Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2012.748977

51 (2013) 3106–3113
April

Taylor & Francis
Taylor & Francis Group

Treatment characteristics and statistical optimization of Chloroform using sonophotocatalysis

J.H. Park

Water Pollution Load Management Research Division, National Institute of Environmental Research,
Kyungseo-dong, Seo-gu, Incheon Metropolitan city 404-170, Korea
Tel. +82 032 560 7361; Fax +82 032 560 7976; email: jhong@korea.ac.kr

Received 27 March 2011; Accepted 4 November 2012

ABSTRACT

The experimental design and response surface methodology were applied to optimization of the sonophotocatalytic degradation of Chloroform. The sonophotocatalytic reactions were mathematically described as a function of parameters such as Chloroform concentration, UV intensity, and TiO_2 concentration using the Box–Behnken method. Statistical analysis showed that the responses of Chloroform removal in sonophotocatalysis were fitted to linear interaction effect model. The response surface methodology using the Box–Behnken method yields the following equation as an uncoded unit: $y = 90.7017 + 5.3371(\mathrm{UV}) - 4.2315(\mathrm{Chloroform}) -0.3550(\mathrm{TiO_2}) - 0.8101(\mathrm{UV})(\mathrm{Chloroform}) + 0.1072(\mathrm{UV})(\mathrm{TiO_2}) + 0.0574(\mathrm{Chloroform})(\mathrm{TiO_2})$. As for main effect factors of the model formula, concentration of Chloroform posted the biggest effects followed by UV intensity and TiO_2 concentration. The impact of various factors on removal rate was higher when Chloroform concentration was lower, TiO_2 concentration was higher, and number of UV lamp was higher.

Keywords: Box–Behnken; Chloroform; Response surface; Sonophotocatalysis; TiO_2; UV intensity

1. Introduction

Chloroform may be released to the air as a result of its formation in the chlorination of drinking water, wastewater, and swimming pools. Other sources include pulp and paper mills, hazardous waste sites, and sanitary landfills. Chemically, it is employed as a solvent for fats, alkaloids, iodine, and other substances. When exposed to sunlight and air, it reacts to form phosgene, a poisonous gas. Due to the nonbiodegradability of Chloroform, conventional biological treatment methods for industrial and municipal wastewater are ineffective. Therefore, it needs to develop an effective treatment process.

Advanced oxidation processes (AOPs) can oxidize and clean organic pollutants rapidly and randomly in aqueous media by creating and utilizing active species like hydroxyl radicals ($OH^{\bullet}$) [1]. The AOPs are being used to various wastewater treatment fields in which conventional methods can hardly be adapted. Among them are nonbiodegradable wastewater and toxic wastewater [2].

Recently, TiO_2 photocatalytic process, which is a part of AOPs, is being widely used to decompose organic pollutants [3–11]. The process utilizes solar or artificial ultraviolet ray lamp and TiO_2 serves as catalyst. Photocatalysis decomposes organic pollutants using $OH^{\cdot}$, which is generated on the surface of TiO_2, thanks to electron transition. Sonophotocatalysis combines photocatalysis and supersonic waves [12]. In the process, organic pollutants are treated through chemical effect generating active species like free radical. Mechanical impacts of supersonic waves increase mass transfer and decrease particle size [13,14]. With this condition, cavitation occurs during rarefaction period [13,15] and small amount of vapors are generated. Then, water is dissociated, generating active species like free radical. The chemical impact of the process makes possible treatment of organic pollutants. Adding supersonic waves to photocatalysis accelerates response rate, generates $OH^{\cdot}$ radical better, and eases mass transfer of reactants and products on the surface of catalyst [12]. Thereby, the method is more efficient in decomposing pollutants compared to conventional photocatalysis [12].

However, most studies have been conducted under subjective judgment of researchers on response variables. And randomization, repetition, and blocking have yet to be conducted to achieve objectivity of experiment planning. In addition, there has been almost no research on accuracy and analysis about error term. And, this type of research is often conducted with one fixed factor but different levels. Therefore, it is difficult to find optimization about response value under specific conditions. And, analyzing and quantifying effects among factors is almost impossible. Accordingly, this study was to optimize response conditions, develop model formula, and provide statistical explanation about factors affecting Chloroform removal rate of sonophotocatalysis with adopting response surface analysis to gain multiple regression analysis and optimal conditions of the test model, which is empirical simulation.

