



A Response Surface Methodology for Styrene Degradation Using Fenton's/UV-Fenton's Oxidation

NUTTAWAN YOSWATHANA

Department of Chemical Engineering, Faculty of Engineering, Mahidol University, Nakornprathom 73170, Thailand

Corresponding author: E-mail: nuttawan.yos@mahidol.ac.th

(Received: 3 September 2012;

Accepted: 29 September 2012)

AJC-12202

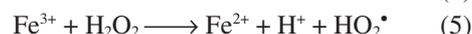
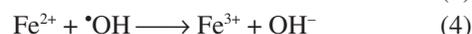
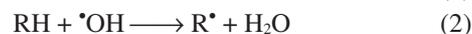
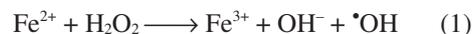
Styrene is one of hazardous wastes sites that purposed on the EPA National Priorities List. Fenton's and UV-Fenton's oxidation for the styrene degradation were investigated by a response surface methodology using central composite Box-Behnken design as a tool for optimization in term of % COD removal. The technical scientific feasibility method was assessed by Fenton's oxidation found that the optimum molar ratio as $[H_2O_2]:[FeSO_4]:[styrene (C_8H_8)]$ was [20]:[1.81]:[1], the COD removal 92.67 % at 30 °C for reaction time 45 min and the reaction rate was zero order with kinetic rate constant of 0.018 mM/min. A response surface methodology was to applied to optimize the Fenton's oxidation conditions: the molar ratio of $[H_2O_2]:[Fe^{2+}]:[C_8H_8]$ was [22.73]:[1.81]:[1.06] at 30 °C, reaction time 42.12 min and the COD removal was 94.90%. In UV-Fenton's oxidation with UV 80 watt, the optimum molar ratio of $[H_2O_2]:[Fe^{2+}]:[C_8H_8]$ was [22.54]:[1.81]:[1.04] at 30 °C for reaction time 29.89 min and the COD removal was 95.03 %. Under these conditions, it was possible to obtain the maximum styrene degradation using optimization from response surface methodology of Fenton's/UV-Fenton's oxidation.

Key Words: Styrene degradation, Fenton's oxidation, UV-Fenton's oxidation.

INTRODUCTION

The styrene (C_8H_8) has been identified in at least 251 of the 1,699 hazardous wastes sites that have been proposed for inclusion on the EPA National Priorities List¹⁻³. The principal sources of styrene releases to water are industrial effluents. The reaction of styrene with peroxy radicals appears to be too slow and no relevant information regarding hydrolyzed in water and abiotic transformations. It has been shown to be biologically degraded in several types of sewage treatment facilities, biofilm reactors, groundwater and lakes^{4,5}. Bridie *et al.*⁶ found that 42 % of the styrene initially present degraded in 5 days when unadapted sewage was used as the source of microorganisms; when an adapted sewage was used, 80 % degradation was observed. Fu and Alexander⁷ showed the rate of styrene biodegradation with 40% mineralization after 30 days. A promising technology for treatment of waste chemicals that promotes the removal contaminants such as toxic and hazardous organic pollutants in aqueous solution could be the advanced oxidation processes (AOPs) such as ozone/UV⁸, hydrogen peroxide/UV^{9,10}, Fenton oxidation¹¹ or Fenton/UV^{9,12,13}. Among them, the Fenton method is cost-effective, easy to apply and effective with relatively low-strength wastewater containing organic compounds and has been applied to different industrial wastewaters, including the pre-oxidation of pharmaceutical wastewaters⁸, treatment of textile wastewaters¹⁴⁻¹⁷,

reduction of polynuclear aromatic hydrocarbons in water¹⁸, degradation of volatile organic compounds in aqueous¹⁹⁻²⁴ or treatment of paper pulp effluents^{12,13}. The oxidation mechanism in the Fenton process involves the reactive hydroxyl radical ($\cdot OH$) generated under acidic conditions by the catalytic decomposition of hydrogen peroxide, which reacts unselectively with organic substances (RH). The reaction mechanism is as follow²⁵⁻²⁷:



