Study on the Decompostion of Dye Wastewaters by Ozonation Process in the presence of Modified Photocatalyst

賴佑昌、申永順

E-mail: 9805415@mail.dyu.edu.tw

ABSTRACT

The purpose of this study is to utilize three kinds of Advanced Oxidation Processes, ozone, ozone/catalyst and ozone/photocatalyst, and treat wastewater containing acid dyes, such as Acid Orange 8, Acid Blue 29 and Acid Blue 113, in order to discuss the impact of operating factors in reaction system, such as initial pH of solution, catalyst level and dye type, on acid dye removal rate and reaction rate. This study also aimed to modify Degussa P-25 photocatalyst by adding various levels of silver nitrate (AgNO3), and prepare metal catalyst by means of Incipient Wet Impregnation and Impregnation methods, coupled with Heat Reduction method and Photocatalytic Synthesis respectively. The results indicated that, preparing metal catalyst by means of Impregnation plus Photocatalytic Synthesis could deposit silver atoms over catalyst surface effectively. Ozone mass transfer and autodecomposition in liquid phase before and after modifying catalyst were studied. Ozone autodecomposition leads to the falling trend of saturation curve, and it also indicates higher oxidizing ability since it can produce strong oxidizing hydroxyl radicals (OH．). As a result, in case of modified catalyst with 5.0wt% Ag-TiO2, solution pH at 3.0, and catalyst addition level at 3.0 g/L, ozone saturation curve drops most significantly. In case of ozone solution pH at 3.0, 5.0, 7.0, 9.0, when catalyst addition level is 1.0 g/L, this catalyst could be most effective to enable ozone autodecomposition. In running batch reaction of acid dye treatment through O3/Catalyst process, adding metal catalyst can allow silver atoms deposited on catalyst surface to catalyze ozone reaction to generate hydroxyl radicals (OH．), and attack dye molecules adsorbed onto catalyst surface. Under reaction conditions such as solution pH of 3.0, 5.0wt% Ag-TiO2 level of 1.0 g/L, initial concentration of Acid Orange 8 at 0.11mM, ozone level at 5 mg/L, Acid Orange 8 could obtain the optimum reaction rate. In running batch reaction of acid dye treatment through O3/UV/Catalyst process, added metal catalyst could produce electrons and electron-hole pairs under UV excitation, silver atoms deposited onto catalyst surface could dissociate electrons from electron-hole pairs quickly. The electrons could react with ozone adsorbed onto catalyst surface to generate hydroxyl radicals (OH．), and attack dye molecules adsorbed onto catalyst surface. Under reaction conditions such as solution pH of 3.0, 5.0wt% Ag-TiO2 level of 1.0 g/L, initial concentration of Acid Orange 8 at 0.11mM, ozone level at 5 mg/L, Acid Orange 8 could obtain the optimum reaction rate. This study compared three kinds of Advanced Oxidation Processes, and found that ozone plus photocatalyst process has the best reaction rate of removing acid dye, ozone/catalyst process followed, and pure ozone process is the worst.

Keywords : Advanced Oxidation Processes、Acid dye、Impregnation、Photocatalyst、Photocatalytic Synthesis、Ag/TiO2