2. Materials and methods

2.1. Reagents

The semiconductor employed as photocatalyst was commercial TiO_2 (BCT-S100-2), which is in granulated form, and was used as received. According to the manufacturer, BCT-S100-2 has a primary particle size of 2 mm, a specific surface area of $50\,m^2/g$, a density of 2.2, and its crystalline mode is 80% anatase.

Chloroform, 99% purity, was obtained from Showa Chemical Co., Japan. Aqueous solutions were prepared using deionized and doubly distilled water.

2.2. Analytical methods

At regular time intervals during the reaction, samples were withdrawn from the reactor using a spring-loaded adjustable syringe (10 mL), and then immediately transferred to a 40 mL vials. The Chloroform was analyzed by a Hewlett-Packard gas chromatography (HP 6890), with flame ionization detector (GC/FID). The column was a HP-5 fused-silica capillary column with dimensions of $50\,m \times 0.2\,mm \times 0.33\,\mu m$. The injection, column, and detector temperature were 270, 120, and 270 °C, respectively.

2.3. Sonophotocatalytic reactor

The sonophotocatalytic reactor has been described in Fig. 1. It consists of an illumination source, sonicator, and blower. The light source used is 40 W UV lamps (Sankyo Denki Co). Ultrasonic irradiation was performed from two sides with a reactor. Blower (1 L/min) was used to prevent photocatalyst from settling.

Sonophotocatalysis operation conditions are described in Table 1.

2.4. Design of experiments for optimization

2.4.1. Concept of response surface analysis method

Response surface explains functional relations of response variable (characteristic) and independent variable (design variables and factor). Response surface formula has not been known yet. With using RSM (response surface methodology), appropriate

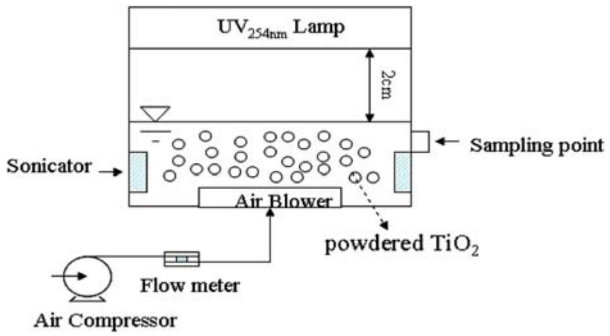


Fig. 1. Schematic diagram of the sonophotocatalytic reactor.

Table 1
Operation conditions of the sonophotocatalysis

Volume	5 L
UV wavelength (UV-C)	254 nm
Total UV lamp (ea)	1, 2, 3
Sonication	40 kHz, 117 V,4.1 amp, 190 W
TiO_2 (mg/L)	25, 50, 100
Chloroform (mg/L)	2, 5, 10

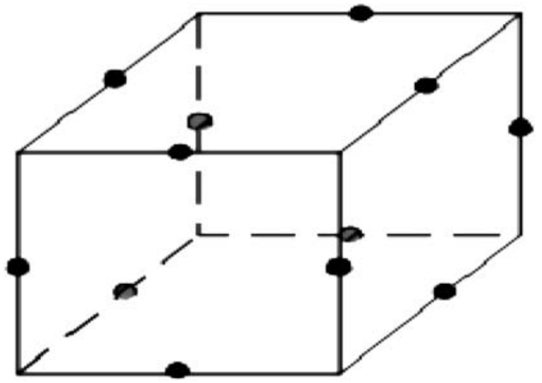


Fig. 2. Design of Box–Behnken method.

statistical model is simulated about response surface and experiments are conducted under various conditions of independent variables. With this process, data are obtained and response surface is estimated through regression analysis. By utilizing estimated response surface formula, sensitivity analysis can be conducted to analyze changes in response variables according to changes in independent variables. Gaining combination of independent variables and maximizing (minimizing) response variables leads to optimization of production and processing.

