Study on the Photoreduction of Cr(VI) in Aqueous Solution by Modified Photocatalytic Processes

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ABSTRACT

The objective of this research is to study the photoreduction behaviors of Cr(VI) ions in aqueous solutions by non-modified and modified photocatalytic processes under various operational factors, such as solution pH values, TiO2 dosages, types and dosages of organic compound (so-called h+-scavenger) with modified TiO2 which were doped with different types and dosages of metals to investigate the removal efficiencies of Cr(VI) in order to determine the optimum conditions of the photoreduction reaction. Experimental results showed that the removal rate of Cr(VI) increased with decreasing solution pH values and with increasing dosages of organic compounds (methanol, ethanol, and isopropane) indicating that the recombination rate of electrons and h+ can be retarded in the reaction systems by the addition of the h+-scavenger, thus the reaction rate of Cr(VI) can be raised. The chemical reaction rate equation of Cr(VI) were established by pseudo-first order kinetic and the kinetic order of TiO2 dosage was found to be almost the same by non-modified and modified UV/TiO2 processes. Comparing the experimental results within modified TiO2 photoreduction systems, the removal rate of Cr(VI) by the UV/Ag-doped TiO2 process was larger than that by to the UV/Cu-doped TiO2 process possibly due to the electron transferring ability of Ag is superior to that of Cu. However, the photoreduction rates of Cr(VI) by the non-modified UV/TiO2 process (Digussa P25) were less than those by modified UV/TiO2 processes possibly because of the competition between the effects of electron transferring and deactivation of deposition of metals onto the surface of TiO2.

Keywords : Cr(VI) ; UV/TiO2 ; h+-scavenger ; photoreduction ; modified photocatalysis

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REFERENCES

1. 王鈴祺, 「以紫外線/La2Ti2O7程序分別處理含染料及異丙醇水溶液之研究」, 國立台灣科技大學化學工程研究所碩士論文(2006)。 2. 王姮娟, 「重金屬廢水處理技術(下)」, 台灣環保產業雙月刊, 第二十七期 (2004)。 3. 行政院環保署放流水標準, 網址 http://www.epa.gov.tw/main/index.asp. (2007)。 4. 李育群, 「半導體光觸媒與吸附劑之複合材料對VOCs處理之研究」, 中原大學化學工程研究所碩士論文(2003) 5. 呂宗昕, 「圖解奈米科技與光觸媒」, 商周出版 (2003)。 6. 周欣穎, 「奈米Ag/TiO2觸媒進行二氧化碳光催化還原反應」, 國立台灣大學化學工程研究所碩士論文(2002)。 7. 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」, 國立台灣工業技術學院化學工程技術研究所碩士論文 (1996)。 8. 曾怡享, 「奈米金屬氧化鈦觸媒光催化還原二氧化碳」, 國立台灣大學化學工程研究所博士論文 (2003)。 9. 勞工安全衛生研究所之物質安全資料表(MSDS), 網址 http://www.iosh.gov.tw (2007)。 10. 潘志弘, 「電鍍業勞工鉻暴露與氧化傷害評估研究」, 勞工安全衛生簡訊, 第70期 (2004)。 11. 環保署環境檢驗所, 「水中六價鉻檢測方法－比色法」, 網址 http://www.niea.gov.tw (2007)。 12. 鄭婉真, 「含銅TiO2觸媒進行二氧化碳光

