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# PERFORMANCE CHARACTERISTICS OF A PACKED-BED OZONE CONTACTOR*

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**ABSTRACT**

Performance characteristics of a packed-bed ozone contactor were investigated. A yellow dye was employed as the tracer to test the dispersion characteristics of the ozone contactor in the single-phase (liquid) and two-phase (countercurrent liquid/air) flow systems. The one-parameter (tanks-in-series) and two-parameter (combined plug-flow/tanks-in-series) models were employed to fit the observed residence time distribution (RTD) functions. It was found that for the one-parameter model, at least twenty well-mixed tanks are required to reasonably fit the observed RTD functions, while for the two-parameter model, only fewer well-mixed tanks plus a plug flow reactor are needed to yield the same fit. The dispersion characteristics of flow in the ozone contactor could also be represented by the dispersion model with appropriate dispersion numbers. The experimental residence time distribution functions were employed in conjunction with the reaction kinetics to determine the discolorization of dyestuff by ozonation in the packed bed reactor. The experimental observations appeared to reasonably confirm the theoretical predictions.

## INTRODUCTION

Chemical oxidation of pollutants has been an attractive method for dealing with various environmental problems. The chemical oxidation process can be

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conducted in various types of reactors, including well-mixed, flow, fluidized bed, or fixed bed types [1, 2]. The wet-air oxidation (WAO) process represents a typical example [3-6]. The WAO process is performed in a well-mixed reactor under high temperatures and pressures.

In recent years, the fixed bed reactor has been widely used in the biological treatment processes of various industrial wastewaters [1, 2]. Lin and Liu have adopted a packed-bed reactor in the treatment of textile wastewater by ozonation [7]. The ozonation reactor employed was found to be superior to other types of reactors because of better air/liquid contact. These authors [7] focused primarily on the studies of overall waste removal efficiencies under various operating conditions. The fundamental aspects of the reactor performance characteristics were not considered. The purpose of the present work is to address this issue by utilizing tracer dye response tests. Theoretical treatment of the experimental residence time distribution (RTD) data is also attempted using a single-parameter (tanks-in-series) or two-parameter (combined plug-flow/tanks-in-series) model. The theoretical model is finally employed to predict ozonation-induced dye discolorization performance in the packed-bed reactor. Good agreement between the predicted and observed results is obtained.

## EXPERIMENTAL STUDIES

The tracer experimental schematic is shown in Figure 1. The packed-bed reactor was a Pyrex glass tube 6 cm in diameter and 1.5 m long. The packing material in the reactor consisted of several structured cylindrical elements of 20 cm long and 6 cm in diameter. Cylindrical elements were made of SS 316 stainless steel strips 2 cm wide. These thin stainless steel strips, which had many punched holes of 0.1 mm in diameter, were twisted and bundled together to form a cylindrical element which looked much like a conventional static mixer. Five sections of these packing elements were inserted into the reactor resulting in a 1 m total packing length. The physical characteristics of the packing elements were given by Lin and Liu [7].

The experimental runs consisted of three types. The first tracer experiment (single phase) used tap water only. The tap water of known flow rate as measured by a rotameter was pumped from the reservoir to the top of the reactor. The water feed was distributed evenly over the top of the packing and allowed to flow through the packing. At time zero, 5 ml of tracer dye solution was injected in an impulse fashion into the feed water at the inlet of packed bed reactor. The tracer dye solution was prepared by dissolving yellow RL dye in deionized water to a concentration of 5000 mg/l. Samples were taken at the reactor exit at the bottom. The dye concentration was determined by a Hitachi UV spectrophotometer (Model U3410, Hitachi Electric, Japan). In the second experiment (two phase), in addition to the water flow, air was pumped to bottom distributor of the reactor rising countercurrent to the water flow. After the countercurrent air/water