2.5. Principle and presumption of experiment design method

Experiment planning method is conducted following three principles and presumption. They are randomization, replication, and blocking. The principle of randomization is that order of experiment should be set randomly. If not, hidden factors (usually depend on time) together with considered factors of experiment can have an impact on the result. Principle of replication is to repeat experiment under the identical condition. This is critical to assume error of experiment and obtain *P* value. This can increase reproducibility of experiment and minimize assessment error which can occur during experiment. Experiment design identifies how considering factors affect response factors. If others have an effect on response factors, assessing impact of considered factors is impossible. In this case, blocking is adopted to block the other factors and obtain better experiment result. This experiment was conducted based on the three designing principles mentioned above.

Table 2
Box–Behnken design for experiment

Level	Code	Explanatory variables		
		UV_{254} (ea)	Chloroform (mg/L)	TiO_2 (mg/L)
Max. level	+1	3	10	100
Central level	0	2	5	50
Min. level	−1	1	2	25

Run order	Coded factor			Uncoded factor		
	UV	Chloroform	TiO_2	UV	Chloroform	TiO_2
1	−1	−1	0	1	2	50
2	1	1	0	3	10	50
3	0	0	0	2	5	50
4	0	0	0	2	5	50
5	−1	1	0	1	10	50
6	1	0	−1	3	5	25
7	0	−1	1	2	2	100
8	−1	0	1	1	5	100
9	1	−1	0	3	2	50
10	−1	0	−1	1	5	25
11	0	1	1	2	10	100
12	0	0	0	2	2	50
13	0	1	−1	2	10	25
14	1	0	1	3	5	100
15	0	−1	−1	2	2	25

2.6. Box–Behnken experiment design

The base of Box–Behnken plan is combining both the balanced incomplete block design (BIBD) and the 2^k full factorial layout design. At the center point, the number of test, n_c, is added to assume the second response surface formula. The test point of vertex is not included (Fig. 2). Box–Behnken plan conducts experiments at the center of hexahedral corners and that of entire experiment area. At level 3 of each factor, experiment is conducted and it sometimes has rotatability. At certain factor numbers, it always has rotatability.

This study utilized Box–Behnken and assumed first-order term and second-order term of response surface efficiently. When numbers of factors are identical, experiment times become lower than that of central composite design. In that case, cost is too high or experiment is not possible. Box–Behnken plan is the useful alternative to that. This is MFAST (multi-factor at the same rime) in which all factors cross with the levels within factors. They are designed randomly with regular interval. The method can search optimized conditions we want and quantify relations between factors and responses.

The three factors identified in the experiment were UV intensity, Chloroform concentration, and TiO_2 concentration. Three levels and three factors were applied as seen in Table 2. As for center point, three times were repeated following the principle of replication.

Table 3
Experimental results of the Box–Behnken design

Run order	Uncoded factor			Chloroform removal (%)
	UV	Chloroform	TiO_2	
1	1	2	50	80.6
2	3	10	50	67.5
3	2	5	50	80.4
4	2	5	50	65.7
5	1	10	50	62.4
6	3	5	25	80.6
7	2	2	100	88.5
8	1	5	100	74.5
9	3	2	50	98.6
10	1	5	25	72.5
11	2	10	100	87.6
12	2	2	50	90.4
13	2	10	25	55.7
14	3	5	100	98.6
15	2	2	25	90.4

Table 4
Regression analysis and response surface model fitting (ANOVA) for second-order equation

Source	DF[a]	Seq. SS[b]	*F*[c]	*P*[d]
Model	9	2,263.8	10.44	0.009
Linear	3	1,736.5	3.78	0.093
Square	3	83.9	2.21	0.395
Cross product	3	443.4	6.14	0.040
Residual error	5	120.4		
Lack of fitness	4	12.4	0.03	0.996
Pure error	1	108.1		
Total	14	2,384.2		

[a]DF: degree of freedom, [b]Seq SS: sum of squares, [c]*F* value = MSR/MSE, and [d]the *P* value is defined as the smallest level of significance leading to rejection of the null hypothesis.

