
Chapter

5

**Optimal
Experimental
Design**

Four to six weeks in a lab can save you an hour in the library.

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5.1 INTRODUCTION

Given the complexity of most chemical processes, in order to find optimal experimental conditions it is important to implement a properly planned set of experiments. The experimental design methodology (Box *et al.*, 1978, Khuri and Cornell, 1987) for the simulation and evaluation of the critical parameters is a modern approach in industrial reactor design. It is based on multivariate methods, which allow more efficient data collection and easier data treatment than the technique of changing the level of one variable at a time, while maintaining other variables at fixed levels. A number of classical experimental designs (experimental matrices) adapted to different types of problems are available. By following this methodology, modeling is possible with only a minimum number of experiments. It is also not necessary to know the detailed reaction mechanism, since the mathematical model is empirical. The magnitude of the interactions between the variables is reflected in the value of the coefficients of the single polynomial expression used to fit the experimental data.

5.2 EXPERIMENTAL

All of the experiments were performed in the reactor system, which is described in detail in Chapter 1 and Alibegic *et al.*, 2001. In the absorption with reaction runs PCE gas was prepared by passing a controlled volume of air through a PCE containing bottle, which was placed in a thermostat. The concentration of the feed gas could therefore be controlled by adjusting the temperature in the thermostat, flow rate of air through PCE containing bottle, and/or main air stream. Gas lines containing the PCE gas and the main line were connected. Gas was then passed through a quartz wool plug (inserted for mixing purposes) and was transferred to the UV bubble column (UV-BCR) through the gas distributor (air stone coil) that was placed around the quartz tube at the bottom of the reactor. Inlet gas samples were taken from the sampling port placed between the quartz wool plug and the reactor with VICI

pressure-lok gas syringe (Series A-2, 500 μ l RN) and analyzed by GC-ECD. Outlet gas samples were taken from the sampling port placed at the exit of the UV-BCR with another syringe. Heating tape was wrapped around the gas exit line to prevent condensation in the effluent section. The effluent stream was then directed into an absorption bottle containing 400 mL of distilled water to trap soluble reaction products. Another flow meter was positioned after the absorption bottle as a control flow meter. Effluent was then passed through an activated carbon adsorption trap and vented. All the gas lines were made of Teflon and connected with either Teflon or Swagelok SS connectors. Special care was taken to prevent any leakage of the gas from the reactor system. In each run 4L of distilled water with a calculated amount of H_2O_2 was input to the UV-BCR. The liquid content of the UV-BCR was recirculated through the reactor with the IWAKI magnetic pump at a flow rate of 5 L/min. Gas and liquid phases were contacted counter-currently. H_2O_2 was continuously supplied into the reactor from an H_2O_2 reservoir using a peristaltic pump at a metered rate in order to maintain the concentration of hydrogen peroxide inside the reacting vessel at a constant value. The hydrogen peroxide concentrations were maintained at values of 0.001, 0.0044 and 0.014 mol/L, which corresponds to approximately 10%, 50% and 90% UV light absorption by hydrogen peroxide, respectively. The hydrogen peroxide degradation rates were previously determined in the same reactor over a wide range of concentrations without any bubbling of the pollutant. Incident photon flow rate measured by the hydrogen peroxide actinometry (Nicole *et al.*, 1990) was determined to be 3.75 $\mu\text{Einstein}/(\text{Ls})$. Gas flow rate was varied from 1 L/min to 2 L/min, however, the inlet PCE gas concentration was kept constant at a value of $6 \times (1 \pm 0.03) \mu\text{mol}/\text{L}$ in order to prevent the direct absorption of UV light by PCE. In a typical experiment UV light was turned on 15 minutes prior to the addition of the gas phase. Therefore, when PCE was sparged into UV-BCR the reaction started immediately. The temperature of the liquid phase was always $25(1 \pm 0.05)^\circ\text{C}$. Typically, experiments were conducted for periods ranging from 1.5 to 2 h. Gas and liquid samples were taken at regular intervals and analyzed for PCE with a GC-ECD (Shimadzu GC-14B). A TC-5 capillary column (GL Science, length 30 m, inner diameter 0.25 mm, film thickness

5 μ m) was used isothermally at 100°C. The injector port and detector were both kept at 200°C. The GC was calibrated for the operating conditions and the linearity was checked weekly. PCE liquid samples were treated with sodium thiosulfate (to quench any active halogen) as described in Glaze *et al.* (1995) and were analyzed by a liquid-liquid micro-extraction method. Cl ion was analyzed by Ion Chromatograph (IC-Yokogawa Hokushin Electric) and HPLC TOSOH, using CM-8010 TC detector, TSK gel column and TSK Eluent IC-Anion-A by TOSOH. H₂O₂ was analyzed by KMnO₄ titration using a 785 DMP Titrino by Methrom, as well as by spectrophotometr (Klassen *et al.*, 1994).