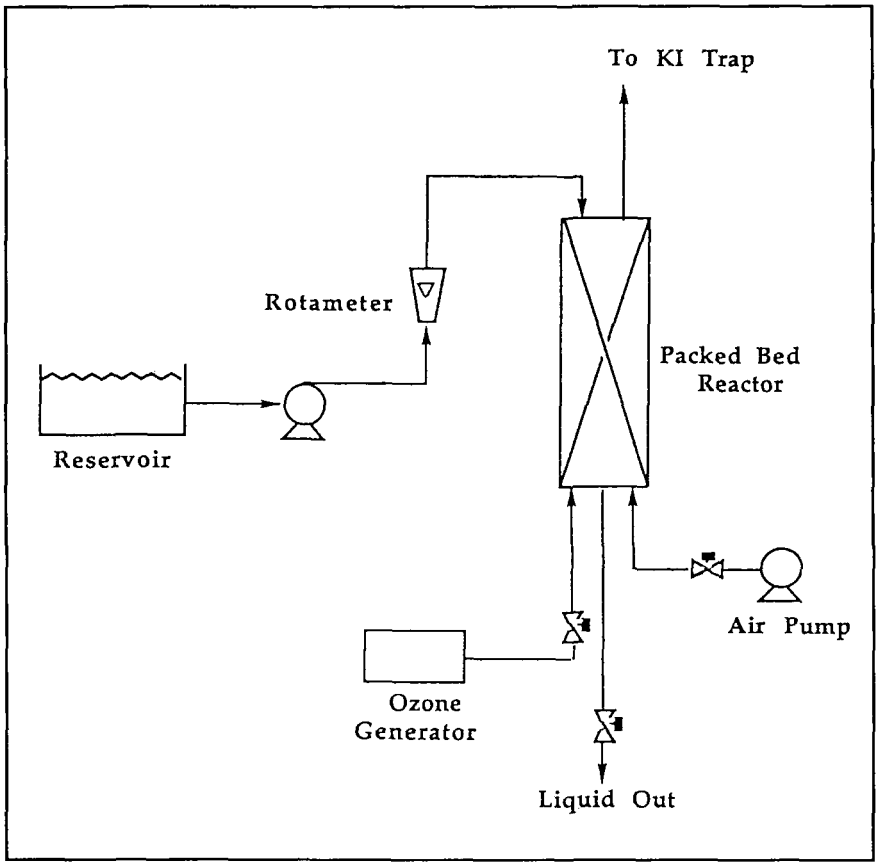


Figure 1. Experimental schematic.

flow reached a steady state, the tracer dye was injected in the sample impulse fashion as the first experiment and the response of tracer at the reactor exit was monitored.

In the third experiment (two-phase ozonation), prepared dye solution was stored in the reservoir and continuously pumped at a fixed flow rate to the top of the reactor. The ozone/air mixture from the Sumitomo ozone generator (Model SG-PSA-01A, Sumitomo Electric, Osaka, Japan) was pumped to the bottom distributor of the reactor. The countercurrent liquid/gas contact also involved chemical reaction due to the dye decomposition by ozone oxidation. The dye concentration at the reactor exit was measured by the Hitachi UV spectrophotometer. The ozone generation system consisted of a pressure swing apparatus (PSA) which was used to clean and dry the incoming air (to a dew point below

–55°C). The dry air from the PSA unit was fed into the Sumitomo ozone generator. The ozone generator is rated at 30 g/hr as its maximum generation capacity. The ozone/air mixture from the ozone generator was then passed to the bottom distributor of the packed bed reactor. The gas effluent exiting the reactor top passed through a potassium iodide (KI) trap before being vented to the atmosphere. The rate of ozone generation as a function of current input as determined by the standard KI absorption method is shown in Figure 2.

## THEORETICAL ASPECTS

The dispersion behavior of flow in a packed-bed reactor is inherently nonideal [8-10]. Such nonideality causes the output response (the E-curve) to an impulse input to deviate from the general Gaussian distribution. To accommodate for the unsymmetrical output response, variations from a simple well-mixed tank or plug

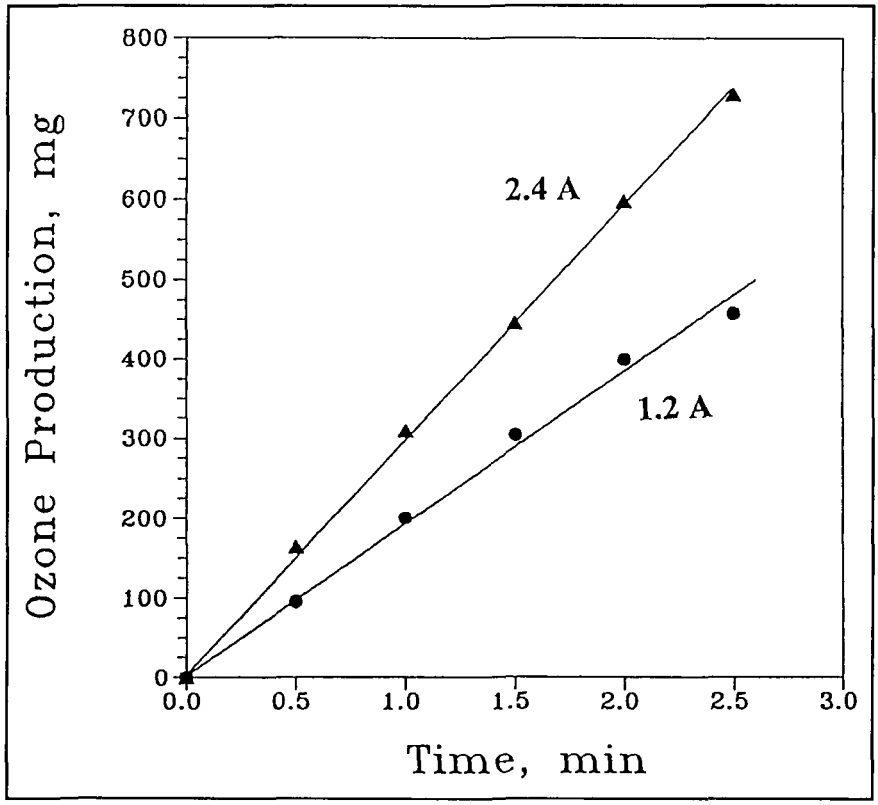


Figure 2. Ozone generation as a function on current input.