Table of Contents

封面內頁 簽名頁 授權書iii 中文摘要iv 英文摘要vi 誌謝viii 目錄ix 圖目錄xv 表目錄xxvi 第一章前言1 1.1研究動機1 1.2研究目的3 第二章理論背景與文獻回顧5 2.1染整廢水5 2.1.1染整廢水簡介5 2.1.2染料之分類8 2.1.3染料之化學結構及發色原理11 2.1.4染整廢水水質特性及現行法規規範12 2.2臭氧之相關特性與反應機制15 2.2.1臭氧物理化學性質15 2.2.2臭氧之自解行為17 2.2.3臭氧之質傳行為18 2.2.4臭氧之反應行為20 2.2.5臭氧相關文獻整理24 2.3光分解反應程序之理論27 2.3.2光化學之反應理論29 2.3.3臭氧/紫外光程序之反應機制34 2.3.4臭氧/觸媒程序之反應機制37 2.4光觸媒反應程序之理論39 2.4.1光觸媒之特性及應用39 2.4.2光觸媒表面吸附現象46 2.4.3臭氧/光觸媒程序52 2.4.4臭氧/光觸媒程序文獻整理54 2.5光觸媒之製備與改質61 2.5.1光觸媒之製備方法61 2.5.2光觸媒之改質文獻整理62 第三章研究目的與架構69 第四章實驗程序與設備71 4.1實驗設備與儀器71 4.2實驗藥品72 4.3實驗裝置73 4.4本研究染料之基本性質74 4.5實驗步驟75 4.5.1光觸媒改質製備75 4.5.2背景實驗77 4.5.3臭氧質傳實驗 78 4.5.4以臭氧程序處理染料水溶液79 4.5.5以臭氧/觸媒程序處理染料水溶液79 4.5.6以臭氧/光觸媒程序處理染料水溶液80 4.6分析測定方法82 4.6.1臭氧測定方法82 4.6.2掃瞄式電子顯微鏡84 4.6.3能量分散式X-射線光譜儀84 4.7各染料之檢量線製作85 第五章結果與討論88 5.1背景實驗88 5.1.1液相中染料穩定性實驗88 5.1.2紫外光直接光解染料實驗89 5.1.3觸媒直接吸附染料實驗90 5.1.4二氧化鈦之定性分析93 5.2 觸媒改質與製備96 5.2.1觸媒改質之製備方法96 5.2.1.1初濕含浸法配合熱還原法96 5.2.1.2含浸法配合熱還原法97 5.2.1.3含浸法配合光催化合成法100 5.2.2光催化合成法之光照時間對觸媒表面銀原子含量之影響107 5.3臭氧於液相中之質傳行為113 5.3.1 單純臭氧質傳行為113 5.3.1.1臭氧劑量效應114 5.3.1.2溶液pH值效應115 5.3.2添加觸媒對臭氧質傳之影響117 5.3.2.1添加TiO2對臭氧質傳之影響117 5.3.2.2添加0.5wt% Ag-TiO2對臭氧質傳之影響119 5.3.2.3添加2.0wt% Ag-TiO2對臭氧質傳之影響121 5.3.2.4添加5.0wt% Ag-TiO2對臭

氧質傳之影響123 5.3.4綜合比較125 5.4臭氧於液相中之自解行為130 5.4.1單純臭氧自解行為131 5.4.2添加觸媒對臭氧自解之影響134 5.4.2.1添加TiO2對臭氧自解之影響134 5.4.2.2添加5.0wt% Ag-TiO2對臭氧自解之影響138 5.4.3綜合比較141 5.5臭氧程序處理染料廢水149 5.5.1溶液初始pH值效應149 5.5.2不同染料種類152 5.6O3/Cata.程序處理染料廢水154 5.6.1以O3/TiO2程序處理染料廢水154 5.6.1.1溶液初始pH值效應154 5.6.1.2觸媒劑量效應158 5.6.1.3不同染料種類160 5.6.2以O3/0.5wt% Ag-TiO2程序處理染料廢水163 5.6.2.1溶液初始pH值效應163 5.6.2.2觸媒劑量效應167 5.6.2.3不同染料種類169 5.6.3以O3/2.0wt% Ag-TiO2程序處理染料廢水171 5.6.3.1溶液初始pH值效應171 5.6.3.3不同染料種類176 5.6.4以O3/5.0wt% Ag-TiO2程序處理染料廢水178 5.6.4.1溶液初始pH值效應178 5.6.4.2觸媒劑量效應181 5.6.4.3不同染料種類 5.6.5綜合比較185 5.6.5.1溶液初始pH值效應185 5.6.5.2觸媒劑量效應190 5.7臭氧結合光觸媒程序處理染料廢水194 5.7.1以O3/UV/TiO2程序處理染料廢水194 5.7.1.1溶液初始pH值效應194 5.7.1.2觸媒劑量效應198 5.7.1.3不同染料種類200 5.7.2以O3/UV/0.5 wt% Ag-TiO2程序處理染料廢水202 5.7.2.1溶液初始pH值效應202 5.7.2.3不同染料種類209 5.7.3以O3/UV/2.0 wt% Ag-TiO2程序處理染料廢水211 5.7.3.1溶液初始pH值效應211 5.7.3.2觸媒劑量效應214 5.7.3.3 不同染料種類216 5.7.4 以O3/UV/5.0 wt% Ag-TiO2程序處理染料廢水218 5.7.4.1溶液初始pH值效應218 5.7.4.2觸媒劑量效應222 5.7.4.3不同染料種類224 5.7.5各反應系統之綜合比較226 5.7.5.1溶液初始pH值效應226 5.7.5.2觸媒劑量效應231 第六章結論與建議236 6.1結論236 6.2建議237 參考文獻238

