

以催化臭氧程序處理含有機物廢水之質傳與反應行為研究

許凱鈞、申永順

E-mail: 9510855@mail.dyu.edu.tw

摘要

中文摘要 臭氧程序在水溶液系統之污染物處理的應用中，臭氧質傳與自解對有機物的去除反應有相當大的影響。為瞭解催化式臭氧程序反應系統中觸媒對於臭氧之質傳係數、自解速率常數和反應速率常數的影響，本實驗使用Al₂O₃、MnO₂、SiO₂和PAC四種觸媒，在不同反應條件下，分別進行單純臭氧自解與質傳，以及在含有機物(Red 4染料)之氧化反應實驗，於催化式臭氧系統中探討不同觸媒在不同操作條件下，對染料去除行為之影響。實驗結果顯示各類觸媒之添加對於臭氧之質傳係數略有增加，臭氧自解速率常數以添加PAC時有最佳促進效果。在本研究範圍內，觸媒劑量對於臭氧質傳係數之促進影響不大，但對臭氧自解常數而言，Al₂O₃與PAC之劑量效應對於臭氧質傳係數之促進情形較為明顯。在低pH條件下，MnO₂觸媒對臭氧之促進質傳較為明顯，添加MnO₂時，臭氧之質傳係數K_{La}值約為0.5488min⁻¹，其質傳效果隨pH之升高而降低。PAC觸媒對臭氧之自解反應速率之影響較其他觸媒更為明顯，臭氧自解之速率隨pH值增高而增加，在pH9添加PAC時，臭氧的自解速率常數k_d值約為2.3141 min⁻¹。實驗發現，以PAC觸媒對增進Red 4脫色反應速率之效率最佳，其餘各類觸媒劑量之增加對於Red 4反應速率之促進並不明顯，在高pH值下觸媒之添加可增加Red 4染料之反應速率，顯示臭氧可藉由觸媒之添加，提升OH⁻與Red 4之間接氧化作用。本研究提出三種反應模式，可合理說明臭氧結合不同觸媒時，對於水中有機物臭氧化反應機制與反應行為之影響。

關鍵詞：質傳係數；自解；臭氧；催化式臭氧程序

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.....	xix 符號說明...
xxiiiv 第一章 前言.....	1 1.1 研究緣起.....
1.1.2 研究目的.....	2 第二章 理論背景.....
及文獻回顧.....	4.2.1 臭氧的自解行為.....
4.2.1.1 臭氧的反應行為.....	4.2.2 臭氧的質傳行為.....
4.2.2.1 活性碳.....	5.2.3.1 金屬氧化物.....
4.2.2.2 異相催化性臭氧化系統之相關文獻.....	5.2.3.2 催化性臭氧化程序之文獻.....
4.2.2.3 MnO ₂ 觸媒.....	5.2.4.1 Al ₂ O ₃ 觸媒.....
4.2.2.4 SiO ₂ 觸媒.....	5.2.4.2 AC 觸媒.....
4.2.2.5 同相催化性臭氧化系統之相關文獻.....	30 第三章 研究目的.....
34 第四章 實驗程序與設備.....	36 4.1 實驗設備.....
36 4.2 實驗藥品.....	37 4.3 實驗裝置.....
38 4.4 實驗步驟.....	39 4.5 分析測定方法.....
41 第五章 結果與討論.....	41 第五章 結果與討論.....
46 5.1 單純O ₃ 自解.....	46 5.1.1 無觸媒條件下臭氧之質傳及自解行為.....
47 5.1.2 有觸媒條件下臭氧之質傳及自解行為.....	50 5.1.2.1 添加Al ₂ O ₃ 觸媒.....
50 5.1.2.2 添加MnO ₂ 觸媒.....	50 5.1.2.2 添加SiO ₂ 觸媒.....
57 5.1.2.3 添加PAC觸媒.....	57 5.1.2.4 添加Al ₂ O ₃ 觸媒.....
64 5.1.2.4 添加SiO ₂ 觸媒.....	64 5.1.2.5 添加PAC觸媒.....
70 5.1.2.5 綜合比較.....	72 5.1.2.6 綜合比較.....
76 5.2 以催化臭氧程序處理含Red 4 水溶液 之反應行為.....	86 5.2.1 無觸媒條件下有機物之臭氧化反應.....
86 5.2.2 有觸媒條件下有機物之臭氧化反應.....	87 5.2.2.1 添加Al ₂ O ₃ 觸媒.....
88 5.2.2.2 添加MnO ₂ 觸媒.....	88 5.2.2.2 添加SiO ₂ 觸媒.....
99 5.2.2.3 添加PAC觸媒.....	99 5.2.2.4 添加Al ₂ O ₃ 觸媒.....
103 5.2.2.4 添加SiO ₂ 觸媒.....	109 5.2.2.5 添加PAC觸媒.....
109 5.2.2.5 添加Al ₂ O ₃ 觸媒.....	113 5.2.2.6 添加SiO ₂ 觸媒.....
119 5.2.2.6 添加PAC觸媒.....	119 5.2.2.7 pH 效應.....

