

# 以連續迴流式紫外線/過氧化氫程序處理含染料及異丙醇廢水之光反應器設計研究

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## 摘要

本研究旨在分別發展與建立以均相(以迴流式UV/H<sub>2</sub>O<sub>2</sub>程序(以染料及異丙醇為目標污染物)水溶液之連續環狀雙套管式光反應器設計方程式, 探討模式係藉由結合光氧化系統中之反應動力、各反應成份之質量平衡方程式, 以及紫外線光強度分佈模式, 並經由不同反應條件(如水力停留時間、氧化劑、光反應器幾何尺寸、水溶液pH值、紫外線光強度及污染物起始濃度等)之實驗驗證, 以及配合計算流體力學(computational fluid dynamics, CFD)軟體進行流場穩態分析所得之結果, 進而評估光反應器設計方程式之合理性與可行性。本研究規劃目的在於將未反應完全的氧化劑H<sub>2</sub>O<sub>2</sub>迴流再利用, 達到最佳的使用效率。經由有機污染物反應速率之分析及氧化劑質量平衡之計算, 在不同迴流比下, 評估氧化劑及紫外線之使用效率, 以做為均相高級氧化程序效能及操作條件之取決依據, 並比較不同類型之有機污染物在光氧化系統中反應特性的差異, 從而建立合理之光反應器設計方程式; 此外, 亦配合以Fluent5.0之CFD軟體進行流場穩態分析, 探討反應器中流體流場分佈與有機污染物反應效率間的關連性。實驗結果顯示, 以迴流式UV/H<sub>2</sub>O<sub>2</sub>程序處理含染料Red141、異丙醇水溶液時, 染料去除率隨染料本身初始濃度之降低、混合後溶液pH值之將低、紫外線光強度之提高、H<sub>2</sub>O<sub>2</sub>添加劑量之提高及光反應器內外半徑比之降低而升高, 其中紫外線光強度與H<sub>2</sub>O<sub>2</sub>添加劑量為主要影響染料光氧化速率之反應因子。在迴流式UV/H<sub>2</sub>O<sub>2</sub>系統中, 結合系統染料及異丙醇之反應動力式、質量守恆方程式及紫外線無限線光源模式, 所推導與建立之光反應器設計方程式, 可合理模擬染料及異丙醇溶液在各操作條件下之分解行為及濃度分佈情形, 可做未來為光反應器設計之基礎。關鍵詞: 高級氧化程序、染料廢水、異丙醇、環狀雙套管式光反應器、設計方程式

