

AN ABSTRACT OF THE THESIS OF

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Title: A Mathematical Model for Adsorptive Bubble-Separation Processes

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Adsorptive bubble-separation processes are used to remove adsorptive contaminants from wastewater. A mathematical model was developed for the adsorptive bubble separation processes in a countercurrent column. The model included an assumption that linear adsorption of the solute occurred on the gas bubbles. Predictions indicated that aqueous column height has less effect on the solute removal efficiency than water flow rates, gas flow rates or bubble size. Increased water flow rates reduce removal efficiency; greater gas flow rates increase removal efficiency. The maximum removal efficiency is determined by adsorption characteristics of the solute; the removal rate is controlled by mass-transfer rate. However, influent concentrations of the solute in the water phase do not affect removal efficiency.

These predictions were tested by means of solvent sublation experiments conducted in a laboratory setting. The data were collected from the sublation of Triton-X100 in a water-ethyl acetate-nitrogen system. Linear regression was used to compare predictions and experimental data with respect to column height. Five column heights ranged from 30 to 100 cm were compared at three water flow rates, 3.0, 5.5 and 13.0 ml/min. The calculated column heights agreed the observed column heights well. As the model predicted, the effect of influent concentration on the removal efficiency was not significant. The surface excess of Triton-X100 ( $0.75 \text{ E-}10$  to  $7.5 \text{ E-}10 \text{ g mole/cm}^2$ ) estimated from the adsorption constant in the model agrees with other published values ( $2.6 \text{ E-}10$  to  $2.8 \text{ E-}10 \text{ g mole/cm}^2$ ). The mass-transfer coefficients of Triton-X100 in water ( $k_L$ , which ranged from 0.50 to 0.60 cm/min) determined from the model and experimental data at 3.0, 5.5, 8.0 and 13.0 ml/min water flows ( $Q_w$ ) are proportional to the 0.124 power of the water flow rates.

$$k_L = 0.0441 Q_w^{0.124}$$

This empirical exponent correlation between mass-transfer coefficients and water flow rates for the adsorption processes is similar to the correlation determined from previous absorption models.

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# **A MATHEMATICAL MODEL FOR ADSORPTIVE BUBBLE-SEPARATION PROCESSES**

## **INTRODUCTION**

The term, adsorptive bubble-separation, was derived from the expression "adsorptive bubble fractionation" (Lemlich, 1966). In adsorptive bubble-separation processes, a gas in the form of bubbles disperses through an aqueous solution. A surface-active solute is adsorbed on the bubble surface. Higher concentrations of the solute appear at the bubble surface compared to the bulk solution. Bubbles rise through the solution, carrying the surface enriched solute to the top of the water column. Many separation methods, such as foam fractionation and solvent sublation, have been proposed to recover the solute at the top of the bulk solution (Lemlich, et al., 1972).

This research examines solvent sublation. To mathematically describe adsorptive bubble-separation processes, process mechanisms must be understood. Although adsorptive bubble-separation appears to be a simple process in which bubbles collect the solute and rise upwards, in fact, complicated mechanisms are involved. Since the process is not at equilibrium, both the solute distribution and solute transfer rates in the solution must be

considered. The mathematical model must incorporate principles of physicochemistry and engineering such as adsorption, mass transfer and mass balance.

Adsorption is a surface phenomena which involves the accumulation of substances at an interface. Any solute which can reduce the free surface energy of a liquid in which it is dissolved will adsorb at the boundary of the liquid phase. The solute is, therefore, a surface-active substance.

A molecule of the surface-active substance usually consists of a hydrophobic group and a hydrophilic group. When the surface-active substance is dissolved in water, it accumulates at the boundary of the water phase, where the molecules of the surface-active substance replace the water molecules and bond with molecules of the non-water phase. The formation of bonds between the hydrophobic group of the surface-active substance and the molecules of the non-water phase reduce the free surface energy.

A thermodynamic relationship between adsorption and solute concentration in bulk solution was first postulated by Gibbs in 1878. The Gibbs' equation is expressed as:

$$\Gamma = - \frac{1}{RT} \frac{d\delta}{d(\ln C)}$$

where:  $\Gamma$  = surface excess, mg/cm<sup>2</sup>;

$R$  = universal gas constant, dyne cm/mg K;

- T = absolute temperature, K;  
 $\delta$  = surface tension, dyne/cm; and  
C = concentration of solute, mg/ml.

Since Gibbs' equation involves differentiation of surface tension with respect to concentration, it is not commonly used in mathematical models involving complex processes.

Three typical isotherm equations that describe the variation in the equilibrium adsorption of solid-water systems with adsorptive solute concentrations in the bulk solution have been confirmed by experimental data. These equations are 1) the Langmuir adsorption model for single layer adsorption and uniform surface energies (Langmuir, 1918), 2) the Brunauer, Emmett, Teller model for multilayer adsorption and uniform surface energies (Brunauer et al., 1938), and 3) the Freundlich model, which is derived from the Langmuir equation, but used for heterogeneous surface energies (Freundlich, 1926). According to these models, adsorption occurs as a result of characteristic properties for a given solid-adsorptive solute-water system. These models consistently suggest a linear relationship between equilibrium adsorption and aqueous concentration for dilute aqueous solutions.

Few studies have been conducted with respect to the equilibrium adsorption for gas-water systems. Most researchers assume that the model for adsorption equilibrium

at the gas-water interface is identical to that found at the solid-water interface. Miller and Lunkenheimer (1982) and Valsaraj et al. (1986) assumed that a linear relationship can be applied in water-gas systems with respect to dilute solutions. This assumption will be used throughout this research.

It is often difficult to determine the rate-controlling step in non-equilibrium bubble-separation processes. There are essentially two consecutive steps for solute adsorption from solution. The first involves transport of the solute through the bulk solution to the exterior of the bubbles. Like the interparticle transport observed in solid-liquid systems (Webber and Morris, 1963), this phenomena can be described by diffusion kinetics. The second step concerns solute adsorption on the surface of bubbles. Many researchers (Defay, R. and Hommelen, 1959; Lange, 1965; and Fainerman, 1978) have shown that surface tension changes with time before equilibrium is reached. The overall rate of adsorption from a water solution represents the combined effects of these two steps. Most mathematical equations describing concentration versus time profiles have been limited to special cases in which only one of these steps controls the overall rate of adsorption (Rosen, 1952; Klinkenberg, 1954 and Goldstein, 1953).

Although both transport in the bulk solution and adsorption have been considered in this research, adsorption kinetics was not included in this model. Unsaturated adsorption at the bubble surface was related to the interfacial concentration of the solute which was controlled by the mass transfer rate in the bulk solution.

To determine the rate of mass transfer towards the bubble surface, it is necessary to predict the mass-transfer coefficients. Film theory (Whitman, 1923) and penetration theory (Higbie, 1935; and Danckwerts, 1951) suggest a relationship between diffusion coefficients and mass-transfer coefficients for transfer between two phases. Unfortunately, the relationship requires parameters which are difficult to measure experimentally, such as the film thickness (Whitman, 1923), the fractional rate of surface renewal (Danckwerts, 1951), and exposure time (Higbie, 1935). Many approaches have been used to develop empirical correlations for mass-transfer coefficients, turbulence and diffusion coefficients through the study of evaporation. The evaporation of organic compounds from seas or lakes has been studied intensively (Redfield, 1948; Sugiura et al. 1963; Quinn and Otto, 1971; Fuller et al., 1977 and Doskey and Andren, 1981). Evaporation in laboratory processes has also been studied (Shulman, et al., 1955; Onda et al., 1968; Deacon, 1977; and Mackay et al., 1986). Since evaporation



involves transfer in both gas and liquid phases, two mass-transfer coefficients must be included in these approaches. It is difficult to study the liquid phase and the gas phase separately.

This research attempted to study the mass-transfer coefficient in the liquid phase ( $k_L$ ) by means of the adsorption process. This approach has rarely been used in mass-transfer coefficient prediction. The advantage of mass-transfer coefficient prediction with respect to the adsorption process is that only one mass-transfer coefficient in the liquid phase is involved at the interface between gas and liquid phases.

The purpose of this research was to create and verify a mathematical model for adsorptive bubble-separation processes. Chapter I discusses the mechanisms of adsorptive bubble-separation. A mathematical model is developed in detail. In the model, the influence of several factors on the removal of an adsorptive solute from aqueous solution was explored. Chapter II describes experimental work in which a bubble separation process, solvent sublation, was designed and used in a laboratory setting. Comparisons of experimental data with model predictions tested the model's validity. In Chapter III, mass-transfer coefficients in the solvent sublation process were obtained by varying water flow rates. A correlation between the mass-transfer

coefficients and water flow rates was determined by means of regression analyses.

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## Chapter I

### **A Design for Adsorptive Bubble-Separation Processes: I Theoretical Development**

#### **Abstract**

A mathematical model is presented for the removal of an adsorptive solute from water by a bubble separation process. The model includes the effect of mass transfer of the solute from the aqueous phase to the bubble surface and the adsorption of the solute to the bubble surface. Mass transfer is based on the film theory. Adsorption is related to the interfacial concentration in the aqueous side of the interface. A linear adsorption function is assumed. Mass-balance differential equations were established using two control volumes in a countercurrent column.

The model was expressed in terms of measurable factors, such as column height, removal percentage of solute, water and gas flow rates and bubble size. A feasible method was proposed for the determination of the specific bubble area. The adsorptive bubble-separation mechanisms were illustrated explicitly by the mathematical description. This model predicted that the increased mass-transfer coefficient of the adsorptive solute in the aqueous solution ( $k_l$ ) enhanced

the removal efficiency, and adsorption constant of the solute ( $k$ ) determined the maximum removal efficiency. The model also predicted that the influence of column height on the removal of the adsorptive solute was less than that of water flow rate, gas flow rate and bubble size. The ratio of water flow rate to gas flow rate played more important role in the bubble-separation process than individual flow rate.

## INTRODUCTION

Bubble separation processes are commonly used to remove volatile organic compounds from wastewater. This paper describes an approach which uses a bubble separation process to remove nonvolatile organic compounds from water based on their adsorptive property. For soluble or slightly soluble organic compounds which contain a hydrophobic and a hydrophilic group, the hydrophobic group accumulates at the interface between the aqueous phase and the gaseous or solid phase. This accumulation is called adsorption. Adsorptive bubble-separation techniques utilize gas bubbles and the adsorptive properties of organic compounds to separate the solute from an aqueous solution.

In an adsorptive bubble-separation process, gas bubbles are dispersed through a water column. As the bubbles rise, the organic solute adsorbs at the surface of the bubbles and moves with the bubbles through the aqueous phase. The adsorbed mass is separated from the aqueous phase by several methods. There are many adsorptive bubble-separation processes. The primary difference between them is the separation method used at the top of the water column which may be classified as foaming or non-foaming (Lemlich, 1972). Based upon specific separation principles, various



mathematical models for individual separation methods have been proposed. Although the separation principles are different, the mechanism in the aqueous phase is identical. It is necessary to determine the mechanism in the aqueous phase that will be suitable for all adsorptive bubble-separation processes.

Obviously, mass transfer of the nonvolatile adsorptive solute occurs in the aqueous phase. In order to enrich and adsorb the solute on the bubble surface, the solute must be transferred from the bulk solution toward the bubbles. According to classical mass-transfer theory, the mass-transfer rate in a fluid depends on fluid turbulence, solute characteristics, and properties of the bulk solution.

The relationship between adsorption and mass transfer must be considered. This research assumes that the removal rate of the adsorptive solute is limited by the mass-transfer rate. Due to transfer in the aqueous phase, the concentration adjacent to the bubble surface is not identical to the concentration in the bulk solution. Consequently, adsorption cannot be directly calculated from the bulk concentration of the solute in the aqueous phase.

The removal efficiency of the solute depends on the retention time of the bubbles in the aqueous phase. As the bubbles rise through the column, the retention time is proportional to the column height. The bulk concentration

of the solute changes with the column height. Since pure bubbles generated at the bottom of the column provide a solute-free surface, the interfacial concentration of the solute at the liquid side is much lower than the concentration in the bulk solution. Therefore the solute removal rate is rapid at the bottom. As the solute gradually accumulates at the bubble surface, the removal slows. Consequently, in countercurrent bubbling operations the bottom portion of the aqueous column is more dilute than the upper portion.

Adsorptive bubble-separation processes can be conducted in a semi-batch column, a concurrent column or a countercurrent column. Due to the non-uniform concentration distribution in the aqueous phase, the countercurrent operation appears to be most efficient. In countercurrent operations, the aqueous solution discharges from the lower portion of the column where the lowest concentration of solute can be found. Large volumes of wastewater can be bubbled and a stable removal of solute from the aqueous solution can be obtained from a small column. Occasionally, very high aqueous flow rates will cause low solute removals. A multiple countercurrent system will increase solute removal.

The objective of this project was to develop a mathematical model to describe adsorption and mass transfer

in adsorptive bubble-separation processes. This model has taken components from other models and organized them in a new form. In a countercurrent aqueous column, two differential mass balance equations were developed. A simple concentration profile explained the surface concentration distribution. Factors which must be considered in the mathematical model are: (1) the size of the bubbles, (2) the water flow rate, (3) the gas flow rate, (4) the height of the aqueous column, (5) the concentration of the solute in the aqueous phase, (6) the mass transfer rate of solute in the aqueous phase, and (7) the adsorption at the bubble surface. Since all adsorptive bubble-separation processes operate in an aqueous column, this model has broader applications than previous models which were specific for one type of process.

## BACKGROUND

### Basic Principles

Like other models, the mathematical model in this paper was derived from basic mass-balance and mass-transfer principles. According to the mass-balance concept, the rate of mass input is equal to the rate of mass output plus the rate of mass accumulation in a control volume. The accumulation in this model was caused by adsorption at the bubble surface.

Mass transfer is based on the classical film model. The film model (Nernst, 1904) was developed for a situation where mass transfer occurs across an interface between phases. It is assumed that the bulk solution is well mixed, and the resistance to mass transfer occurs only in a narrow region adjacent to the interface. The narrow region is regarded as a stagnant film. For example, a water solution flows past a pure gas surface. The flux of solute toward the interface from the bulk solution is proportional to the difference between the concentration of the solute in the bulk liquid ( $C_l$ ) and the concentration at the interface ( $C_{l,i}$ ), i.e. the driving force is  $(C_l - C_{l,i})$ . The ratio of the flux to the driving force is defined as a mass-transfer coefficient ( $k_l$ ), such that:

$$\text{Flux} = k_L (C_L - C_{L,i}) \quad (1)$$

The mass-transfer coefficient is a function of turbulence in the bulk solution and properties of the solution, such as viscosity and density.

### Early Mathematical Models for Adsorptive Bubble-Separation Processes

Foam Fractionation Models      Foam fractionation is a typical foaming process in bubble separation. Many surfactant solutions create foams during bubbling processes. If the surfactant concentration is sufficient, a stable foam layer can be generated on top of the bubbled solution. The fractionation apparatus consists of two portions: an aqueous column at the bottom and a foam column at the top. The foam can be easily removed from the top of the foam column. Past attempts at modeling continuous foam fractionation were developed for the foam column. The liquid column was assumed to be a column of infinite height. These models included two types of columns: single stage and multistage.

In single-stage models, no mass transfer was considered in the foam column. The solute surface excess at the surface of bubbles, which is the saturated adsorption per unit surface area ( $\Gamma$ ) was presumed to be constant within the entire foam column (Brunner and Lemlich, 1963; Leonard and

Lemlich, 1965; Valdes-Krieg et al., 1975; and Kato et al., 1977). Therefore, no effects of the aqueous or foam column heights were considered in these models.

Multi-stage models propose mass transfer within the foam column. The foam column height was described as a product of two parts: the number of transfer units, NTU, and the height of transfer units, HTU. The number of transfer units, which represents the difficulty in removing solute from the aqueous phase, can be calculated from the concentrations in the interstitial stream and at the bubble surface. The height of a transfer unit, which is related to the mass-transfer rate between the interstitial stream and the bubble surface, was determined by dividing the column height by the number of transfer units (Haas and Johnson, 1965; Banfield et al., 1965; Goldberg and Rubin, 1972). Since the interstitial stream may originate from the aqueous column, the feed solution, the reflux, and the bubble coalescence, these models reported variation in HTU values. The variation was caused by the number of variables involved and different assumptions.

Adsorption was considered as an important separation mechanism in both single stage and multistage models. If the adsorption at the bubble surface is assumed to be constant in a single-stage column, the surface excess can be determined independently based on surface tension and the

concentration of the solute in the aqueous column or in the feed solution. The surface excess does not appear to depend on the nature of the foam and has no relationship to the solute concentration in the interstitial liquid.

The linear-isotherm or Langmuir-isotherm adsorption equation (Goldberg, 1972; Jashnani and Lemlich, 1973; and Kato et al., 1977) indicates an equilibrium relationship between the solute concentrations in the interstitial liquid and the surface. However, the finite mass transfer rate in the interstitial liquid may prevent adsorption from reaching equilibrium. Goldberg (1972) created a non-uniform solute-concentration profile adjacent to the bubble surface. He assumed that the solute concentration in the liquid film was slightly reduced before reaching the high adsorption surface region. He utilized an average concentration in his model. Wilson et al. (1976) proposed a model that included a difference between the saturated and unsaturated surface excesses. In addition to diffusive mixing, the model contained many unknown parameters and required experimental support.

Solvent Sublation Models. Solvent sublation is a non-foaming separation process. In solvent sublation, an organic solvent layer floats on the top of the water column. When the enriched bubbles reach the solvent layer the

adsorbed solute dissolves into the solvent because of high solubility.

Several models for solvent sublation have been developed (Stachurski and Szeglowski, 1974; Lionel et al., 1981; Womack et al., 1982; Wilson and Valsaraj, 1982-1983; Valsaraj and Wilson, 1983; and Huang et al., 1983). Most of the models were written for semi-batch operations. The sublation aqueous column was modeled by dividing it into many sections and the solute concentration in each section was assumed to be uniform. Differential equations were developed to describe the solute concentration in each section with respect to time. Since the solute concentration changed with the column height, a finite-difference mass balance approach was taken.

These solvent-sublation models were based on the stagnant-film theory. Equilibrium adsorption on the bubble surface was described by the Langmuir isotherm. Due to the finite mass transfer between the bulk aqueous phase and the bubble surface, adsorption was in equilibrium with the interfacial concentration in the stagnant film, instead of with the bulk concentration. Unfortunately only a few experimental data were reported to support these models.

The adsorptive bubble-separation model in this paper utilizes a steady state mass balance rather than a finite-difference mass balance approach. The adsorptive bubble-



separation model is similar to the solvent sublation models with respect to adsorption, except that linear adsorption occurs in the adsorptive bubble-separation model rather than that depicted by the Langmuir isotherm.

### MATHEMATICAL MODEL

For mass transfer in the aqueous phase in a non-equilibrium process, the solute transfers from the bulk solution to the bubble surface over the whole column. Since the film theory is used to describe the mass transfer, resistances to mass transfer are confined to a thin stagnant film adjacent to the surface of the bubbles.

Due to the adsorption of the solute at the interface, it is assumed that another enriched surface film exists where the average concentration in the film is defined as the surface concentration,  $C_s$  (Fig. I-1). Obviously,  $C_s$  increases as the bubbles rise along the column.

