

紫外光/二氧化鈦/超音波程序對染整廢水處理之研究 = Decolorization of Textile Wastewater by The Hybird UV/TiO₂/Ultrasound..

鍾富鳳、吳忠信

E-mail: 9901113@mail.dyu.edu.tw

摘要

本研究以紫外光/二氧化鈦(UV/TiO₂)為實驗基礎，並結合震盪式超音波(ultrasonic bath, USB)及探針式超音波(ultrasonic probe, USP)，對染整廢水之處理進行脫色研究，以了解光催化處理染整廢水之可行性及結合超音波是否能增加反應速率。本研究之目標污染物為C.I. Reactive Red 2 (RR2)，探討參數包含染料初始濃度、TiO₂劑量、溶液pH值、燈光波長及結合USB及USP。實驗結果顯示降解速率隨初始濃度和pH值下降而增加；研究發現TiO₂最適添加量為2 g/L，脫色反應符合擬一階反應速率式；降解速率以波長254 nm之UV照射高於365 nm；此外溶液中添加鹽類對UV/TiO₂程序的降解能力具促進效果。脫色速率呈現UV/TiO₂/USB/USP > UV/TiO₂/USB > UV/TiO₂/USP > UV/TiO₂，由實驗數據可知USB和USP系統有助於增加UV/TiO₂之降解速率。光催化實驗中，以UV/TiO₂/USB/USP具有最佳之光降解效果，反應時間經過120 min，於254 nm UV照射下，可達到約80%之脫色效率。C₂H₅OH添加對UV/TiO₂相關系統造成明顯之抑制效應，實驗結果推測氫氧自由基是主要氧化有機物之物種，但反應速率並未因C₂H₅OH添加而完全停止，故電洞之氧化能力於UV/TiO₂相關系統中亦扮演重要之角色。

關鍵詞：二氧化鈦；超音波；可行性；速率式；紫外光

目錄

目錄 封面內頁 簽名頁 授權書.....	iii 中文摘要.....
.....iv 英文摘要.....	v 誌謝.....
.....vi 目錄.....	
.....vii 圖目錄.....	x 表目錄.....
.....xv 第一章 前言.....	1 1-1 研究緣起.....
.....1 1-2 研究動機.....	1 第二章 文獻回顧.....
.....3 2-1 染整廢水.....	3 2-1 染整廢水.....
.....3 2-1-1 染整廢水對台灣河川污染情況.....	3 2-1-2 染料介紹.....
.....5 2-1-3 反應性染料.....	6 2-1-4 染整廢水之處理.....
.....7 2-2 二氧化鈦/紫外光之光催化反應.....	13 2-2-1 光化學理論.....
.....13 2-2-2 光化學反應類型.....	13 2-2-3 光化學氧化技術.....
.....15 2-2-4 二氧化鈦物化特性.....	20 2-2-5 二氧化鈦之用途及應用.....
.....21 2-3 超音波.....	22 2-3-1 超音波簡介.....
.....22 2-3-2 超音波應用型態.....	24 2-4 高級氧化程序之相關文獻整理.....
.....26 2-4-1 TiO ₂ 劑量影響.....	27 2-4-2 pH值影響.....
.....27 2-4-3 溫度的影響.....	28 第三章 實驗材料與方法.....
.....34 3-1 實驗材料.....	34 3-2 實驗設備.....
.....34 3-3 實驗步驟.....	35 3-3-1 前置作業.....
.....35 3-3-2 背景實驗.....	36 3-3-3 異相光催化反應.....
.....38 3-3-4 實驗結合.....	40 3-4 實驗試程
.....44 第四章 結果與討論.....	47 4-1 光催化反應背景實驗.....
.....47 4-1-1 直接光解實驗.....	47 4-1-2 未照光實驗.....
.....49 4-1-3 超音波實驗.....	50 4-2 異相光催化實驗.....
.....52 4-2-1 RR2濃度效應.....	52 4-2-2 TiO ₂ 濃度效應.....
.....54 4-2-3 pH效應實驗.....	56 4-3 複合系統實驗.....
.....58 4-3-1 UV/TiO ₂ /USB不同初始濃度.....	58 4-3-2 UV/TiO ₂ /USB 不同TiO ₂ 劑量添加.....
.....60 4-3-3 UV/TiO ₂ /USB 之溶液pH值的影響.....	62 4-3-4 UV/TiO ₂ /USP不同初始濃度.....
.....64 4-3-5 UV/TiO ₂ /USP 不同TiO ₂ 劑量添加.....	66 4-3-6 UV/TiO ₂ /USP 之溶液pH值的影響.....
.....68 4-3-7 UV/TiO ₂ /USB/USP 不同初始濃度的影響.....	70 4-3-8 UV/TiO ₂ /USB/USP不