關鍵詞: 高級氧化程序; 染料廢水; 異丙醇; 環狀雙套管式光反應器; 設計方程式

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## 參考文獻

- 工業技術研究院化學工業研究所「半導體業環境技術手冊」，民國八十八年。王登楷，“以高級氧化程序處理揮染整廢水之光反應器設計研究”，碩士論文，大葉大學環工所，民國九十年。王春盛，“半導體高濃度廢水之高級氧化處理與有機廢液之異丙醇回收”，元智大學化工所，民國九十一年。王文，“以新式光纖反應器進行UV/TiO<sub>2</sub>程序處理揮發性有機污染物反應行為之研究”，臺灣科技大學化工所，民國九十二年。林奇璋，“以紫外線/臭氧程序處理染料廢水之光反應器設計研究”，碩士論文，大葉大學環工所，民國九十一年。申永順，“以紫外線/過氧化氫程序處理含氯酚類有機溶液反應行為之研究”，碩士論文，國立台灣科技大學化工所，民國八十一年。申永順，“以高級氧化程序處理揮發性有機污染物反應行為及光反應器設計及研究”，博士論文，國立台灣科技大學化工所，民國八十七年。莊連春，“紫外光/過氧化氫程序分解水中毒性污染物研究”，國立中央大學土木工程所，民國八十五年。廖志祥，工業廢水物化處理新技術講習會，民國九十一年。經濟部環保署工業減廢聯合輔導小組，「工業減廢技術手冊4-染整工業」，第21-23頁，民國八十四年。Akehata, T., Shiral, T., Ishizoki, N., and Ito, K. (1973) “Average Light Intensity in an Annular Photochemical Reactor”, *Kag. Kog.*, Vol.37, pp.1026-1031. Alfano, O. M., Romero, R. L., and Cassano, A. E. (1984) “Radiation Field Inside a Cylindrical Photoreactor Irradiation From the Bottom”, *Chem. Eng. Rea.*, Vol.1, pp.506-522. Alfano O. M., Martinez M. J., Brandi R. J., and Cassano A. E. (2001) “Effects of the H<sub>2</sub>O<sub>2</sub> Concentration and Spectral Distribution of the UV Lamp Output Power on the Photooxidation of a Water Pollutant”, *Water Science and Technology :Water Supply.*, Vol.1, No.2, pp 73-82. Alfano O. M., Brandi R. J., Cassano A. E. (2001) “Dagradation kinetics of 2,4-D in Water Employing Hydrogen Peroxide and UV Radiation”, *Chemical Engineering.*, Vol.82, pp.209-218. Alaton A., Ferry I. J. L.(2002) “Application of polyoxotungstates as environmental catalyts: wet air oxidation of acid dye Orange”, *Dyes and Pigments.* Arce, P. E., Cassano A. E., and Irazoqui H. A. (1988) “The Tubular Reactor with Laminar Flow Regime:An Integral Equation Approach- Homogeneous Reaction with Arbitrary Kinetics”, *Comput. Chem. Engng.*, Vol.12, No.11, pp.1103-1113. Bolton, J. R. (1999) “Calculation of Ultraviolet Fluence Rate Distributions in an Annular Reactor: Significance of Refraction and Reflection”, *Wat. Res.*, Vol.13, No.34, pp.3315-3324. Borup, M. B. and Middlebrooks E. J., (1987) “Photocatalyed Oxadation of Toxic Organics”, *Wat. Sci. Tech.*, Vol.19, No.4, pp.381-390. Carlos, A. M., Cabrera, M. I., Alfano O. M., and Cassano, A. E. (1997) “Photochemical Decomposition of 2,4-Dichlorophenoxyacetic acid (2,4-D) in Aqueous Solution . Reactor Modeling and Verification”, *Wat. Sci. Tech.*, Vol.35, No.4, pp.197-205. Colonna, G. M., Caronna, T., Milano, B. M. (1998) “Oxidative Degradation of Dyes by Ultraviolet Radiation in the Presence of Hydrogen peroxide”, *Cabrera, M. I., Martin, C. A., Alfano, O. M., and Cassano, A. E. (1997) “Photochemical Decomposition of 2,4-dichlorophenoxyacetic acid (2,4-d) in Aqueous Solution. Kinetic Study”, *Wat. Sci.Tech.*, Vol.35, No.4, pp.31-39. Cisneros, R. L., Abel, E. G., Litter, M. I.(2002) “Phtodegradation of an Azo Dye of the Textile Industry”, *Chemosphere.* Chu, W., Ma, C. W. (1998) “Reaction Kinetics of UV-decolourization for Dye Materials”, *Chemosphere.*, Vol.37, No.5, pp.961-974. Fung, P. C., Huang, Q., Tsui, S. M., Poon, C. S. (1999) “Treat-ability Study of Organic and Colour Removal in Desizing/dyeing Wastewater by UV/us System Combined with Hydrogen Peroxide”, *Water Sci. Technol.*, Vol.40, No.1, pp.153-160. Georgiou D. P. M., Aivasidis A., Gimouhopoulos K. (2002) “Degradation of Azo-reactive Dyes by Ultraviolet Radiation in the Presence of Hydrogen Peroxide”, *Dyes and pigments.*, Vol.52, pp.69-78. Galindo, C., Kalt A. (1999) “UV/H<sub>2</sub>O<sub>2</sub> Oxidation of Azodyes in Aqueous Media:Evidence of a Structure-Degradability Relationship”, *Dyes and Pigments.*, Vol.42, pp.199-207. Galindo, C., Kalt A. (1998) “UV-H<sub>2</sub>O<sub>2</sub> Oxidation of Monoazo Dyes in Aqueous Media:a Kinetic Study”, *Dyes and Pigments.*, Vol.40, pp.27-35. Grau, P., (1991) “Textile Industry Wastewaters Treatment”, *Journal Water Sci. Technol.*, Vol.24, No.1, pp.97-103. Horacio, A., Irazoqui, M. A. I., and Cassano, A. E. (2000) “Simplified Extense Source Model for Photoreactor Analysis and Design”, *Dyes and Pigments.*, Vol.41, pp.211-220. Horning, R. H., (1997) “Characterization and Treatment of Textile Dyeing Wastewater”, *Textile Chemist and Colorist.*, Vol.9, No.4, pp.24-27. Herrera, F., Lopez, A., Kiwi, J. (2000) “Photochemically Activated Degradation of Reactive Dyes Statical Modeling of the Reactor Performance”, *Journal of Photochemistry and Photobiology A:Chemistry.*, Vol.135, pp.45-51. Ince N. H., Stephen M. I., Bolton J. R. (1997) “UV/ degradation and Toxicity Reduction of Textile Azo Dyes. *Journal. Adv. Oxid. Technol.*”, Vol.2, No.3, pp.442-448. Jacob, S. M., and Dranoff, J. S. (1966) “Radial Scale-up of Perfectly Mixed Photochemical Reactors”, *Chem. Eng. Prog. Symp. Ser.*, Vol.62. Jacob, S. M., and Dranoff, J. S. (1968) “Design and Analysis of Perfectly Mixed Photochemical Reactors”, *Chem. Eng. Prog. Sym. Ser.*, Vol.64, pp.54-63. Jacob, S. M., and Dranoff, J. S. (1970) “Light Intensity Profiles in an Elliptical Photoreactor”, *AIChE. Journal.*, Vol.16, pp.359-363. Jain, R., Graessley, W. W., and Dranoff, J. S., (1971) “Design and Analysis of a Photoreactor for Styrene Polymerization”, *Ind. Eng. Chem. Prod. Res.*, Vol.10, pp.293-298. Kurbus, T., Slokar, Y. M., Marechal, A. M. L. (2002) “The Study of the Effects of the Variables on H<sub>2</sub>O<sub>2</sub>/UV Decoloration of Vinsulphonedye:part”, *Dyes and Pigments.*, Vol.54, pp.67-78. Li, X. Z. and Zhao, Y. G. (1999) “Advanced Treatment of Dyeing Wastewater for Reuse”, *Wat. Sct. Tech.*, Vol.39, No.10, pp.249-255. Martin C. A., Alfano, O. M., and Cassano A. E., (2001) “Water decolorization using UV radiation and hydrogen peroxide:a kinetic study”, *Water Science and Technology:Water Supply.*, Vol.44, No.5, pp.53-60. Martin, G. C. A., Camera R., Santarelli, F. (1999) “Effective Design of Photocatalytic Reactors:Influence of Radiative Transfer on Their Performance”, *Catalysis Today.*, Vol.48, pp.307-313.*