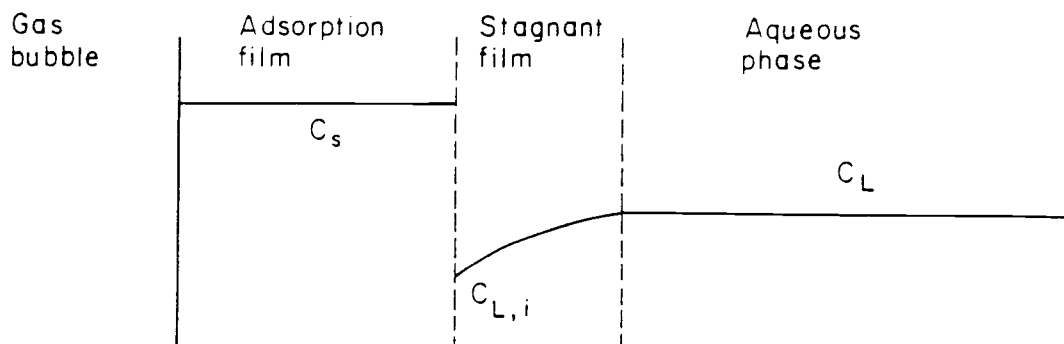


Figure I-1 Mass Transfer Profile for an Adsorptive Compound

Two mass-balance differential equations are applied. The control volume in the first mass-balance equation is a differential element in a bubbled aqueous column (Fig. I-2).

The concentration of solute in each differential volume is assumed to be well mixed and is uniform.

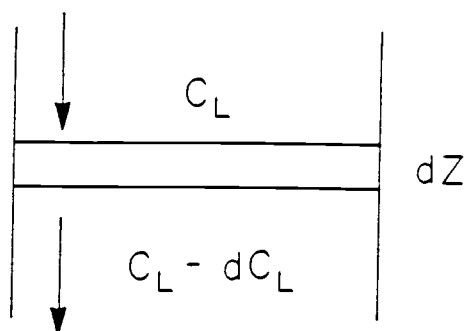


Figure I-2 Mass Balance in a Differential Element

The mass balance for the liquid phase is:

$$A \, dZ \, \frac{dC_L}{dt} = Q_w C_L - Q_w (C_L - dC_L) - k_L (C_L - C_{L,i}) S A \, dZ \quad (2)$$

where:  $A$  = column intercept area,  $\text{cm}^2$ ;  
 $Z$  = column height,  $\text{cm}$ ;  
 $C_L$  = concentration of solute in the bulk aqueous phase,  $\text{ml/min}$ ;  
 $t$  = time,  $\text{min}$   
 $Q_w$  = water flow rate,  $\text{ml/min}$ ;  
 $k_L$  = mass transfer coefficient,  $\text{cm/min}$ ;  
 $C_{L,i}$  = interfacial concentration at aqueous side,  $\text{ml/min}$ ; and

$S$  = specific interfacial area,  $\text{cm}^2/\text{cm}^3$ , the total bubbles' surface area per unit column volume.

At steady state,

$$dC_L/dt = 0.$$

By solving Equation 2 for  $Z$ , it becomes

$$\int_0^{Z_0} dZ = \frac{Q_w}{S A k_L} \int_{C_{out}}^{C_{in}} \frac{dC_L}{C_L - C_{L,i}} \quad (3)$$

where:  $Z_0$  = total height of the aqueous column, cm;  
 $C_{in}$  = influent concentrations of solute, mg/ml;  
 and  
 $C_{out}$  = effluent concentrations of solute, mg/ml.

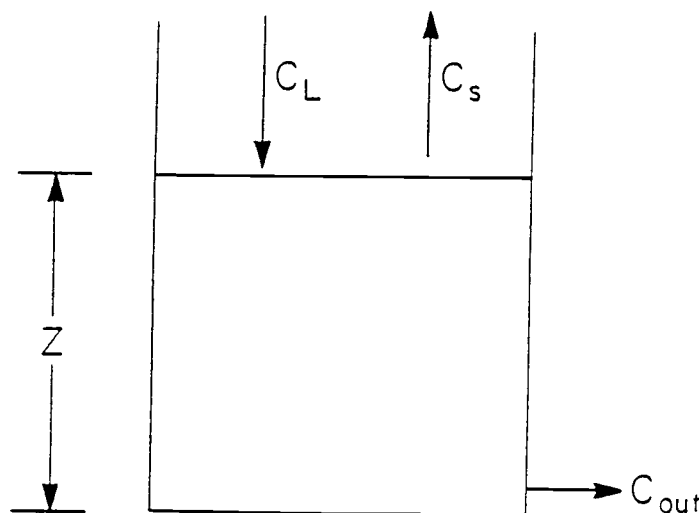


Figure I-3 Mass Balance in the Aqueous Column

The control volume in the second mass balance equation is taken from the bottom of the column to an arbitrary height in the column (Fig. I-3). At steady state, the second mass balance equation can be expressed as follows:

$$A \int \frac{dC_L}{dt} = Q_w C_L - Q_w C_{out} - \Gamma_s N_b S_b = 0 \quad (4)$$

where:  $\Gamma_s$  = enriched surface mass of solute per bubble surface area, mg/cm<sub>2</sub>;

$N_b$  = total number of bubbles generated per minute,  $N_b = Q_g/V_b$ ; and

$Q_g$  = gas flow rate, ml/min.

The change in bubble size in a short aqueous column is negligible. Assume that there is no bubble collapse and coalescence in the column, and all bubbles are spherical, so

$V_b$  = volume of a single bubble,  $V_b = 4 \pi r_b^3/3$ , cm<sup>3</sup>

$S_b$  = surface area of a single bubble,

$S_b = 4 \pi r_b^2$ , cm<sup>2</sup>; and

$r_b$  = radius of bubble, cm.

$\Gamma_s$  is the unsaturated adsorptive mass per unit bubble surface area relative to the bulk concentration. ( $\Gamma_s$  is proportional to the surface concentration ( $C_s$ ) in Figure I-1 and I-3.) It is different from the surface excess ( $\Gamma$ ) which is the saturated or equilibrium adsorptive mass per

unit area. In very dilute solutions, the surface excess is linearly related to the bulk solution concentration. In this case, assume that  $\Gamma_s$  is proportional to the interfacial concentration in the aqueous phase.

$$\Gamma_s = k C_{L,i} \quad (5)$$

where:  $k$  = adsorption constant, cm.

Substituting  $\Gamma_s$  from Equation 5 into Equation 4, then solving for  $C_{L,i}$ , yields

$$C_{L,i} = M (C_L - C_{out}) \quad (6)$$

where  $M$  is adsorptive separation factor, a mathematical substitute of  $r_b Q_w / (3 k Q_g)$ .

Then substituting Equation 6 into Equation 3, and integrating, gives:

$$Z_o = \frac{Q_w}{A S k_L (1 - M)} \ln [(1 - M) C_{in}/C_{out} + M] \quad (7)$$

Most factors in the model are measurable in the laboratory, such as the height of the aqueous column ( $Z_o$ ), the flow rates of gas and water ( $Q_g$  and  $Q_w$ , respectively), the concentrations of the solute in the influent and effluent ( $C_{in}$  and  $C_{out}$ ), and the average bubble radius ( $r_b$ ).

The specific interfacial area ( $S$ ) is calculated from the bubble rise velocity and the gas flow rate.

$$U_w = Q_w/A \quad (8)$$

$$U_b = 60 u - U_w \quad (9)$$

$$N_b = Q_g / (4 \pi r_b^3 / 3) \quad (10)$$

$$S = 4 \pi r_b^2 N_b / A U_b \quad (11)$$

where:  $U_w$  = water velocity relative to the column,  
cm/min;

$U_b$  = bubble rise velocity relative to the column,  
cm/min;

$u$  = bubble velocity relative to water, cm/sec;  
and

$N_b$  = bubble number generated per unit time, min<sup>-1</sup>.

In the range of Reynolds numbers of 0 to 10<sup>4</sup>, the velocity of rising bubbles in a liquid is given by Fair et al. (1968).

$$u = \frac{2}{9\mu} r_b^2 g \rho \left[ 1 + \frac{1}{4} \left( \frac{r_b \rho u}{2 \mu} \right)^{1/2} + \frac{0.34 \rho r_b u}{12 \mu} \right]^{-1} \quad (12)$$

where:  $g$  = gravitational constant, cm/sec<sup>2</sup>;

$\rho$  = density of the aqueous phase, g/ml; and

$\mu$  = viscosity of the aqueous phase, g/cm.sec.

Substituting S into Equation 7, the final expression of the mathematical model is

$$Z_o = \frac{U_b k M}{k_L (1 - M)} \ln \left[ (1 - M) \frac{C_{in}}{C_{out}} + M \right] \quad (13)$$

This model is only suited for dilute solutions and short column heights. The model includes the following assumptions:

1. At a given column height, the bulk solution is well mixed, and resistance to mass transfer occurs only in a narrow interfacial region in the water solution. The solute transfer rate in the water phase is proportional to the concentration in the bulk solution (film theory).
2. A hypothetical adsorption film at the bubble surface is proposed. The unsaturated excess of solute in the film is uniform and proportional to the interfacial concentration in the water phase. The unsaturated excess does not equilibrate with the concentration in the bulk solution, but will equilibrate with the interfacial concentration.
3. The model assumes steady state is achieved.
4. In the mass-balance equation, the solute concentration in each differential volume is uniform.
5. All bubbles are spherical and identical in the column. There is no bubble collapse and coalescence in the column.
6. The viscosity and density of the aqueous phase does not change as the solute concentration changes.



7. Equation 13 is used for the system in the range of Reynolds numbers of 0 to  $10^4$ . Equation 7 has no this limit.

## THEORETICAL RESULTS AND DISCUSSION

This model can be used to evaluate experimental data, using Equations 7 and 13. Based on Equation 11 and Equation 12, a method is provided to calculate the specific surface area using the bubble rise velocity. Equation 13 is the final expression. If the specific area can be measured by alternate methods, Equation 7 can be used directly.

Many factors are included in the mathematical model. However, there are only two unknown parameters that must be determined, the mass-transfer coefficient ( $k_L$ ) and the adsorption constant ( $k$ ). These two unknown parameters are not difficult to estimate from experimental data. Statistical methods, such as non-linear regression analyses, are commonly used for estimating parameters based on measurable data. All other factors are experimentally measurable.

In wastewater treatment processes, the most important information is the efficiency of solute removal from the aqueous column. If rearranged, Equation 13 can be expressed as

$$R = \frac{e^{Z_0 k_L (1-M)/(M u_b k)} - 1}{e^{Z_0 k_L (1-M)/(M u_b k)} - M} \quad 100\% \quad (14)$$

where:  $R$  = solute removal efficiency, %.

The test conditions given in Table I-1 were selected to demonstrate the model predictions.

Table I-1 Test Conditions for Theoretical Analyses

$\rho$	1	g/cm <sup>3</sup>	$Q_w$	10	ml/min
$\mu$	0.01	g/cm.sec	$Q_g$	5	ml/min
A	5	cm <sup>2</sup>	$r_b$	0.05	cm
$k_l$	0.1	cm/min*	k	0.01	cm

\* For simplification,  $k_l$  is assumed constant for different water flow rates.

The influence of column height, the mass-transfer coefficient and the adsorption constant on the solute removal efficiency is shown in Fig. I-4. Greater column height results in increased removal efficiency. However, the removal efficiency is not proportional to column height. As the maximum removal efficiency is reached, increased column height no longer influences removal efficiency.

The maximum removal efficiency is determined by the adsorption constant ( $k$ ). In Fig. I-4, when  $k$  increases from 0.01 to 0.05 cm, the maximum removal efficiency increases from 30% to 70%. As the bubbles rise in the countercurrent column, solute adsorption on the bubble surface increases. When adsorption reaches saturation, or the adsorption rate is equal to the desorption rate, accumulation ceases. Higher  $k$  values provide elevated levels of adsorption, so

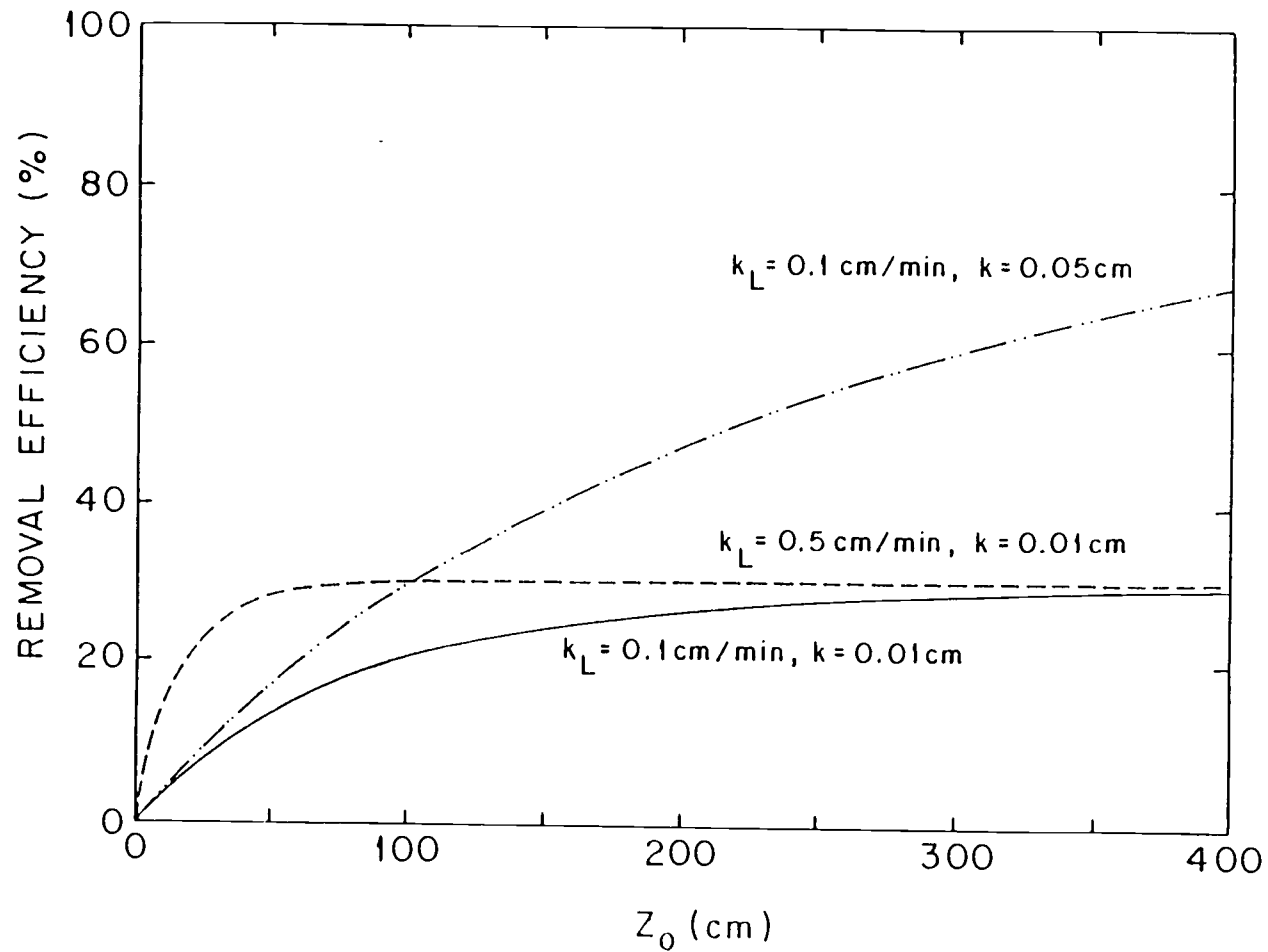


Figure I-4 The Influence of 1) Column Height; 2) Mass-Transfer Coefficient ( $k_L$ ) and 3) Adsorption Constant ( $k$ ) on Removal Efficiency at Test Conditions Given in Table I-1.

that an increased maximum removal efficiency will be obtained.

Fig. I-4 also shows that removal efficiency is related to the mass-transfer coefficient ( $k_L$ ). When  $k_L$  increases from 0.1 to 0.5 cm/min, removal nearly doubles at a column height of 50 cm. However, there is little difference in the maximum removal.

The adsorptive separation factor,  $M [ r_b Q_w / (3 k Q_g) ]$ , is an important component of this mathematical model.  $M$  depends on the ratio of the water flow rate to the gas flow rate. Regardless of the water flow rate, there is an insignificant change in solute removal efficiency for a given factor  $M$  or a given ratio of  $Q_w/Q_g$  (Fig. I-5). However, changes in  $M$  influence the removal efficiency significantly. When  $Q_w/Q_g$  increases from 0.5 to 2 or  $M$  increases from 0.83 to 3.3 in a 30-cm column, the removal efficiency increases 24% (from approximately 9% to 33%).

Increases in column height enhance the effect of  $M$  on the removal efficiency. In a 50-cm column, the increase in  $M$  from 0.83 to 3.3 provides a 32% increase in removal efficiency (from 13% to 45%). In a 30-cm column, this increase in  $M$  results in a 24% increase, which is 8% less.

Equation 14 reveals that the influence of the elements in the adsorptive separation factor ( $M$ ), such as  $r_b$ ,  $Q_w$ ,  $Q_g$

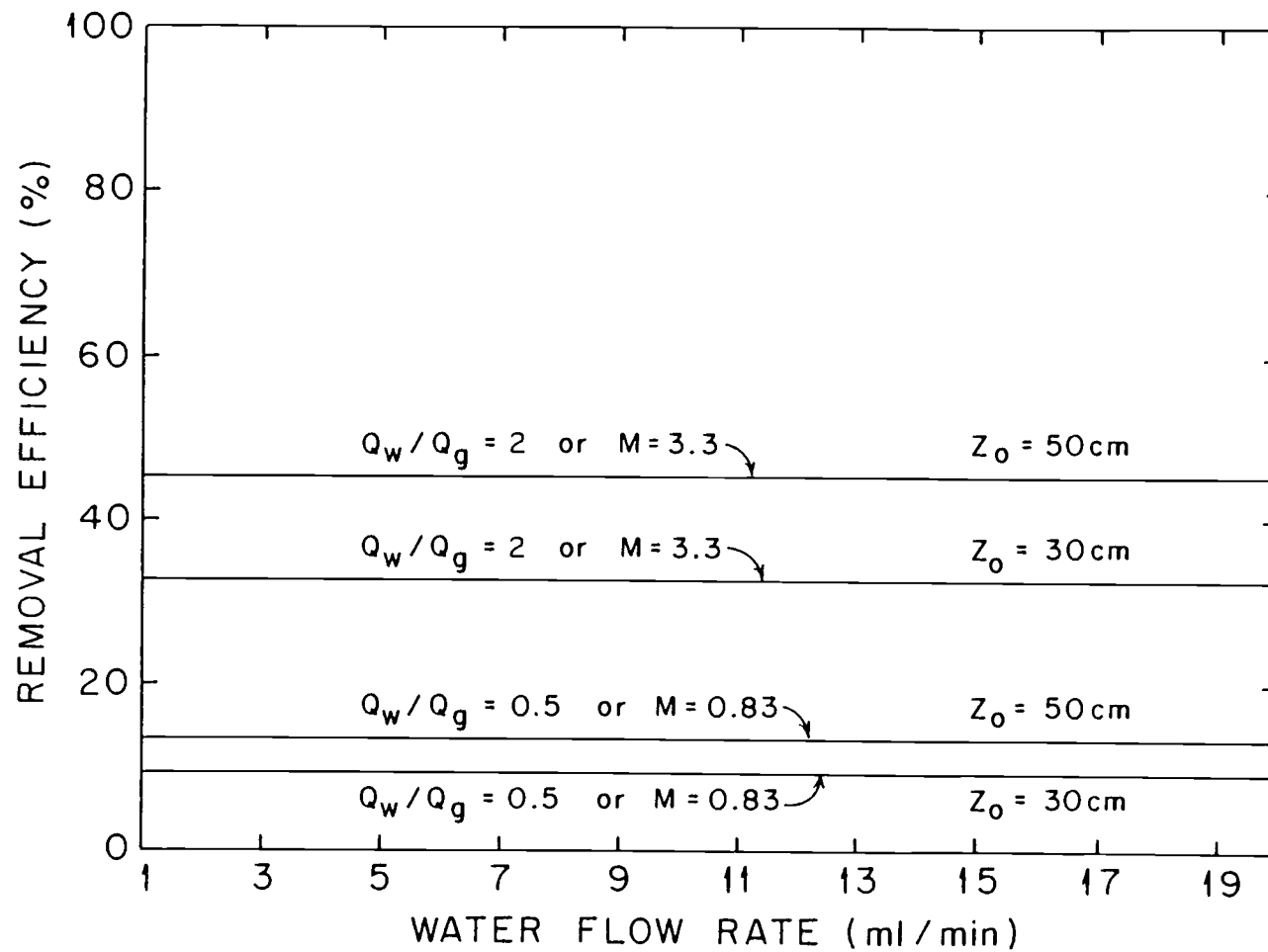


Figure I-5 The Effect of Bubble Adsorption Factor (M) on Removal Efficiency under Test Conditions Given in Table I-1.

are more significant than the column height ( $Z_0$ ). Actually, their ratio is the key factor in determining removal efficiency rather than their individual values.

