in the same range as that of a biofilter (10 - 160

Table 4.10 Design example of a PAC - activated sludge system for MEK removal.

Design parameters	design results	equations used
$\theta_c = 10 \text{ d}$	$S_e = 0.84 \text{ g/m}^3$	(4.31)
$q_{\max} = 0.66 \text{ d}^{-1}$	$q_e = 6.02 \times 10^{-3} \text{ g/g}$	(4.1)
$k_s = 1.37 \text{ g/m}^3$	$C_e = 8,000 \text{ g/m}^3$	
$y = 0.6 \text{ gVSS/gMEK}$	$X_w = 10,000 \text{ g/m}^3$	
$K_d = 0.05 \text{ d}^{-1}$	$Q_w = 0.0396 \text{ m}^3/\text{d}$	(4.33)
$X = 2,000 \text{ gVSS/m}^3$	$V = 1.98 \text{ m}^3$	(4.34)
$C_w = 40,000 \text{ g/m}^3$	PAC dosage (g/d) = 1584 g/d	(4.26)
$\frac{C_e}{C_w} = \frac{X}{X_w} = \frac{1}{5}$	liquid-phase wasted MEK = 0.033 g/d	
scrubbed MEK = 1000 g/d	solid-phase wasted MEK = 9.54 g/d	
$\theta_c = 2.5 \text{ d}$	$S_e = 1.78 \text{ g/m}^3$	(4.31)
$q_{\max} = 0.66 \text{ d}^{-1}$	$q_e = 8.71 \times 10^{-3} \text{ g/g}$	(4.1)
$k_s = 1.37 \text{ g/m}^3$	$C_e = 8,000 \text{ g/m}^3$	
$y = 0.6 \text{ gVSS/gMEK}$	$X_w = 10,000 \text{ g/m}^3$	
$K_d = 0.05 \text{ d}^{-1}$	$Q_w = 0.0524 \text{ m}^3/\text{d}$	(4.33)
$X = 2,000 \text{ gVSS/m}^3$	$V = 0.65 \text{ m}^3$	(4.34)
$C_w = 40,000 \text{ g/m}^3$	PAC dosage (g/d) = 2096 g/d	(4.26)
$\frac{C_e}{C_w} = \frac{X}{X_w} = \frac{1}{5}$	liquid-phase wasted MEK = 0.093 g/d	
scrubbed MEK = 1000 g/d	solid-phase wasted MEK = 18.3 g/d	

g/m³/h). Deshusses (1995) reported that MEK biodegradation rates ranged from zero to 120 g/m³/h when MEK loading rates ranged from zero to 150 g/m³ volume/h. At the loading rates higher than 150 g/m³/h, the biodegradation rates reached a maximum of 120 g/m³/h. The breakthrough loading rate was 100 g/m³ volume/h, and the removal efficiency decreased when the loading rate was higher than 100 g/m³ volume/h. The difference of a CSTR activated sludge reactor and a biofilter is: a CSTR aeration tank operates at a low MEK concentration ($S_e \approx k_s$), while a biofilter operates at a much higher sludge concentration (20-40 kg/m³) and a plug flow condition.

Although it is assumed that equilibrium prevails in the aeration tank, desorption does take some time in a real scenario. As results of the adsorption rate test show, 60% equilibrium was reached in one minute and higher percentage of equilibrium was reached after 15 minutes. Therefore, the hydraulic retention time of PAC(the average regeneration time of PAC), as described by the following equation, should not be too small:

$$HRT_{PAC} = V/[(Q_w + L)(C_w/C_e)] \quad (4.35)$$

Assuming a flow rate of $L = 11 \text{ m}^3/\text{d}$, as given in the design example of co-current spray chamber. The average regeneration time of PAC in this design is 0.86 or 0.28 hours at sludge retention time of 10 days and 2.5days, respectively, long enough for desorption to occur.

The model shows that the residual VOC in waste water is quite small since both S_e and Q_w are small. Most of the residual VOC is on PAC due to high PAC concentration

in waste sludge. This is favorable considering that VOC loss before the final treatment of waste sludge (by incineration) is limited by adsorption. The removal efficiency of the system is very high, with a residual discharge of 0.95% and 1.8% at sludge retention time of 10 days and 2.5 days, respectively. To increase the volumetric loading of the aeration tank, lower sludge retention time and higher S_e can be used, but the residual discharge will also increase.

The cell growth on the PAC surface was ignored in this model. However, since PAC has the same retention time as biomass, a retention time of 10 days generally results in cell growth on PAC, which could block some of the micropores and reduce the adsorption capacity of PAC. Meanwhile, competitive adsorption of organic cell residuals and inorganics can reduce the adsorption capacity of the VOC. Therefore, fresh carbon dosage should be decided by the adsorption capacity supplementation and the need to maintain PAC concentration in the aeration tank. This issue needs further investigation. The system can also operate at a lower sludge retention time, but the waste of PAC will increase and the cost will increase.

Generally, the model prediction indicates that the PAC - activated sludge process is feasible for biodegradable VOC removal and PAC regeneration. As future work, capital and operational cost can be estimated based on this model.