flow model have been suggested [8-10]. In the present study, two models were employed, the systems of tanks-in-series and plug-flow/tanks-in-series, as shown in Figure 3. The residence time distribution (RTD) function $E(\theta)$ for the tanks-in-series model can be represented by

$$E(\theta) = \frac{(\theta N)^N}{\theta (N-1)!} \exp(-\theta N) \tag{1}$$

where N is the number of well-mixed tanks, $\theta$ the dimensionless time ($t/\tau$), and $\tau$ the mean residence time (V/Q). Equation (1) was obtained from the material balance of the tanks-in-series system and is generally known as the one-parameter model because the number of well-mixed tanks (N) is the only adjustable variable [8, 9]. The RTD function for the combined plug-flow/tanks-in-series (two-parameter) model can be similarly derived as

$$E(\theta) = \frac{N^N}{(N-1)!} \left(\frac{1}{1-\alpha}\right)^N (\theta - \alpha)^{N-1} \exp\left[-N\left(\frac{\theta-\alpha}{1-\alpha}\right)\right] \tag{2}$$

in which the additional parameter $\alpha$ is defined as $V_1/(V_1+V_2)$ with $V_1$ and $V_2$ being the volumes of plug flow reactor and N well-mixed tanks, respectively. The

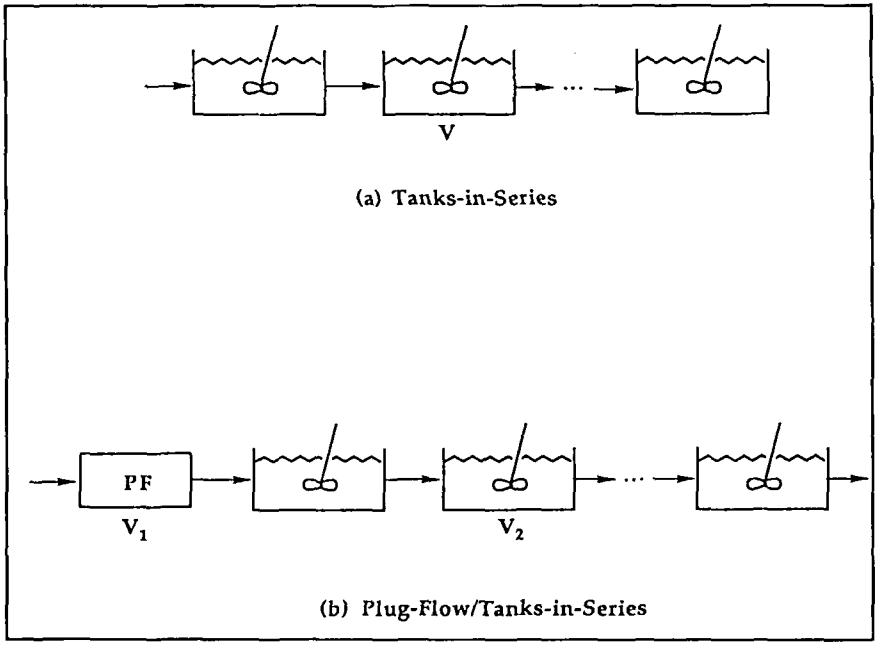


Figure 3. The tanks-in-series and the plug-flow/tanks-in-series systems.

above two equations were employed to fit the experimental residence time distribution functions by properly adjusting N in eq. (1) or N and $\alpha$ in eq. (2) using an IMSL nonlinear least square curve fitting package.

## DISCUSSION OF RESULTS

Figure 4 shows the unsymmetrical residence time distribution function for single phase at a liquid flow rate of 1.5 l/min. Also shown in this figure is the theoretical prediction using single-parameter (tanks-in-series) model. Apparently, eq. (1) with twenty-two well-mixed tanks fits the unsymmetrical RTD function reasonably well. In fact, the two-parameter (plug-flow/tanks-in-series) model yielded essentially identical fit, as shown in Figure 5. In this case, the parameters, N and $\alpha$, were found to be 7 and 0.41, respectively. The volume ratio of the plug-flow reactor to the well-mixed tanks ($V_1/V_2$) is about 0.7 based