5.3 RESULTS AND DISCUSSION

As shown in Chapter 3, the hydrogen peroxide concentration to pollutant ratio is an important parameter in the UV/H₂O₂ process. In batch operating reactors initial hydrogen peroxide concentration needs to be high to ensure the presence of peroxide throughout the reaction. However, as it was shown in Chapter 2, H₂O₂ itself can act as a radical scavenger and this in a great way reduces the efficiency, and therefore cost performance, of the system. For these two reasons I have developed a UV-Bubble Column Reactor (UV-BCR) in which H₂O₂ can be added in to the reactor continuously and kept on an optimum level throughout the reaction and optimum value searched.

5.3.1 H₂O₂ degradation kinetics

As shown earlier the overall decay rate of pure H₂O₂ solution can be given by the combination of the Beer-Lambert law and the definition of quantum yield as

$$r_{\text{H}_2\text{O}_2} = -\frac{dc_{\text{H}_2\text{O}_2}}{dt} = \phi_T I_0 (1 - 10^{-D}) \quad (5-1)$$

where optical density ($D = \epsilon l_{eff} c_{H_2O_2}$) primarily depends on the hydrogen peroxide concentration. The rate expression can be simplified when D is either very small or very large as follows.

When D is small, the decomposition of hydrogen peroxide can be described by the first order kinetics derived from the Taylor series expansion of Eq.(5-1),

$$r_{H_2O_2} = 2.303 \epsilon l_{eff} \phi_T I_0 c_{H_2O_2} = k_{5-2} c_{H_2O_2} \quad (5-2)$$

however, when $D > 2$ the rate can be expressed as a zero order:

$$r_{H_2O_2} = \phi_T I_0 = k_{5-3} \quad (5-3)$$

The data analysis has shown that all of the experimental results of hydrogen peroxide degradation could be fit to either zero or first order kinetics or the integrated form of Eq.(5-1).

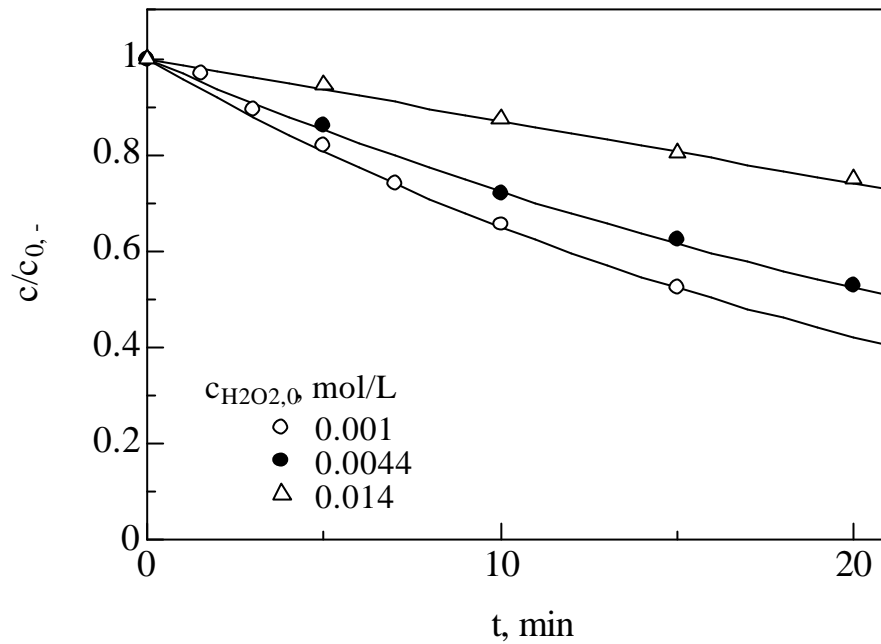


Figure 5.1. Influence of initial hydrogen peroxide concentration on the H_2O_2 degradation rate.