效應.....	119	2.劑量效應.....	123	5.2.2.5 綜合比較-pH效應....
.....129 第六章 結果與建議.....			152	參考文獻.....
.....154				

參考文獻

參考文獻 Tong, S. P., Liu, W. P., Leng, W. H., and Zhang Q. Q., " Characteristics of MnO₂ catalytic ozonation of sulfosalicylic acid and propionic acid in water " , Chemosphere , Vol. 50, pp. 1359-1364 (2003). Kasprzyk-Hordern, B., Dabrowska, A., Swietlik, J., and Nawrocki, J., " The application of the perfluorinated bonded alumina phase for natural organic matter catalytic ozonation " , J. Environ Eng. Sci. , Vol. 3, pp. 41-50 (2004). Kasprzyk-Hordern, B., Andrzejewski, P., and Mawroki, J., " Ether degradation in water using catalytic ozonation in the presence of perfluorinated alumina " , International Conference Barcelona (2004). Park, J. S., Choi, H., and Cho, J., " Kinetic decomposition of ozone and para-chlorobenzoic acid (pCBA) during catalytic ozonation " , Water Research Vol. 38, pp. 2285-2292 (2004). Craeynest, V.K., Dewulf, J., Donck, H., Beuf, D.K., and Langenhove, V.H., " Application of the peroxone process for the removal of chlorinated volatile organic compounds from waste gases in an advanced oxidative scrubber. Experimental results. " , International Conference Barcelona (2004). Lee, J.E., Jin, B.S., Cho, S.H., Han, S.H., Joo, O.S., and Jung, K.D., " Catalytic Ozonation of Humic Acids with Fe/MgO " , Korean J. chem. Eng., Vol. 22, pp. 536-540 (2005). Ernst, M., Lurot, F., and Schrotter, J.C., " Catalytic ozonation of refractory organic model compounds in aqueous solution by aluminum oxide " , Applied Catalysis B:Environmental, Vol. 47, pp. 15-25 (2004). Fujita, H., Izumi, J., Sagehashi, M., Fujii, T., and Sakoda, A., " Decomposition of trichloroethene on ozone-adsorbed high silica zeolites " , Water Research, Vol.38, pp. 166-172 (2003). Fujita, H., Izumi, J., Sagehashi, M., Fujii, T., and Sakoda, A., " Adsorption and decomposition of water-dissolved ozone on high silica zeolites " , Water Research, Vol.38, pp. 159-165 (2004). Ma, J., Sui, M., Zhang, T., and Guan, C., " Effect of pH on MnO_x/GACcatalyzed ozonation for degradation of nitrobenzene " , Water Research, Vol.39, pp. 779-786 (2005). Lin, J., Kawai, A., and Nakajima, T., " Effective catalysts for decomposition of aqueous ozone " , Applied Catalysis B:Environmental, Vol.39, pp. 157-165 (2002). Song, S.S., Oh, B.S., Na, S.J., Lee, E.T., and Kang, J.W., " Heterogeneous catalytic ozonation of oxalic acid using Mn-doped GAC as a catalyst " , International Conference Barcelona (2004). Einaga, H., and Futamura, S., " Oxidation behavior of cyclohexane on alumina-supported manganese oxides with ozone " , Applied Catalysis B:Environmental, Vol.60, pp. 49-55 (2005). Andreozzi, R., Insola, A., Caprio, V., Marotta, R., and Tufano, V., " The use of manganese dioxide as a heterogeneous catalyst for oxalic acid ozonation in aqueous solution " , Applied Catalysis A:General, Vol.138, pp. 75-81 (1996). Beltran, F.J., Rivas F.J., and Montero-de-Espinosa R., " Iron type catalysts for the ozonation of oxalic acid in water " , Water Research, Vol.39, pp. 3553-3564 (2005). Alebic-Juretic, A., Cvitas, T., and Klasinc, L., " Kinetics of heterogeneous ozone reactions " , Chemosphere, Vol.41, pp. 667-670 (2000). Einaga, H., and Futamura, S., " Catalytic oxidation of benzene with ozone over alumina-supported manganese oxides " , Journal of Catalysis, Vol.227, pp. 304-312 (2004). Legube, B., and Leitner, N.K.V., " Catalytic ozonation: a promising advanced oxidation technology for water treatment " , Catalytic Today, Vol.53, pp. 61-72 (1999). Parisheva, Z., and Demirev, A., " Ozonation of ethanolamine in aqueous medium " , Wat. Res., Vol.34, pp. 1340-1344 (2000). Andreozzi, R., Insola, A., Caprio, V., and D'Amore, M. G., " The Kineticsof Mn(II)-Catalysed Ozonation of Oxalic Acid in Aqueous Solution " , Wat. Res., Vol. 26, No. 7, pp. 912-917 (1992). Gracia, R., Araguees, J. L., and Ovelleiro, J. L., " Study of the catalytic ozonation of humic substances in water and their ozonation byproducts " , Wat. Res., Vol. 18, No. 3, pp. 195-208 (1996). Andreozzi, R., Caprio, V., Insola, A., Marotta, R., and Tufano, V., " The Ozonation of Pyruvic Acid in Aqueous Solutions Catalyzed by Suspended and Dissolved Manganese " , Wat. Res., Vol. 32, No. 5, pp. 1492-1496 (1998). Cortes, S., Sarasa, J., Ormad P., and Ovelleiro, J. L., " Comparative Efficiency of the Systems O₃/high pH and O₃/Catalyst for the Oxidation of Chlorobenzens in Water " , Conference of Ozonation and AOPs in Water Treatment, pp. 23-25 (1998). Ma, J., Graham, and Nigel, J. D., " Degradation of Atrazine by Manganese-catalyzed Ozonation:Influence of Humic Substances " , Wat. Res., Vol. 33, No. 3, pp. 785-793 (1999). Andreozzi, R., Caprio, V., D'Amore, M. G., Insola, A., and Tufano, V., " Analysis of complex reaction networks in gas-liquid systems , the ozonation of 2-hydroxypyridine in aqueous solutions " , Industrial Engineering and Chemical Research, Vol. 30, pp. 2098-2104 (1991). Beltra'n, F. J., Garcia-Araya, J. F., and Acedo, B. , " Advanced oxidation of atrazine in water – . Ozonation " , Water Research, Vol. 28, pp. 2153-2164 (1994). Beltra'n, F. J., " Theoretical aspects of the kinetics of competitive first order reactions of ozone in the O₃/H₂O₂ and O₃/UV oxidation Processes " , Ozone Science & Engineering, Vol. 19, pp. 13-37 (1997). Benitez, F. J., Beltra'n-Heredia, J., and Gonzalez, T., " Ozonation of aqueous solution of fenuron " , Industrial Engineering and Chemical Research , Vol. 30, pp. 2390-2395 (1991). Buxton, G. V., Greenstock, C. L., Helman, W. P., and Ross, A. B., " Critical review of rate constants for reaction of hydrated electrons , hydrogen atoms and hydroxyl radicals (OH / O -) in aqueous solutions " , Journal of Physical Chemistry Reference Data , Vol. 17, pp. 513-886 (1988). Gurol, M. D., and Nekouinaini, S., " Kinetic behaviour of ozone in aqueous solutions of substituted phenols " , Industrial Engineering and Chemical Research, Vol. 16, pp. 377-383 (1984). Haag, W. R. , and Yao, C. C. D., " Rate constants for reaction of hydroxyl radicals with several drinking water contaminants " , Environmental Science & Technology, Vol. 26, pp. 1005-1013 (1992). Hoigne, J., Bader H., Haag, W. R., and Staehelin, J., " Rate constants of reaction of ozone with organic and inorganic compounds in water- . Inorganic compounds and radicals " , Water Research , Vol. 19, pp. 993-1004 (1985). Hoigne, J., and Bader, H., " Ozonation of water : oxidation competition values of different types of waters used in Switzerland " , Ozone Sciwnce and Engineering, Vol. 1, pp. 357-372 (1979). Hoigne, J., and Bader, H., " Ozonation of water : role of hydroxyl radical reactions in ozonation processes in aqueous