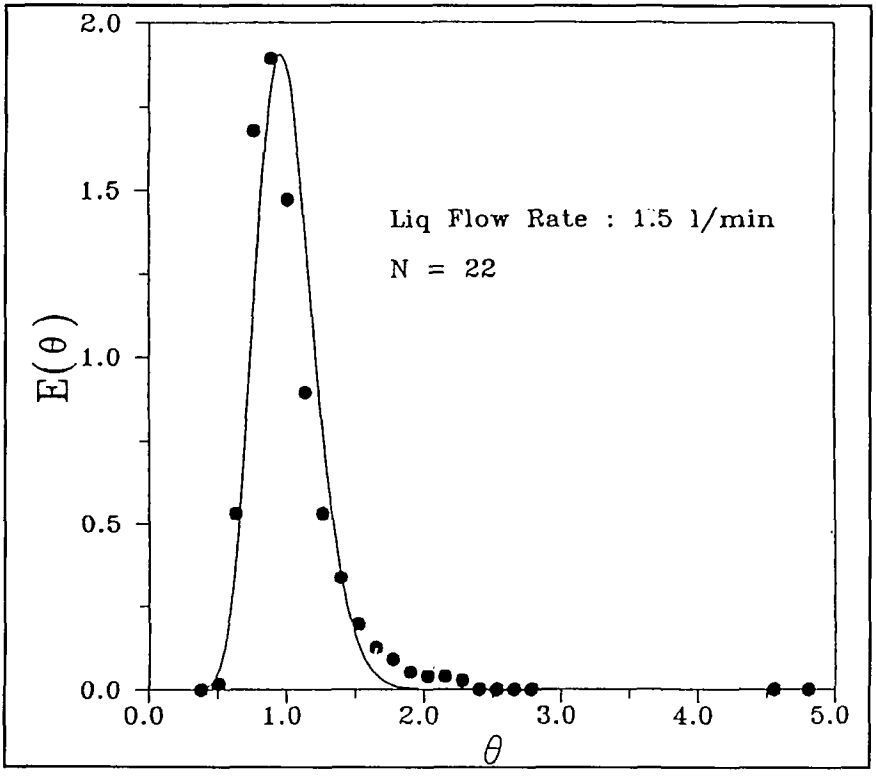


Figure 4. The RTD function of single-phase system with Q = 1.5 L/min fitted by the tanks-in-series model.

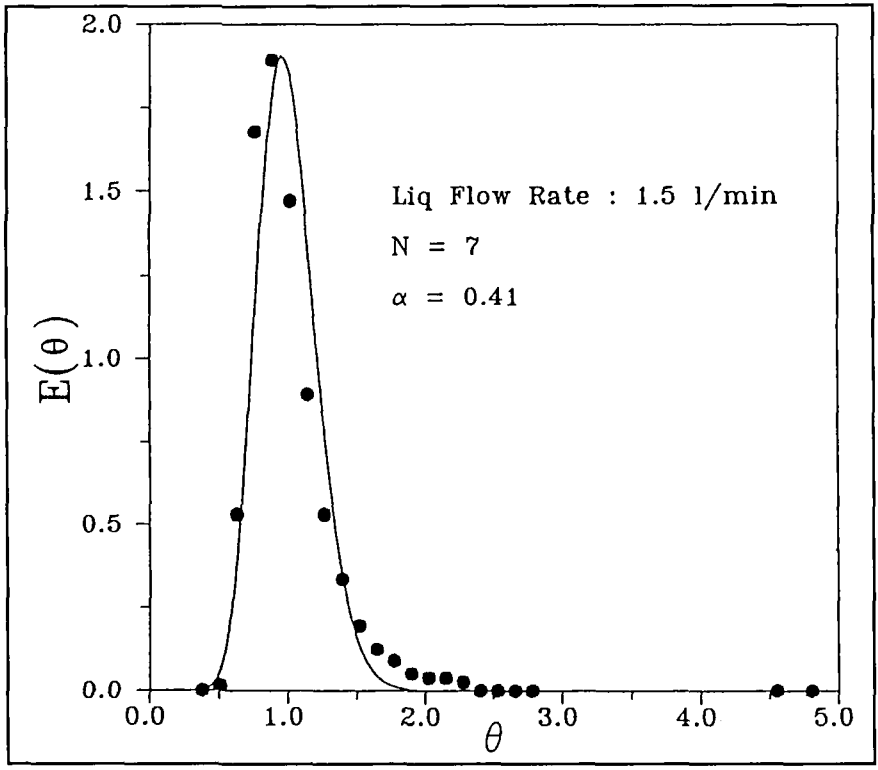


Figure 5. The RTD function of single-phase system with $Q_1$ = 1.5 L/min fitted by the plug-flow/tanks-in-series model.

on $\alpha = 0.41$. The tanks-in-series model is easy to use because only one parameter is involved. The combined plug-flow/tanks-in-series model, however, has more flexibility because of the presence of additional parameter ($\alpha$) which enables the model to fit the unsymmetrical RTD functions over a wider range of operating conditions.