REFERENCES

1.和田洋六，水處理技術（應用篇），地人書館 (1992)。 2.經濟部環保署工業減廢聯合輔導小組，「工業減廢技術手冊1-染整工業」，第20-43頁 (1993)。 3.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 (1995)。 4.顧洋，“紫外線/臭氧氧化程序在廢水處理上之應用”，工業污染防治第十四卷，第四期，第248-261頁 (1995)。 5.台灣區綿布/絲綢印染整理工業同業公會，「染整業1998年放流水標準合理性修訂之研議」，(1999)。 6.經濟部工業局編印，「染整業污染防治與環境管理系統實務手冊」，(2002)。 7.徐新華，趙傳榮，「水與廢水的臭氧處理」，化學工業出版社 (2003)。 8.呂宗昕，「圖解奈米科技與光觸媒」，商周出版 (2003)。 9.?田博史,「光觸媒圖解」，商周出版 (2003)。 10.行政院環境保護署，「中華民國法規資料中心」，網址 http://law.epa.gov.tw/zh-tw/ (2008)。 11.殷榮堅，「以紫外線/臭氧程序處理2-氯酚溶液反應行為之研究」，碩士論文，國立台灣工業技術學院化工所 (1994)。 12.莊英良，「以紫外線/二氧化鈦程序分別處理含六價鉻及亞素靈水溶液反應行為之研究」，碩士論文，國立台灣工業技術學院化學工程技術研究所 (1996)。 13.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，國立台灣工業技術學院化工所 (1997)。 14.林鴻祥，「臭氧的質傳行為對以臭氧及紫外線/臭氧程序處理福瑞松水溶液之影響」，碩士論文，國立台灣工業技術學院化工所(1997)。 15.洪佳敬，「以臭氧相關程序處理含酚類水溶液反應及臭氧質傳行為之研究」，碩士論文，國立台灣科技大學化工所 (1998)。 16.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之研究」，博士論文，國立台灣科技大學化工所(1998)。 17.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)。 18.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)。 19.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 (2000)。 20.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 (2001)。 21.曾怡享，「奈米金屬氧化鈦觸媒光催化還原二氧化碳」，博士論文，國立台灣大學化學工程研究所 (2003)。 22.曾裕森，「在臭氧程序中添加二氧化鈦及二氧化錳對處理甲酚水溶液之影響」，碩士論文，國立台灣科技大學化學工程研究所(2004)。 23.許凱鈞，「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」，碩士論文，大葉大學環境工程學系研究所 (2006)。 24.陳聖翰，「異相臭氧催化反應對草酸降解之研究」，碩士論文，逢甲大學環境工程與科學學系研究所 (2007)。 25.Abe, K. and Tanaka, K.,“Effect of Fe2+ on UV-illuminated Ozonation of Nitrophenolic Compounds”, Chemosphere, Vol. 38, pp. 2747-2752 (1999). 26.Agustina, T. E., Ang, H. M., and Vareek, V. K.,“A review of Synergistic Effect of Photocatalysis and Ozonation on Wastewater Treatment”, Journal of Photochemistry and Photobiology C: Photochemistry Reviews, Vol. 6, pp. 264-273 (2005). 27.Bulanin, K. M., Lavalley, J. C., and Tsyganenko, A. A.,“Catalytic Ozonation of Oxalic Acid in an Aqueous TiO2 Slurry Reactor”, Journal of Photochemistry & Photobiology, A: Chemistry., Vol. 99, pp. 10294(1995). 28.Bouzazam, A., and Laplanche, A.“Photocatalytic Degradation of Toluene in the Gas Phase: Comparative Study of Some TiO2 Supports”, Journal of photochemistry and PhotoBiology A: Chemistry, Vol. 150, pp. 207-212 (2002). 29.Beltran, F. J., Rivas, F. J. and Montero-de-Espinosa, R.,“Catalytic Ozonation of Oxalic Acid in an Aqueous TiO2 Slurry Reactor”, Applied Catalysis B: Environmental, Vol. 39, pp. 221-231 (2002). 30.Choi, W., Termin, A., and Hoffmann, M.R.,“The Role of Metal Ion Dopants in Quantum-Sized TiO2:Correlation between Photoreactivity and Charge Carrier Recombination Dynamics” Journal of Physical Chemistry, Vol. 98, pp. 13669-13679 (1994). 31.Chedeville, O., Debacq, M., Almanza, M. F., and Porte, C.,“Use of an Ejector for Phenol Containing Water Treatment by Ozonation”, Separation and Purification Technology, Vol. 57, pp. 201-208 (2007). 32.Chen, Y.S., Zhang, X. S., Dai, Y.C. and Yuan, W. K.,“Pulsed High-Voltage Discharge Plasma for Degradation of Phenol in Aqueous Solution”, Separation and Purification Technology, Vol.34, pp. 5-12 (2004). 33.Chu, L. B., Xing, X. H., Yu, A. F., Zhou, Y. N., Sun, X. L., and Jurcik, B.,“Enhanced Ozonation of Simulated Dyestuff Wastewater by Microbubbles”, Chemosphere, Vol. 68, pp. 1854-1860 (2007). 34.Dussert, B. W., and“Advenced Oxidation:Ultraviolet Light Helps Advenced Oxidation Technologies Outshine Other Treatment Systems for Organics in Wastewater and Groundwater”, Industrial Wastewater, pp.29-35 (1997). 35.Grau, P.,“Textile Industry Wastewaters Treatment”, Water Science and Technology, Vol. 24, pp. 97-103 (1991) . 36.Gao, Min-Tian., Hirata, Makoto., Takanashi, Hirokazu., and Hano, Tadashi.,