The effects of water flow rate and column height on removal efficiency is shown in Fig. I-6. When water flow rates are increased to greater than 15 ml/min, or three times the gas flow rate, there is little effect of column height on removal efficiency. For the test conditions given in Table I-1, all removal efficiencies are less than 10% when the column heights are less than 60 cm and the water flow rate is larger than 15 ml/min.

At flow rates between 5 and 15 ml/min, removal efficiencies vary between 10% and 20% for column heights between 30 and 60 cm. Each 10-cm increase in column height results in less than a 5% increase in removal efficiency.

The curves representing column heights are steepest for water flow rates between 1 and 5 ml/min. The water flow rates in this range are less than the gas flow rate. Differences in removal efficiency between individual column heights tested are 5% to 10%.

The greatest influence of water flow rate on removal efficiency occurs for the 60 cm column height followed by the 50, 40 and 30 cm columns, respectively. In summary, lower water flow rates provide higher removal. When water flow rates are greater than three times the gas flow rate,

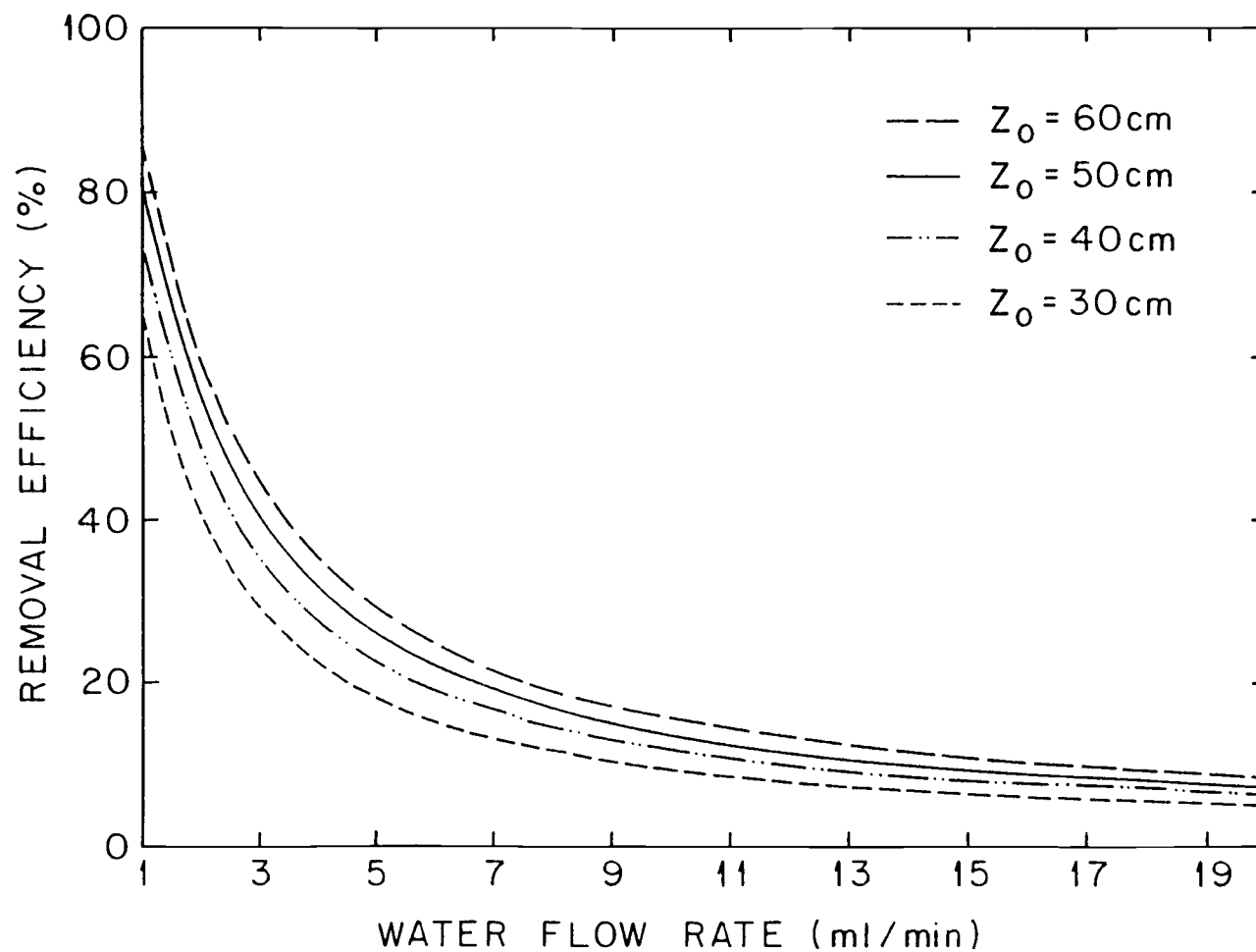


Figure I-6 The Effects of Water Flow Rate and Column Height on Removal Efficiency under Test Conditions Given in Table I-1.



the influence of further increase in water flow rate on removal is very small. The effect of column height on removal is less than that of water flow rate.

Gas flow rate should be another important element in the adsorptive separation factor. Since bubble size depends on the pore size of the bubble generator, larger pore sizes generate larger bubbles. However, it is noted that variation in gas flow rates also leads to changes in bubble size, even when the same generator pore size is used. Therefore, the influence of gas flow rate on removal efficiency is complex.

If the bubble size is kept constant by means of adjusting the bubble generator pore size while the gas flow rate is varied in the manner depicted in this test case, the effect caused only by the gas flow rate can be predicted. The effect of gas flow rate on removal under these conditions is showed in Fig. I-7. For a given bubble size and water flow rate, higher gas flow rates increase the removal. Because higher gas flow rates can produce more bubbles, a larger specific area is obtained. Subsequently, the adsorption increases, which, in turn, causes an increase in removal efficiency. At the given test conditions in Table I-1, when the gas flow rate increases from 1 ml/min to 20 ml/min, the removal efficiency increases approximately 40% for a 60-cm column. In contrast, the effect of column

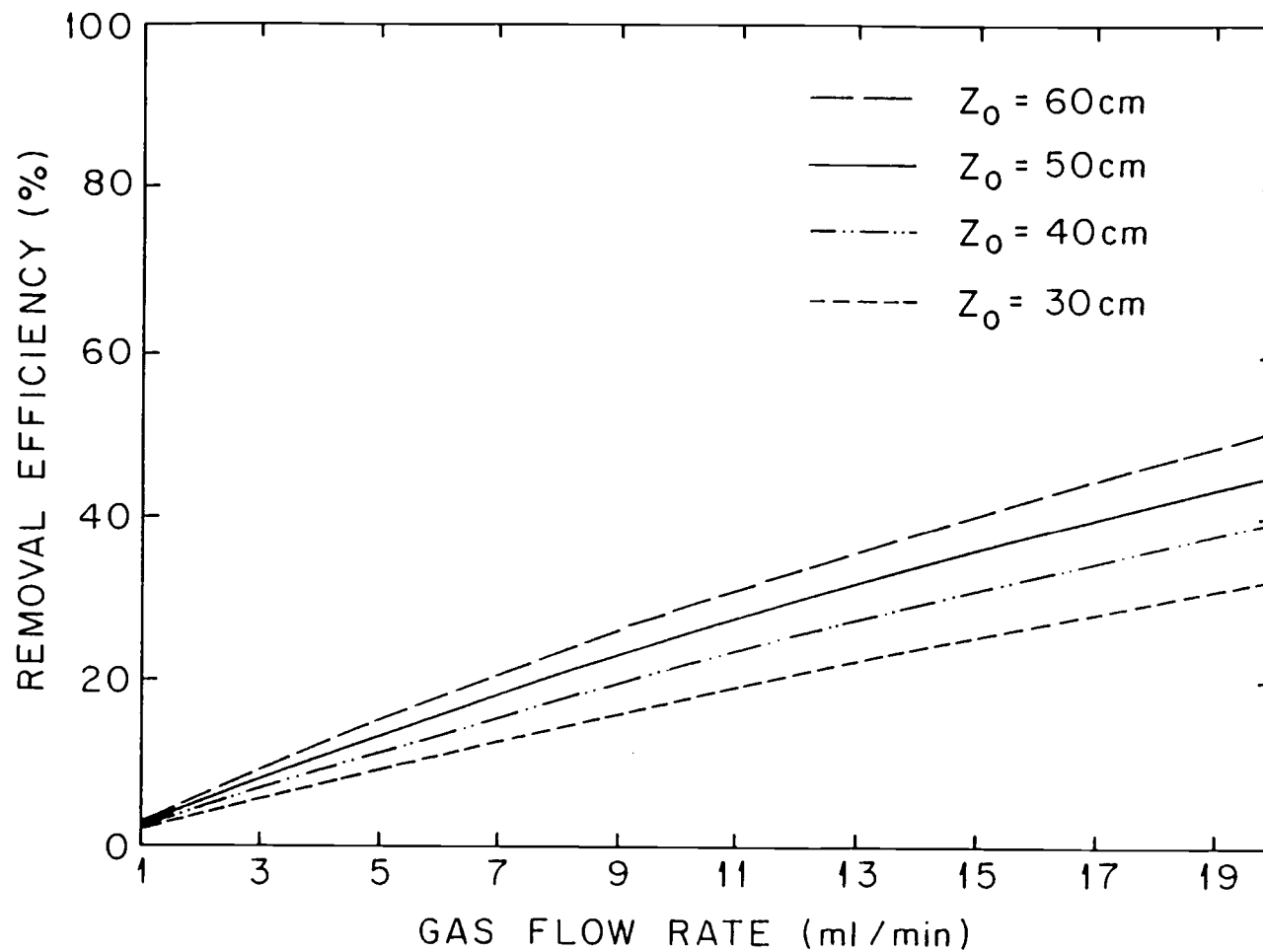


Figure I-7      The Effects of Column Height and Gas Flow Rate on Removal Efficiency under Test Conditions Given in Table I-1.

height on removal is not as significant as the effect of the gas flow rate. With each 10-cm increase in column height, the removal efficiencies increase only 2% at low gas flow rates, and 20% at 20 ml/min gas flow.

Bubble size has a greater impact on removal than water flow rate (Fig. I-8). As the bubble radius is reduced from 0.1 cm to 0.01 cm, removal percentages increase from approximately 10% to 100% at  $Q_w$  equal to 4.5 ml/min. It is not difficult to explain the influence of bubble size on removal. At a given gas flow rate, the smaller the bubble size, the greater the total bubble numbers produced. Smaller bubble sizes provide more surface area for adsorption. Moreover, small bubbles have slower rising velocities than larger bubbles (Fair et al. 1968). The change in bubble size causes a change in the specific surface area per unit aqueous phase. Both the bubble size and the specific area in the model vary simultaneously. Therefore, bubble size has a significant effect on solute removal.

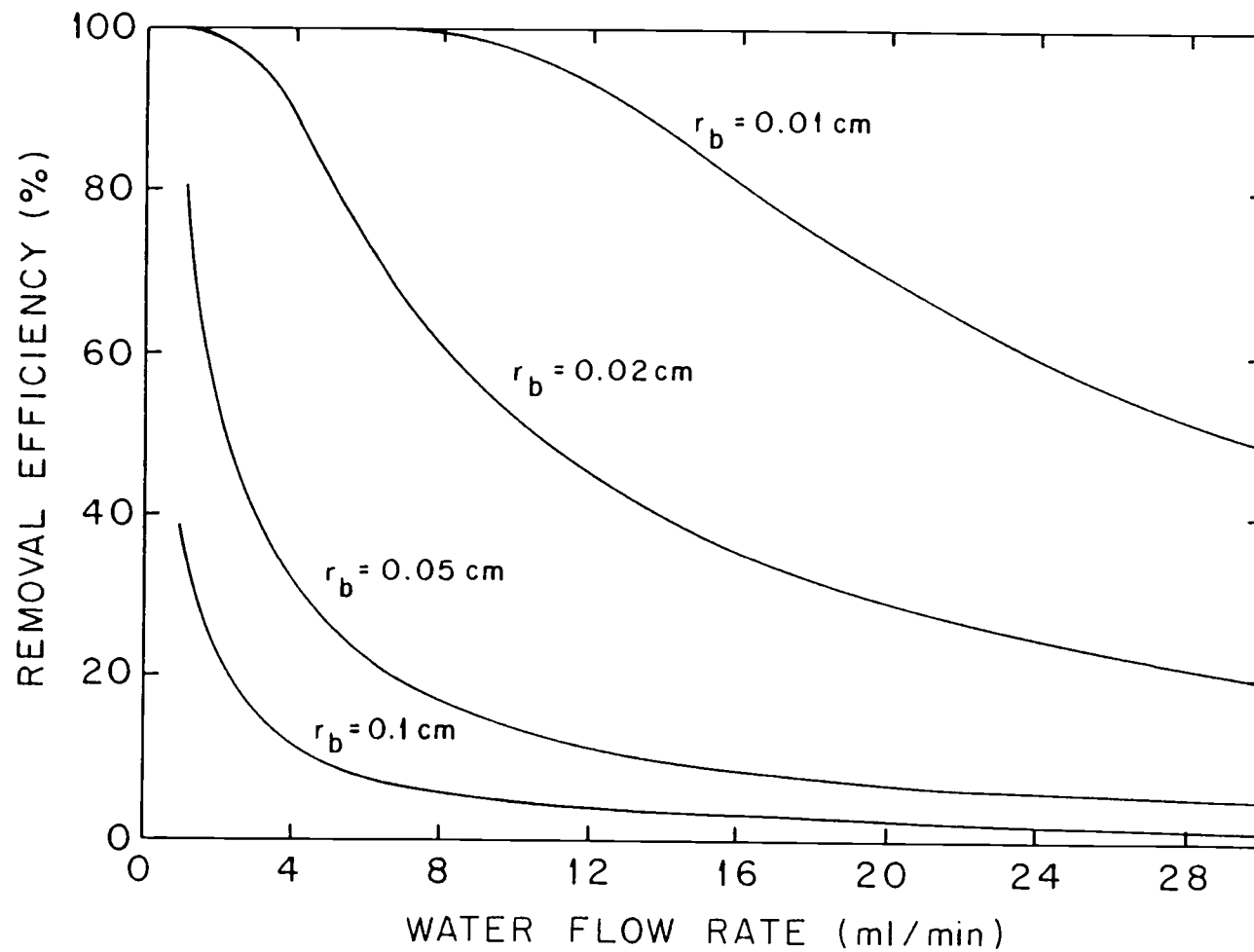


Figure I-8 The Effect of Water Flow Rates and Bubble Size on Removal Efficiency under Test Conditions Given in Table I-1.

## CONCLUSIONS

When gas bubbles pass through a water column containing an adsorptive solute, the column is not at equilibrium. The solute transfers from the bulk solution to the bubble surface before it adsorbs on the bubbles. Therefore, the adsorption rate of the solute is limited by the transfer rate in bulk solution.

A mathematical model was developed to describe the behavior of the adsorptive solute in the bubbling process. Stagnant film theory and mass balance equations were used. A linear relationship was assumed between adsorption on the bubbles and interfacial concentrations in solution. Countercurrent operations simplified the mass balance approach. The model can be expressed in three forms (Equations 7, 13 and 14). The model predicted that the adsorptive separation factor ( $M$ ) is a critical and effective factor in designing adsorptive bubble-separation processes. Larger values of  $M$  produces higher removal efficiencies. Within the adsorptive factor, bubble size is an important element influencing removal efficiency. Both water and gas flow rates can change the removal efficiency, but their ratio is the key factor. Provided that the ratio of  $Q_w/Q_g$  is kept constant, variation in water flow rate does not influence the removal significantly. The model also

demonstrated that increases in column height can increase removal efficiencies. However, the maximum removal efficiency depends on the adsorption constant ( $k$ ).

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## Chapter II

### **A Design for Adsorptive Bubble-Separation Processes: II Experimental Verification**

#### **Abstract**

An adsorptive bubble-separation experiment, solvent sublation, was used to test a mathematical model developed in Chapter I. Nitrogen was bubbled through an aqueous solution containing an adsorptive solute, Triton-X100. An organic solvent, ethyl acetate, floated at the top of the water column, dissolved and removed the Triton-X100 from the bubble surface. The removal efficiencies of the Triton-X100 from the aqueous solution were measured at various column heights, influent concentration and water flow rates.

Experimental results showed that the removal efficiencies increased with water column heights. Five water column heights calculated from the mathematical model were compared to five observed column heights at 30, 40, 50, 60 and 100 cm with 13.0, 5.5 and 3.0 ml/min water flow rates, respectively. The predicted column heights agreed with the observed heights. The experimental data also showed that the influent concentration did not affect the removal efficiency as the model prediction.

Based on the model and the experimental data, adsorption constant and mass transfer coefficients were estimated. The surface excess of Triton-X100 obtained from the adsorption constant ranged from  $0.75 \text{ E-}10$  to  $7.5 \text{ E-}10 \text{ g mole/cm}^2$ . These values were consistent with values presented by previous researchers ( $2.6 \text{ E-}10$  to  $2.8 \text{ E-}10 \text{ g mole/cm}^2$ ). The mass-transfer coefficients were  $0.05\text{-}0.06 \text{ cm/min}$ , which fell within the accepted range ( $10^{-4}$  to  $10^{-1}$ ) for gas/liquid contacting devices. As a result, the mathematical model is a good predictive tool for adsorptive bubble-separation processes.

## INTRODUCTION

A conceptual and mathematical model (Tang and Woods, 19xx) was evaluated for use in adsorptive bubble-separation processes. The mathematical model suggested that it is possible to calculate solute removal efficiency from column height, bubble size, water flow rate and gas flow rate. To test the reliability of the mathematical model, an appropriate laboratory bubble-separation process was required. The variables in the model, such as column height, can be obtained either by measurement in the laboratory or predicted from models with other given data. The purpose of this research, therefore, was to validate the mathematical model. This was done by comparing the calculated column heights with the observed column heights.

Not all adsorptive bubble-separation processes are suitable to be used in laboratory tests. Adsorptive bubble-separation processes can be classified into foaming and non-foaming types (Karger et al., 1967).

In foaming processes, a foam layer exists at the top of the column, provided the concentration of the surface-active solute is sufficient to support a stable foam layer. The foam layer, with the solute attached to its surface, is skimmed off the top of the column. Foam fractionation is a typical foaming process (Grieves, 1975).