A CSTR activated sludge reactor may not be the most efficient type of reactor. If stripping is still negligible in plug-flow type, then plug-flow should be used. The sludge concentration in activated sludge system is not as high as in fixed bed system. Therefore,

a submerged fixed-film aeration tank should be considered, especially when biodegradation is slow. Another possible advantage of a submerged fixed-film bioreactor is: much less biomass will be in the suspended form, therefore the separation of PAC slurry for making up the feeding to a spray chamber will be more efficient, also the adsorption capacity of PAC inside a droplet could be less affected by bacteria slurry. If a facility is available for separating the PAC from being contacting with sludge while maintaining good diffusion of VOCs in liquid, such as a membrane, then the process will be more efficient.

CHAPTER V

CONCLUSIONS AND SUGGESTIONS

Based on an experimental study of the fundamental mechanisms and theoretical investigation, a combined spray chamber - activated sludge system is considered to be feasible for capturing and biodegrading of relatively soluble and biodegradable VOCs. The following conclusions are obtained:

(1) Based on experimental results, aqueous adsorption of VOCs onto PAC can be very fast. Using PAC slurry as solvent, gas-to-liquid mass transfer of VOCs can be greatly enhanced. Lower liquid flow or spray chamber volume can be achieved.

(2) Based on experimental results and literature information, if bacteria slurries are used as solvent, the cell adsorption and biodegradation in a spray chamber can be negligible. Bacteria slurries have little enhancement for mass transfer process in the spray chamber.

(3) In co-current or horizontal cross-flow spray chambers, gas retention time only needs to be in less than 10 seconds to achieve high efficiency MEK removal. The required volume of a spray chamber can be in the order of 10 to 60 times smaller than a comparable biofilter. Smaller droplet diameters are preferred in both water only and PAC slurry solvent situations. A single-stage cocurrent flow spray chamber may not be feasible for removal of VOCs with Henry's constant higher than 10^{-3} atm·m³/mol in this

combined process. PAC slurry is recommended as the capture solvent for less soluble VOCs.

(4) Compared with biodegradation, the stripping loss of MEK from the aeration tank is negligible. This combined process can operate at feasible overall efficiency with water only as solvent for relatively soluble and easily biodegradable VOCs.

(5) Based on experimental results, PAC has no retardation or enhancement to the biodegradation of MEK. Biological regeneration of PAC is feasible if the adsorption of VOC is readily reversible. Fate of VOCs in the PAC - activated sludge system can be a simple combination of adsorption and biodegradation. A feasible design for MEK removal is provided.

Further work needs to be conducted in the following area:

(1) the gas-to-liquid mass transfer rate of a spray chamber as a function of variation of PAC concentration, droplet size, flow pattern and/or other operational parameters;

(2) the feasibility of using other bioreactors for volume reduction and operation optimization.

LIST OF REFERENCES

LIST OF REFERENCES

1. Awata, M; and Kimura J., 1984. Jpn. Kokai Tokkyo Koho JP 60,206,428 (Cl. B01D53/54) 18 Oct 1985, Appl. 84/62406, 30 Mar 1984.
2. Benedek, P., Major, V., and Takacs, I., 1985. Mathematical Model Suggested for a Carbon-Activated Sludge System. Water Research, Vol. 19, No. 4.
3. Benefield, L. D., and Randall C. W., Biological Process Design for Wastewater Treatment, 1987. Copyright © 1985 by Benefield L. D., and Randall C. W.. Inprint Inc., Charlottesville, Virginia.
4. Buonicore, A. J., Davis, T, and Reed G.D, 1984. Spray Drier/Baghouse Experience on a 1000 ACFM Pilot Plant, fifth Symposium on the Transfer and Utilization of Particle Control Technology.
5. Burglund, R. L. (Union Carbide Corp.), 1983. Biochemical Enhanced Absorption System for Volatile Organic Materials. Eur. Pat. Appl. EP 74,100 (Cl. B01D53/54), 16 Mar 1983. US Appl. 2999,327, 04 Sep. 1981, 18pp.
6. Burant, W. Jr., Copa, W. M. (Sterling Drug Inc.) Ger. Offen, 2,839,137 (Cl. B01D52/02), 29 Mar 1979, US Appl. 833,465, 15 Sep 1977, 18pp.
7. Calvert, S., Mehta, D., and Ressel, R., 1969. Gas Scrubbing with Suspensions of Adsorption or Chemical Reactive Particles. American Industrial Hygiene Association Journal, January-February, 1969.