The unsymmetrical RTD function for a lower liquid flow rate 0.5 l/min is shown in Figure 6. The response peak in this figure is seen to be lower than that in the previous one. Theoretical fit by the one-parameter model requires twenty well-mixed tanks. Again, the two-parameter model with $N = 7$ and $\alpha = 0.37$ yielded essentially identical fit and the $V_1/V_2$ ratio became slightly less than 0.6.

The countercurrent air/liquid interaction in the two-phase experiments tends to cause much more dye dispersion. Comparison of Figures 6 and 7 reveals that the spread of the residence time distribution function of the two-phase case is significantly wider than that of the one-phase case. The two-parameter model with

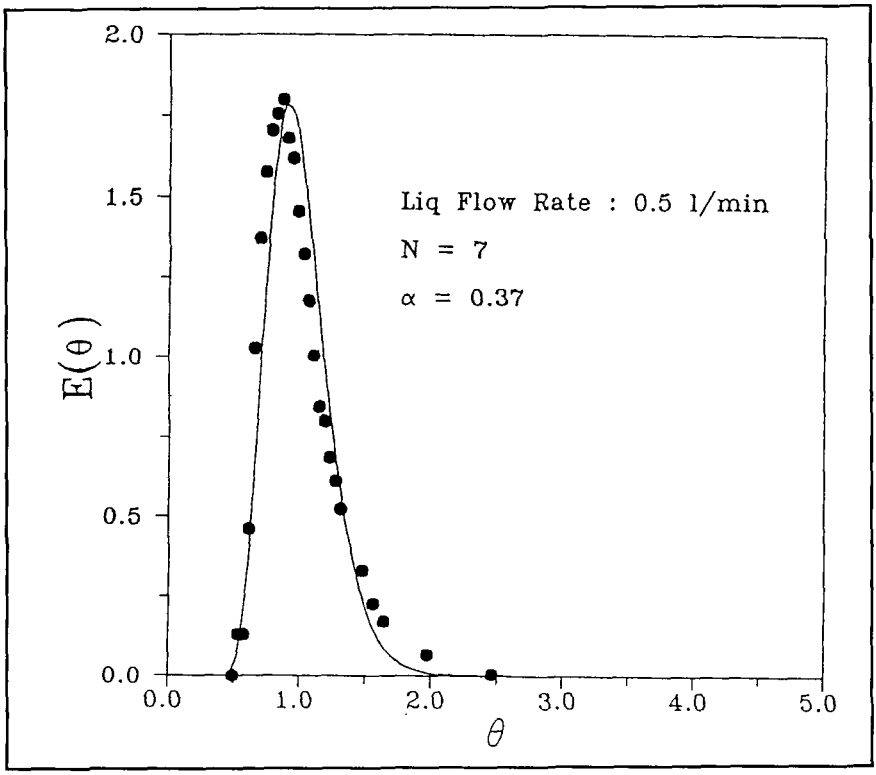


Figure 6. The RTD function of single-phase system with $Q_1$ = 0.5 L/min fitted by the plug-flow/tanks-in-series model.

N = 1.5 and $\alpha$ = 0.2 fits the observed curve reasonably well. The $V_1/V_2$ ratio became 0.25. This parameter set represents a significant decrease in both the number of well-mixed tanks and the volume ratio parameter $\alpha$ from their values in the single-phase case.

Figure 8 demonstrates the RTD function for the same two-phase experiment with a quadruple reduction in the air flow rate. The curve is narrower than that in Figure 7, but the peak is apparently higher. The theoretical model fit reveals that the number of well-mixed tanks remains unchanged, but the $V_1/V_2$ ratio is increased to 0.33 from 0.25 of the previous one.

In Figure 8, the liquid to gas flow rate ratio is 1:0.5. Figure 9 shows the RTD function for the two-phase system with a liquid to gas flow rate ratio of 0.5:1. Comparison of Figures 8 and 9 shows that there is a significant increase in the spread of the residence time distribution in the former case. The theoretical model fit indicates that the $V_1/V_2$ volume ratio was reduced by more than one half from