Generally, the foam layer includes not only the surface of the ascending bubbles, but the interstitial stream. Collapse and coalescence of bubbles in the foam occurs frequently, changing the condition of the foam layer. A portion of the interstitial liquid and the liquid produced by the collapsed foam eventually returns to the aqueous phase. As a result, it is difficult to accurately measure the separation efficiency.

In non-foaming processes, the adsorptive solute concentration is too small to support a foam layer. When the bubbles carry the solute to the top of the aqueous column, the upper portion of the aqueous column may be enriched with the adsorptive solute. Solute separation from the aqueous solution can occur by two methods: bubble fractionation or solvent sublation. In bubble fractionation, the enriched aqueous portion flows directly out at the column top (Kubota et al., 1984). In solvent sublation, an immiscible solvent layer is floated at the top of the aqueous column, collecting the enriched solute from the bubble surface (Sebba, 1962).

The liquid overflowing during bubble fractionation contains not only the solute adsorbed on the bubbles, but the aqueous solution surrounding the bubbles. Therefore, bubble fractionation can result in higher removal

efficiencies than those due only to the removal by rising bubbles.

The solvent sublation system consists of two immiscible phases and gas bubbles in a column. Usually, the lower and larger portion of the column is an aqueous phase, while the upper smaller portion is a less dense organic phase floating on top of the aqueous column. The solvent is deliberately chosen so that the solubility of the solute in the solvent phase is much greater than its solubility in the aqueous phase. When the ascending bubbles reach the solvent phase, they release the adsorbed mass into the solvent. Therefore, solvent sublation is an ideal experimental method to collect solute from the bubble surface. Since solvent sublation is able to quantitatively separate the adsorbed solute mass on the bubble surface from the water solution, it was chosen as the appropriate experimental method to test the model.

Although solvent sublation is also able to remove volatile solutes, or a solute with both adsorptive and volatile properties, this research will focus on the sublation of a non-volatile adsorptive solute.

## EXPERIMENTAL METHODS

### Reactor Description

The solvent sublation apparatus consisted of a glass column fitted with several glass and Teflon ports. Five columns, 2.54 cm (1 inch) in diameter, were tested at heights of 30, 40, 50, 60 and 100 cm. Influent and effluent ports were provided for the water and solvent. The location of the upper water port depended on the height of the water columns. Another water port was located at the bottom of the water column. Two solvent ports were fitted above the water column, so that the solvent would not mix with the water solution and the contact area between solvent and water was minimized. Medium fritted glass used as a gas diffuser was placed at the bottom of each column. In order to prevent the solvent from evaporating on the top of the column, the gas travelled through a solvent saturator before entering the gas diffuser.

### Experimental Procedures

A continuous countercurrent operation was conducted. The water solution entered the column at the designated height and flowed downward. The effluent samples were taken

from the port near the frit located at the bottom of the column. The solvent flowed into the column at the top near the water phase, then overflowed along the highest port. A schematic of the reactor is shown in Fig. II-1.

Ethyl acetate (HPLC Grade) was used as the organic solvent. It is a non-toxic solvent suitable to be used for the non-ionic surfactant. Nitrogen was used as the insoluble gas.

A surfactant, Triton-X100<sup>1</sup>, was chosen as the adsorptive solute in a dilute water solution. The initial aqueous solution of Triton-X100 was prepared by adding a stock solution with 1 g/l Triton-X100 to distilled water which had been previously saturated with ethyl acetate. The influent concentration of Triton-X100 ranged from 0.007 mg/ml to 0.07 mg/ml.

The absorbance of Triton-X100 was measured at 276 nm by a Heath Model EU-721-11 spectrophotometer. The slit width was 300 microns. A silica rectangular cell with 10 mm light path was used.

Since the concentration of Triton-X100 in the water was too low to be measured by ultraviolet spectrophotometry, the water samples required further concentration. For water

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<sup>1</sup> Triton-X100 is a non-ionic surfactant produced by Rohm and Haas, Philadelphia, PA. It is p-(1,1,3,3-tetra-methyl-butyl) phenyl-polyoxy-ethylene ethanol with an average ethylene oxide chain length of 9-10 units. The average molecular weight is 628.

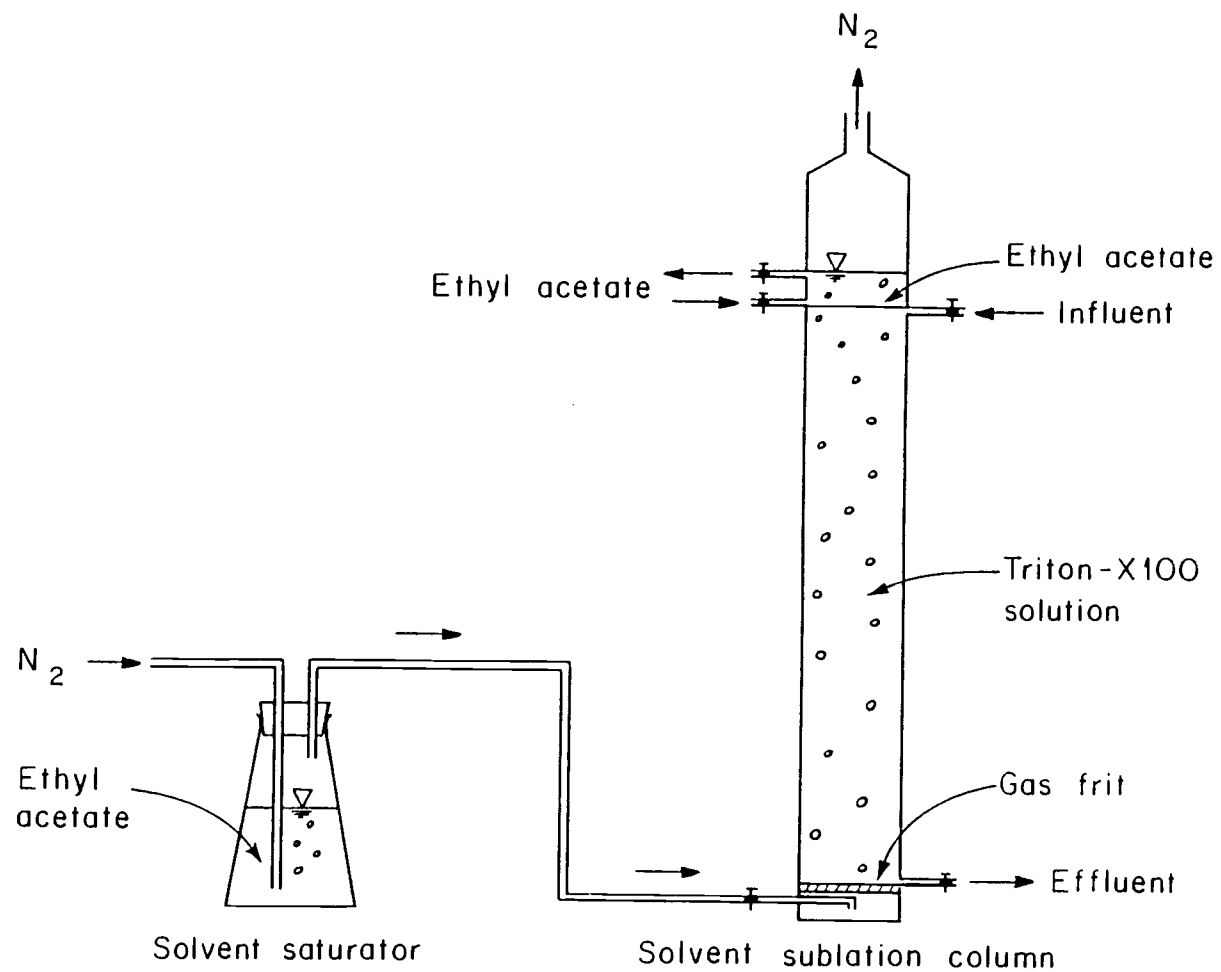


Figure II-1 Schematic of the Solvent Sublimation Process.



samples with concentrations higher than 0.01 mg/ml, the procedure involved evaporating 25-ml samples to 2 to 3 ml on a hot plate, then bringing the sample to a final volume of 5-ml in a volumetric flask after cooling to room temperature. The absorbance of Triton-X100 was read from the 5-ml concentrated solution. The correlation coefficient for the standard curve was 0.9999. For aqueous concentrations lower than 0.01 mg/ml, 100-ml aqueous samples were extracted with 5-ml ethyl acetate. The absorbance of the ethyl acetate extract was compared to the standard curve in order to determine the concentration in the water phase. The correlation coefficient for the standard curve was 0.9987.

A volumetric flask and a stop watch were used to measure the water flow rates. The water flow rates were 3.0 to 13.0  $\pm 0.2$  ml/min, and the nitrogen flow rate was 6.4  $\pm 0.2$  ml/min. The nitrogen flow rate was adjusted with a needle valve and soap film flowmeter. Both the nitrogen and water flow rates were monitored frequently during the sublation process.

The mean bubble radius, 0.0294 cm, was calculated from 769 bubbles appearing in three photographs taken at  $Q_g$  equal to 6.4 ml/min and  $C_{in}$  equal to 0.070 mg/ml. The sampling distribution of the bubble size was approximately normal, and the relative standard deviation was 29%. The effect of

water head on the bubble size was negligible if the column was not higher than 100 cm (Appendix A).

The water solution viscosity was obtained by means of a Cannon-Fenske viscometer. Water density was obtained by dividing the sample weight by the volume. All operations were run at room temperature,  $23 \pm 1.0$  °C. The calculation of specific interfacial area (S) was described in the previous paper (Tang and Woods, 19xx).

In the model, the value of the adsorption constant (k) and mass-transfer coefficient ( $k_L$ ) were determined by a non-linear least squares method, ZXSSQ (International Mathematics and Statistics Libraries, 1976). This is a modified Levenberg-Marquardt algorithm (Levenberg, 1944 and Marquardt, 1963) for finding the minimum sum of squares for M functions with N variables.

## EXPERIMENTAL RESULTS

Results of the sublation experiments are shown in Fig. II-2. Fig. II-2a, II-2b, and II-2c are comparisons of the calculated column heights with the observed column heights at  $Q_w = 13.0, 5.5$  and  $3.0$  ml/min, respectively. The influent Triton-X100 concentration was  $0.07 \pm 0.005$  mg/ml.

Values for the adsorption constant ( $k$ ) and the mass-transfer coefficient ( $k_L$ ) at  $Q_w$  equal to  $13.0$  ml/min were determined simultaneously based on the data presented in Figure II-2a. A non-linear least squares statistical program (Appendix B) was written in Fortran language. Fifteen independent sets of data were used to develop fifteen equations with two unknowns ( $k$  and  $k_L$ ) based on the mathematical model. The diagonal line in Fig. II-2a indicates an ideal situation where all the calculated column heights were equal to the observed column heights. The data in Fig. II-2a show that the observed column heights from the experiments are almost identical to the calculated column heights.

Fig. II-2b and II-2c depict alternative water flow rates. Since the adsorption constant depends on the properties of the solute only, changes in water flow rate will not affect adsorption behavior. Therefore, the value of  $k$ , which was determined at  $Q_w$  equal to  $13$  ml/min, can be

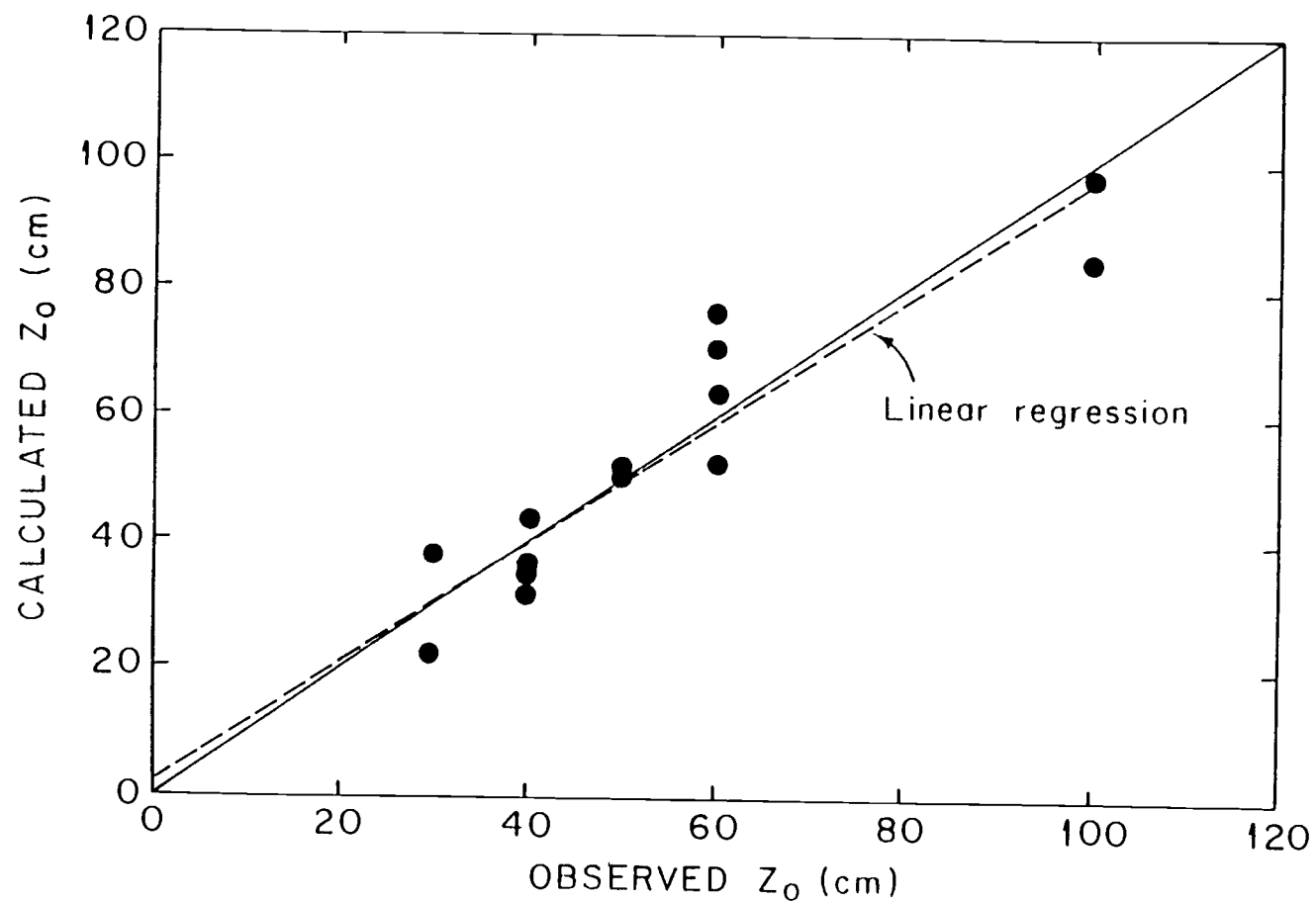


Figure II-2a Comparison of Calculated Column Heights with Observed Column Heights at  $Q_w$  Equal to 13.0 ml/min. The Estimated  $k$  is 0.006513 cm, and  $k_L$  is 0.6054 cm/min.

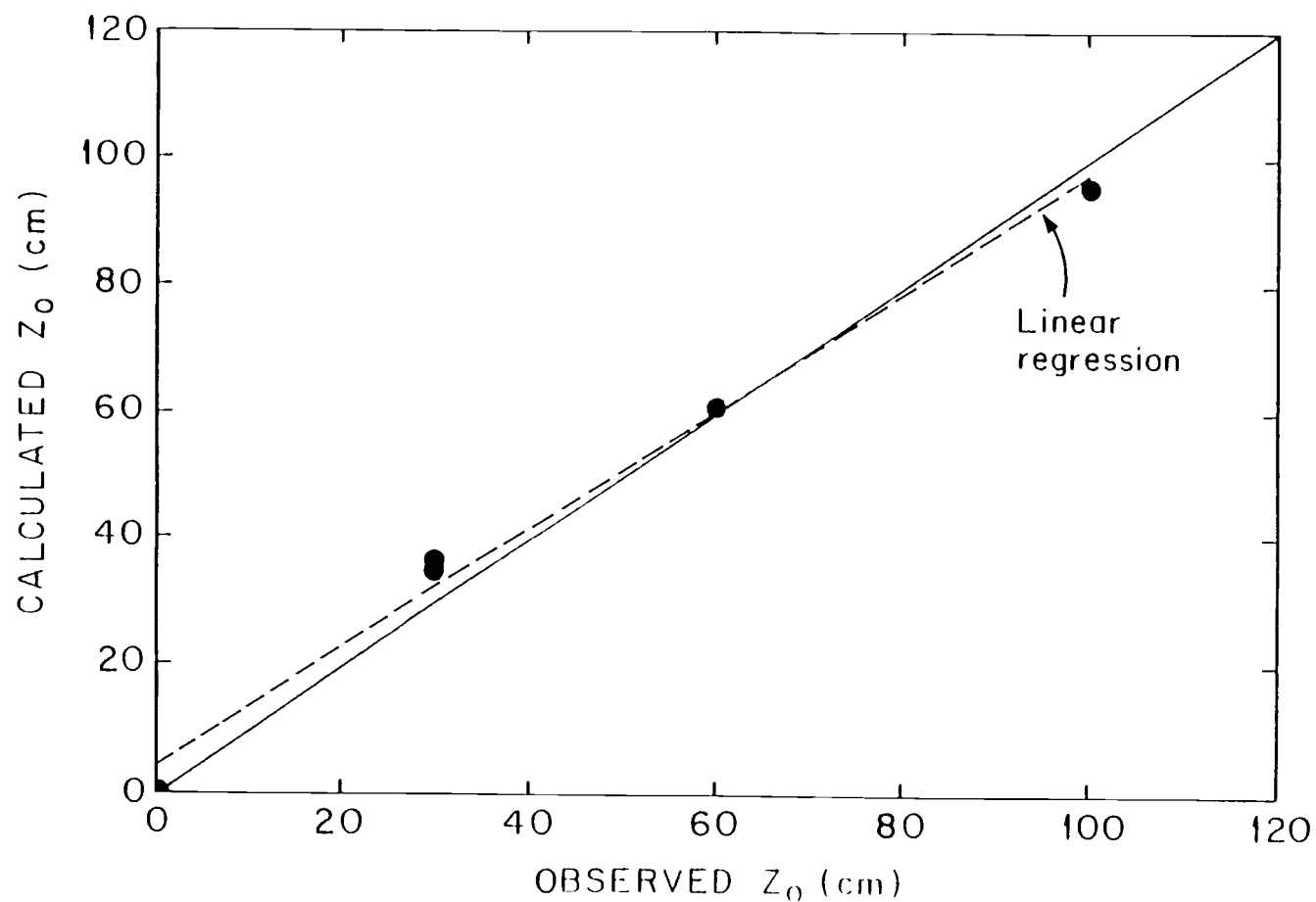


Figure II-2b      Comparison of Calculated Column Heights with Observed Column Heights at  $Q_w$  Equal to 5.5 ml/min. The Estimated  $k$  is 0.006513 cm, and  $k_L$  is 0.5417 cm/min.