同TiO ₂ 劑量添加.....	75	4-3-9 UV/TiO ₂ /USB/USP 之溶液pH值的影響.....	80	4-3-10 鹽類添加.....
.....86 4-3-11 溫度的影響.....			89	4-3-12 抑制劑添加的影
響.....		94 第五章 結論與建議.....	96	5-1 結論.....
.....96 5-2 建議.....			97	參考文
獻.....		98 附錄.....		
	...104			

參考文獻

參考文獻 Alnuaimi, M. M., Rauf, M. A., and Ashraf, S. S. A comparative study of Neutral Red decoloration by photo-Fenton and photocatalytic processes, 2008, Dyes and Pigments, 76, 332-337 Arslan-Alaton,I., Gursoy, B. H., and Schmidt, J. E. Advanced oxidation of acid and reactive dyes: Effect of Fenton treatment on aerobic, anoxic and anaerobic processes, 2008, Dyes and Pigments, 78, 117-130 Berlan, J.and Mason, T. J. Sonochemistry: from research laboratories to industrial plants, 1992, Ultrasonics, 30, 203-212 Bandara, J., Nadtochenko, V., Kiwi, J.and Pulgarin, C. Dynamics of oxidant addition as a parameter in the modeling of dye mineralization (Orange 2) via technologies., 1997, Water Science and Technology, 35(4), 87-99. Brillas, E., Cabot, P. L., Rodriguez, R. M., Arias, C., Garrido, J. A. and Oliver, R. Degradation of the herbicide 2,4-DP by catalyzed ozonation using the O₃/Fe²⁺/UVA system, 2004, Applied Catalysis B: Environmental , 51, 117 – 127 Bejarano-Perez, N. J.,and Suarez-Herrera, M. F. Sonophotocatalytic degradation of congo red and methyl orange in the presence of TiO₂ as a catalyst, 2007, Ultrasonics Sonochemistry, 14, 589 – 595 Chen, R.and Pignatello, J. J., Role of quinone intermediates as electron shuttles in fenton and photoassisted fenton oxidations of aromatic compounds. Environ Science and Technology, 1997, 31(8), 2399-2406. Cho, I. H. and Zoh, K. D. Photocatalytic degradation of azo dye (Reactive Red 120) in TiO₂/UV system: Optimization and modeling using a response surface methodology (RSM) based on the central composite design, 2007, Dyes and Pigments, 75, 533-543 Chen, C., Wang, Z., Ruan, S., Zou, B., Zhao, M. and Wu, F. Photocatalytic degradation of C.I. Acid Orange 52 in the presence of Zn-doped TiO₂ prepared by a stearic acid gel method, 2008, Dyes and Pigments, 77, 204-209 Chu, W., and Wong C. C. The photocatalytic degradation of dicamba in TiO₂ suspensions with the help of hydrogen peroxide by different near UV irradiations, 2004, Water Research, 38, 1037-1043 Dominguez, J. R., Beltran, J. and Rodriguez, O. Vis and UV photocatalytic detoxification methods (using TiO₂, TiO₂/H₂O₂, TiO₂/O₃, TiO₂/S₂O₈²⁻, O₃, H₂O₂, S₂O₈²⁻, Fe³⁺/H₂O₂ and Fe³⁺/H₂O₂/C₂O₄²⁻) for dyes treatment, 2005, Catalysis Today, 101, 389 – 395 Ince, N. H., Tezcanli, G., Belen, R. K. and Apikyan, I. G. Ultrasound as a catalyst of aqueous reaction systems:the state of the art and environmental applications, 2001, Applied Catalysis B: Environmental, 29, 167-176 Jozwiak, W., Mitros, M., Czaplinska, J. K. and Tosik, R. Oxidative decomposition of Acid Brown 159 dye in aqueous solution by H₂O₂/Fe²⁺ and ozone with GC / MS analysis, 2007, Dyes and Pigments, 74, 9-16 Jiang, Y., Sun, Y., Liu, H., Zhu, F. and Yin, H. Solar photocatalytic decolorization of C.I. Basic Blue 41 in an aqueous suspension of TiO₂-ZnO, 2008, Dyes and Pigments, 78, 