A response surface methodology is a statistical technique for designing experiments, building and analyzing models, evaluating the simultaneous effects of several factors and thus searching optimum conditions. Moreover, the efficiency of a selected treatment method can be evaluated with a limited number of experiments by taking into account of influencing parameters on the process efficiency²⁸. The objective of this work was to evaluate the performance of Fenton's and UV-Fenton's oxidation in term of percentage of removal of chemical oxygen demand (COD) for styrene treatment with optimization by the response surface methodology using central composite Box-Behnken experimental design.

EXPERIMENTAL

The stock solution of iron sulfate was prepared by dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ salt in deionized water to 0.2 N and diluting H_2O_2 from 18 wt % to 3 wt %. Any pH adjustments (sample or standard solutions) were performed with 1 M H_2SO_4 and 1 M NaOH solutions. A power of UV lamp was 80 watts.

Experiments were performed in a batch mode and carried out in 100 mL bottle with a solution volume of 50 mL that consisted of COD was 968 mg/L. A 0.2 N $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ stock solution was added in the bottle with required amount from calculation. Then 3 wt % H_2O_2 was added with required amount from calculation and was standardized just before the experiments. The Fenton reaction time was initiated by the addition of 3 wt % H_2O_2 and then 1 M H_2SO_4 solution for adjust pH of 3 to the mixture. The reaction was stopped with adding 1 M NaOH in the solution with pH of 11. The COD measured in the samples taken from the sample bottle. The UV-Fenton experiment was only to bring the sample bottle into UV box.

Experimental design and statistical analysis: Fenton's and UV-Fenton's oxidation were optimized by applying the response surface methodology [h] using central composite Box-Behnken design (BBK). The COD removal was used as the variable to be optimized. The initial design involved 16 tests, based on a $(n \times 2^{n-1})$ factorial with $(n+1)$ center runs for a second phase of steepest ascent. When n were 3 factors: molar of styrene, molar of hydrogen peroxide and reaction time. The total design for Fenton's and UV-Fenton's oxidation were outlined in Tables 1 and 2, in which notation of the operating variables are coded as x_i .

TABLE-1
BOX-BEHNKEN DESIGN FOR THE EFFECTS OF THE VARIABLES AFFECTING THE COD REMOVAL BY FENTON'S OXIDATION

Exp. No.	Styrene (X_1)	H_2O_2 (X_2)	Time (X_3)	Code (X_1)	Code (X_2)	Code (X_3)
1	0.50	20	40	-1	0	-1
2	0.50	30	45	-1	1	0
3	0.50	10	45	-1	-1	0
4	0.50	20	50	-1	0	1
5	1.00	10	40	0	-1	-1
6	1.00	10	50	0	-1	1
7	1.00	30	40	0	1	-1
8	1.00	30	50	0	1	1
9	1.50	20	40	1	0	-1
10	1.50	10	45	1	-1	0
11	1.50	30	45	1	1	0
12	1.50	20	50	1	0	1
13	1.00	20	45	0	0	0
14	1.00	20	45	0	0	0
15	1.00	20	45	0	0	0
16	1.00	20	45	0	0	0

Analytical methods: The analytical of COD was performed in accordance with standard methods²⁹. Hydrogen peroxide was determined by the permanganate titration method.

RESULTS AND DISCUSSION

Effects of H_2O_2 dose for Fenton's oxidation: The effects of H_2O_2 dose were investigated at an initial pH of 3, a reaction time of 45 min, the ratio of $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ of [11]:[1] and initial COD of 968 mg/L (Fig. 1).