Table 5
Regression coefficients analysis for second-order equation

Source	Coefficient	*P*
Constant	116.3349	0.002
UV	−4.449	0.722
Chloroform	−7.995	0.033
TiO_2	−0.693	0.085
UV × UV	2.447	0.396
Chloroform × Chloroform	0.302	0.161
$TiO_2 \times TiO_2$	0.003	0.279
UV × Chloroform	−0.810	0.238
UV × TiO_2	0.107	0.153
Chloroform × TiO_2	0.058	0.014

Table 6
Regression analysis and response surface model fitting (ANOVA) for "linear + cross product"

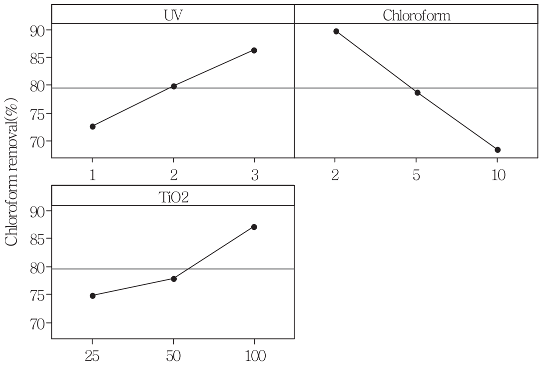
Source	DF[a]	Seq. SS[b]	*F*[c]	*P*[d]
Model	6	2,176.0	13.94	0.001
Linear	3	1,736.5	7.83	0.009
Cross product	3	439.5	5.63	0.023
Residual error	8	208.2		
Lack of fitness	7	100.1	0.13	0.971
Pure error	1	108.0		
Total	14	2,384.2		

[a]DF: degree of freedom, [b]Seq SS: sum of squares, [c]*F* value = MSR/MSE, and [d]the *P* value is defined as the smallest level of significance leading to rejection of the null hypothesis.

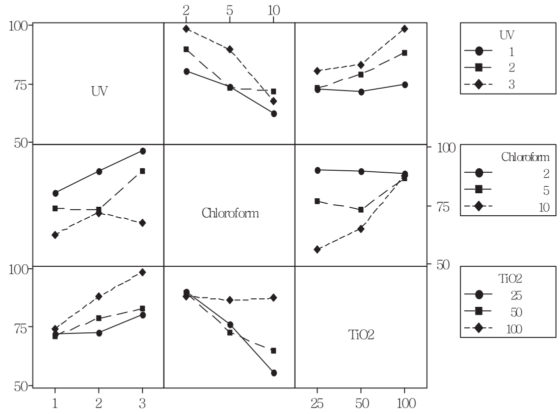
Optimal response conditions are determined with surface plot or contour plot.

Table 7
Regression coefficients analysis for "linear + cross product"

Source	Coefficient	*P*
Constant	90.702	0.000
UV	5.337	0.359
Chloroform	−4.232	0.030
TiO_2	−0.355	0.066
UV × Chloroform	−0.810	0.233
UV × TiO_2	0.107	0.144
Chloroform × TiO_2	0.057	0.008



(a) Main effect plot



(b) Interaction effect plot

Fig. 3. Main effect (a) and interaction effect (b) plot for Chloroform removal (%).