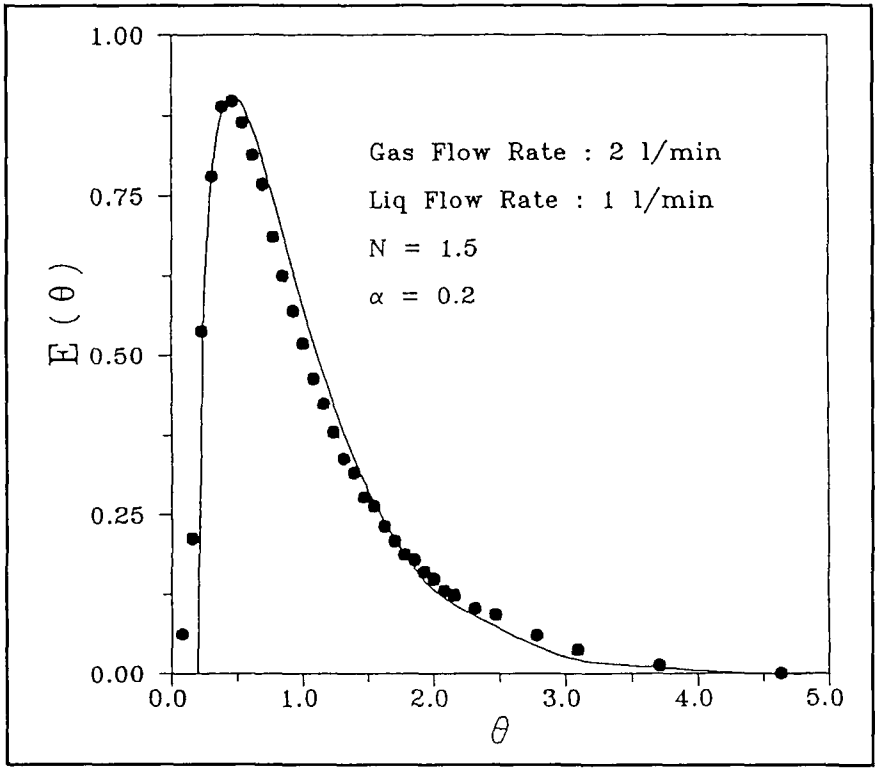


Figure 7. The RTD function of two-phase system with $Q_g$ = 2 L/min and $Q_l$ = 1 L/min fitted by the plug-flow/tanks-in-series model.

0.25 in Figure 8 to 0.12 in Figure 9 while the number of well-mixed tanks was increased slightly to 2 from 1.5 of the previous case.

Characterization of the residence time distribution by either the tanks-in-series model or the combined plug-flow/tanks-in-series model, in fact, can also be represented by the dispersion model [8-10]. The RTD function E(θ) obtained previously can be employed to compute the variance by

$$\sigma^2 = \int_0^\infty (\theta - 1)^2 E(\theta)\, d\theta \tag{3}$$

which is related to the dispersion number (D/uL) by

$$\sigma^2 = 2\left(\frac{D}{uL}\right) - 2\left(\frac{D}{uL}\right)^2 \left[1 - \exp\left(-\frac{uL}{D}\right)\right] \tag{4}$$

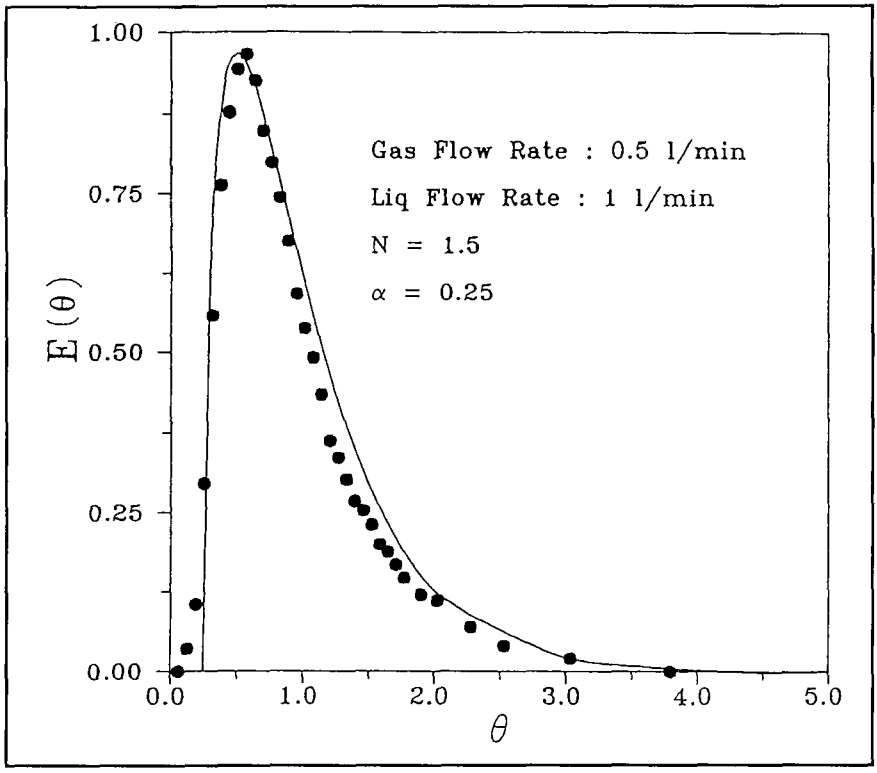


Figure 8. The RTD function of two-phase system with $Q_g$ = 0.5 L/min and $Q_l$ = 1 L/min fitted by the plug-flow/tanks-in-series model.

where D is the dispersion coefficient, u the superficial velocity of liquid, and L the length of the packed bed reactor. The dispersion number was determined iteratively using the above equation and the E(θ) functions shown in Figures 4 through 9. Table 1 lists the computed dispersion numbers for the single-phase and two-phase flow systems. The number is seen to decrease mildly with an increase in the liquid flow rate for the single-phase system, as anticipated. The small dispersion numbers shown here for the single-phase system imply that the present flow system is closer to the plug flow model. This also accounts for the narrow RTD functions. For the two-phase case, the dispersion numbers are significantly larger than these of the single-phase one, reflecting the wider RTD functions. They increase with increasing gas flow rate. It is of interest to note that even when the air/liquid flow rate ratio is fixed for the two-phase flow, the dispersion number still increases with simultaneously increasing air and liquid flow rates due primarily to stronger mixing action at the higher air and liquid flow rates.