8. Card, T. R., and Corsi, R. L., 1992. A Flexible Fate Model for VOCs in Wastewater. *Water Environment & Technology*, March 1992.
9. Cini., R., Pantani, B. and Sorace, G., 1980. Physicochemical Aspects of the Use of Activated Carbon in Drinking Water Treatment. Activated Carbon Adsorption, Vol. 1., p425. Copyright © 1980 by Ann Arbor Science Publishers, Inc. Ann Arbor, Michigan.
10. Corsi, R. L., and Card, T. R., 1991. Estimation of VOC Emissions Using the BASTE Model. *Environmental progress*, Vol. 10, No. 4.
11. Corsi, R. L., 1996. VOC Emissions From Sewer Junction Boxes and Drop Structures: Estimation Methods and Experimental Results. *Journal Air Waste Mgmt. Assoc.* Vol. 46, March 1996.
12. Damle A. S., 1985. Modeling of SO₂ Removal in Spray Dryer Flue Gas Desulfurization System, EPA-600/7-85-038, December 1985.
13. Davis, W. T., Reed, G. D., and Lillestolen T.. Spray Dryer/Baghouse Experiences on a 1000 ACFM Pilot Plant. Fifth Symposium on the Transfer and Utilization of Particulate Control Technology, August 1984.
14. Davis, W. T., Reed, G. D. et al, June 1985. Comparison of Pilot Plant Data with Predictions From the USEPA SPRAYMOD Computer Program, Ninth Symposium on Flue Gas Desulfurization, Cincinnati, Ohio.
15. Danckwerts, P. V., and Gillham, A. J., *Trans. Inst. Chem. Engrs.*, 1966, 44, T42.

16. Damle, Ashok S. 1985. Modeling of SO₂ Removal in Spray Dryer Flue Gas Desulfurization System. EPA-600/7-85-038, December 1985.
17. Deshusses, M. A., Hamer, G., and Dunn, I. J., 1995. Behavior of Biofilters for Waste Air Biotreatment. 1. Dynamic Model Development. Environmental Science and Technology, Vol. 29, No. 4.
18. DeWalle, F. B., and Chian, E. S. K., 1976. Biological Regeneration of Powdered Activated Carbon Added to Activated Sludge Units. Water Research, Vol. 11.
19. DeWalle, F. B., Chian, E. S. K., and Small, E. M., 1977. Organic Matter Removal by Powdered Activated Carbon Added to Activated Sludge. Journal WPCF, April 1977.
20. Dvorak, B. I., Lawler, D. F., Fair, J. R., and Handler, N. E., 1996. Evaluation of Onda Correlations for Mass Transfer with Large Random Packing. Environmental Science and Technology, Vol. 30.
21. Furusawa, T. and Smith, M., 1973. Fluid-Particle and Intraparticle Mass Transfer Rates in Slurries. Ind. Eng. Chem. Fundam., Vol. 12, No. 2.
22. Howard, Philip H., 1990. Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Copyright © 1990 by Lewis Publishers, Inc. Lewis Publishers, Inc., Chelsea, Michigan.
23. Hutchison, D. H., and Robinson C., 1990. A microbial Regeneration Process for Granular Activated Carbon—Process Modeling. Water Research, Vol. 24, No. 10.

24. LaGrega M. L., Buchingham P. L., and Evans, J. C., 1994. Hazardous Waste Management. Copyright © 1994 by McGraw-Hill Inc., McGraw-Hill Inc., New York.
25. Jonas, L. A., Tewari, Y. B., and Sansone E. B., 1978. Prediction of Adsorption Rate Constants of Activated Carbon for Various Vapors. J. Cat., Vol. 17, 1978.
26. Kanezashi, Hiroyasu; Okada, Kazuo (Fuji Kasui Kogyo K. K., Japan). Biological Deodorization Application to Shell Molding Plants. Akushu no Kenkyu 1980, 9(44), 28-38 (Japan).
27. Kim, B. R., and Pingel, L. J., 1989. Removal of Toluene from Air Using PAC/Water Slurry Reactor. Journal of Environmental Engineering, Vol. 115, No. 5.
28. Kim, B. R., and Cognata, M. B., 1989. PAC Addition As a Means of Regeneration GAC in a GAC Fluidized-Bed Reactor. Water Research, Vol. 24, No. 1.
29. Kohler, Herbert; Homans, Willem Jan; and Bartke, Dieter. Deodorization of intensely-odorous industrial waste gases with activated-sludge methods. GWF, 1979, 120(6), 282-7.
30. Kyosai, S., and Rittmann, B.E., 1991. Effect of Water-surface Desorption on Volatile Compound Removal under Bubble Aeration. Journal WPCF, Vol. 63, No. 6.
31. Lackey L. W., 1992. Mathematical Model Based On Film Theory To Predict The Adsorption Of Sulfur Dioxide By A Calcium Hydroxide Slurry In A Spray Dryer During The Falling Rate Period. Thesis, University of Tennessee, May 1992.