Figure 5.1 shows the influence of the initial hydrogen peroxide concentration on the H_2O_2 degradation rate. Data could be well fit to zero or pseudo-first order kinetic rate expressions with high regression coefficients (ranging from 0.994 and 0.999 for 14 mmol/L and 1 mmol/L). It can be observed that increasing the initial H_2O_2 concentration decreases the rate of hydrogen peroxide degradation. This indicates that in addition to decreasing the pollutant degradation rate, increasing the initial hydrogen peroxide concentration decreases the rate of H_2O_2 consumption. This leads to high level of hydrogen peroxide residual in the treated water and therefore to an increase in the operating cost. Since the rate of H_2O_2 degradation and consequent OH production is proportional to the light intensity (Eqs. 5-1 to 5-3) an increase in UV power will probably have a direct positive effect on the H_2O_2 consumption constant. Due to the constraints of available equipment in this work I have however performed experiments at the constant, maximum light output. On the other hand, Crittenden *et al.* (1999) reported that the operating cost also increases with increasing UV power. The balance

between light power and hydrogen peroxide concentration needs to be obtained. This fact again indicates the importance of optimization of the level of H_2O_2 with regard to the initial concentration of pollutant.

In batch reactors the light absorption characteristics vary with changes in concentration of the light absorbing species ($D = \epsilon l c_{\text{H}_2\text{O}_2}$); therefore the operating conditions are always at unsteady state, except when interpolated to time zero or when operated in a total absorption conditions ($D > 2$) for all reaction times. In our work, in order to study the effects of both, H_2O_2 concentration and the rate of UV light absorption I ensured that the concentration of hydrogen peroxide was kept constant at values which gave 10%, 50% and 90% light absorption by hydrogen peroxide, by continuous addition of concentrated H_2O_2 solution to make-up for that which had reacted. The mass balance for the hydrogen peroxide can be written as:

$$\text{Accumulation} = \text{Inlet} - \text{Outlet} - \text{Reaction} \quad (5-4)$$

With the Accumulation and Outlet terms set to zero (constant bulk liquid concentration and no flow out) the amount of H_2O_2 addition can be calculated from

$$r_{\text{H}_2\text{O}_2} V_R = Q_{\text{H}_2\text{O}_2, \text{IN}} c_{\text{H}_2\text{O}_2, \text{IN}} \quad (5-5)$$

where the hydrogen peroxide reaction rate for a given H_2O_2 concentration was selected from the results shown in Fig. 5.1. The inlet flow rate ($Q_{\text{H}_2\text{O}_2, \text{IN}}$) of the make-up hydrogen peroxide solution ($c_{\text{H}_2\text{O}_2, \text{IN}}$) was set to ratio of the sample size and sampling time in order to maintain the reaction volume as constant as possible throughout the time of the experimental periods. By doing this I have ensured that the volume of reacting (irradiated) solution changed at most for 1.5% between the two sampling times. Make-up H_2O_2 concentration was calculated for a given set of operating conditions from Eq. (5-5) and the H_2O_2 solution was continuously

introduced into the UV-BCR with a peristaltic pump as shown in the schematic of the reaction apparatus.

5.3.2 Experimental methodology

Response surface methodology (Khuri and Cornell, 1987) was used for the evaluation of the influence of H_2O_2 concentration and gas flow rate on PCE gas removal in the UV-BCR, as the effect of one variable depends on the setting of another one and *vice-versa*. Simply speaking, there are interactions between variables. The absorption of PCE gas into the reaction medium can be enhanced by flow rate (higher mass transfer coefficient) and by the reaction of PCE with OH radicals (which affects the concentration gradient between the PCE in the gas phase and PCE dissolved in the bulk liquid). On the other hand, the concentration of available OH radicals (which are responsible for the oxidation) depends on the absorption characteristics of the reacting medium (which change in the presence of a gas phase), and on the ratio of H_2O_2 and PCE concentrations in the bulk liquid as has been demonstrated earlier.

A 3^k Factorial Design has been applied in this work to investigate the two input variables (gas flow rate and hydrogen peroxide concentration, respectively; $k=2$) over the range determined in a previous work (Alibegic, 2001). 3^k Factorial Design requires that the responses be observed at all possible input level combinations of the k input variables, which have three levels each. In this case, that meant nine experiments, in which gas flow rate was varied between 1, 1.5 and 2 L/min, and H_2O_2 concentration between 0.001, 0.0044 and 0.014 mol/L (corresponding to 10%, 50% and 90% UV light absorption by hydrogen peroxide, respectively). In these preliminary runs the inlet gas concentration was however kept constant at $6(1\pm0.03)$ $\mu\text{mol/L}$. This concentration was selected such that the direct absorption of UV light by PCE was negligible in order to suppress the Cl radical-initiated chain reaction in the gas phase which usually results in the production of stable intermediates (Alibegic, 2001).