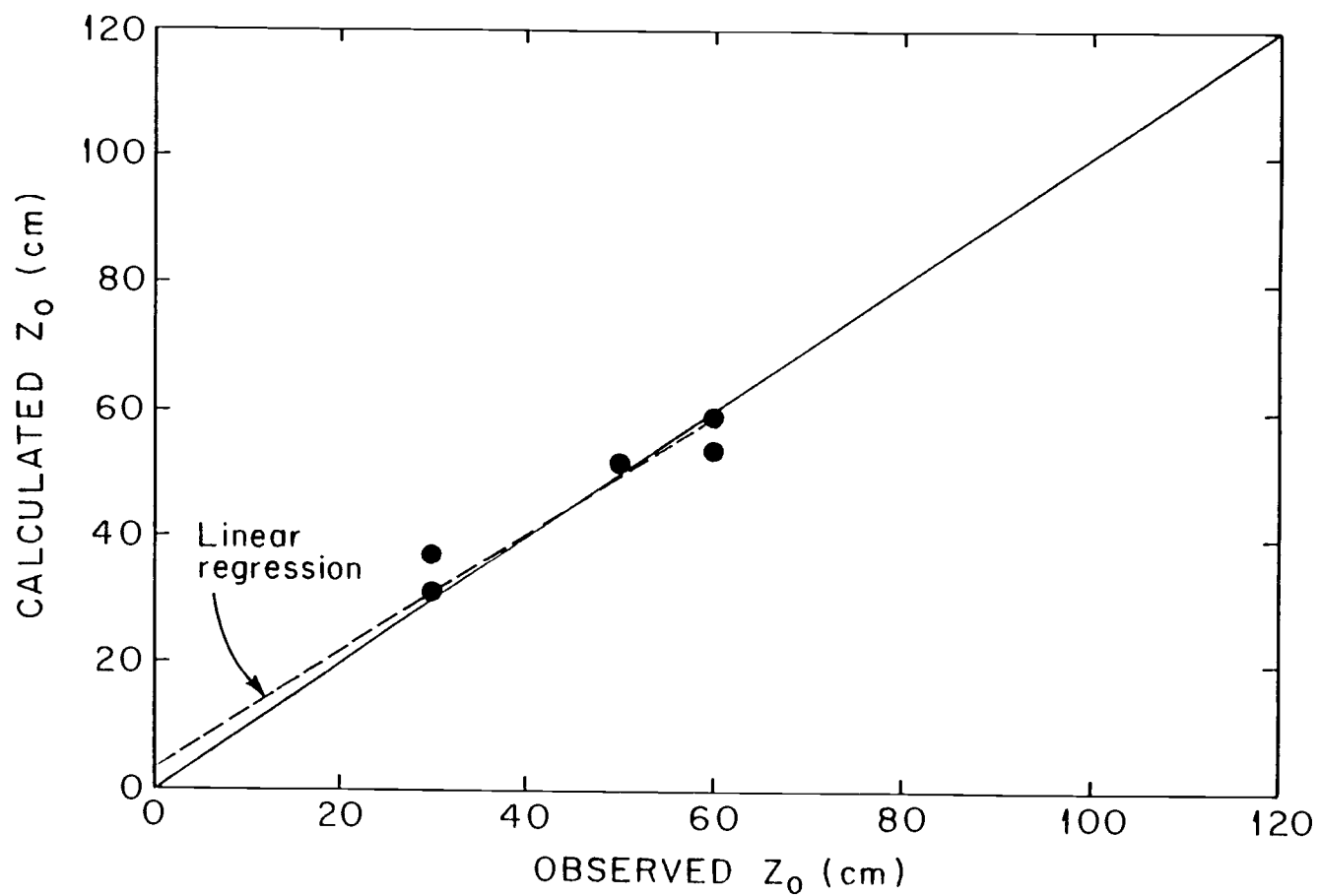


Figure II-2c      Comparison of Calculated Column Heights with Observed Column Heights at  $Q_w$  Equal to 3.0 ml/min. The Estimated  $k$  is 0.006513 cm, and  $k_L$  is 0.5041 cm/min.

used at both  $Q_w$  equal to 5.5 ml/min and  $Q_w$  equal to 3.0 ml/min. Only mass-transfer coefficients require determination for the latter two flow rates. The same statistical method as that used for  $Q_w$  equal to 13 ml/min was employed to determine mass-transfer coefficients at the other two flow rates. Table II-1 summarizes the estimated values of  $k$  and  $k_L$ . Fig. II-2b and II-2c show that the calculated column heights compare favorably with the observed heights.

Table II-1      The Estimated Adsorption Constant ( $k$ )  
and Mass-Transfer Coefficient ( $k_L$ )

$Q_w$ ml/min	$k$ cm	$k_L$ cm/min
13.0	0.006513	0.06054
5.5		0.05417
3.0		0.05041

Linear regression results based on the experimental data at varying water flow rates and column heights is shown in Table II-2. The regression coefficients for the three regression lines are close to 1.0. The average correlation coefficient was 0.98.

Table II-2 Column Height Regression

Flow rate ml/min	Number of Observation	Slope	Intercept	Correlation Coefficient
13.0 <sup>1</sup>	15	0.95	2.10	0.9475
5.5 <sup>2</sup>	5	0.93	4.58	0.9954
3.0 <sup>3</sup>	6	0.93	3.40	0.9834

1. Figure II-2a  
3. Figure II-2c

2. Figure II-2b

The model predicted that variations in the influent concentration would not affect removal. In other words, if all other factors in the model are kept constant, the ratio between influent and effluent concentrations will not be affected by changes in influent concentration. During the laboratory experiments, no significant influent concentration effects were found in removal at the given column heights and water flow rates (Fig. II-3). As the influent concentrations increased from 0.007 mg/ml to 0.070 mg/ml, effluent concentrations also increased proportionally. Therefore, removal was independent of influent concentration within this concentration range.



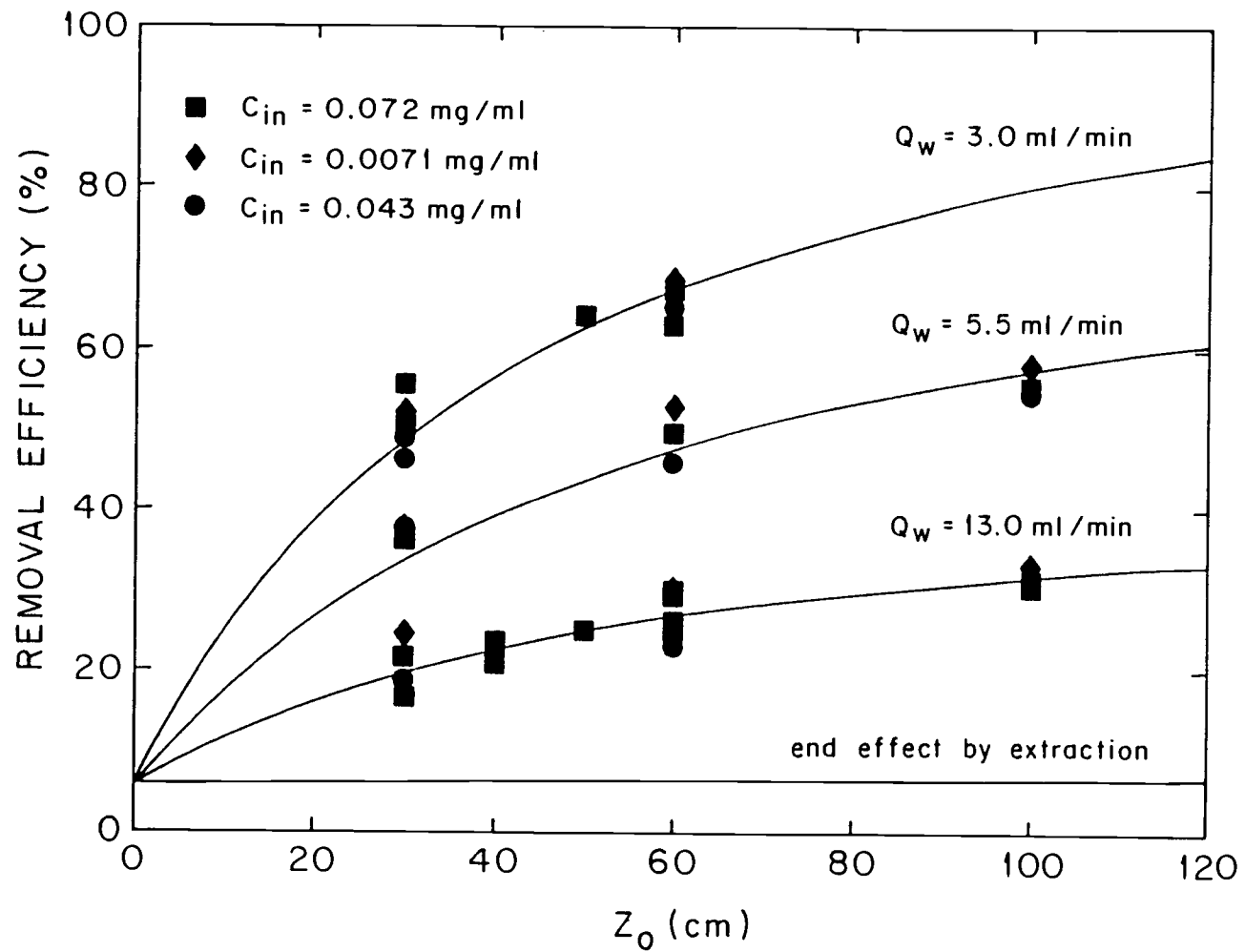


Figure II-3 The Effect of Influent Concentration on Removal Efficiency.

## DISCUSSION

### Adsorption Effects on the Column Wall

The effect of Triton-X100 adsorption on the glass wall was insignificant over the course of a steady state experiment. Although adsorption on the glass wall is significant at the beginning of the sublation process, its rate declines with time. After approximately one hour, adsorption on the glass wall slows because of near saturated conditions. In continuous flow sublation tests, all samples were taken at steady state, which was realized after one hour or more in a 30-cm water column. Taller water columns require periods in excess of one hour to reach equilibrium. Samples from the effluent in the 30-cm water column were taken within one hour during each run; standard deviations for the output concentration were less than 10%. Most standard deviations, in fact, were less than 2%. These small standard deviations indicated that steady state was reached, and that adsorption on the glass wall was negligible.

### The End Effect on $Z_0$

In Fig. II-2, the slopes of the three regression lines are slightly less than 1.00, and the intercepts slightly more than 0.00. This result can be explained by the end effect occurring at the bottom of the column. A certain amount of Triton-X100 adsorbs immediately on the bubbles when they first form from the frit. The removal rate of Triton-X100 from the water solution at the bottom appears to be slightly higher than the rate at other positions in the column. According to the relationship of the ratio  $C_{in}/C_{out}$  to the column height ( $Z_0$ ), the additional removal that occurs at initiation of the bubbling process requires a short hypothetical column height to be incorporated into the model calculation. Therefore, the calculated height becomes a little larger than the observed experimental height at low  $Z_0$  values.

The end effect at the top of the column is due to extraction of the solute from the water phase. Extraction occurs due to the contact between the aqueous phase and solvent phase at the top of the column. Extraction was determined by running control experiments with similar water flow rates but without bubbling. The average extraction removal efficiency in the control experiments was 6.35%. This removal was deducted from the influent concentration in

calculations of column height and sublation removal efficiencies.

### Influent Concentration

The adsorption assumption,  $\Gamma_s = k C_{L,i}$ , is valid for dilute solutions and infers that nonlinear adsorption is negligible in such dilute concentration ranges. Therefore, the influent concentration must be within a certain dilute range for use of this model.

The slightly lower value of  $Z_{obs}$  in relation to  $Z_{calc}$  found for taller columns may be caused by nonlinear adsorption. As the column height increases, the interfacial concentration ( $C_{L,i}$ ) increases at the top of the column. As  $C_{L,i}$  approaches  $C_{in}$ ,  $\Gamma_s$  may be less than  $(k C_{L,i})$  at the top of taller columns. Therefore, the removal efficiencies in taller columns may lower than the predictions, i.e. the calculated column heights may higher than the observed heights. This also accounts for the fact that the slopes in Fig. II-2 are less than 1.00.

### Evaluation of k

Surface excess ( $\Gamma$ ) is an equilibrium adsorption character expressed as mass per unit area ( $\text{mg}/\text{cm}^2$ ). The

surface excess can be determined by Gibbs adsorption equation (Gladstone, 1946).

$$\Gamma = - \frac{1}{RT} \frac{d \delta}{d(\ln C_L)} \quad (1)$$

Where:  $\Gamma$  = surface excess, mg/cm<sup>2</sup>;  
 $R$  = gas constant, dyne cm/mg K;  
 $T$  = absolute temperature, K;  
 $\delta$  = surface tension of the solution, dyne/cm;  
 and  
 $C_L$  = concentration of adsorptive solute in liquid phase, mg/ml.

Jashnani and Lemlich have investigated the surface excess of Triton-X100 with the Gibbs equation (Jashnani and Lemlich, 1973). Moreover, Lemlich and his colleagues have determined the surface excess by means of foam fractionation (Lemlich, 1968; Fanlo and Lemlich, 1965; Leonard and Lemlich, 1965).

The estimated adsorption constant ( $k$ ) is related to the surface excess. In a bubble separation system, adsorption equilibrium will be reached as the bubbles rise to a certain height. Beyond this threshold, no mass transfer occurs. In Fig. II-3, the model lines tend to be horizontal when equilibrium is reached. Consequently, the solute stops transferring from the bulk solution to the bubble surface, and  $C_{L,i} = C_L = C_{in}$ . The equilibrium enriched mass or surface

excess ( $\Gamma$ ) will be proportional to  $C_{in}$  based on the adsorption assumption in the model.

$$\Gamma = k C_{in}. \quad (2)$$

Table II-3 shows a comparison of the calculated  $\Gamma$  based on an estimate of  $k$  and previously published values. The two values are approximately equal. This fact strengthens the validity of the mathematical model.

Table II-3 Surface Excess Comparisons

Sources	Surface Excess g mole/cm <sup>2</sup>	Concentration of Triton-X100, mg/ml
Gibbs Equation	2.67 E-10*	0.043~0.26
Foam Fractionation	2.7 E-10** 2.8 E-10***	0.314
Calculated from $k$	0.75~7.5 E-10	0.007~0.071

\* Jashnani and Lemlich, 1973.

\*\* Fanlo and Lemlich, 1965; Leonard and Lemlich, 1965.

\*\*\* Shih and Lemlich, 1967.

The surface excess calculated from  $k$  brackets the range of published values. Two possible explanations are: 1) different concentration ranges were used in the published data, and 2) the solvent on the top of the column is not absolutely immiscible. The solvent dissolves in the aqueous phase and adsorbs on the bubble surface. The adsorption of the solvent changes the surface properties of the bubble.

As a result, more Triton-X100 adsorbs on the bubble surface. This may explain the higher surface excesses observed in this research.

#### Evaluation of $k_l$

The published values for mass-transfer coefficients have a large range, depending on the compounds and the systems. Typically,  $k_l$  value ranges from  $10^{-4}$  to  $10^{-1}$  cm/min in common gas-liquid contacting devices for volatile compounds. (This is in contrast with  $k_l$  values reported in natural water systems - lakes, rivers and oceans - which range from  $10^{-7}$  to  $10^{-5}$  cm/min for mass transfer of low-molecular-weight organic compounds.) The estimated  $k_l$  from the model is  $10^{-2}$  cm/min, which falls within the currently accepted range for gas/liquid contacting devices.

The estimated  $k_l$  decreases with lower water flow rates. When the water flow rate is reduced, the subsequent reduction in turbulence causes a lower mass-transfer rate. Research on the correlation between mass-transfer coefficients and water flow rates will be discussed in Chapter III.

## CONCLUSIONS

The following conclusions can be drawn:

1. Predictions from the model agree with the data obtained by solvent sublation experiments with various column heights, water flow rates and influent concentrations.
2. The removal efficiency of adsorptive compounds in dilute solutions is dependent on column height and water flow rate, but independent of influent concentration.
3. The adsorption constants and mass-transfer coefficients determined by fitting the model to experimental data fall within previous published ranges.
4. Solvent sublation provides a good method to test the adsorptive bubble-separation mathematical model.



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### Chapter III

## **The Influence of Liquid Flow Rate on Mass Transfer in an Adsorptive Bubble-Separation Process**

### **Abstract**

Mass transfer was evaluated in a countercurrent adsorptive bubble-separation process. In this process, the adsorptive solute, Triton-X100, was transferred from an aqueous solution to the surface of the bubbles. As the aqueous solution flowed downwards, the bubbles rose to top of the solution column where the solute was dissolved into a floating organic solvent. When gas flow rate held constant, the solute transfer rate was affected by the aqueous flow rate.

The effects of gas flow rate and water flow rate on solute removal from an aqueous solution were tested in a 60-cm countercurrent column. Removal efficiency increased as expected with increasing gas flow rates and decreasing water flow rates.

Mass-transfer coefficients were determined at four water flow rates, 3.0, 5.5, 8.0 and 13.0 ml/min, respectively, while other experimental conditions were

held constant. An empirical relationship was developed to express mass-transfer coefficients in the liquid phase as a function of water flow rates. The constant and exponent for the correlation equation were computed by linear regression, resulting in the following expression:

$$k_L = 0.044 Q_w^{0.124}$$

where  $k_L$  = mass-transfer coefficient, cm/min; and  
 $Q_w$  = water flow rate, ml/min.

The correlation coefficient for the regression line was 0.99. This exponent correlation was similar to those correlation equations yielded by previous studies on absorption processes.

## INTRODUCTION

Adsorptive bubble-separation is a well known practice for water treatment and water pollution control. In a countercurrent column, wastewater flows from the top to the bottom of a column. Clean gas bubbles are dispersed from a diffuser at the base of the column. As the gas bubbles rise through the water column, the adsorptive contaminant in the water adsorbs at the bubble surface due to its surface activity. This results in mass transfer from the bulk solution toward the interface between the water and the gas bubble.

Mass transfer in an adsorptive bubble-separation column is related to several mechanisms of transfer: turbulence due to eddy and molecular diffusion in the bulk solution and molecular diffusion in the stagnant film adjacent to the interface between the water and gas phases. Eddy diffusion is analogous to molecular diffusion, but contributes more mixing or transport of the solute than molecular diffusion. The water flow at any point in the bulk solution is subjected to irregular fluctuations in both direction and velocity. Thus, these fluctuations bring about mixing of different parts of the solution. Therefore, transport in the solution is rapid and effective in reducing concentration gradients by means

of random eddies. The concentration gradients in the bulk solution are negligible, because of fully developed turbulence. Near the bubble surface, turbulence is progressively dampened, and transfer is largely by molecular diffusion. The main resistance to solute transfer occurs within the boundary stagnant film near the bubble surface where eddy diffusion is diminishing (Towle and Sherwood, 1939).

Engineers commonly express the rate of mass transfer per unit area as a product of the mass-transfer coefficient and a driving force. The mass-transfer coefficient is a result of the bulk motion contribution, and the driving force is expressed as the difference between the concentrations at both edges of the stagnant film. The mass-transfer coefficient obviously increases with increased turbulence that promotes eddy diffusion and reduces the thickness of the stagnant film. In a continuous-flow operation, turbulence is a complicated process and is influenced by many factors, among which flow rate is one of the most important factors.

Although extensive research (Calderbank, 1959; Cornell et al., 1960; Hughmark, 1967; Onda et al., 1968; Fair et al., 1973; Trybal, 1980 and Roberts et al., 1985) has been conducted on turbulence related to gas absorption processes, especially to air stripping, few studies focus

on adsorption-bubble separation processes. The objective of this paper, therefore, is 1) to measure the influence of water and gas flow rates on the removal efficiency for a solute under a countercurrent operation; and 2) to determine the correlation between the water flow rate and the mass-transfer coefficient for the adsorption process based on experimental data.