TABLE-2
BOX-BEHNKEN DESIGN FOR THE EFFECTS OF THE VARIABLES AFFECTING THE COD REMOVAL BY UV-FENTON'S OXIDATION

Exp. No.	Styrene (X_1)	H_2O_2 (X_2)	Time (X_3)	Code (X_1)	Code (X_2)	Code (X_3)
1	0.50	20	25	-1	0	-1
2	0.50	30	30	-1	1	0
3	0.50	10	30	-1	-1	0
4	0.50	20	35	-1	0	1
5	1.00	10	25	0	-1	-1
6	1.00	10	35	0	-1	1
7	1.00	30	25	0	1	-1
8	1.00	30	35	0	1	1
9	1.50	20	25	1	0	-1
10	1.50	10	30	1	-1	0
11	1.50	30	30	1	1	0
12	1.50	20	35	1	0	1
13	1.00	20	30	0	0	0
14	1.00	20	30	0	0	0
15	1.00	20	30	0	0	0
16	1.00	20	30	0	0	0

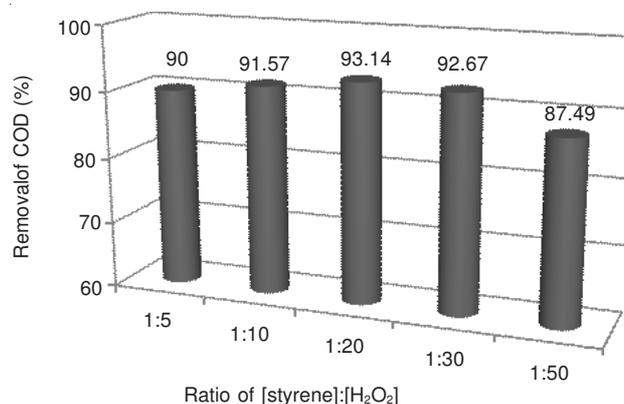


Fig. 1. Removal of COD of styrene with different initial H_2O_2

From Tang and Huang²¹, the ratio of $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ of [11]:[1] was the optimum for oxidation of volatile organic compounds (VOCs). The removal of COD depended on the initial H_2O_2 dose. The maximum COD removal was 93.14 % at the ratio of $[\text{C}_8\text{H}_8]:[\text{H}_2\text{O}_2]$ of [1]:[20]. At the higher ratio of $[\text{C}_8\text{H}_8]:[\text{H}_2\text{O}_2]$ from [1]:[30] and [1]:[50], COD removal decreased to 92.67 and 87.49 %, respectively. It was presumably that residual H_2O_2 affected.

Effects of temperature for Fenton's oxidation: Typically, the temperature has effect for chemical reaction. This work studied at the initial pH of 3, the ratio of $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]:[\text{C}_8\text{H}_8]$ of [20]:[1.81]:[1], a reaction time of 45 min and initial COD of 968 mg/L as shown in Fig. 2.

From Fig. 2, the temperature was not significantly effect to Fenton reaction. However, the highest removal of COD was 30 °C and got 93.77 %. In addition, the experimental temperature for removal styrene using Fenton's oxidation could do at ambient temperature in Thailand.

Kinetic reaction rate for Fenton's oxidation: Where the initial concentration of styrene was 0.47 mM, the order of reaction and kinetic rate constant for Fenton's oxidation were investigated in Fig. 3.