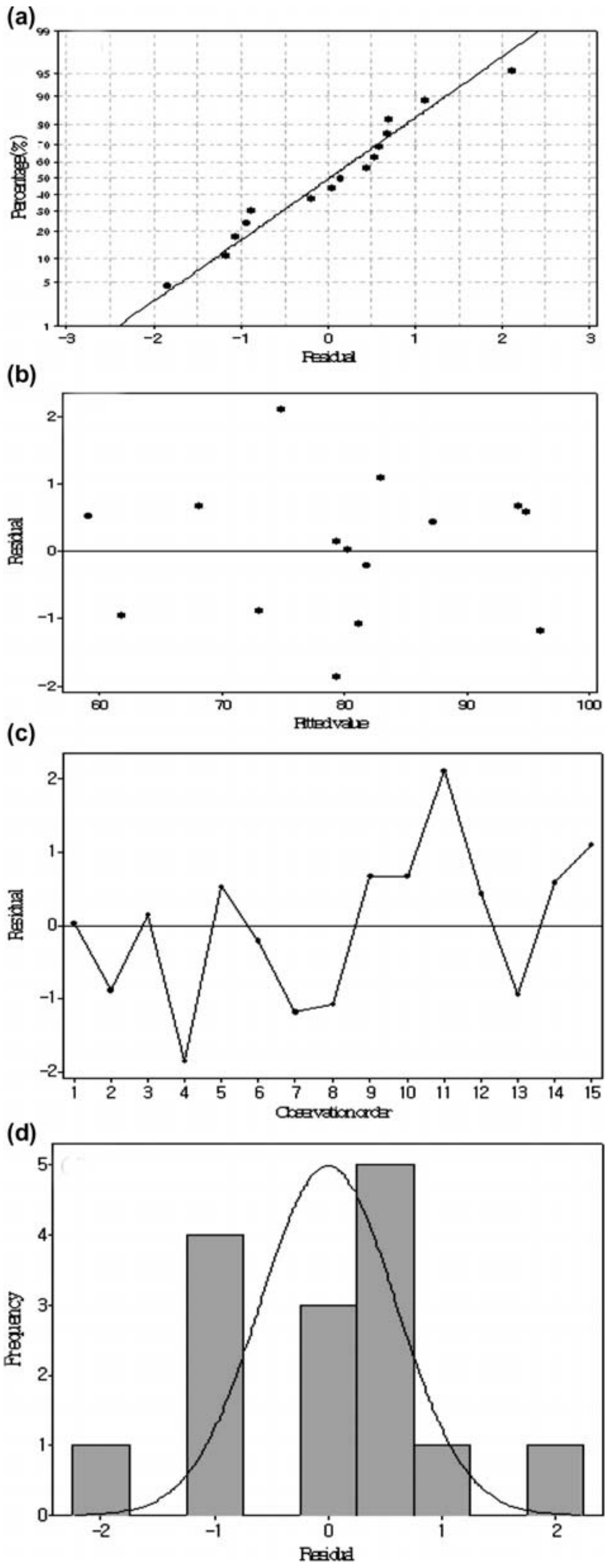


Fig. 4. Residual plot of model for error values ((a) normal probability, (b) residuals vs. the response, (c) residuals vs. the order of the data, and (d) histogram).

3. Results and discussion

3.1. *Presumption of response model by response surface analysis*

It needs 15 experiments which is considered randomization and repletion at the central point. Experimental results of the Box–Behnken design are shown in Table 3. When the results of Table 3 were analyzed to second-order equation (Tables 4 and 5), *P* value for square order was 0.395. It means significance was very low. However, the results were fitted to "linear + cross product" term (Tables 6 and 7), i.e. P value for lack of fitness was 0.971 and revised R^2 was 84.7%. Moreover, analysis of variance was conducted to evaluate the fitness. The result showed that P value for linear term was 0.009 and P value for cross product term was 0.023.

The reaction models encoded variables in Table 6 were shown in Eqs. (1) and (2).

Parameter estimate from coded data:

$$\begin{aligned} y = {} & 77.473 - 1.188(\mathrm{UV}) - 13.013(\mathrm{Chloroform}) \\ & + 6.800(\mathrm{TiO_2}) - 7.300(\mathrm{UV})(\mathrm{Chloroform}) \\ & + 15.125(\mathrm{UV})(\mathrm{TiO_2}) + 2.125(\mathrm{Chloroform}) \\ & \times (\mathrm{TiO_2}) \end{aligned} \tag{1}$$

Parameter estimate from uncoded data:

$$\begin{aligned} y = {} & 90.7017 + 5.3371(\mathrm{UV}) - 4.2315(\mathrm{Chloroform}) \\ & - 0.3550(\mathrm{TiO_2}) - 0.8101(\mathrm{UV})(\mathrm{Chloroform}) \\ & + 0.1072(\mathrm{UV})(\mathrm{TiO_2}) + 0.0574(\mathrm{Chloroform}) \\ & \times (\mathrm{TiO_2}) \end{aligned} \tag{2}$$

3.2. Main effect and interaction effect of response model factors

Fig. 3 shows impacts of each factor on the estimated value and interaction effects of factors. Main effect is caused by changes in level of factors and also refers to discrepancy of level average of each factor. When the discrepancy is large, main effects exist. If not, we can tell there is no main effect.

The larger the main effects, the bigger the gradients, as seen in Fig. 3(a). Chloroform concentration has the largest impacts, followed by UV intensity and initial TiO_2 concentration.