solution ” , Water Research , Vol. 10, pp. 377-386 (1976). Hoigne, J., and Bader, H., “ Rate constants of reaction of ozone with organic and inorganic compounds in water- . Non-dissociated organic compounds ” , Water Research, Vol. 17, pp. 173-183 (1983 a). Hoigne, J., and Bader, H., “ Rate constants of reaction of ozone with organic and inorganic compounds in water- . Dissociated organic compounds ” , Water Research, Vol. 17, pp. 184-195 (1983 b). Li, K. Y., Kuo, C. H., and Weeks, J. L., ” A kinetic study of ozone-phenol reation in aqueous solution “ , American Institute of Chemical Engineers Journal, Vol. 25, pp. 583-591 (1979). Minchew, E. P., Gould, J. P, and Saunder, F. M., ” Multistage decomposition kinetics of ozone in dilute aqueous solutions “ , Ozone Sciwnce & Engineering , Vol. 9, pp. 165-177 (1987). 胡冠華，「以三(正辛基)胺硫酸鹽萃取酚之質傳研究」，博士論文，清華大學化學工程研究所(1992)。楊平義，「金屬離子對臭氧化分解2-氯酚效能增進之探討與研究」，碩士論文，國立交通大學環境工程研究所(1999)。賴朝文，「新型捲氣式反應器之臭氧質傳研究」，碩士論文，國立台灣科技大學化學工程研究所(1999)。方長福，「染整廢水以新型反應器進行臭氧脫色研究」，碩士論文，國立台灣科技大學化學工程研究所(1997)。陳修斌，「氣泡形成對臭氧質傳及其對含2-氯酚水溶液分解反應行為之影響」，碩士論文，國立台灣科技大學化學工程研究所(2000)。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，私立大葉大學環境工程研究所(2002)。柯雅雯，「臭氧處理對自來水中消毒副產物與有機前質之去除研究」，國立台灣大學環境工程學研究所博士論文(1999) 徐新華，趙傳榮，「水與廢水的臭氧處理」，化學工業出版社(2003)。