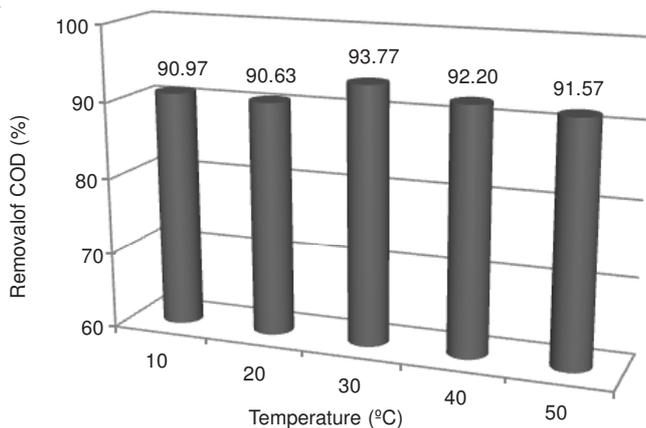


Fig. 2. Removal of COD of styrene with various temperatures

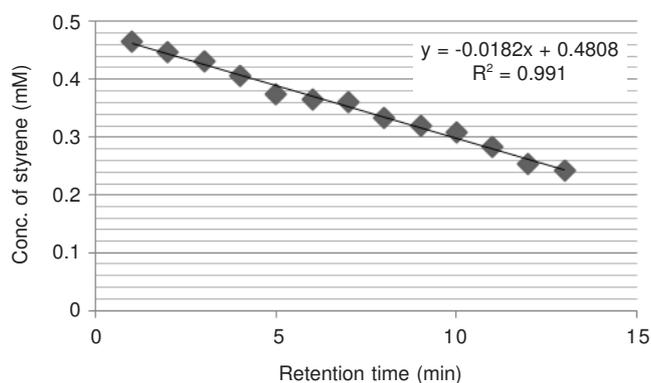


Fig. 3. Concentration of styrene with various reaction times

Fig. 3 showed the kinetic fitting of the concentration of styrene data *versus* times was a linear with R^2 of 0.991, which the experiments conditions were 30 °C, pH of 3, the ratio of $[H_2O_2]:[Fe^{2+}]:[C_8H_8]$ of [20]:[1.81]:[1] and initial COD of 968 mg/L. In addition, the reaction rate of removal styrene using Fenton's oxidation was zero order with kinetic rate constant of 0.018 mM/min.

Effects of reaction time for Fenton's/UV-Fenton's oxidation: The reaction time was varied between 15 to 90 min. The initial pH of 3, the ratio of $[H_2O_2]:[Fe^{2+}]:[C_8H_8]$ of [20]:[1.81]:[1] and initial COD of 968 mg/L. The results were shown in Fig. 4.

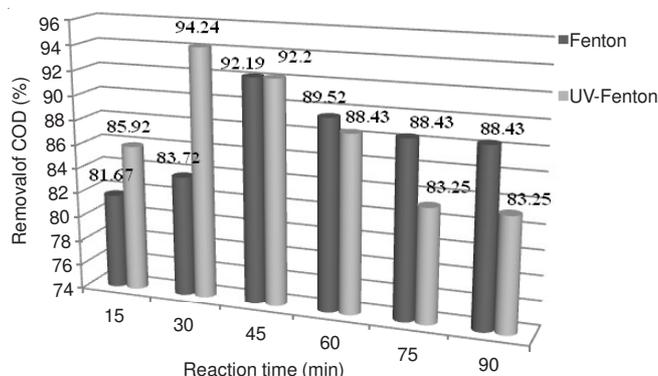


Fig. 4. Removal of COD of styrene with various reaction times

At 30 min, the COD removal for UV-Fenton's oxidation was the maximum at 94.24 %, while Fenton's oxidation

degraded the maximum COD at 92.19 % for 45 min. After those times, the % removal of COD were lower. Thus, the optimum reaction time for removal of styrene was 30 min with UV-Fenton's oxidation.

Optimization of affected conditions for Fenton's oxidation: The model for a response surface in terms of the coded variables x_i is demonstrated in eqn. 6. The results from experiments were shown in Fig. 5.

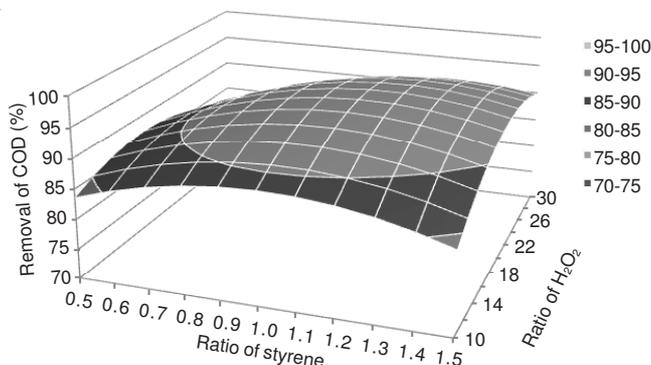


Fig. 5. % Removal of COD of styrene with Fenton using RSM

$$\hat{Y} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (6)$$

When eqn. 6 was evaluated which based on the experimental results of the COD removal by Fenton's oxidation. It was reduced to eqn. 7 as following:

$$Y = 94.36944 + 0.654108X_1 + 2.420199X_2 + 0.196232X_3 + 2.354788X_1X_2 + (-0.78493)X_1X_3 + (-0.13082)X_2X_3 + (-5.10204)X_1^2 + (-4.97122)X_2^2 + (-6.27943)X_3^2 \quad (7)$$

The results showed that the optimum molar ratio of $[H_2O_2]:[Fe^{2+}]:[C_8H_8]$ was [22.73]:[1.81]:[1.06] at 42.12 min, the % estimated removal styrene was 94.74 % with R^2 of 0.970 and the % experimental removal styrene was 94.90 %.

Optimization of affected conditions for UV-Fenton's oxidation: The affected conditions for removal styrene were the molar of $[H_2O_2]$ and $[C_8H_8]$ and reaction times by using UV-Fenton were shown in Fig. 6.

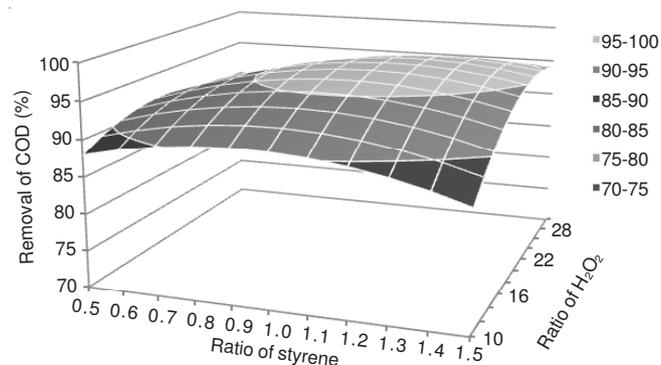


Fig. 6. Removal of COD of styrene with UV-Fenton using RSM

From eqn. 6, the model for a response surface which based on the experimental results of the COD removal by UV-Fenton's oxidation was reduced to eqn. 8:

$$Y = 94.7619 + 0.784929X_1 + 2.55102X_2 + 0.327054X_3 + 2.093145X_1X_2 + (-1.04657)X_1X_3 + (0.130822)X_2X_3 + (-5.42909)X_1^2 + (-5.03663)X_2^2 + (-6.34485)X_3^2 \quad (8)$$

In UV-Fenton's oxidation with UV 80 watt, the optimum molar ratio of $[H_2O_2]:[Fe^{2+}]:[C_8H_8]$ was $[22.54]:[1.81]:[1.04]$ at 29.89 min, the % estimated removal COD was 95.12 % with R^2 of 0.969 and the % experimental removal COD was 95.03 %.

Conclusion

The removal of styrene with UV-Fenton reaction was more valuable than only Fenton reaction. The shorter time for removal COD of UV-Fenton reaction was nearly 1.5 times of Fenton reaction. The response surface methodology was shown to be a valuable approach to process optimization based on UV-Fenton reaction. The small number of experiments needed to do which compared with technical scientific method. In addition, the statistical model obtained was suitable for predicting and optimizing removal within the range of variables used.

ACKNOWLEDGEMENTS

The author is grateful to Faculty of Engineering, Mahidol University for the financial and research facilities.