32. Lee, J. S., and Johnson, W. K., 1979. Carbon-slurry Activated Sludge for Nitrification-denitrification. Journal WPCF, Vol. 51.
33. Little, J. C., and Marinas B. J., 1997. Cross-flow versus Counterflow Air-stripping Towers. Journal of Environmental Engineering, July 1997.
34. Mattson, J. S. and Mark, H. B., 1971. Activated Carbon — Surface Chemistry and Adsorption From Solution. Copyright © 1971 by Marcel Dekker, Inc.. Marcel Dekker Inc., New York.
35. Mehta, D. S., and Calvert, S., 1967. Gas Sorption by Suspension of Activated Carbon in Water. Environmental Science and Technology, Vol. 1, No. 4, 1967.
36. Namkung, E., and Rittman B. E., 1987. Estimating Volatile Organic Compound Emissions from Publicly Owned Treatment Works. Journal WPCF, Vol. 59, No. 7.
37. Ockeloen, H. F., Overcamp, T. J., and Grady, Jr. C. P. L., 1996. Engineering Model for Fixed-Film Bioscrubbers. Journal of Environmental Engineering, March 1996.
38. Overcamp, T. J., Chang, H. C., and Grady, C. P. L. Jr., 1993. An Integrated Theory For Suspended Growth Bioscrubbers. Journal Air and Waste Mgmt. Assoc., Vol 43, No. 5.
39. Onda, K., et al., Journal Chem. Eng. Japan, vol 1, 1968.
40. Onda, K., Takeuchi, H., and Okumotao, Y., 1968. Mass Transfer Coefficients Between Gas and Liquid Phases in Packed Columns. J. Chem. Engrg. of Japan, 1(1).
41. Ottengraf, S.P.P., 1986. Exhaust Gas Purification. Biotechnology, H. J. Rehm and G. Reed, eds., Chapter 12, Vol. 8, 426-452.

42. Parker, W. J., Monteith, H. D., and Melcer, H., 1996. VOCs in Fixed Film Processes. II: Model Studies. *Journal of Environmental Engineering*, July 1996.
43. Partridge G. P., 1987. A Modeling Spray Dryer mathematical Model Based on Film Theory to Predict SO₂ Absorption and Reaction by a Ca(OH)₂ Slurry in the Contact Rate Period. PhD. Dissertation, University of Tennessee, Knoxville, December 1985.
44. Perry's Chemical Engineers' Handbook, 6th edition. Copyright © 1984 by McGraw-Hill Inc. McGraw-Hill Book Company series, New York.
45. Rehrmann, J. A., and Jonas, L. A., 1977. Desorption of Gas Adsorption Rate on Carbon Granule Size and Linear Flow Velocity. *Carbon*, Vol. 16, No. 1-D.
46. Rice R.G. and Robson C.M., Biological Activated Carbon. Copyright © 1982 by Ann Arbor Science. Ann Arbor, Michigan.
47. Roberts, P. V., Dandliker, P., and Matter-Muller, C. Volatilization of Organic Pollutants in Wastewater Treatment—Model Studies. EPA-600/2-84-047. U.S. EPA, Cincinnati, 1984.
48. Schultz, J. R., and Keinath T. M., 1984. Powered Activated Carbon Treatment Process Mechanism. *Journal WPCF*, Vol. 56, No. 2.
49. Sigurdson, S. P., and Robinson, C. W., Substrate-inhibited Microbiological Regeneration of Granular Activated Carbon. *The Canadian Journal of Chemical Engineering*, Vol. 56, June, 1978.
50. Masters, K., Spray Drying Handbook, 3rd edition, 1976. Copyright © 1976 by K. Masters. John Wiley & Sons Inc., New York.

51. Sundstrom, D. W., Herbert, E. K., Tien, T., and Suresh, N., Response of Biological Reactors to The Addition of Powdered Activated Carbon. Water Research, Vol. 13.
52. Swanson, W. J. and Reymond, C. Loehr, 1997. Biofiltration: Fundermentals, Design and Opertion Principles, and Applications. Journal of Environmental Engineering. Vol. 123 No. 6.
53. Treybel R. E., Mass-Transfer Operations. 2th edition. Copyright © 1968 by McGraw-Hill Inc. McGraw-Hill Book Company series, New York.
54. American Water Works Association, Water Quality and Treatment, 4th edition. Copyright © 1990 by McGraw-Hill Book Company series. New York.
55. Water, Jr., Copa, Wiliam Marvin (Sterling Drug, Inc.) Ger. Offen. 2,839,173 (Cl. B01D53/02), 29 Mar 1979, US Appl. 833,465, 15 Sep 1977; 18pp.
56. Wet Scrubber System Study, Volume I: Scrubber Handbook, EPA-R2-72-118a, U.S. EPA, 1972.
57. Ying, W., and Weber, W. J. Jr.. Bio-Physicochemical Adsorption Of Model Systems For Wastewater Treatment. Journal WCF, 51, Nov. 1979.
58. Zhang, X., Wang, Z., and Gu, X., 1991. Simple Combination of Biodegradation and Carbon Adsorption - The Mechanism of The Biological Activated Carbon Process. Water Research, Vol. 25, No. 2.
59. Zierold Kristina M., 1996. Henry's Law Constant Of Selected VOCs: Experimental Determined And Estimated Values. Master Thesis, Vanderbuilt University, 1996, p22.

APPENDIXES

APPENDIX A

Equilibrium concentrations of MEK adsorption on PAC at 22°C.