“ Ozone Mass Transfer in a New Gas – Liquid Contactor – Karman Contactor ” , Separation and Puri?cation Technology, Vol. 6942, pp. 145-149 (2005). 37.Gupta, A. K., Anjali, P., and C.Sahoo., “ Photocatalytic Degradation of a Mixture of Crystal Violet (Basic Violet 3) and Methyl Red Dye in Aqueous Suspensions Using Ag+ Doped TiO2 ” , Dye and Pigments, Vol. 69, pp. 224-232 (2006). 38.Hoigne, J., and Bader, H., “ Rate Constants of Reaction of Ozone with Organic and Inorganic Compounds in Water-I.Dissociated Organic Compounds ” , Water Research, Vol. 17, pp. 173-183 (1983). 39.Hoigne, J., and Bader, H., “ Rate Constants of Reaction of Ozone with Organic and Inorganic Compounds in Water-Ⅱ.Dissociated Organic Compounds ” , Water Research, Vol. 17, pp. 185-194 (1983). 40.Horikoshi, S., Watanabe, N., Onishi, H., Hidaka, H., and Serpone, N., “ Photodecompsoition of Nonylphenol Polyethoxylate Surfactant in a Cylindrical Photoreactor with TiO2 Immobilized Fiberglass Cloth ” , Applied Catalysis B: Environmental, Vol. 37, pp.117-129 (2002). 41.Hernandez -Alonso, M. D., Coronado, J. M., Maira, A. J., Soria, J., Loddo, V., and Augugliaro, V., “ Ozone Enhanced Activity of Aqueous Titanium Dioxide Suspensions for Photocatalytic Oxidation of Free Cyanide Ions ” , Applied Catalysis B, Environmental, Vol. 39, pp. 257-267(2002). 42.Jones, B. M., Langlois, G. W., and Sakaji, R. H., “ Effect of Ozonation and UV Irradiation on Biorefractory Organic Solutes in Oil Shale Retort Water ” , Environmental Program, Vol. 4, pp. 252 (1985). 43.Kin, K. T., DeGenova, J., and Shadman, F., “ Oxidation of Organic Impurities in the Recycle and Reclaim Loops of Ultra-Pure Water Plant ” , Clean Processes, Vol. 1, pp. 31-38 (1998). 44.Kopf, P., Gilbert, E., and Eberle, S. H., “ TiO2 Photocatalytic Oxidation of Monochloroacetic Acid and Pyridine: Influence of Ozone ” , Journal of Photobiology A: Chemistry, Vol. 136, pp. 163-168 (2000). 45.Kidak, R., and Ince, N.H., “ Catalysis of Advanced Oxidation Reactions by Ultrasound: A Case Study with Phenol ” , Journal of Hazardous Materials, Vol. 146, pp. 630-635 (2007). 46.Lewis, W., and Whitman, W. G., “ Principles of Gas Absorption ” , Industrial and Engineering Chemistry, Vol. 16, pp. 1215-1219 (1924). 47.Lin, S.H. and Yeh, K.L., “ Looking to Treat Wastewater Try Ozone ” , Chemical Engineering., May, pp. 112-116 (1978). 48.Langlais, B., Reckhow, D. A., and Brink, D. R., “ Ozone in Water Treatment Application and Engineering ” , Lewis, Michigan, U.S.A. (1991). 