REFERENCES

- HazDat. 2007, Styrene. HazDat Database: ATSDR's Hazardous Substance Release and Health Effects Database. Atlanta, GA: Agency for Toxic Substances and Disease Registry. <http://www.atsdr.cdc.gov/hazdat.html>. May 21 (2007).
- EPA, Health and Environmental Effects Profile for Styrene, O.H. Cincinnati, U.S. Environmental Protection Agency, Environmental Criteria and Assessment Office, EPA600X84325 (1984).
- EPA, Frequency of Organic Compounds Identified in Water, G.A. Athens, U.S. Environmental Protection Agency, Office of Research and Development, EPA600476062, PB265470 (1975).
- H.R. Pahren and D.E. Bloodgood, *J. Water Pollut. Control Fed.*, **33**, 233 (1961).
- E.D. Pellizzari, N.P. Castillo, S. Willis, D. Smith and J.T. Bursley, *ASTM Spec. Tech. Publ.*, **686**, 256 (1979).
- A.L. Bridie, C.J. Wolff and M. Winter, *Water Res.*, **13**, 627 (1979).
- M.H. Fu and M. Alexander, *Environ. Sci. Technol.*, **26**, 1540 (1992).
- C. Holf, S. Sigl, O. Specht, I. Wurdack and D. Wabner, *Water Sci. Technol.*, **35**, 257 (1997).
- M. Perez, F. Torrades, X. Domenech and J. Peral, *Water Res.*, **36**, 2703 (2002).
- F.J. Benitez, J. Beltran-Heredia and J.L. Rubio, *J. Chem. Technol. Biotechnol.*, **76**, 312 (2001).
- J. Rodriguez, C. Parra, D. Contreras, J. Freer and J. Baeza, *Water Sci. Technol.*, **44**, 251 (2001).
- M. Perez, F. Torrades, J.A. Garcia-Hortal and X. Domenech, *Appl. Catal. B: Environ.*, **36**, 63 (2002).
- E.C. Catalkaya and F. Kargi, *J. Hazard. Mater.*, **139**, 244 (2007).
- P.C. Vendevivere, R. Bianchi and W. Verstraete, *J. Chem. Technol. Biotechnol.*, **72**, 289 (1998).
- S.-F. Kang, C.-H. Liao and M.-C. Chen, *Chemosphere*, **26**, 923 (2002).
- C.L. Hsueh, Y.H. Huang, C.C. Wang and C.Y. Chen, *Chemosphere*, **58**, 1409 (2005).
- S. Meric, D. Kaptan and T. Olmez, *Chemosphere*, **54**, 435 (2004).
- F.J. Beltran, M. Gonzalez, F.J. Rivas and P. Alvarez, *Water Air Soil Pollut.*, **105**, 685 (1998).
- X.R. Xu, Z.Y. Zhao, X.Y. Li and J.D. Gu, *Chemosphere*, **55**, 73 (2004).
- N.R. Mohanty and I.W. Wei, *Hazard. Waste Hazard. Mater.*, **10**, 171 (1993).
- W.Z. Tang and C.P. Huang, *J. Environ. Tech.*, **17**, 1371 (1996).
- P.R. Gogate and A.B. Pandit, *Adv. Environ. Res.*, **8**, 501 (2004).
- J.C. Lou and S.S. Lee, *Hazard. Waste Hazard. Mater.*, **12**, 185 (1995).
- N.S.S. Martinez, J.F. Fernandez, X.F. Segura and A.S. Ferrer, *J. Hazard. Mater.*, **B101**, 315 (2003).
- W.G. Barb, J.H. Baxendale, P. George and K.R. Hargave, *J. Chem. Soc. Trans. Faraday Soc.*, **47**, 462 (1951).
- Y.W. Kang and K.Y. Hwang, *Water Res.*, **34**, 2786 (2000).
- C. Walling, *Acc. Chem. Res.*, **8**, 125 (1975).
- E.C. Catalkaya and F. Kargi, *Chemosphere*, **69**, 485 (2007).
- Standard Methods, Standard Methods for the Examination of water and wastewater, American Public Health Association/American Water Works association/Water Environmental Federation, Washington, DC, edn 20 (1998).