### Theory of Mass Transfer for an Adsorptive Bubble-Separation Process

An equation was derived for the general case of adsorption on bubbles (Tang and Woods 19xx a):

$$Z_o = \frac{Q_w}{A S k_L (1 - M)} \ln \left[ (1 - M) \frac{C_{in}}{C_{out}} - M \right] \quad (1)$$

where

- $Z_o$  = water column height, cm;
- $Q_w$  = water flow rate, ml/min;
- $A$  = water column intercept area,  $\text{cm}^2$ ;
- $S$  = specific interfacial surface area,  $\text{cm}^2/\text{cm}^3$ ;
- $k_L$  = mass-transfer coefficient, cm/min;
- $M$  = adsorptive separation factor, dimensionless;  $M = r_b Q_w / (3 k Q_g)$ ;
- $Q_g$  = gas flow rate, ml/min;

- $r_b$  = average of bubbles' radii, cm;  
 $k$  = adsorption constant,  $k = \Gamma_s/C_{L,i}$ , cm;  
 $\Gamma_s$  = unsaturated adsorptive mass per unit surface area, mg/ml;  
 $C_{L,i}$  = interfacial concentration at liquid side, mg/ml;  
 $C_{in}$  = influent concentration of solute, mg/ml;  
 $C_{out}$  = effluent concentration of solute, mg/ml.

This equation was based on the film theory and an assumption that solute adsorption at the bubble surface is linear with respect to the interfacial concentration of solute in the water phase. The mass-transfer coefficient ( $k_L$ ) represents turbulence in the water phase. The adsorption constant ( $k$ ) governs the adsorption equilibrium on the bubble surface. The constants can be determined by fitting experimental data with Equation 1.

#### Comparison of the Adsorptive Bubble-Separation Model with Air-Stripping Model

Equation 1 is similar to equation developed for air stripping, or the design of absorption columns. The expression for the air stripping is as follows (Sherwood et al., 1975; Trybal, 1980 and Robert et al., 1982):



$$Z_o = \frac{Q_w}{A K_L a (1 - S_t)} \ln \left[ (1 - S_t) \frac{C_{in}}{C_{out}} + S_t \right] \quad (2)$$

where  $K_L$  = overall mass-transfer coefficient, cm/min;  
 $a$  = specific interfacial area,  $\text{cm}^2$ ;  
 $S_t$  = stripping factor,  $S_t = Q_w / (Q_g H)$ ,  
dimensionless; and  
 $H$  = Henry's Law constant,  $H = C_g / C_L$ ,  
dimensionless.

Both Equations 1 and 2 express the column height as a product of two elements. The first element, the height of a theoretical unit (HTU), is the ratio of the water flow rate to the product of the specific surface area, column intercept area and mass-transfer coefficient. HTU equals  $Q_w / (A k_L S)$  for adsorptive bubble separation and  $Q_w / (A K_L a)$  for air stripping.

The second element, the number of theoretical units (NTU), is a unitless logarithmic component incorporating the aqueous concentrations of the solute in the influent and effluent.

For adsorption bubble-separation processes:

$$NTU = \frac{1}{(1 - M)} \ln \left[ (1 - M) \frac{C_{in}}{C_{out}} - M \right]$$

For air stripping processes:

$$NTU = \frac{1}{(1 - S_t)} \ln \left[ (1 - S_t) \frac{C_{in}}{C_{out}} + S_t \right]$$

Obviously, there are two major differences between the adsorptive bubble separation model and the air stripping model: 1) different mass-transfer coefficients were used; and 2) the adsorptive separation factor,  $M$ , in Equation 1 replaces the stripping factor,  $S_t$  in Equation 2. Both the stripping factor ( $S_t$ ) and the adsorptive separation factor ( $M$ ) are influential in mathematical models (Roberts et al., 1985 and Tang and Woods, 19xx a). Both factors depend on the ratio of  $Q_w$  and  $Q_g$ . These two factors also are involved in the specific properties of each process.  $S_t$  involves the Henry's Law constant ( $H$ ), [ $S_t = Q_w / (Q_g H)$ ], whereas,  $M$  involves the bubble radius ( $r_b$ ) and adsorption constant ( $k$ ), [ $M = r_b Q_w / (3 k Q_g)$ ].

Since the air stripping design is used for volatile solutes, Henry's Law governs phase equilibrium. The overall mass-transfer coefficient ( $K_L$ ) in the air stripping design combines mass-transfer resistance in both aqueous and gas phases.

$$K_L^{-1} = k_L^{-1} + (k_g H)^{-1} \quad (3)$$

where  $k_g$  is the mass-transfer coefficient in gas phase, cm/min.

In order to investigate the effect of either gas flow rate or water flow rate on the mass-transfer coefficient, it is necessary to separate the two resistances. However, it is difficult to measure the two resistances independently for a volatile compound.

For a nonvolatile solute in an adsorptive bubble-separation column, mass transfer occurs in the aqueous phase, but not in the gas phase. Therefore, only the mass-transfer coefficient ( $k_l$ ) in Equation 1 applies to the aqueous phase. It simplifies the evaluation of the correlation between the flow rate and mass transfer.

The air stripping model is only suitable for a packed column. The specific interfacial area ( $a$ ) is not identical to the total specific packing surface area. It is a wetted packing surface area and is a function of the flow rate, packing characteristics and liquid solution properties. When the correlation involving the flow rate and mass transfer was evaluated, it entailed separation of  $k_l$ ,  $k_g$  and  $a$ . Therefore, the correlation between the flow rate and mass-transfer coefficient for the air stripping design is related to the turbulence in both gas and water phases and the wetted specific packing area.

The specific area ( $S$ ) in adsorptive bubble-separation can be calculated from bubble size, bubble rise velocity and water flow rate (Tang and Woods, 19xx a).  $k_l$  and  $S$

are independent of each other in the adsorptive bubble-separation design. Therefore, it is possible to determine a correlation between mass-transfer coefficients and water flow rates.

## EXPERIMENTAL METHODS

The adsorptive bubble-separation process was conducted in a glass column. Triton-X100 (Rohm and Haas, 1986) was used as a nonvolatile solute. Nitrogen gas bubbles were generated at the base of a water column, which contained the surfactant, Triton-X100. An immiscible organic liquid, ethyl acetate, was floated at the top of the water. As the nitrogen bubbles rose in the column, Triton-X100 adsorbed at the bubble surface. The solute Triton-X100 was transferred from the bubbles to the floating solvent, ethyl acetate, as the bubbles reached the top layer. The process separated Triton-X100 from the water phase. Experimental procedures and analytical methods are described in Chapter II (Tang and Woods, 19xx b).

The effect of gas and liquid flow rates on removal of Triton-X100 from the aqueous solution was tested experimentally. All experiments were conducted with a 60 cm water column. A glass frit with medium porosity was fixed at the bottom of the column. Thus, bubble size was kept constant for a given gas flow rate. The influent solution contained 0.071 mg/ml Triton-X100. The effluent concentrations at steady state for Triton-X100 were measured as a function of liquid and gas flow rates.

The effect of water flow rate on the mass-transfer coefficient in the liquid phase was evaluated by means of the adsorptive bubble-separation process. Equation 1 was used to calculate the mass-transfer coefficient for five column heights ( $Z_0$ ) 30, 40, 50, 60 and 100 cm. Each column was operated individually. The gas flow rate was held constant at 6.4 ml/min. The mean bubble size was measured from three photographs that included a total of 769 bubbles. The average bubble radius ( $r_b$ ) was 0.0294 cm. The viscosity of the water solution was obtained by means of a Cannon-Fenske viscometer. The density of the aqueous solution was obtained by dividing the sample weight by the volume. All operations were run at room temperature,  $23 \pm 1.0$  °C.

The value of the mass-transfer coefficient ( $k_l$ ) in Equation 1 was determined by a non-linear least squares fit of the data, using a statistical method, ZXXSQ (International Mathematics and Statistics Libraries, 1976). This program is based on a modified Levenberg-Marquardt algorithm for determining the minimum sum of squares for several functions (Levenberg, 1944 and Marquardt, 1963).

Since there are two unknowns in Equation 1, the mass-transfer coefficient ( $k_l$ ) and the adsorptive constant ( $k$ ), the adsorption constant was determined at a constant water

flow rate equal to 13.0 ml/min. The adsorption constant ( $k$ ) will remain constant if the test conditions are unchanged even though water flow rates are varied. The mass-transfer coefficient ( $k_l$ ) was determined at varying water flow rates.

## EXPERIMENTAL RESULTS

Experimental results are shown in Fig. III-1 and III-2. The effect of water flow rate on removal efficiency for a 6.4-ml/min gas flow rate is shown in Fig. III-1. The removal of Triton-X100 from the water increased with decreased water flow rates. Removal at a water flow rate of 13 ml/min was only approximately 30%, whereas at 3 ml/min, removal increased to 65%. Fig. III-2 shows the effect of gas flow rate on removal for a constant 13.0 ml/min water flow rate. Removal efficiency increased with increased gas flow rate. When the gas flow rates increased from 3 ml/min to 11.6 ml/min, removal efficiency increased from 16% to 40%.

Operations were conducted at four water flow rates to produce four estimates of the mass-transfer coefficient. For the sake of precision, the operation at each water flow rate in individual columns was repeated two to four times. The variation of column height did not affect the turbulence in the column, but yielded different removal efficiencies. The mass-transfer coefficients ( $k_L$ ) increased with greater water flow rates ( $Q_w$ ) (Fig. III-3). This result is consistent with the mass-transfer theories discussed above. The curve in Fig. III-3 indicates an exponential relationship between the mass-transfer



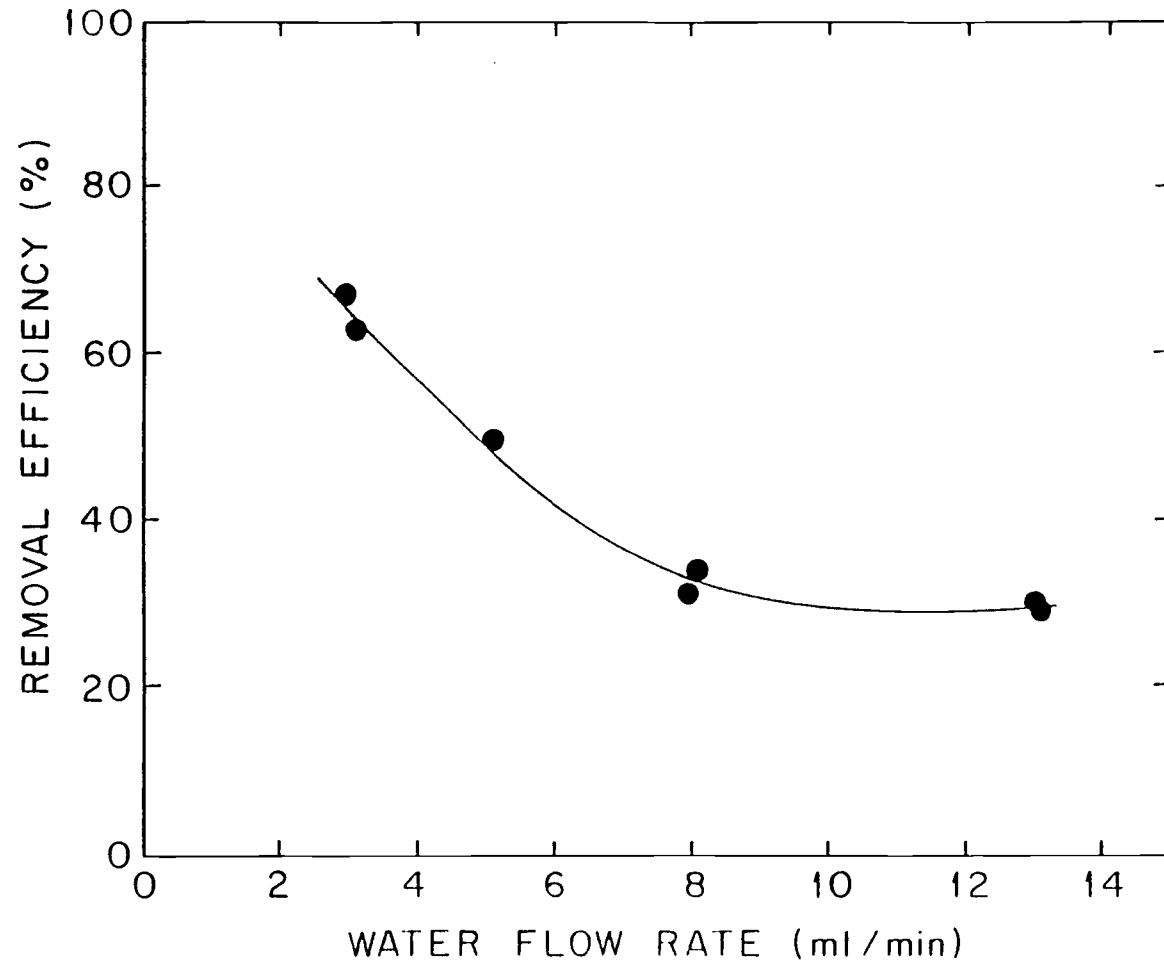


Figure III-1 The Effects of Water Flow Rate on Removal Efficiency at  $Z_0$  Equal to 60 cm and  $Q_g$  Equal to 6.4 ml/min.

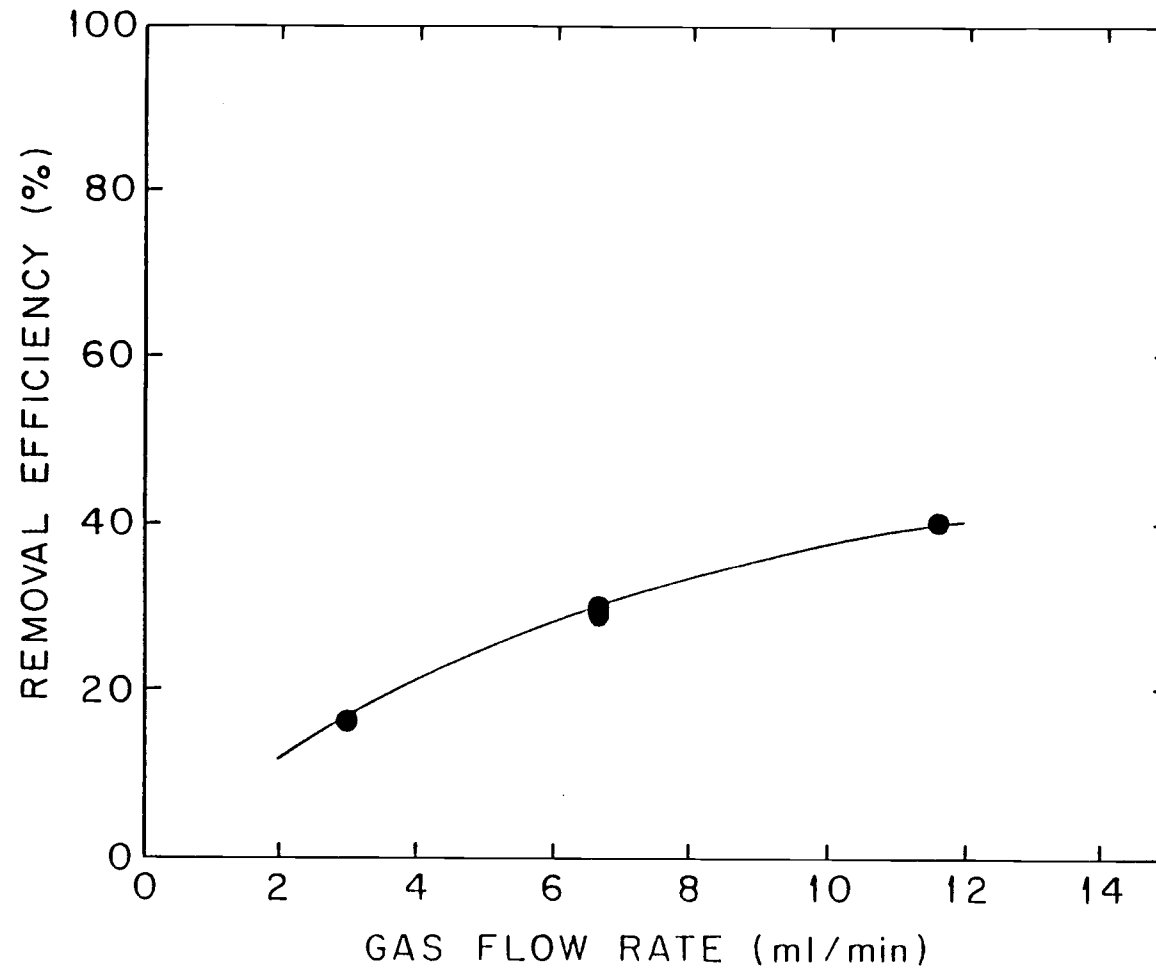


Figure III-2 The Effects of Gas Flow Rate on Removal Efficiency at  $Z_0$  Equal to 60 cm and  $Q_w$  Equal to 13.0 ml/min.

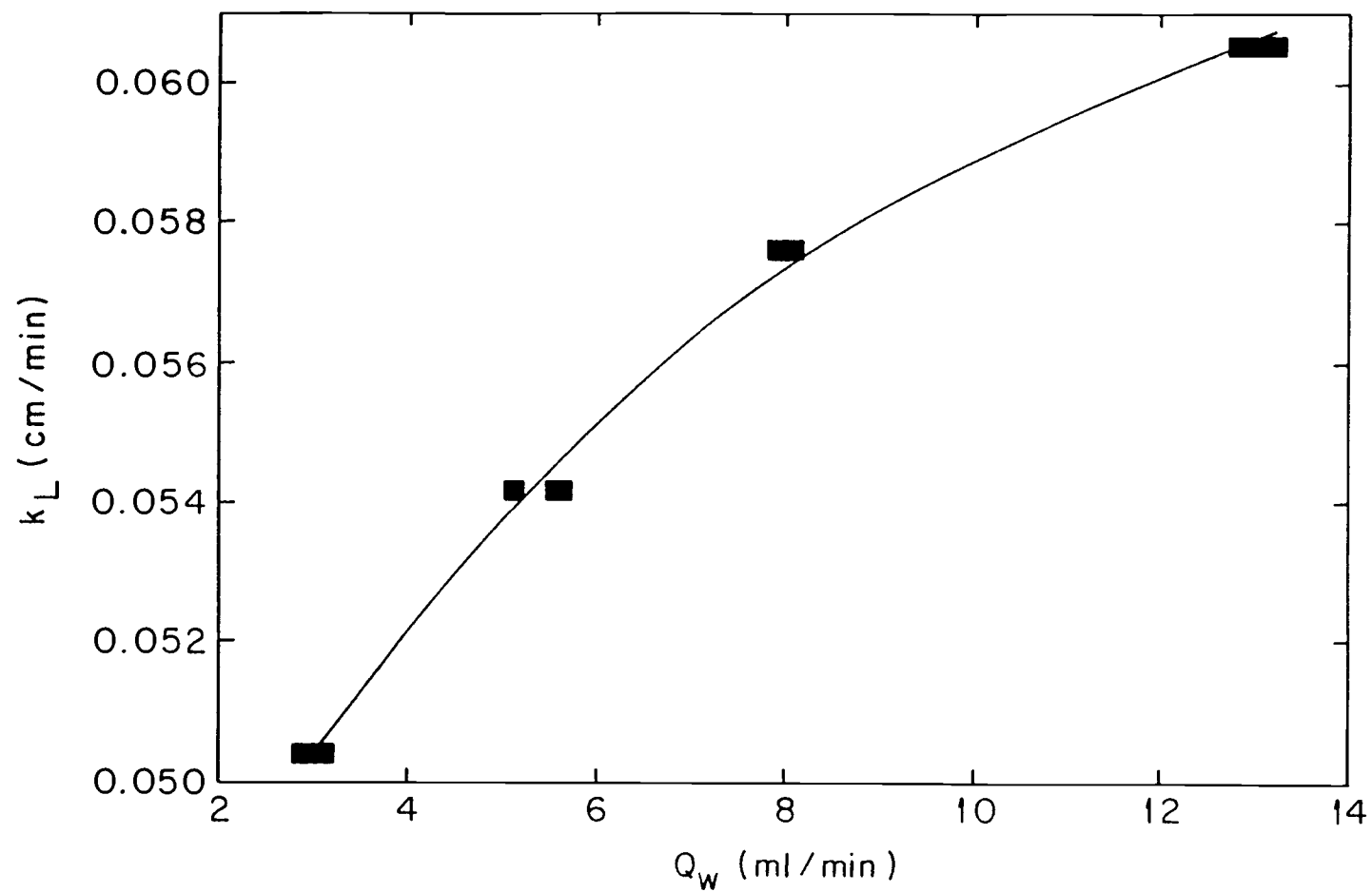


Figure III-3 Relationships Between Mass Transfer Coefficients and Water Flow Rates  
at  $Q_g$  Equal to 6.4 ml/min and  $r_b$  Equal to 0.0294 cm.

coefficient and water flow rate. Logarithmic transformations of  $k_L$  and  $Q_w$  suggest the empirical relationship described by Equation 4 (Fig. III-4).

$$k_L = 0.044 Q_w^{0.124} \quad (4)$$

The correlation coefficient in Fig. III-4 is 0.997.