77-83 Konstantinou, I.K. and Albanis, T.A. TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations—a review, 2004, Applied Catalysis B: Environmental, 49, 1 – 14. Ku, Y., Lee, W.H. and Wang, W.Y. Photocatalytic reduction of carbonate in aqueous solution by UV / TiO₂ process, 2004, Journal of Molecular Catalysis A : Chemical, 212, 191-196 Kaur, S. and Singh, V. TiO₂ mediated photocatalytic degradation studies of Reactive Red 198 by UV irradiation, Journal of Hazardous Materials, 141, 230 – 236 Liu, W., Chen, S., Zhao, W. and Zhang, S. Titanium dioxide mediated photocatalytic degradation of methamidophos in aqueous phase, 2009 Journal of Hazardous Materias, 164, 154-160 Muruganandham, M. and Swaminathan, M. Photocatalytic decolourisation and degradation of Reactive Orange 4 by TiO₂-UV process, 2006, Dyes and Pigments, 68, 133-142 Muruganandham, M., Sobana, N. and Swaminathan, S., Solar assisted photocatalytic and photochemical degradation of Reactive Black 5, 2006, Journal of Hazardous Materials, B137, 1371 – 1376 Oturan, N., Trajkovska, S., Oturan, M. A., Couderchet, M. and Aaron, J. J. Study of the toxicity of diuron and its metabolites formed in aqueous medium during application of the electrochemical advanced oxidation process ‘ ‘ electro-Fenton ” , 2008, Chemosphere, 73, 1550-1556. Rao, R. N. and Venkateswarlu, N. The photocatalytic degradation of amino and nitro substituted stilbenesulfonic acids by TiO₂/UV and Fe²⁺/H₂O₂/UV under aqueous condition, 2008, Dyes and Pigments, 77, 590-597 Sadik, W. A., Poznyak, S., Kulak, A. and Pichat, P. TiO₂-In₂O₃ photocatalysts: preparation, characterisations and activity for 2-chlorophenol degradation in water, 2004, Journal of Photochemistry and Photobiology A: Chemistry, 162, 423-430 Sadik, W. A. Effect of inorganic oxidants in photodecolourization of an azo dye, 2007, Journal of Photochemistry and Photobiology A: Chemistry, 191, 132-137 Tezcanli-Guyer, G. and Ince, N. H. Individual and combined effects of ultrasound, ozone and UV irradiation: a case study with textile dyes, 2004, Ultrasonics, 42, 603 – 609 Voncina, D. B. and Majcen-Le-Marechal, A. Reactive dye decolorization using combined ultrasound/H₂O₂, 2003, Dyes and Pigments, 59, 173-179 Vajnhandl, S. and Marechal, A. M. L. Ultrasound in textile dyeing and the decolouration/mineralization of textile dyes, 2005, Dyes and Pigments, 65, 89-101 Watanabe, N., Horikoshi, S., Hidaka, H. and Serpone, N., On the recalcitrant nature of the triazinic ring species, cyanuric acid, to degradation in Fenton solutions and in UV-illuminated TiO₂ (naked) and fluorinated TiO₂ aqueous dispersions, 2005, Journal of Photochemistry and Photobiology A: Chemistry 174, 229 – 238 Wu, C.H. and Chang, C. L. Decolorization of Reactive Red 2 by advanced oxidation processes:Comparative studies of homogeneous and heterogeneous systems, 2006, Journal of Hazardous Materials, B128, 265 – 272. Wu, C. H. Decolorization of C.I. Reactive Red 2 in O₃, Fenton-like and O₃/Fenton-like hybrid systems, 2008, Dyes and Pigments, 77, 24-30 Wu, C. H. Effects of operational parameters on the