Liquid-phase concentration C (mg/l)	solid-phase concentration q (mg/g)
72.0	57.9
76.2	60.3
93.6	61.5
108	63.3
123	65.2
136	67.4
147	70.3
148	80.1
195	85.6
245	92.7
299	102
338	123
452	129
548	160

Results of MEK stripping test using water as solvent.

time(sec)	MEK concentration(mg/l)
0	240
20	209
43	192
60	179
90	157
120	135
156	119
182	109
214	91
241	83
270	74
300	67

Results of MEK biodegradation and stripping in batch aeration test.

Time (sec)	MEK concentration (mg/l)
0	215
22	165
42	123
63	73
82	26
100	0

Calculation of the accumulated amount of MEK stripped and biodegraded in the aeration test.

T (min.)	C (mg/l)	C (mg/l) =215 - 2.2896T	c _{ave.} (mg/l)	$\Delta C/\Delta T$ (mg/(l·min))	stripping ΔC (mg/l)	accumulated stripping (mg/l)	accumulated biodegradation (mg/l)
0	215	215				0	0
1		212.7104	213.8552	-0.94096	-0.94096		
2		210.4208	211.5656	-0.93089	-0.93089		
3		208.1312	209.276	-0.92081	-0.92081		
4		205.8416	206.9864	-0.91074	-0.91074		
5		203.552	204.6968	-0.90067	-0.90067		
6		201.2624	202.4072	-0.89059	-0.89059		
7		198.9728	200.1176	-0.88052	-0.88052		
8		196.6832	197.828	-0.87044	-0.87044		
9		194.3936	195.5384	-0.86037	-0.86037		
10		192.104	193.2488	-0.85029	-0.85029		
11		189.8144	190.9592	-0.84022	-0.84022		
12		187.5248	188.6696	-0.83015	-0.83015		
13		185.2352	186.38	-0.82007	-0.82007		
14		182.9456	184.0904	-0.81	-0.81		
15		180.656	181.8008	-0.79992	-0.79992		
16		178.3664	179.5112	-0.78985	-0.78985		
17		176.0768	177.2216	-0.77978	-0.77978		
18		173.7872	174.932	-0.7697	-0.7697		
19		171.4976	172.6424	-0.75963	-0.75963		
20		169.208	170.3528	-0.74955	-0.74955		
21		166.9184	168.0632	-0.73948	-0.73948		
22	165	164.6288	165.7736	-0.7294	-0.7294	18.4	32
23		162.3392	163.484	-0.71933	-0.71933		
24		160.0496	161.1944	-0.70926	-0.70926		
25		157.76	158.9048	-0.69918	-0.69918		
26		155.4704	156.6152	-0.68911	-0.68911		
27		153.1808	154.3256	-0.67903	-0.67903		
28		150.8912	152.036	-0.66896	-0.66896		
29		148.6016	149.7464	-0.65888	-0.65888		
30		146.312	147.4568	-0.64881	-0.64881		
31		144.0224	145.1672	-0.63874	-0.63874		
32		141.7328	142.8776	-0.62866	-0.62866		
33		139.4432	140.588	-0.61859	-0.61859		
34		137.1536	138.2984	-0.60851	-0.60851		
35		134.864	136.0088	-0.59844	-0.59844		
36		132.5744	133.7192	-0.58836	-0.58836		
37		130.2848	131.4296	-0.57829	-0.57829		

(to be continued, 1 of 3)

(continued, 2 of 3)

T (min.)	C (mg/l)	c (mg/l) =215 - 2.2896T	c _{ave.} (mg/l)	$\Delta C/\Delta T$	stripping ΔC (mg/l)	accumulated stripping (mg/l)	accumulated biodegradation (mg/l)
39		125.7056	126.8504	-0.55814	-0.55814		
40		123.416	124.5608	-0.54807	-0.54807		
41		121.1264	122.2712	-0.53799	-0.53799		
42	123	118.8368	119.9816	-0.52792	-0.52792	30.8	62
43		116.5472	117.692	-0.51784	-0.51784		
44		114.2576	115.4024	-0.50777	-0.50777		
45		111.968	113.1128	-0.4977	-0.4977		
46		109.6784	110.8232	-0.48762	-0.48762		
47		107.3888	108.5336	-0.47755	-0.47755		
48		105.0992	106.244	-0.46747	-0.46747		
49		102.8096	103.9544	-0.4574	-0.4574		
50		100.52	101.6648	-0.44733	-0.44733		
51		98.2304	99.3752	-0.43725	-0.43725		
52		95.9408	97.0856	-0.42718	-0.42718		
53		93.6512	94.796	-0.4171	-0.4171		
54		91.3616	92.5064	-0.40703	-0.40703		
55		89.072	90.2168	-0.39695	-0.39695		
56		86.7824	87.9272	-0.38688	-0.38688		
57		84.4928	85.6376	-0.37681	-0.37681		
58		82.2032	83.348	-0.36673	-0.36673		
59		79.9136	81.0584	-0.35666	-0.35666		
60		77.624	78.7688	-0.34658	-0.34658		
61		75.3344	76.4792	-0.33651	-0.33651		
62		73.0448	74.1896	-0.32643	-0.32643		
63	73	70.7552	71.9	-0.31636	-0.31636	39.6	106
64		68.4656	69.6104	-0.30629	-0.30629		
65		66.176	67.3208	-0.29621	-0.29621		
66		63.8864	65.0312	-0.28614	-0.28614		
67		61.5968	62.7416	-0.27606	-0.27606		
68		59.3072	60.452	-0.26599	-0.26599		
69		57.0176	58.1624	-0.25591	-0.25591		
70		54.728	55.8728	-0.24584	-0.24584		
71		52.4384	53.5832	-0.23577	-0.23577		
72		50.1488	51.2936	-0.22569	-0.22569		
73		47.8592	49.004	-0.21562	-0.21562		
74		45.5696	46.7144	-0.20554	-0.20554		
75		43.28	44.4248	-0.19547	-0.19547		
76		40.9904	42.1352	-0.18539	-0.18539		
77		38.7008	39.8456	-0.17532	-0.17532		
78		36.4112	37.556	-0.16525	-0.16525		
79		34.1216	35.2664	-0.15517	-0.15517		
80		31.832	32.9768	-0.1451	-0.1451		