Interaction effect, which means the impact of certain factor, is adjusted due to the level of the other factors. In other words, if the effect caused by factor A shows consistently B1 and B2, which are another level of B, there is no interaction effect between A and B. Meanwhile, when the effect caused by B shows level B1 and A shows B2, it has interaction effect between A and B.

As shown in Fig. 3(b), response model factors had interaction effect, because the factors were not parallel, even though if the graphs show parallel, it had not interaction effect among the factors. These results

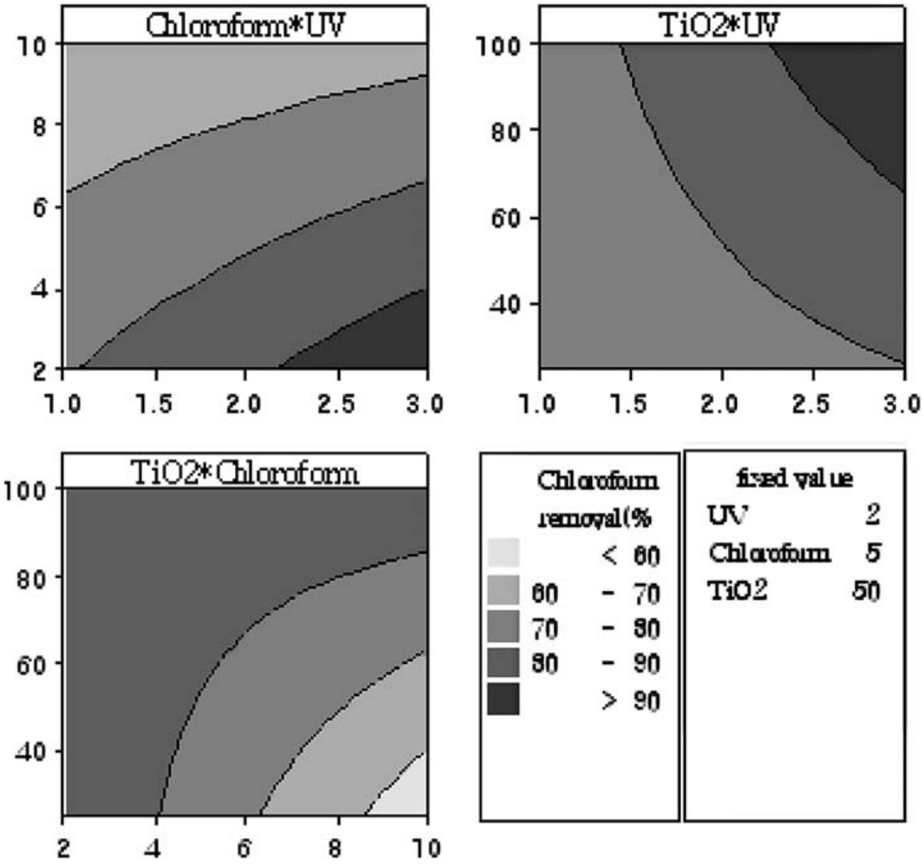


Fig. 5. Response surface contour plot (2D) of Chloroform removal (%) in decoded value.

are the same as P value of interaction shows 0.023 (<0.05) in Table 4.

3.3. Residual analysis of response model

Fig. 4 shows normal probability (a), residual- fitted value (b), residual-data observation order (c), and histogram (d) which are used to evaluate suitability of response model. Normal probability is used to evaluate normal distribution of data, effect by another variable, and characteristic of data. Residual-fitted value is used to evaluate regularity of variation nonlinear relationship and characteristic of data. Residual-data observation order is used to evaluate the effect of data which is acquired to time or data collection order. Histogram is used to evaluate inclination of data or characteristic of data.

The results demonstrated that all the data showed normal distribution as they were straightly distributed between −2 and 2 of residual in normal probability. As shown in residual-fitted value, residuals were ideally distributed around zero. Histogram also showed normal distribution. Furthermore, residual-data observation order showed that all data distributed between −2 and 2 of residual. Therefore, the model is satisfied with four assumptions on error term, i.e. normality, equal variation, independence, and linearity. Therefore, the model is applicable to analysis of sonophotocatalysis process.