49.Legube, B., and Karpel Vel Leitner, N., “ Catalytic Ozonation: a Promising Advanced Oxidation Technology for Water Treatment ” , Catalysis Today, Vol. 53, pp. 61-72(1999). 50.Leiknes, T., Phattaranawik, J., Boller, M., Gunten, U. Von., and Pronk, W., “ Ozone Transfer and Design Concepts for NOM Decolourization in Tubular Membrane Contactor ” , Chemical Engineering Journal, Vol. 111, pp. 53-61 (2005). 51.Li, L., Zhu, W., Chen, L., Zhang, P., and Chen, Z., “ Photocatalytic Ozonation of Dibutyl Phthalate Over TiO2 Film ” , Journal of Photochemistry and Photobiology A: Chemistry, Vol. 175, pp. 172-177 (2005). 52.Lackey, Laura W., Mines, Richard O., McCreanor, and Philip T., “ Ozonation of Acid Yellow 17 Dye in a Semi-Batch Bubble Column ” , Journal of Hazardous Materials B, Vol. 138, pp. 357-362 (2006). 53.Lopez-Lopez, A., Pic, J.-S., Benbelkacem, H., and Debellefontaine, H., “ In?uence of t-butanol and of pH on Hydrodynamic and Mass Transfer Parameters in an Ozonation Process ” , Chemical Engineering and Processing, Vol. 46, pp. 649-655 (2007). 54.Lopez-Lopez, A., Pic, J.S., and Debellefontaine, H., “ Ozonation of Azo Dye in a Semi-Batch Reactor: A Determination Of the Molecular and Rradical Contributions ” , Chemosphere, Vol. 66, pp. 2120-2126 (2007). 55.Marco, A., Esplugas, S., and Saum, G., “ How and Why Combine Chemical and Biological Processesfoe Wastewater Treatment ” , Water Science and Technology, Vol. 35, pp. 321-327 (1997). 56.Ma, C.W. and Chu, W., “ Photodegradation Mechanism and Rate Improvement of Chlorinated Aromatic Dye in Non-ionic Surfactant Solutions ” , Water Research, Vol.35, pp.2456-2459 (2001). 57.Martin, M. A., Raposo, F., Borja, R., and Martin, A., “ Kinetic Study of the Anaerobic Digestion of Vinasse Ppretreated with Ozone, Ozone Plus Ultraviolet Light in the Presence of Titanium Dioxide ” , Process Biochemistry, Vol. 37, pp. 699-706 (2002). 58.Muthukumar, M., and Selvakumar, N., “ Studies on the effect of inorganic salts on decolouration of acid dye effluents by ozonation ” , Dye and Pigments, Vol. 62, pp. 221-228 (2004). 59.Ollis, D. F., ” Comparative Aspects of Advance Oxidation Process ” , Paper presented at ACS , I & EC Division Special Sym., Atlanta Georgia,Oct. 1-3 (1991). 60.Obee, T. N., and Hay, S.O., “ Effects of Moisture and Temperature on the Photooxidation of Ethylene on Titania ” , Environmental Science and Technology, Vol.31, pp.2034 -2038(1997). 61.Pengyi, Z., Fuyan, L., Gang, Y., Qing, C., Wanpeng, Z., “ A comparative Study on Decomposition of Gaseous Toluene by O3/UV, TiO2/UV and O3/TiO2/UV ” , Journal of Photochemistry and Photobiology A: Chemistry Vol. 156, pp. 189-194 (2003). 