Another advantage of UV-BCR is the fact that if Cl radical-initiated reaction in the gas phase proceeds via the phosgene branch, the later was shown to hydrolyzes with water ($k_{\text{Phosgene,H}_2\text{O}} = 9 \text{ s}^{-1}$) to form hydrochloric acid and carbon dioxide, the desirable products of the oxidation.

In order to avoid having different units for different variables U_i , the real variables (U_1 = Flow rate (L/min) and U_2 =UV light absorption (%)) were transformed into the following reduced centered dimensionless variables: X_1 (normalized flow rate) and X_2 (normalized UV light absorption, which corresponds to the H_2O_2 concentration). Calling the $U_0=(U_{i,\min}+U_{i,\max})/2$ the value of U_i at the center of the experimental region, i.e. the average of the maximum and minimum used during the experiments, we define $X_i=(U_i-U_{i0})/\Delta U_i$, with the step size being defined as $\Delta U_i=(U_{i,\max}-U_{i,\min})/2$.

Assuming the *pseudo*-first-order reaction rate constant for the reaction of PCE in the liquid phase to be 0.01 s^{-1} and a mass transfer coefficient between 10^{-5} and 10^{-4} m/s we can calculate the Hatta number to be between 0.028 and 0.28, corresponding to the slow bulk liquid reaction regime, with reaction occurring mainly in the bulk liquid, at a rate affected by the mass transfer rate across the liquid film. In such a system the concentration of the bulk liquid phase is very important. As the Ha number alone does not provide much information about the system, it is convenient to define a new variable, the degree of saturation of the liquid bulk, η_{SAT} . The degree of saturation of the liquid bulk is defined as the ratio of the PCE liquid concentration to the liquid phase concentration of PCE when the liquid phase is saturated (Elk *et al.*, 2000). If Henry's law holds, this can be represented in the form $\eta_{\text{SAT}} = mc_{\text{PCE}}^{\text{L}} / c_{\text{PCE}}^{\text{G,IN}}$. For increasing reaction rate or decreasing mass transfer rate, the degree of saturation will approach a certain minimum and for decreasing reaction rate or increasing mass transfer rate the degree of saturation will approach a maximum.

Table 5.1. Experimental matrix for 3^k factorial design.

Experiment	Coded variables		Real variables		Experimental responses	
No.	X_1 ,	X_2 ,	Q,	A,	X_G	η_s
	/	/	L/min	/	/	/
1	-1	-1	1.0	0.1	72-78	0.098
2	0	-1	1.5	0.1	77-82	0.081
3	1	-1	2.0	0.1	54-61	0.132
4	-1	0	1.0	0.5	69-73	0.04
5	0	0	1.5	0.5	68-70	0.08
6	1	0	2.0	0.5	50-58	0.13
7	-1	1	1.0	0.9	55	0.15
8	0	1	1.5	0.9	56	0.113
9	1	1	2.0	0.9	54	0.414

The experimental data (values averaged over the time of the experimental run) as shown in Table 5.1 were used to develop regression equations to quantitatively describe the PCE gas removal efficiency ($X_G = 1 - c_{PCE}^{G,OUT} / c_{PCE}^{G,IN}$) and the degree of saturation of the liquid phase, η_{SAT} . The data fit was evaluated based on the correlation (R^2) of the final regression equations. When compared to the experimental data, regression coefficients of 0.99 and 0.96 were obtained for Eqs. (5-1) and (5-2) respectively.

$$X_G = 0.704 - 0.0495X_1 - 0.0803X_2 - 0.0475X_1^2 - 0.0455X_2^2 + 0.0278X_1X_2 \quad (5-1)$$

$$\eta_{SAT} = 0.0549 + 0.0599X_1 + 0.0675X_2 + 0.0540X_1^2 + 0.0765X_2^2 + 0.0514X_1X_2 \quad (5-2)$$

The resulting regression equations, plotted as a contour plots (curves of constant response) using SYSTAT software, are presented in Figs. 5.2a and 5.2b. Figure 5.2a represents the influence of flow rate and UV light absorbed (hydrogen peroxide concentration) on the PCE gas removal in absorption with reaction runs. Increases in both gas flow rate and hydrogen

peroxide concentration have a negative effect on the gas removal efficiency. The predicted optimum is outside the experimental region for pollutant concentration. Figure 5.2b shows that the minimum degree of saturation (less than 0.05) is predicted for flow rates between 1 and 1.5 L/min and H_2O_2 concentrations between 3 and 8 mmol/L, respectively. It can also be observed that the degree of saturation increases for all flow rates once H_2O_2 concentration is higher than 8 mmol/L, which might be explained by the increased scavenging effect of hydrogen peroxide itself. The highest removal efficiency (70-75%) in a single flow-through with the lowest degree of saturation of the liquid phase is predicted for flow rates between 1.2 and 1.5 L/min and hydrogen peroxide concentrations about 3 mmol/L. Lower hydrogen peroxide concentrations did not likely afford sufficient OH radical concentration in solution for the reaction to proceed favorably.