3.4. Determination of optimal reaction conditions

The effect of Chloroform removal efficiency by reaction factors using response surface contour plot (2D) and response surface plot (3D) in sonophotocatalysis process was shown in Figs. 5 and 6. It could be known that how could the reaction factors of the model be effected to the dependent variable from Figs. 5 and 6.

Fig. 5 showed that the lower initial Chloroform concentration, higher TiO_2 concentration, and more number of UV lamp stimulated higher Chloroform removal. Moreover, Chloroform removal efficiency was more affected by initial Chloroform concentration than UV lamp number or TiO_2 concentration judging from slope of each contour.

As shown in Fig. 6, Chloroform removal was more effective at the minimum Chloroform concentration and maximum TiO_2 concentration in case of interaction between Chloroform and TiO_2. In case of Chloroform and UV lamp number, Chloroform removal was more effective at the minimum Chloroform concentration and maximum UV lamp number, and more effective Chloroform concentration than UV lamp number. In case of interaction between TiO_2 and UV lamp number, Chloroform removal was more effective at the maximum TiO_2 concentration and maximum UV lamp number, and more effective TiO_2 concentration than UV lamp number.

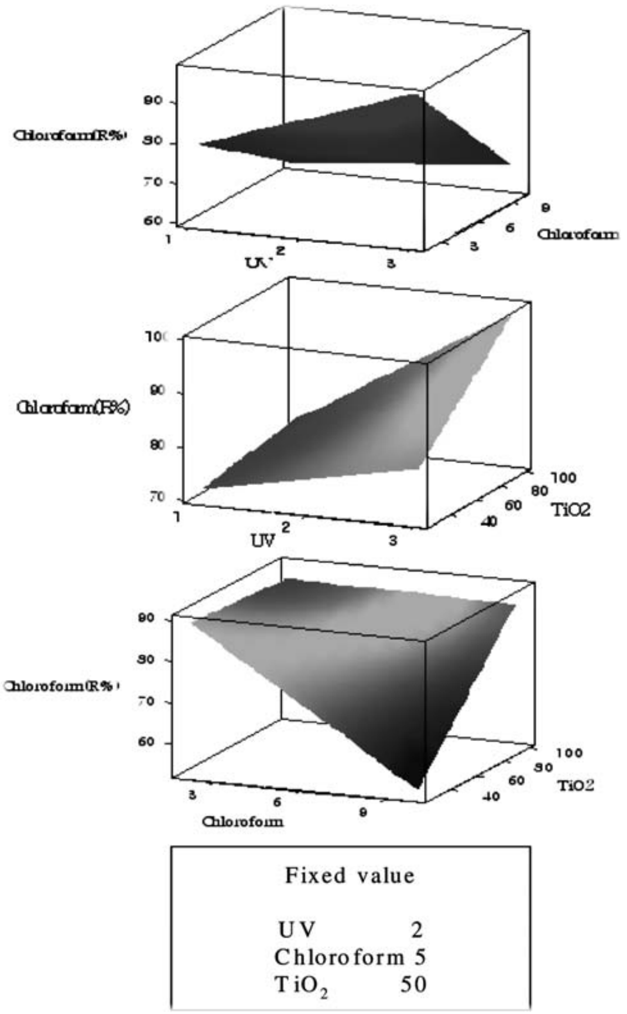


Fig. 6. Response surface plot (3D) Chloroform removal (%) in decoded value.

4. Conclusion

This study treated Chloroform through the use of sonophotocatalysis. The experimental results obtained from this study were as follows:

(1) "Linear + Cross product" model equation deduced by experiment design method for sonophotocatalysis of Chloroform was more suitable than second-order equation, and, moreover, P value (0.001) and R^2 (84.7) showed high correlation.