(to be continued)

(continued, 3 of 3)

T (min.)	C (mg/l)	c (mg/l) =215- 2.2896T	c _{ave.} (mg/l)	$\Delta C/\Delta T$	stripping ΔC (mg/l)	accumulated stripping (mg/l)	accumulated biodegradation (mg/l)
81		29.5424	30.6872	-0.13502	-0.13502		
82	26	27.2528	28.3976	-0.12495	-0.12495	43.7	145
83		24.9632	26.108	-0.11488	-0.11488		
84		22.6736	23.8184	-0.1048	-0.1048		
85		20.384	21.5288	-0.09473	-0.09473		
86		18.0944	19.2392	-0.08465	-0.08465		
87		15.8048	16.9496	-0.07458	-0.07458		
88		13.5152	14.66	-0.0645	-0.0645		
89		11.2256	12.3704	-0.05443	-0.05443		
90		8.936	10.0808	-0.04436	-0.04436		
91		6.6464	7.7912	-0.03428	-0.03428		
92		4.3568	5.5016	-0.02421	-0.02421		
93		2.0672	3.212	-0.01413	-0.01413		
94	0	-0.2224	0.9224	-0.00406	-0.00406	44.4	171

Results of MEK stripping from water in desorption rate test.

Time (min)	gas phase MEK concentration (ppm)
0	228
34	212
64	191
113	181
141	178
236	159
283	151

Results and calculation of MEK stripping from PAC slurry in desorption rate test.

time (min)	gas-phase concentration (ppm)	accumulated desorption (mg/g)	solid-phase concentration q (mg/g)	liquid-phase equilibrium concentration C_s (mg/l)	liquid-phase concentration C (mg/l)
0	228	0	80.2	164	164
34	212	1.672522	78.52748	156.6924	159.9298
64	191	3.31338	76.88662	150.0984	144.0877
113	181	5.010967	75.18903	143.4281	136.5439
141	178	5.856998	74.343	140.1615	134.2807
236	159	8.890056	71.30994	128.7649	119.9474
283	151	10.24721	69.95279	123.8246	113.9123

Results of Warburg Respirometer test .

sample	time (min)	Temp (°C)	α	KO ₂	Δh (mm)	Δh (mm)	ΔO_2 (10 ⁻³ ml)	accumulative O ₂ (10 ⁻³ ml)
[MEK] = 0 g/l	0				0	0	0	0.0
	70	14	0.035114	10.6077	-1.9	-1.9	20.15462	20.2
	130	17.25	0.03266	10.48603	-1.25	-1.45	14.15615	34.3
	190	21.1	0.030318	10.34608	-1	-1.25	11.63934	46.0
[PAC] = 0 g/l	250	22.25	0.0297	10.30508	-1.48	-1.58	15.76678	61.7
	310	22.75	0.029431	10.28736	-1.38	-1.38	14.19655	75.9
	422	23.4	0.029081	10.2644	-2.82	-2.82	28.94560	104.9
	482	23.4	0.029081	10.2644	-1.75	-1.75	17.96270	122.8
	545	23	0.029296	10.27851	-1.13	-1.43	13.15650	136.0
	1265	23	0.029296	10.27851	-14.35	-12.9	140.0448	276.0
[MEK] = 81 g/l	0				0	0	0	0.0
	70	14	0.035114	10.6077	-3.8	-3.35	37.92251	37.9
	130	17.25	0.03266	10.48603	-1.45	-3.25	24.64218	62.6
	190	21.1	0.030318	10.34608	-1.25	-1.3	13.19126	75.8
[PAC] = 0 g/l	250	22.25	0.0297	10.30508	-1.58	-1.28	14.73627	90.5
	310	22.75	0.029431	10.28736	-1.38	-1.58	15.22529	105.7
	422	23.4	0.029081	10.2644	-2.82	-2.97	29.71543	135.4
	482	23.4	0.029081	10.2644	-1.75	-1.95	18.98914	154.4
	545	23	0.029296	10.27851	-1.43	-1.43	14.69828	169.1
	1265	23	0.029296	10.27851	-13.25	-14.25	141.3296	310.4
[MEK] = 81 g/l	0				0	0	0	0
	70	14	0.035114	10.6077	-2.5	-4.2	35.53578	35.5
	130	17.25	0.03266	10.48603	-3.15	-1.6	24.90433	60.4
	190	21.1	0.030318	10.34608	-1.2	-1.2	12.4153	72.9
[PAC] = 5 g/l	250	22.25	0.0297	10.30508	-1.43	-1.68	16.02441	88.9
	310	22.75	0.029431	10.28736	-1.63	-1.73	17.28276	106.2
	422	23.4	0.029081	10.2644	-2.97	-3.12	31.25509	137.4
	482	23.4	0.029081	10.2644	-1.75	-2.55	22.06845	159.5
	545	23	0.029296	10.27851	-1.03	-0.88	9.815981	169.3
	1265	23	0.029296	10.27851	-13.2	-12.65	132.8498	302.2