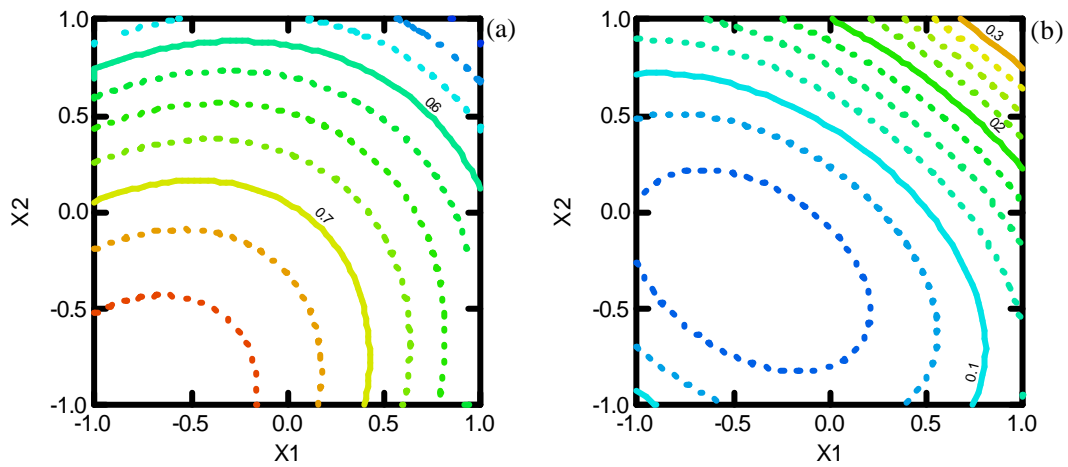


Figure 5.2. 2D-contour plot of (a) gas removal efficiency derived from the Eq. (5-1) and (b) the degree of saturation of the liquid phase derived from the Eq. (5-2) with centered and reduced variables X_1 (levels -1, 0 and 1 corresponding to the gas flow rates of 1, 1.5 and 2 L min^{-1}) and X_2 (levels -1, 0 and 1 corresponding to the UV light absorption rate by H_2O_2 10, 50 and 90%). Conditions: $c_{\text{PCE,G-IN}} = 6 \mu\text{mol L}^{-1}$, $T=25^\circ\text{C}$, $I_0 = 3.75 \mu\text{Einstein L}^{-1}\text{s}^{-1}$, $\text{pH}_0 = 7$.

The increase of the PCE gas removal efficiency for flow rates below 1.5 L/min and hydrogen peroxide concentrations less than 3 mmol/L, coupled with a simultaneous increase in the degree of saturation is somewhat uncommon. It could be however explained by the increased mass transfer rate due to an increase in the hydrophobic character of the reacting solution caused by the presence of a higher concentration of PCE in the bulk liquid. Gurol and Nekouinaini (1985) reported that the presence of the hydrophobic phase in the liquid could in addition contribute to the enhancement of mass transfer, as it can reduce the bubble coalescence rate (bubble size) and therefore increase the interfacial surface area. (The octanol-water partition coefficient (K_{ow}), an indicator of hydrophobicity, of PCE is 2.88). It should be noted that even though higher flow rates cause the introduction of greater amount of PCE into reactor, the maximum overall mineralization of pollutant will be achieved by balancing combination of gas removal efficiency and resulting liquid bulk concentration.

5.4 CONCLUSIONS

In the experiments where PCE gas was absorbed into a UV-BCR, the influence of two critical parameters, gas flow rate and hydrogen peroxide concentration (absorption of radiation energy), was investigated using the experimental design methodology. For the operational conditions in this study it was observed that both gas flow rate and hydrogen peroxide concentration had a negative effect on the PCE gas removal efficiency, and the predicted maximum was outside the experimental region. The highest PCE gas removal efficiency with the lowest degree of bulk liquid saturation was predicted for flow rates between 1.2 and 1.5 L/min and hydrogen peroxide concentrations about 3 mmol/L. Further studies of the process with regard to the initial pollutant concentration, gas flow rate, hydrogen peroxide concentration and the proper modeling of light absorption and the reactor system are still needed, from not only an empirical but from a scientific point of view.