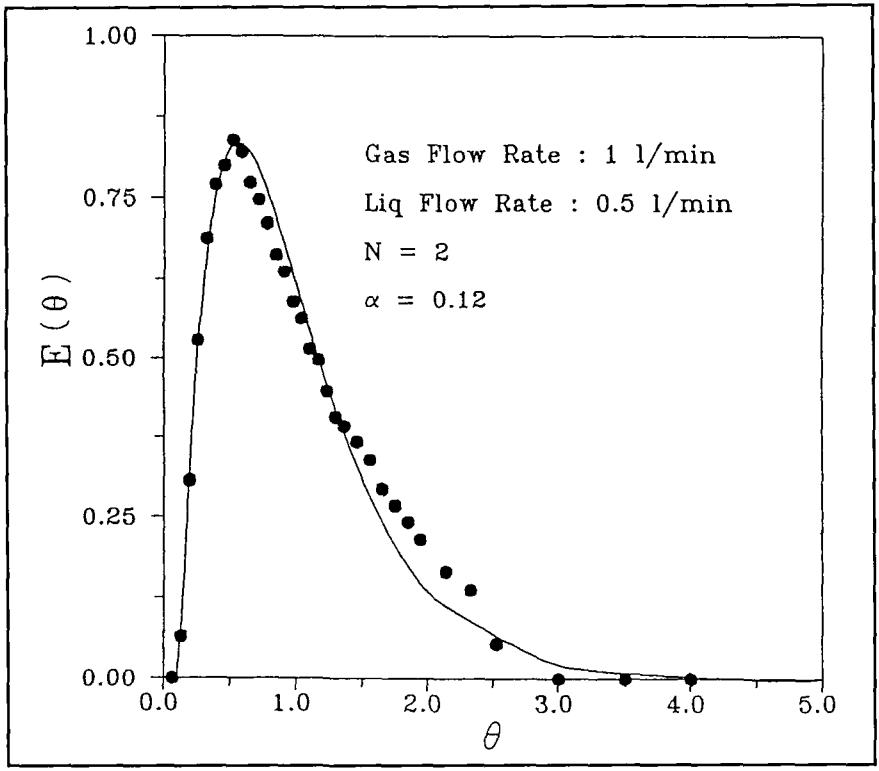


Figure 9. The RTD function of two-phase system with $Q_g$ = 1 L/min and $Q_l$ = 0.5 L/min fitted by the plug-flow/tanks-in-series model.

According to Wen and Fan, the dispersion coefficient for a liquid flow at 0.88 cm/s in fixed bed reactor packed with aluminium or glass beads was about 12.1 $cm^2/s$ [10]. From Table 1, the dispersion coefficient estimated here was 20.2 $cm^2/s$. The difference between these two figures was due primarily to the difference in the packing materials employed.

The RTD function can be employed to determine the exit concentration of a reacting system in the packed bed reactor. As mentioned earlier, ozone is an excellent oxidant for dye discolorization. Efficiency of dye discolorization in a packed bed ozone contactor had been shown to be quite high [7]. In this case, the gas that entered the reactor bottom came from the ozone generator as a mixture of air and ozone instead of plain air. The reaction kinetics between ozone and the yellow dye was determined separately in a batch reactor to be of first order, as shown in Figure 10 which is represented by

$$\frac{C}{C_0} = \exp(-0.71\ t) \tag{5}$$

The exit dye concentration is then computed from

$$\frac{C_{exit}}{C_0} = \int_0^\infty \frac{C}{C_0} E(\theta)\, d\theta \tag{6}$$

The $C_{exit}/C_0$ values computed from the above equation for liquid/gas flow rate ratios of 3/1.5, 2/1, and 1/0.5 were $4.29\times10^{-11}$, $8.04\times10^{-14}$, and $1.41\times10^{-17}$, respectively. The corresponding experimental dye concentrations for these cases were below the detection limit of the Hitachi UV spectrophotometer (approximately $10^{-4}$ mg/l) because the originally strong tracer dye color of the liquid stream had completely faded away at the reactor exit. The exit liquid samples taken had identical UV spectra like those of pure water employed for dye solution preparation.