(to be continued, 1 of 2)

(continued, 2 of 2)

sample	time (min)	Temp (°C)	α	K _{O2}	Δh (mm)	Δh (mm)	ΔO_2 (10 ⁻³ ml)	accumulative O ₂ (10 ⁻³ ml)
[MEK] = 269mg/l	0				0	0	0	0
	70	14	0.035114	10.6077	-2.75	-4.25	37.12694	37.1
	130	17.25	0.03266	10.48603	-2.45	-3.45	30.9338	68.1
[PAC] = 0 g/l	190	21.1	0.030318	10.34608	-2.5	-3.55	31.2969	99.4
	250	22.25	0.0297	10.30508	-2.98	-3.98	35.8617	135.2
	310	22.75	0.029431	10.28736	-1.68	-5.08	34.77127	170.0
	422	23.4	0.029081	10.2644	-2.22	-6.02	42.28932	212.3
	482	23.4	0.029081	10.2644	-1.7	-2.25	20.27218	232.6
	545	23	0.029296	10.27851	-0.83	-1.68	12.89954	245.5
	1265	23	0.029296	10.27851	-12.3	-16.25	146.7258	392.2
[MEK] = 269mg/l	0				0	0	0	0
	70	14	0.035114	10.6077	-4.2	-3.95	43.22636	43.2
	130	17.25	0.03266	10.48603	-3.95	-3.3	38.01187	81.2
[PAC] = 5 g/l	190	21.1	0.030318	10.34608	-3.4	-0.345	19.37304	100.6
	250	22.25	0.0297	10.30508	-3.88	-3.58	38.43797	139.0
	310	22.75	0.029431	10.28736	-3.58	-3.48	36.31437	175.4
	422	23.4	0.029081	10.2644	-4.32	-3.97	42.54593	217.9
	482	23.4	0.029081	10.2644	-1.95	-1.8	19.24574	237.2
	545	23	0.029296	10.27851	-1.83	-1.43	16.75398	253.9
	1265	23	0.029296	10.27851	-15.35	-14.25	152.122	406.0
[MEK]= 1885mg/l	0				0	0	0	0
	70	14	0.035114	10.6077	-3.8	-3.95	41.10482	41.1
	130	17.25	0.03266	10.48603	-3.95	-2.85	35.65252	76.8
[PAC] = 0 g/l	190	21.1	0.030318	10.34608	-3.2	-2.8	31.03825	107.8
	250	22.25	0.0297	10.30508	-3.38	-3.58	35.8617	143.7
	310	22.75	0.029431	10.28736	-4.38	-3.78	41.97241	185.6
	422	23.4	0.029081	10.2644	-8.72	-8.12	86.42623	272.1
	482	23.4	0.029081	10.2644	-4.85	-4.6	48.49928	320.6
	545	23	0.029296	10.27851	-5.23	-4.33	49.1313	369.7
[MEK]= 1885mg/l	0				0	0	0	0
	70	14	0.035114	10.6077	-3.95	-3.2	37.92251	37.9
	130	17.25	0.03266	10.48603	-2.35	-3.45	30.4095	68.3
[PAC] = 5 g/l	190	21.1	0.030318	10.34608	-2.8	-2.8	28.96903	97.3
	250	22.25	0.0297	10.30508	-3.43	-3.48	35.60407	132.9
	310	22.75	0.029431	10.28736	-3.93	-4.18	41.71523	174.6
	422	23.4	0.029081	10.2644	-8.47	-8.62	87.70928	262.3
	482	23.4	0.029081	10.2644	-4.95	-5.35	52.86165	315.2
	545	23	0.029296	10.27851	-4.83	-5.53	53.2427	368.4

APPENDIX B

Estimation of mass transfer coefficient k'_L and k'_G for test number 5.