(2) The evaluation results on main effect factor of the model equation showed that Chloroform initial concentration is the most effective factor, and UV lamp number and TiO_2 concentration are the next.
(3) Interaction effect of response model factors was shown as *P* value for interaction was 0.023 (<0.05) in model equation.
(4) The results of residual analysis on error term of the reaction model showed that it was satisfied normality, equal variation, independence, and linearity. Therefore, the model was acceptable.
(5) The experiments were performed with various UV lamp number, Chloroform initial concentration, and TiO_2 on sonophotocatalysis process. The results using response surface contour plot (2D) showed that the lower Chloroform initial concentration, higher UV lamp number, and TiO_2 concentration stimulated higher Chloroform removal.
(6) From response surface plot (3D), Chloroform removal was more effective at the minimum Chloroform concentration and maximum TiO_2 concentration in case of interaction between Chloroform and TiO_2, more effective Chloroform concentration than UV lamp number in case of interaction between Chloroform and UV lamp number, and more effective TiO_2 concentration than UV lamp number in case of interaction between TiO_2 and UV lamp number.

References

[1] J.H. Park, E.S. Choi, I.H. Cho, Y.G. Kim, Solar light induced degradation of trichlorethlylene (TCE) using TiO_2: Effect of solar light intensity and seasonal variation, J. Environ. Sci. Health, Part A A38 (2003) 1915–1926.
[2] E.S. Choi, I.H. Cho, J.H. Park, The effect of operational parameters on the photocatalytic degradation of pesticide, J. Environ. Sci. Health, Part B B39 (2004) 53–64.
[3] J.H. Park, E.S. Choi, K.I. Gill, Removal of reactive dye using UV/TiO_2 in circular type reactor, J. Environ. Sci. Health, Part A A38 (2003) 1389–1399.
[4] U.S. Akpan, B.H. Hameed, Photocatalytic degradation wastewater containing acid red 1 dye by titanium dioxide: Effect of calcination temperature, Desalin. Water Treat. 43 (2012) 84–90.
[5] A. Rezaee, H. Masoumbaigi, R.D.C. Soltania, A.R. Khataee, S. Hashemiyan, Photocatalytic decolorization of methylene blue using immobilized ZnO nanoparticles prepared by solution combustion method, Desalin. Water Treat. 44 (2012) 174–179.
[6] S.K. Sharma, H. Bhunia, P. Kumar, Photocatalytic decolorization kinetics and adsorption isotherms of a mixture of two anionic azo dyes: Reactive Red 120 and Reactive Black 5, Desalin. Water Treat. 44 (2012) 261–268.
[7] T. Visa, M. Sanchez, V.L. Grimau, R. Navarro, S. Reche, M.C. G. Boouzan, Photocatalysis with titanium dioxide to remove colour of exhausted reactive dyebaths without pH modification, Desalin. Water Treat. 45 (2012) 91–99.
[8] S.R. Patil, U.G. Akpan, B.H. Hameed, S.K. Samdarshi, A comparative study of the photocatalytic efficiency of Degussa P25, Qualigens, and Hombikat UV-100 in the degradation kinetic of congo red dye, Desalin. Water Treat. 46 (2012) 188–195.
[9] A. Dhir, N.T. Prakash, D. Sud, Comparative studies on TiO2/ZnO photocatalyzed degradation of 4-chlorocatechol and bleach mill effluents, Desalin. Water Treat. 46 (2012) 195–204.
[10] M.H. Habibi, R. Kamrani, Photocatalytic Mineralization of methylene blue from water by a heterogeneous copper-titania nanocomposite film, Desalin. Water Treat. 46 (2012) 278–284.
[11] K. Umar, A.A. Dar, M.M. Haque, N.A. Mir, M. Muneer, Photocatalysed decolourization of two textile dye derivatives, Martius Yello and Acid Blue 129, in UV-irradiated aqueous suspensions of Titania, Desalin. Water Treat. 46 (2012) 205–224.
[12] M. Kaneko, I. Okura, Sonophotocatalysis-Joint System of Sonochemical and Photocatalytic Reactions, Kodansha, Tokyo, 2002, pp. 203–221.
[13] J. Lindley, (Ed.), Sonochemistry, The Royal Society of Chemistry, Cambridge, 1997.
[14] T.J. Mason, (Ed.), Current Trends and Future Prospects, The Royal Society of Chemistry, Cambridge,. p. 171 1992.
[15] H. Harada, C. Hosoki, A. Kudo, Overall water splitting by sonophotocatalytic reaction: The role of powdered photocatalyst and an attempt to decompose water using a visible-light sensitive photocatalyst, J. Photochem. Photobiol. A141 (2001) 219–224.