Mariana N., Ilie, S., Antonius, K. (1999) " Kinetics of nitromusk compounds degradation in water by ultraviolet radiation and hydrogen peroxide " ,Chemosphere. Majcen, A. L. M., Taufer, Y. M. S. T., (1997) " Decoloration of Chlorotriazine Reactive Azo Dyes with H<sub>2</sub>O<sub>2</sub>/UV " ,Dyes and Pigments., Vol.33, No.4, pp.281-298. Mariana N., Ilie S., Ayyfer Y., Antonius K. (2002) " Kinetics of decolorization and mineralization of reactive azo dyes in aqueous solution by the UV/H<sub>2</sub>O<sub>2</sub> oxidation " ,Dyes and Pigments. Nilsun H. I., (1998) " Critical Effect of Hydrogen Peroxide in Photochemical Dye Degradation " ,Wat. Res., Vol.33, No.4, pp.1080-1084. Octave L. " Chemical Reaction Engineering, Third Edition pp.136-140 Spadoni, G., stramigioli, C., Santarelli, F. (1979) " Rigorous and Simplified Approach the Modelling of Continuous Photoreactor " ,Chemical Engineering Science., Vol.35, pp.925-931. Sundstrom, D. W., Weir, B. A. (1990) " Destruction of Mixtures of Pollutants by UV-Catalyzed Oxidation with Hydrogen Peroxide " ,ACSSymp. Series., No.422, pp.67-76. Tanaka K, Padermpole K, Hisanaga T.(2000) " Photocatalytic degradation of Commercial Azo Dyes " ,Water Res., Vol.34, pp.327-333. William J., Dolan C. A., Dranoff, J. S. (1965) " Dimensional Analysis in Photochemical Reactor Design " ,AIChE Journal. Yue, P. L. (1997) " Oxidation Reactors for Water And Wastewater Treatment " ,Wat. Sci. Tech., Vol.35, No.4, pp.189-196.