$$k'_L = 0.0051 \left(\frac{L}{a_i \mu_L} \right)^{2/3} (\mu_L / \rho_L D_L)^{-0.5} (a_i d_p)^{0.4} (\rho_L / \mu_L g)^{-1/3} \quad \text{equation (2.22)}$$

$$k'_G = 5.23 [(G/a_i \mu_G)^{0.70} (\mu_G / \rho_G D_G)^{1/3} (a_i d_p)^{-2.0} (a_i D_G)] / RT \quad \text{equation (2.23)}$$

$$L = 0.467 \text{ gpm} \times 3.785 \text{ kg/gpm} \times \text{min}/60\text{sec} / 0.0324 \text{ m}^2 = 0.909 \text{ kg}/(\text{m}^2 \cdot \text{s})$$

$$\mu_L = 0.001 \text{ kg}/(\text{m} \cdot \text{s})$$

$$\rho_L = 998 \text{ kg}/\text{m}^3$$

$$D_L = 1.07 \times 10^{-9} \text{ m}^2/\text{s} \text{ (from Wilke-Lee Method)}$$

$$a_i = 180 \text{ m}^2/\text{m}^3$$

$$\text{calculated } k'_L = 6.93 \times 10^{-5} \text{ m/s}$$

$$G = 43 \text{ acfm} \times 0.0283 \text{ m}^3/\text{ft}^3 \times 1.20 \text{ kg}/\text{m}^3 / 0.0324 \text{ m}^2 \times \text{min}/60\text{s} = 0.751 \text{ kg}/(\text{m}^2 \cdot \text{s})$$

$$\mu_G = 1.81 \times 10^{-5} \text{ kg}/(\text{m} \cdot \text{s})$$

$$\rho_G = 1.20 \text{ kg}/\text{m}^3$$

$$D_G = 9.56 \times 10^{-6} \text{ m}^2/\text{s} \text{ (from Wilke-Lee Method)}$$

$$\text{calculated } k'_G = 6.88 \times 10^{-3} \text{ m/s}$$

$$= 6.88 \times 10^{-3} \text{ m/s} \times (\text{mol gas}) / (0.0240 \text{ m}^3 \text{ gas}) \times 60\text{s}/\text{min} \times 0.0929 \text{ m}^2/\text{ft}^2$$

$$= 1.57 \text{ mol}/(\text{ft}^2 \cdot \text{min})$$

Dimensionless Henry's Law constant H:

$$H = 0.45 \text{ atm} \cdot (\text{mol gas}/\text{mol air}) / (\text{mol gas}/\text{mol water})$$

$$\times (\text{mol air} / 0.0240 \text{ m}^3 \text{ air}) \times (\text{m}^3 \text{ water} / 55600 \text{ mol})$$

$$= 0.45 \times 7.49 \times 10^{-4} (\text{mol gas}/\text{m}^3 \text{ air}) / (\text{mol gas}/\text{m}^3 \text{ water})$$

$$= 3.37 \times 10^{-4} (\text{mol gas}/\text{m}^3 \text{ air}) / (\text{mol gas}/\text{m}^3 \text{ water})$$

gas phase resistance :

$$1/k'_G = 1/6.88 \times 10^{-3} \text{ m/s} = 145 \text{ s/m}$$

liquid phase resistance:

$$H/k'_L = 3.37 \times 10^{-4} (\text{mol gas}/\text{m}^3 \text{ air}) / (\text{mol gas}/\text{m}^3 \text{ water}) / 6.93 \times 10^{-5} \text{ m/s} = 4.86 \text{ s/m}$$

APPENDIX C

Experimentally inferred k_v and regression of k_v versus PAC mass loading in packed tower operation with PAC slurry.

Test	[PAC]L	$-\ln(y_2/y_1)$	$G/(SZ)$	$\frac{G/(SZ)}{-\ln(y_2/y_1)}$	$k_v p_T/RT$	k_v	estimated k_v	estimated y_2/y_1	real y_2/y_1
number	(g/min)		(mol/ft ³ /min)	(mol/ft ³ /min)	(mol/ft ³ /min)	(1/min)	(1/min)		
9	25.9	0.77	67.8	52.5	16.5	14.4	12.6	0.5253	0.5386
10	17.4	0.63	67.8	42.0	7.0	6.0	8.45	0.4906	0.4691
11	17.5	0.67	66.2	44.4	8.4	7.2	7.17	0.4994	0.4888
12	34.3	0.84	66.2	55.7	19.7	16.8	16.7	0.5661	0.5689
13	52.7	0.92	66.2	50.9	24.9	21.6	25.7	0.6287	0.6012
14	47.3	1.05	67.8	71.6	35.6	30.6	23.0	0.6023	0.6517
15	66.4	1.05	67.8	71.0	35.0	30.6	32.3	0.6603	0.6489
16	139.0	1.36	66.2	90.1	54.1	46.8	67.5	0.8213	0.7437

Note: estimated $k_v = 0.486[\text{PAC}]L$.

VITA

Ke Liu was born in Chengdu, China. She graduated from Tsinghua University with a Bachelor of Science degree in Environmental Engineering in 1994. In August 1995, she entered the Graduate School at the University of Tennessee at Knoxville. She worked as a graduate research assistant in the Civil and Environmental Engineering Department, while she pursued an Master of Science degree in Environmental Engineering. She received the degree in December, 1997.