## CONCLUSIONS

Residence time distribution functions for a packed-bed ozone contactor were determined experimentally using tracer dye in both the single-phase and the

Table 1. Dispersion Numbers of the Flow Systems

| Single Phase | |
|---|---|
| Liquid Flow Rate (L/min) | Dispersion Number (D/uL) |
| 0.5 | 0.0423 |
| 1 | 0.0345 |
| 1.5 | 0.0249 |
| **Two Phase** | |
| Air/Liquid Flow Rate Ratio | Dispersion Number (D/uL) |
| 0.5/1 | 0.1299 |
| 1/1 | 0.1643 |
| 2/1 | 0.2 |
| 1/0.5 | 0.1391 |
| 2/1 | 2 |
| 3/1.5 | 0.2322 |

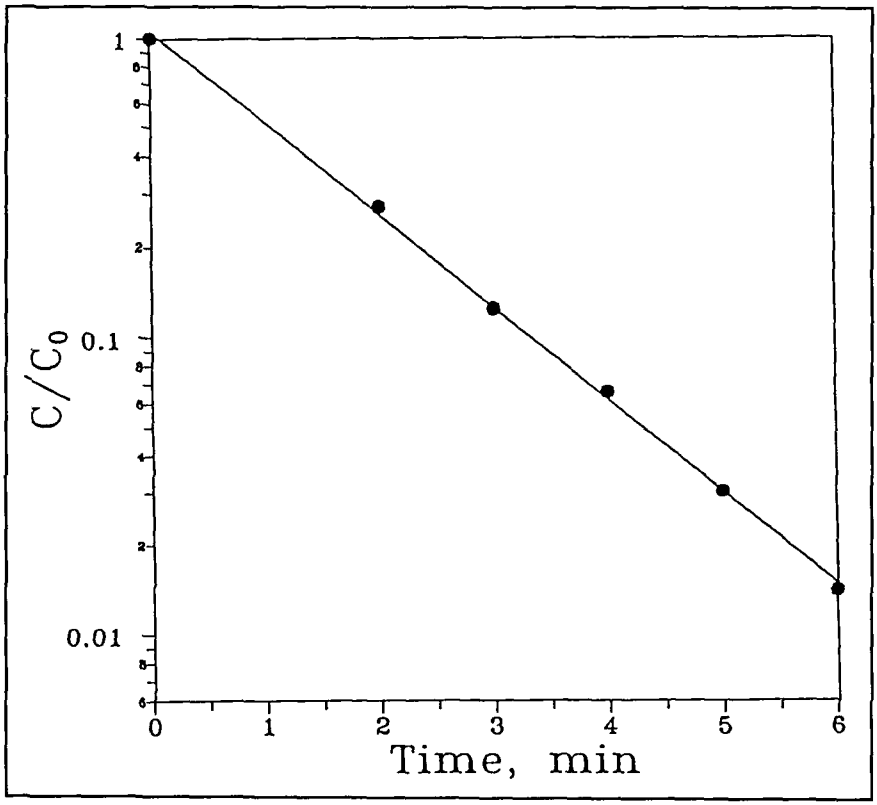


Figure 10. First-order reaction kinetics of yellow dye discolorization by ozonation.

two-phase flow systems. The observed functions were theoretically fitted using the tanks-in-series and the combined plug-flow/tank-in-series models. It is found that the tanks-in-series model requires at least twenty well-mixed tanks to yield a reasonable fit to the observed RTD functions. The combined plug-flow/tanks-in-series model requires significantly fewer well-mixed tanks to fit the observed functions. The RTD functions are also employed to determine the dispersion number of the dispersion model. The dispersion numbers for the two-phase system are nearly double those of the single-phase system.

In conjunction with the reaction kinetics of dye discolorization, the RTD function was employed to predict the exit dye concentration of the ozonation system. The predicted exit dye concentration using the experimental RTD functions is reasonably confirmed by the experimental observations.

## NOMENCLATURE

| | |
|---|---|
| $C$ | dye concentration (mg/L) |
| $C_0$ | inlet dye concentration (mg/L) |
| $C_{exit}$ | exit dye concentration (mg/L) |
| $D$ | dispersion coefficient ($cm^2/s$) |
| $E(\theta)$ | residence time distribution function |
| $L$ | length of packed bed reactor (cm) |
| $N$ | number of well-mixed tanks |
| $Q$ | volumetric flow rate ($cm^3/s$) |
| $Q_g$ | volumetric flow rate of gas mixture ($cm^3/s$) |
| $Q_l$ | volumetric flow rate of liquid ($cm^3/s$) |
| $t$ | time (s) |
| $u$ | superficial liquid velocity (cm/s) |
| $V_1$ | volume of plug-flow reactor ($cm^3$) |
| $V_2$ | total volume of N well-mixed tanks ($cm^3$) |

**Greek symbols**

| | |
|---|---|
| $\alpha$ | volume ratio parameter, $V_1/(V_1+V_2)$ |
| $\theta$ | dimensionless time, $t/\tau$ |
| $\tau$ | mean residence time, V/Q (s) |

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