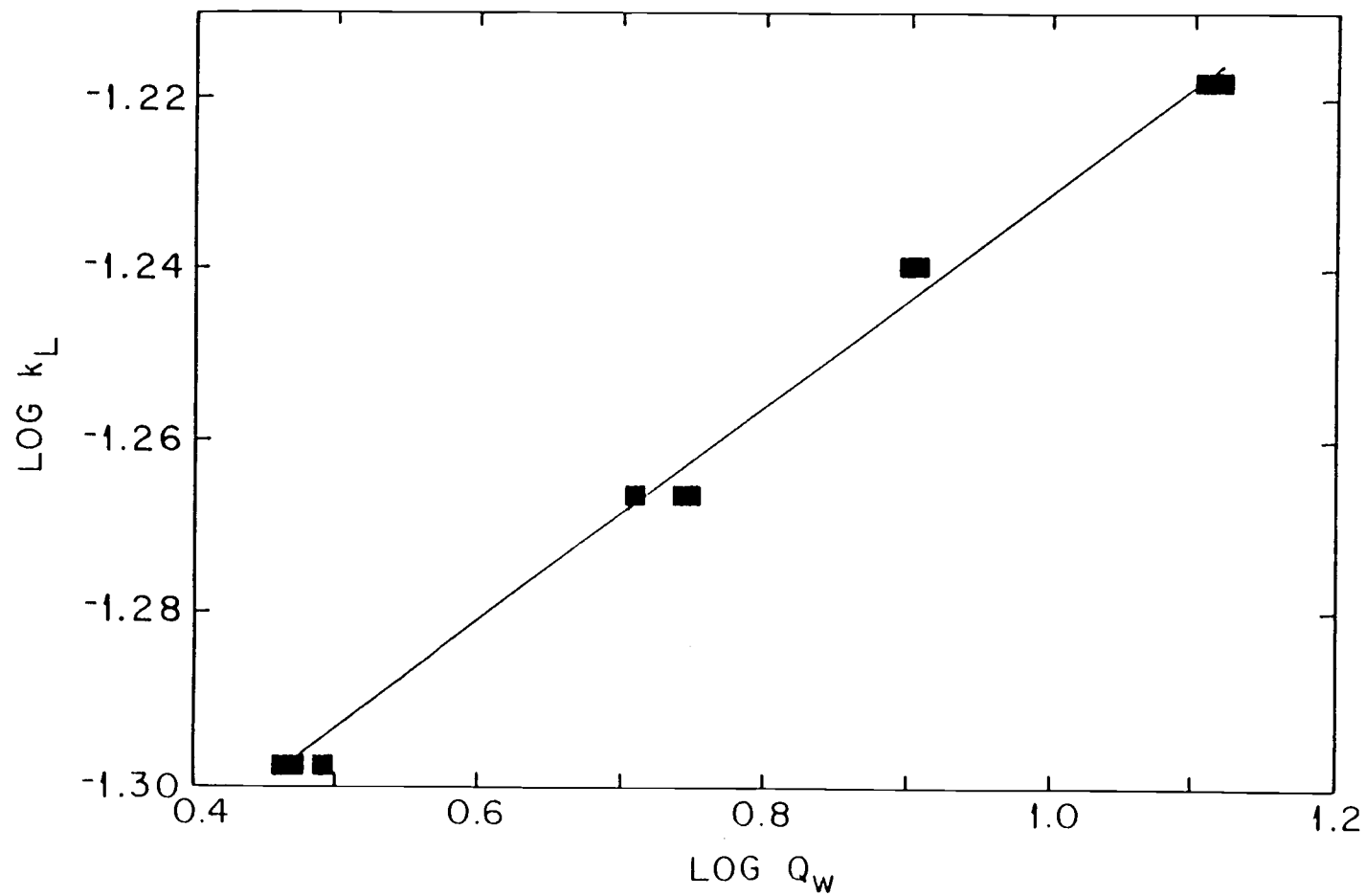


Figure III-4 Linear Regression of the Logarithm of Mass-Transfer Coefficients and Water Flow Rate.

## DISCUSSION

For engineering designs, turbulence is usually expressed in terms of a dimensionless parameter, or Reynolds number. The Reynolds number involves four factors: velocity, length, density and viscosity. The velocity and density factors for turbulence in a water column can be expressed in terms of the water flow rate. The length factor is the bubble size. The viscosity of the Triton-X100 solution is almost identical to the viscosity of water because the solution is dilute. Since the bubble size and viscosity are constant in this research, the study of turbulence merely focuses on the effect of water flow rate.

Much effort has been spent in developing the measurement of eddy diffusion by the Reynolds number. Experimental data are usually obtained with various equipment by measurement of the evaporation rate of a volatile liquid or a volatile solute into a gas stream over a known surface. There are dozens of well-known correlations, which reveal that the mass-transfer coefficients in the liquid phase have an exponential relationship with the water flow rates in air stripping packed columns. For example, the Sherwood-Holloway model (1940) assumed that the transfer resistance in the gas

phase was negligible in an air-stripping system. This model indicated that the product of a specific area ( $a$ ) and the liquid transfer coefficient ( $k_L$ ) in the liquid phase is proportional to the water flow rate with a  $1-n$  exponent.

$$\frac{k_L a}{D_L} = 10.764 \alpha \left( \frac{0.3048 L_M}{\mu} \right)^{1-n} \left( \frac{\mu}{\rho D_L} \right)^{0.5}$$

where  $k_L$  = mass-transfer coefficient in liquid phase, m/sec; ( According to the assumption, the  $k_L$  equals the overall transfer coefficient,  $K_L$ .)

$\alpha$  = constant depending on packing materials, unitless;

$D_L$  = diffusion coefficient,  $m^2/sec$ ;

$L_M$  = liquid mass flux,  $L_M = Q_w \rho/A$ ,  $kg/m^2 sec$ ;

$\mu$  = liquid viscosity, Pa sec; and

$\rho$  = liquid density,  $kg/m^3$ .

Values of the exponent ( $n = 0.28$ ) and constant ( $\alpha = 150$ ) were empirically determined and called packing parameters which are only suitable for 1/2-in ceramic Berl saddle packing (Sherwood and Holloway, 1940). Use of different gases, liquid and packing material would result in a variation in the constants and exponents (Morris and Jackson, 1953; Vivian and King, 1964 and Norman, 1961).

A further effort was made to try to separate  $k_L$  and  $a$  in the correlation equation by Onda and his colleagues (Onda et al., 1968). An estimation of the wetted specific area ( $a$ ) was proposed, and the exponent correlation between  $k_L$  and  $Q_w$  was further confirmed.

$$k_L \left( \frac{\rho}{\mu g} \right)^{1/3} = 0.0051 \left( \frac{L_M}{a \mu} \right)^{2/3} \left( \frac{\mu^2}{\rho D_L} \right)^{0.5} (a_t d_p)^{0.4}$$

Where  $a_t$  = total specific surface area of packing,  
 $m^2/m^3$ ;

$$a/a_t = 1 - \exp\{-1.45(\delta_c/\delta_L)^{0.75} [L_M/(a_t \mu)]^{0.1} [L_M^2 a_t/(\rho^2 g)]^{-0.05} [L_M^2/(\rho \delta a_t)]^{0.2}\}$$

$d_p$  = nominal packing size, m;

$\delta_c$  = critical surface tension of packing  
 material, dynes/cm;

$\delta_L$  = surface tension of liquid;

$\delta$  = surface tension, dyne/cm; and

$g$  = gravitational constant,  $m/hr^2$ .

The water flow rate exponent in the Onda model was 0.67 which included rings, spheres, rods, and saddles, varying in size from 4 to 50 mm.

Comparing with previous research results mentioned above, Equation 4 proposes a similar exponent relationship between mass-transfer coefficients and water flow rates for adsorption processes. Although the fundamental basis



for Equation 4 is unknown, it fits the data well for varying water flow rates. It seems impossible that the exponent in Equation 4 can be similar to the above exponents obtained from air stripping models, because the bubble size is much smaller than the packing size. However, Equation 4 indicated, at least, that the exponent correlation suits the adsorption column. A larger data base is required to further determine the exact nature of the exponent.

Theoretically, the gas flow rate does not affect the mass-transfer coefficient in the aqueous phase. However, many other factors related to transfer in the bubbling column are influenced by gas flow rate, such as bubble size and bubble velocity. As the gas flow rate increases, the bubble numbers increase, and the bubble size also increases even with the same orifices (Leibson et al. 1956). As seen in Fig. III-2, the removal of Triton-X100 increases with increased gas flow rates because with greater gas flow rates, more bubbles are generated. More bubbles provide a greater surface area for solute adsorption. On the other hand, the increase in bubble size also causes an increase in bubble velocity. The bubble velocity further affects 1) specific area estimation, based on the calculation of the specific area ( $S$ ) in Equation 1 (Tang and Woods, 19xx a); and 2) the

total bubble numbers in a certain volume of water, due to the change in bubble retention time. The change in bubble size modifies the Reynolds number, as well the turbulence. With these analyses, change in gas flow rate will affect the removal efficiency and the water mass-transfer coefficient. Although gas flow rate effects have been considered in Equation 1, all  $k_L$ 's in the present work were determined at a single gas flow rate. Therefore, Equation 4 does not include any gas flow rate component.

Although the increased water flow rate can elevate mass-transfer rates, the greater water flow rates reduce the removal as shown in Fig. III-1. The reduced removal can be explained by the change in water retention time. If the gas flow rate and bubble size are held constant, the bubble specific area is constant. With the same bubble specific area, greater water flow rates reduce the contact time between the gas bubbles and the water solution. Reduced adsorption occurs at the bubble surface. Therefore, total mass removal from the water solution by bubble adsorption declines.

## CONCLUSIONS

Mass-transfer rates depend on turbulence in the system. Turbulence in an adsorption bubble column is a function of gas and liquid flow rates. This research proposed a correlation between water flow rate and the mass-transfer coefficient based on a mathematical model and experimental data. At 6.4 ml/min gas flow rate and 0.0294 cm average bubble radius, correlation within the 3- to 13-ml/min water flow rate range is expressed by the equation

$$k_L = 0.044 Q_w^{0.124} \quad (4)$$

The empirical correlation is similar to the form of correlations proposed for other absorption processes. However, the correlation obtained from adsorptive bubble-separation processes is more reliable than that determined for other absorption processes, because mass transfer only occurs in the liquid side .

The effects of both gas and water flow rates on the removal of an adsorptive solute were investigated with a countercurrent operation. The removal increased with higher gas flow rates, and decreased with increased water flow rates. These results were explained by the changes in turbulence and bubble surface area.

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## **APPENDICES**

## Appendix A      The Effect of Hydraulic Head on Bubble Size

According to the Gas Law,  $P_1 V_1 = P_2 V_2$ , the bubble size must change with the depth of an aqueous column.

Assume that condition 1 is atmospheric conditions, and that condition 2 represents the condition inside the aqueous phase. The atmosphere pressure,  $P_1$ , is 1.013 E6 dyne/cm<sup>2</sup>. Therefore, the pressure at a given column height might be expressed as

$$P_2 = P_1 + g p Z + g p_s Z_s$$

where  $g$  = the gravitational constant, cm/sec<sup>2</sup>;

$p$  = the density of aqueous phase, g/cm<sup>3</sup>;

$p_s$  = the density of solvent phase, g/cm<sup>3</sup>;

$Z$  = the height of the aqueous phase, cm; and

$Z_s$  = the height of the solvent phase, cm.

For a 100 cm water column, the pressure on the nitrogen bubbles at the bottom of the column is

$$\begin{aligned} P_2 &= 1.013 \text{ E6} + 9.8 (0.995 * 100 + 0.902 * 6) \\ &= 1.014 \text{ E6 dynes/cm}^3 \end{aligned}$$

So the error caused by the depth of the liquid with respect to the bubble size is

$$\frac{V_2 - V_1}{V_1} = \frac{P_1 - P_2}{P_1} = 0.1 \%$$

This error is a small. It can be ignored in my model.

## Appendix B Computer Program for Non-linear Least Squares Regression

The program was written in Fortran language as following

( $Q_{\text{L}}$  = 13.0 ml/min):

```

C      NON-LINEAR LEAST SQUARES PROGRAM
C      IMSL ROUTINE NAME - ZXSSQ
C      MINIMUM OF THE SUM OF SQUARES OF M FUNCTIONS IN N
C      VARIABLES
C      USING A FINITE DIFFERENCE LEVENBERG-MARQUARDT
C      ALGORITHM
$DEBUG
      PROGRAM TRITON
      EXTERNAL FUNC
      INTEGER M,N,IXJAC,NSIG,MAXFN,IOPT,I,INFER,IER,J
      REAL PARM(4),X(2),F(14),XJAC(14,2),XJTJ(3),WORK(41),
*      EPS,DELTA,SSQ,Qw(14),Qg(14),CIN(14),COUT(14),Z(14)
      COMMON /SSQ/Z,Qw,Qg,CIN,COUT,J
C      INPUT NUMBER OF OBSERVATIONS
      M=14
C      INPUT NUMBER OF UNKNOWN PARAMETERS
      N=2
C      INPUT ROW DIMENSION OF MATRIX XJAC EXACTLY
      IXJAC=14
C      THE FIRST CONVERGENCE CRITERION: THE PARAMETER
C      ESTIMATES AGREE TO NSIG DIGITS.
      NSIG=5
C      THE SECOND CONVERGENCE CRITERION: THE DIFFERENCE
C      BETWEEN SSQ'S OF TWO SUCCESSIVE ITERATIONS IS LESS
C      THAN OR EQUAL TO EPS.
      EPS=0.001
C      THIRD CONVERGENCE CRITERION: THE NORM OF THE
C      APPROXIMATE GRADIENT IS LESS THAN OR EQUAL TO
C      DELTA.
      DELTA=0.001
C      INPUT MAXIMUM NUMBER OF FUNCTION EVALUATIONS ALLOWED
      MAXFN=1000
C      INPUT OPTIONS PARAMETER: 0 BROWN'S ALGORITHM WITHOUT
C      STRICT DESCENT;
C      1 STRICT DESCENT AND DEFAULT
C      VALUES FOR INPUT VECTOR
C      PARM;
C      2 STRICT DESCENT WITH USER
C      PARAMETER CHOICES IN INPUT
C      VECTOR PARM.
      IOPT=1

```

```

C      X1=k
C      X2=k1
      DO 20 I=1,14
20  READ (5,*) Z(I),Qw(I),Qg(I),CIN(I),COUT(I)
      READ (5,*) (X(I),I=1,2)
C      SUBROUTINE WHICH CALCULATES THE RESIDUAL VECTOR F(I)
C      FOR GIVEN PARAMETER VALUE X(I)
      CALL FUNC(X,M,N,F)
C      SUBROUTINE WHICH IS LIBRARY FUNCTION
      CALL ZXSSQ(FUNC,M,N,NSIG,EPS,DELTA,MAXFN,IOPT,PARM,X,
*      SSQ,F,XJAC,IXJAC,XJTJ,WORK,INFER,IER)
C      OUTPUT
      7 FORMAT(3X,'The result is:')
      8 FORMAT(5X,6Hk*x = ,F8.5; 5HkL = ,F7.5)
      9 FORMAT(3X,'The minimum of the sum of squares is:')
10  FORMAT(5X,6HSSQ = ,F10.3)
11  FORMAT(3X,'The fourteen residual vectors are:')
12  FORMAT(1X,7F10.4)
13  FORMAT(5X,7HINFER = ,I2)
14  FORMAT(5X,4HJ = ,I2)
      X(1)=rb/(3*X(1))
      WRITE(6,7)
      WRITE(6,8) (X(I),I=1,2)
      WRITE(6,*)
      WRITE(6,9)
      WRITE(6,10) SSQ
      WRITE(6,*)
      WRITE(6,11)
      WRITE(6,12) (F(I),I=1,14)
C      THE SATISFIED CRITERION:
C      1 FIRST CRITERION WAS SATISFIED
C      2 SECOND CRITERION WAS SATISFIED
C      3 5 6 7 MORE THAN ONE OF THE CRITERIONS WERE SATISFIED
C      4 THIRD CRITERION WAS SATISFIED
C      SIMULTANEOUSLY
      WRITE(6,*)
      WRITE(6,13) INFER
C      ACTUAL NUMBER OF CALLS TO FUNC
      WRITE(6,14) J
      STOP
      END
      SUBROUTINE FUNC(X,M,N,F)
      INTEGER M,N,I,J
      REAL X(N),F(M),Qw(14),Qg(14),M1(14),M2(14),
*      CIN(14),COUT(14),Z(14),AS(14),rb
      COMMON /SSQ/Z,Qw,Qg,CIN,COUT,J
      J=J+1
      rb=0.0294
      DO 30 I=1,14
      Ub(I) = 7.4005*60-Qw(I)/5.0671
      AS(I)=3*Qg(I)/(Ub*rb)

```

```
M1(I)=rb*Qw(I)/(3*X(1)*Qg(I))
M2(I)=(1-M1(I))*Cin(I)/Cout(I)+M1(I)
M2(I)=log(M2(I))
F(I)=Qw(I)*M2(I)/(AS(I)*X(2)*(1-M1(I)))-Z(I)
30 CONTINUE
RETURN
END
```



# Appendix C    Data for Theoretical Model Prediction

Table C-1    Test Conditions for Theoretical Analyses  
in Chapter I

p	1	g/cm <sup>3</sup>
$\mu$	0.01	g/cm-sec
$r_b$	0.05	cm
A	5	cm <sup>2</sup>
$Q_w$	10	ml/min
$Q_g$	5.1	ml/min
$Z_o$	50	cm
$k_L$	0.1	cm/min
k	0.01	cm