decolorization of C.I. Reactive Red 198 in UV/TiO₂-based systems, 2008, Dyes and Pigments, 77, 31-38 Wu, C. H., Chang, C. L. and Kuo, C. Y. Decolorization of Procion Red MX-5B in electrocoagulation (EC), UV/TiO₂ and ozone-related systems, 2008, Dyes and Pigments, 76, 187-194 Wu, C. H. and Yu, C. H. Effects of TiO₂ dosage, pH and temperature on decolorization of C.I. Reactive Red 2 in a UV/US/TiO₂ system, 2009, Journal of Hazardous Materials. Yang, H.G., Li, C.Z., Gu, H.C. and Fang, T.N. Rheological Behavior of Titanium Dioxide Suspensions, 2001, Journal of Colloid and Interface Science, 236, 96-103 Zhang, H., Duan, L., Zhang, Y. and Wu, F. The use of ultrasound to enhance the decolorization of the C.I. Acid Orange 7 by zero-valent iron, 2005, Dyes and Pigments, 65, 39-43 小西謙三原著，張明基譯，1987，工業合成染料化學，復漢出版社有限公司。工業污染防治技術服務團隊，染整業廢水污染防治技術，1993，經濟部工業局。中國技術服務社編，化學混凝處理單元設計與操作，1990，經濟部工業局。中國技術服務社編，活性碳處理，1993，經濟部工業局。中國技術服務社編，廢水處理功能生物診斷技術，1995，經濟部工業局。中國技術服務社編，工業廢水逆滲透處理，1996，經濟部工業局。行政院環境保護署，放流水標準，2007年6月修正。邱永亮譯，染料之合成與特性，1989，財團法人徐氏基金會。宋心琦、周福添、劉劍波，光化學，2004，五南圖書出版股份有限公司。翁志聖，高級氧化程序在廢水處理上的應用，1993，經濟部工業局。張淑芳、高思懷，Fenton法之原理與應用，1995，工業污染防治第56期。橋本和仁著，張立群譯，光清境革命-活耀的二氧化鈦光觸媒，1996，協志工業叢書。賴耿陽，高週波工業應用技術，1993，復漢出版社。蘇宏毅、洪錫勳，UV/H₂O₂技術在化工業上之應用，1995，工業污染防治56期。曹怡，張建成，光化學技術，2007，新文京開發出版社。曾迪華、莊連春、郭家倫、楊志堅，UV/H₂O₂氧化程序於水處理，1995，工業污染防治第56期。廖盛焜，反應性染料之發展動向，紡織科學期刊44期，1982。顏上惟，紡織染整業推行ISO環境管理系統之先期審查，品值月刊，2000。鄭振東，超音波工程，1999，全華科技圖書股份有限公司。謝永旭，光催化處理程序，1995，工業污染防治第56期。顧洋，紫外線/臭氧氧化程序在廢水處理上之應用，1995，工業污染防治第56期。