62.Sotelo, J. L., Beltran, F. J., Benitez, F. J., and Beltran-Heredia, J., “ Ozone Decomposition in Water:Kinetic Study ” , Industrial and Engineering Chemistry Research, Vol. 26, pp. 39-43 (1987). 63.Shu, H. Y. and Huang, C. R., “ Degradation of Commercial Azo Dyes in Water Using Ozonation and UV Enhanced Ozonation Process ” , Chemosphere, Vol. 31, pp. 3813-3825 (1995). 64.Sanchez, L., Peral, J., Domenech, X., “ Aniline Degradation by Combined Photocatalysis and Ozonation ” , Applied Catalysis B: Environmental, Vol. 19, pp. 59-65 (1998). 65.Song, K. Y., Kwon, Y. T., Choi, G. J., and Lee, W. I., “ Photocatalytic Activity of Cu/TiO2 with Oxidationstate of Surface Loaded Copper ” , Bulletin of the Korean Chemical Society 20, pp. 975 (1999). 66.Sahoo, C., Gupta, A.K., and Anjali Pal., “ Photocatalytic Degradation of Crystal Violet (C.I. Basic Violet 3) on Silver Ion Doped TiO2 ” , Dye and Pigments, Vol. 66, pp. 189-196 (2005). 67.Sobana, N., Muruganadham, M., and Swaminathan, M., “ Nano-Ag Particles Doped TiO2 for Efficient Photodegradation of Direct Azo Dyes ” , Journal of Molecular Catalysis A: Chemical, Vol. 258, pp. 124-132 (2006). 68.Senthilkumaar, S., Porkodi, K., Gomathi, R., Geetha Maheswari, A., and Manonmani, N., “ Sol-gel Derived Silver Doped Nanocrystalline Titania Catalysed Photodegradation of Methylene Blue from Aqueous Solution ” , Dye and Pigments, Vol. 69, pp. 22-30 (2006). 69.Seery, M. K., George, R., Floris, P., Pillai, S. C., “ Silver Doped Titanium Dioxide Nanomaterials for Enhanced Visible Light Photocatalysis ” , Journal of Photobiology A: Chemistry, Vol. 189, pp. 258-263 (2007). 70.Sun, L., Lu, H., Zhou, J., “ Degradation of H-acid by Combined Photocatalysis and Ozonation Processes ” , Dye and Pigments, Vol. 76, pp. 604-609 (2008). 71.Tomiyasu, H., Fukutomi, H., and Gordon, G., “ Kinetics and Mechanism of Ozone Decomposition in Basic Aqueous Solution ” , Inorganic Chemistry, Vol. 24, pp. 2962-2974 (1985). 72.Villasenor, J., Reyes, P., and Pecchi G., “ Catalytic and Photocatalytic Ozonation of Phenol on MnO2 Suooortid Catalysts ” , Catalysis Today, Vol. 76, pp. 121-131 (2002). 73.Yang,

Y., Ma, J., Qin, Q., Zhai, X., " Degradation of Nitrobenzene by Nano-TiO2 Catalyzed Ozonation ", Journal of Molecular Catalysis: A Chemical, Vol. 267, pp. 41-48 (2007). 74.Yang, X., Xu, L., Yu, X., and Guo, Y., " One-Step Preparation of Silver and Indium Oxide Co-Doped TiO2 Photocatalyst for the Degradation of Rhodamine B ", Catalysis Communications, Vol. 9, pp. 1224-1229 (2008).