Table C-2    Background Data for Fig. I-4

$Z_o$ cm	Removal% k = 0.001 $k_L$ = 0.1 cm/min	Removal% $k_L$ = 0.5 cm/min	Removal% k = 0.005
0	0.00%	0.00%	0.00%
5	1.91%	8.18%	1.96%
10	3.67%	13.80%	3.85%
15	5.29%	17.82%	5.69%
20	6.79%	20.77%	7.47%
25	8.18%	22.97%	9.19%
30	9.47%	24.65%	10.86%
35	10.67%	25.93%	12.49%
40	11.79%	26.92%	14.06%
45	12.83%	27.70%	15.59%
50	13.80%	28.30%	17.08%
55	14.71%	28.78%	18.53%
60	15.57%	29.15%	19.93%
65	16.37%	29.45%	21.30%
70	17.12%	29.69%	22.63%
75	17.82%	29.87%	23.92%
80	18.48%	30.02%	25.18%
85	19.11%	30.14%	26.41%
90	19.69%	30.23%	27.61%
95	20.25%	30.31%	28.77%
100	20.77%	30.37%	29.91%
105	21.26%	30.41%	31.02%

Table C-2 Background Data for Fig. I-4 (Continued)

Zo cm	Removal% k = 0.001 k <sub>L</sub> = 0.1 cm/min	Removal% k <sub>L</sub> = 0.5 cm/min	Removal% k = 0.005
110	21.72%	30.45%	32.10%
115	22.16%	30.48%	33.15%
120	22.58%	30.51%	34.18%
125	22.97%	30.52%	35.19%
130	23.34%	30.54%	36.17%
135	23.70%	30.55%	37.13%
140	24.03%	30.56%	38.06%
145	24.35%	30.57%	38.98%
150	24.65%	30.58%	39.87%
155	24.93%	30.58%	40.75%
160	25.20%	30.58%	41.60%
165	25.45%	30.59%	42.44%
170	25.70%	30.59%	43.26%
175	25.93%	30.59%	44.06%
180	26.15%	30.59%	44.84%
185	26.36%	30.59%	45.61%
190	26.55%	30.60%	46.36%
195	26.74%	30.60%	47.10%
200	26.92%	30.60%	47.82%
205	27.09%	30.60%	48.53%
210	27.26%	30.60%	49.22%
215	27.41%	30.60%	49.90%
220	27.56%	30.60%	50.56%
225	27.70%	30.60%	51.21%
230	27.83%	30.60%	51.85%
235	27.96%	30.60%	52.48%
240	28.08%	30.60%	53.10%
245	28.19%	30.60%	53.70%
250	28.30%	30.60%	54.29%
255	28.41%	30.60%	54.87%
260	28.51%	30.60%	55.44%
265	28.60%	30.60%	56.00%
270	28.69%	30.60%	56.55%
275	28.78%	30.60%	57.09%
280	28.86%	30.60%	57.62%
285	28.94%	30.60%	58.15%
290	29.01%	30.60%	58.66%
295	29.09%	30.60%	59.16%
300	29.15%	30.60%	59.65%
305	29.22%	30.60%	60.14%
310	29.28%	30.60%	60.62%
315	29.34%	30.60%	61.09%
320	29.40%	30.60%	61.55%

Table C-2 Background Data for Fig. I-4 (Continued)

$Z_o$ cm	Removal% $k = 0.001$ $k_L = 0.1$ cm/min	Removal% $k_L = 0.5$ cm/min	Removal% $k = 0.005$
325	29.45%	30.60%	62.00%
330	29.50%	30.60%	62.45%
335	29.55%	30.60%	62.89%
340	29.60%	30.60%	63.32%
345	29.64%	30.60%	63.74%
350	29.69%	30.60%	64.16%
355	29.73%	30.60%	64.57%
360	29.77%	30.60%	64.97%
365	29.80%	30.60%	65.37%
370	29.84%	30.60%	65.76%
375	29.87%	30.60%	66.15%
380	29.91%	30.60%	66.53%
385	29.94%	30.60%	66.90%
390	29.97%	30.60%	67.27%
395	29.99%	30.60%	67.63%
400	30.02%	30.60%	67.99%

Table C-3      Background Data for Fig. I-5

$Q_w$ ml/min	$Q_g=0.5Q_w$ ml/min	Removal% $Z_o=60$ cm	Removal% $Z_o=30$ cm	$Q_g=2Q_w$ ml/min	Removal% $Z_o=60$ cm	Removal% $Z_o=30$ cm
1	0.5	13.53%	9.27%	2	45.39%	32.69%
2	1	13.53%	9.28%	4	45.40%	32.70%
3	1.5	13.53%	9.28%	6	45.41%	32.71%
4	2	13.53%	9.28%	8	45.41%	32.71%
5	2.5	13.54%	9.28%	10	45.42%	32.72%
6	3	13.54%	9.28%	12	45.43%	32.72%
7	3.5	13.54%	9.28%	14	45.43%	32.73%
8	4	13.54%	9.29%	16	45.44%	32.74%
9	4.5	13.55%	9.29%	18	45.45%	32.74%
10	5	13.55%	9.29%	20	45.45%	32.75%
11	5.5	13.55%	9.29%	22	45.46%	32.75%
12	6	13.55%	9.29%	24	45.47%	32.76%
13	6.5	13.56%	9.30%	26	45.47%	32.77%
14	7	13.56%	9.30%	28	45.48%	32.77%
15	7.5	13.56%	9.30%	30	45.49%	32.78%
16	8	13.56%	9.30%	32	45.50%	32.78%
17	8.5	13.56%	9.30%	34	45.50%	32.79%
18	9	13.57%	9.31%	36	45.51%	32.79%
19	9.5	13.57%	9.31%	38	45.52%	32.80%
20	10	13.57%	9.31%	40	45.52%	32.81%

Table C-4 Background Data for Fig. I-6

$Q_w$ ml/min	Removal% $Z_o=60$ cm	Removal% $Z_o=50$ cm	Removal% $Z_o=40$ cm	Removal% $Z_o=30$ cm
1	85.50%	80.65%	73.97%	64.62%
2	59.59%	54.23%	47.76%	39.82%
3	44.47%	39.99%	34.74%	28.51%
4	35.26%	31.54%	27.22%	22.16%
5	29.16%	26.00%	22.36%	18.12%
6	24.84%	22.10%	18.96%	15.32%
7	21.62%	19.22%	16.46%	13.27%
8	19.14%	17.00%	14.54%	11.70%
9	17.17%	15.23%	13.02%	10.47%
10	15.57%	13.80%	11.79%	9.47%
11	14.24%	12.62%	10.77%	8.64%
12	13.12%	11.62%	9.91%	7.95%
13	12.16%	10.77%	9.18%	7.36%
14	11.33%	10.03%	8.55%	6.85%
15	10.61%	9.39%	8.00%	6.41%
16	9.97%	8.83%	7.52%	6.02%
17	9.41%	8.33%	7.09%	5.68%
18	8.91%	7.88%	6.71%	5.37%
19	8.46%	7.48%	6.37%	5.10%
20	8.05%	7.12%	6.06%	4.85%

Table C-5      Background Data for Fig. I-7

$Q_g$ ml/min	Removal% $Z_o=30$ cm	Removal% $Z_o=40$ cm	Removal% $Z_o=50$ cm	Removal% $Z_o=60$ cm
1	1.92%	2.41%	2.84%	3.21%
2	3.81%	4.77%	5.61%	6.34%
3	5.67%	7.08%	8.32%	9.40%
4	7.50%	9.35%	10.96%	12.38%
5	9.29%	11.57%	13.55%	15.28%
6	11.06%	13.74%	16.07%	18.11%
7	12.79%	15.87%	18.53%	20.86%
8	14.49%	17.95%	20.94%	23.54%
9	16.17%	19.99%	23.28%	26.15%
10	17.81%	21.98%	25.57%	28.68%
11	19.43%	23.94%	27.80%	31.15%
12	21.02%	25.85%	29.97%	33.54%
13	22.58%	27.71%	32.09%	35.87%
14	24.11%	29.54%	34.16%	38.13%
15	25.62%	31.33%	36.17%	40.32%
16	27.09%	33.08%	38.13%	42.45%
17	28.55%	34.78%	40.03%	44.51%
18	29.97%	36.45%	41.89%	46.51%
19	31.37%	38.09%	43.70%	48.45%
20	32.75%	39.68%	45.45%	50.33%

Table C-6 Background Data for Fig. I-8

$r_b$ cm	0.1	0.05	0.02	0.01
$u$ cm/min	1323.3	770.94	287.4	102.18
$Q_w$ ml/min	Removal%	Removal%	Removal%	Removal%
1	39.03%	80.65%	100.00%	100.00%
2	21.67%	54.23%	99.46%	100.00%
3	14.96%	39.99%	95.81%	100.00%
4	11.42%	31.54%	89.13%	100.00%
5	9.24%	26.00%	81.47%	100.00%
6	7.75%	22.10%	74.09%	99.97%
7	6.68%	19.22%	67.47%	99.85%
8	5.87%	17.00%	61.69%	99.49%
9	5.23%	15.23%	56.69%	98.72%
10	4.72%	13.80%	52.35%	97.42%
11	4.30%	12.62%	48.58%	95.57%
12	3.95%	11.62%	45.28%	93.22%
13	3.65%	10.77%	42.38%	90.49%
14	3.39%	10.03%	39.82%	87.51%
15	3.17%	9.39%	37.54%	84.40%
16	2.98%	8.83%	35.50%	81.25%
17	2.80%	8.33%	33.66%	78.14%
18	2.65%	7.88%	32.01%	75.12%
19	2.51%	7.48%	30.50%	72.21%
20	2.39%	7.12%	29.13%	69.43%
21	2.28%	6.79%	27.88%	66.80%
22	2.17%	6.49%	26.72%	64.32%
23	2.08%	6.22%	25.66%	61.97%
24	1.99%	5.97%	24.68%	59.76%
25	1.92%	5.73%	23.77%	57.68%
26	1.84%	5.52%	22.93%	55.72%
27	1.78%	5.32%	22.14%	53.88%
28	1.71%	5.13%	21.41%	52.14%
29	1.65%	4.96%	20.72%	50.51%
30	1.60%	4.80%	20.08%	48.96%

# Appendix D Experimental Data and Regression Results

Table D-1 Extraction Effect at Top of Water Column  
(End Effect, at  $Q_g = 0$ )

$Q_w$ ml/min	$C_{in}$ A	$C_{out}$ A	$C_{in}$ mg/ml	$C_{out}$ mg/ml	Removal %
3.0	0.698	0.660	0.06777	0.06406	5.47%
3.0	0.753	0.698	0.07300	0.06778	7.16%
5.5	0.723	0.661	0.07016	0.06423	8.46%
5.5	0.532	0.493	0.05182	0.04807	7.23%
13.0	0.727	0.694	0.07053	0.06734	4.53%
13.0	0.766	0.725	0.07429	0.07037	5.26%
Average					6.35%

Concentration Standard Curve Equation:

$$C = 0.09586 A + 0.00084$$



Table D-2 Data Determined by Experimentation

$Q_w$ ml/min	$Q_g$ ml/min	$C_{in}$ A	$C_{out}$ A	$C_{in}$ mg/ml	$(1-6.35\%)C_{in}$	$C_{out}$ mg/ml	$Z_o$ cm
13.1745	6.3261	0.751	0.587	0.07287	0.06824	0.05715	30.0
13.0750	6.2391	0.740	0.615	0.07173	0.06717	0.05975	30.0
12.9418	6.2831	0.753	0.590	0.07302	0.06838	0.05737	40.0
12.9771	6.5035	0.736	0.584	0.07134	0.06681	0.05677	40.0
12.9441	6.4143	0.732	0.557	0.07100	0.06649	0.05425	40.0
13.1289	6.4564	0.719	0.565	0.06975	0.06532	0.05499	40.0
13.0350	6.3258	0.756	0.565	0.07329	0.06863	0.05504	50.0
13.0512	6.3166	0.727	0.536	0.07051	0.06603	0.05150	60.0
13.0250	6.2570	0.722	0.540	0.07005	0.06560	0.05263	60.0
13.0899	6.6373	0.747	0.528	0.07242	0.06782	0.05142	60.0
13.0094	6.6465	0.747	0.521	0.07242	0.06782	0.05078	60.0
12.7996	6.2599	0.767	0.574	0.07435	0.06963	0.05587	50.0
13.1609	6.3961	0.716	0.491	0.06951	0.06510	0.04789	100.0
13.0152	6.5675	0.701	0.484	0.06804	0.06372	0.04722	100.0
Average:							
13.03	6.40			0.07145			
5.5384	6.3855	0.767	0.487	0.07439	0.06967	0.04750	30
5.5243	6.3586	0.704	0.443	0.06835	0.06401	0.04326	30
5.1187	6.3512	0.758	0.378	0.07347	0.06880	0.03708	60
5.5998	6.4097	0.700	0.306	0.06798	0.06366	0.03021	100
Average:							
5.45	6.37			0.07105			

Table D-2 Data Determined by Experimentation (Continued)

$Q_w$ ml/min	$Q_g$ ml/min	$C_{in}$ A	$C_{out}$ A	$C_{in}$ mg/ml	$(1-6.35\%)C_{in}$	$C_{out}$ mg/ml	$Z_o$ cm
3.0948	6.3595	0.757	0.275	0.07339	0.06873	0.02719	60
2.9595	6.3630	0.676	0.216	0.06567	0.06150	0.02154	60
2.9420	6.3793	0.700	0.247	0.06794	0.06362	0.02450	50
2.9019	6.3639	0.769	0.338	0.07452	0.06979	0.03326	30
2.9041	6.3212	0.719	0.352	0.06977	0.06534	0.03453	30
Average:							
2.96	6.36			0.07026			
8.0695	6.3657	0.728	0.496	0.07058	0.06609	0.04836	40.0
7.9580	6.4130	0.736	0.488	0.07139	0.06686	0.04764	40.0
8.0904	6.3564	0.736	0.452	0.07139	0.06686	0.04412	60.0
7.9622	6.3756	0.737	0.472	0.07151	0.06696	0.04605	60.0
8.0045	6.4082	0.718	0.459	0.06962	0.06519	0.04484	60.0
8.0154	6.3678	0.682	0.477	0.06617	0.06196	0.04656	30.0
7.9821	6.4400	0.745	0.559	0.07224	0.06765	0.05442	30.0
8.0096	6.3215	0.730	0.408	0.07082	0.06632	0.03999	100.0
Average:							
8.01	6.38			0.070			
Concentration Standard Curve Equations:							
				$C = 0.09586 A + 0.00084$ , at $C > 0.01$ mg/ml			
				$C = 0.0205 A - 0.0003$ , at $C < 0.01$ mg/ml			

Table D-3 Regression Data for Fig. II-2

Fig. II-2a		$Q_w = 13.0 \text{ ml/min}$ $k' = 0.006513 \text{ cm}$ $k_l = 0.06054 \text{ cm/min}$	
$Z_{\text{obs}} (X)$	$Z_{\text{calc}} (Y)$	Regression	
40.0	36.18	Constant	2.095
30.0	21.63	Std Err of Y Est.	8.434
50.0	51.29	R Squared	0.898
60.0	70.68	No. of Observations	15
60.0	76.01	Degrees of Freedom	13
40.0	31.13	X Coefficient(s)	0.9458
30.0	37.29	Std Err of Coef.	0.0884
50.0	50.40	Correlation Coef.	0.9476
100.0	98.02		
100.0	84.24		
40.0	43.55		
60.0	63.27		
60.0	52.03		
40.0	34.52		
0.0	0.00		

Table D-3 Regression Data for Fig. II-2 (Continued)

Fig. II-2b		$Q_w = 5.5 \text{ ml/min}$ $k = 0.006513 \text{ cm}$		$k_L = 0.05417 \text{ cm/min}$	
$Z_{\text{obs}} (X)$	$Z_{\text{calc}} (Y)$	Regression			
30.0	34.98	Constant		4.582	
30.0	36.14	Std Err of Y Est.		3.924	
60.0	60.99	R Squared		0.991	
100.0	95.30	No. of Observations		5	
0.0	0.00	Degrees of Freedom		3	
		X Coefficient(s)		0.9295	
		Std Err of Coef.		0.0519	
		Correlation Coef.		0.9954	

Fig. II-2c		$Q_w = 3.0 \text{ ml/min}$ $k = 0.006513 \text{ cm}$		$k_L = 0.05041 \text{ cm/min}$	
$Z_{\text{obs}} (X)$	$Z_{\text{calc}} (Y)$	Regression			
60.0	53.73	Constant		3.397	
60.0	59.11	Std Err of Y Est.		4.414	
50.0	51.7	R Squared		0.967	
30.0	37.1	No. of Observations		6	
30.0	31.21	Degrees of Freedom		4	
0.0	0.00	X Coefficient(s)		0.9238	
		Std Err of Coef.		0.0852	
		Correlation Coef.		0.9834	

Table D-4 Background Data for Fig. III-1 and III-2

$Q_w = 13.0$  ml/min,  $Q_g = 6.4$  ml/min,  $C_{in} = 0.071$  mg/ml,  $Z_o = 60$  cm

Removal %	$Q_g$ , ml/min	Removal %	$Q_w$ , ml/min
40.33%	11.5879	28.99%	13.0899
28.99%	6.6373	29.88%	13.0094
29.88%	6.6465	34.01%	8.0904
16.14%	2.9798	31.22%	7.9622
		49.53%	5.1187
		62.95%	3.0948
		67.19%	2.9595

Table D-5 Background Data for Fig. III-3 and III-4

$k_L$	$Q_w$	$\log k_L(Y)$	$\log Q_w(X)$	Regression	
0.06054	12.9418	-1.21794	1.111994		
0.06054	13.0750	-1.21794	1.116441	Constant	-1.3551
0.06054	13.0350	-1.21794	1.115111	Std Err of Y Est.	0.0024
0.06054	13.0899	-1.21794	1.116936	R Squared	0.9936
0.06054	13.0094	-1.21794	1.114257	No. of Observations	31
0.06054	12.9771	-1.21794	1.113177	Degrees of Freedom	29
0.06054	13.1745	-1.21794	1.119734	X Coefficient(s)	0.1240
0.06054	12.7996	-1.21794	1.107196	Std Err of Coef.	0.0018
0.06054	13.1609	-1.21794	1.119285	Correlation Coef.	0.9968
0.06054	13.0152	-1.21794	1.114450		
0.06054	12.9441	-1.21794	1.112071	$\log k_L = -1.3551 + 0.124 \log Q_w$	
0.06054	13.0512	-1.21794	1.115650		
0.06054	13.0250	-1.21794	1.114777	$\log k_L = \log 0.0441 + 0.124 \log Q_w$	
0.06054	13.1289	-1.21794	1.118228		
0.05760	8.0695	-1.23957	0.906846		
0.05760	7.9580	-1.23957	0.900803		
0.05760	8.0904	-1.23957	0.907969		
0.05760	7.9622	-1.23957	0.901033		
0.05760	8.0045	-1.23957	0.903334		
0.05760	8.0154	-1.23957	0.903925		
0.05760	7.9821	-1.23957	0.902117		
0.05760	8.0096	-1.23957	0.903610		
0.05417	5.5998	-1.26628	0.748172		
0.05417	5.5384	-1.26628	0.743384		
0.05417	5.5243	-1.26628	0.742277		

Table D-5 Background Data for Fig. III-3 and III-4 (Continued)

$k_L$	$Q_w$	$\log k_L (Y)$	$\log Q_w (X)$	Regression
0.05417	5.1187	-1.26628	0.709159	
0.05041	3.0948	-1.29747	0.490632	
0.05041	2.9595	-1.29747	0.471218	
0.05041	2.9420	-1.29747	0.468642	
0.05041	2.9019	-1.29747	0.462682	
0.05041	2.9041	-1.29747	0.463011	