催化還原反應」，國立台灣大學化學工程研究所碩士論文 (2001)。 13. 劉安治，「近紫外光／二氧化鈦催化分解氣相中低濃度四氯乙烯之操作參數探討」，國立中山大學環境工程與科學系碩士論文(1997) 14. 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). 15. Chen, S. and Cao, G.,“ Study on the Photocatalytic reduction of dichromate and photocatalytic oxidation of dichlorvos ”, Chemosphere, Vol. 60, pp.1308-1315 (2005). 16. Colon, G., Hidalgo, M.C., Navio, J.A.,“ Photocatalytic deactivation of commercial TiO2 samples during simultaneous photoreduction of Cr(VI) and photooxidation of salicylic acid ”, Journal of Photochemistry and Photobiology A: Chemistry, Vol. 138, pp.79-85 (2001). 17. Das, D.P., Parida, K. and De, B.R.,“ Photocatalytic reduction of hexavalent chromium in aqueous solution over titania pillared zirconium phosphate and titanium phosphate under solar ratiation ”, Journal of Molecular Catalysis A: Chemical Vol. 245, pp.217-224 (2006). 18. Daneshvar, N., Rabbani, M. Modirshahla, N., and Behnajady, M. A.,“ Kinetic modeling of photocatalytic degradation of Acid Red27 in UV/TiO2 process ”, Journal of Photochemistry and Photo-biology A: Chemistry, Vol.168, pp.39-45(2004). 19. Foster, N. S., Noble, R. D., Koval, C. A.,“ Reversible photoreductive Deposition and Oxidative Dissolution of Copper Ions in Titanium Dioxide Aqueous Suspensions ”, Environ. Sci. Technol. Vol. 27, pp.350-356(1993) 20. Hung, C.H. and MariNas, B.J.,“ Role of Chlorine and Oxygen in the Photocatalytic Degradation of Trichloroethylene Vapor on TiO2 Films ”, Environ. Sci. Technol., Vol.31, pp.562 -568(1997) 21. 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). 22. Ishibashi, K., Fujishima, A., Watanabe, T., and Hashimoto, K.,“ Quantum yields of active oxidative species formed on TiO2 photocatalyst ”, J. Photochem. Photobiol. A, Vol. 134, pp139-142 (2000). 23. Jose, A.N., Gerardo, C., Maria, T., Jose, P., Xavier, D., Juan J, T., Javier, P., Diana, R. and Marta I, L.,“ Heterogeneous photocatalytic reactions of nitrite oxidation and Cr(VI) reduction of iron-doped titania prepared by the wet impregnation method ”, Applied Catalysis B: Environmental Vol.16, pp.187-196 (1998). 24. Jiang, F., Zheng, Z., Xu, Z., Zheng, S., Guo, Z. and Chen, L.,“ Aqueous Cr(VI) photo-reduction catalyzed by TiO2 and sulfated TiO2 ”, Journal of Hazardous Materials B134, pp.94-103 (2006). 25. Ku, Y. and Jung, I. L.,“ Photocatalytic reduction of Cr(VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide ”, Wat. Res. Vol.35, No.1, pp.135-142(2001). 26. Khalil, L.B., Mourad, W.E. and Rophael, M.W.,“ Photocatalytic reduction of environmental pollutant Cr(VI) over some semiconductors under UV/visible light illumination ”, Catalysis B: Environmental Vol. 17, pp.267-273 (1998). 27. Liu, Y., Deng, L., Chen, Y., Wu, F. and Deng, N.,“ Simultaneous photocatalytic reduction of Cr(VI) and oxidation of bisphenol A induced by Fe(III)-OH complexes in water ”, Journal of Hazardous Materials B139, pp.399-402 (2007). 28. Munoz, J. and Domenech, X.“ TiO2 Catalysed reduction of Cr(VI) in aqeous solutions under ultraviolet illumination ”, Journal of App. Electrochem., Vol.20, pp.518-521(1990). 29. Mohapatra, P., Samantaray, S.K. and Parida, K.,“ Photocatalytic reduction of hexavalent chromium in aqueous ”, Journal of Photochemistry and Photobiology A: Chemistry Vol. 170, pp.189-194 (2005). 30. Navio, J.A., Colon, G., Macias, M., Campelo, J.M., Romero, A.A. and Marinas, J.M.,“ Catalytic properties of sulfated and non-sulfated ZrO2-SiO2: effects of the sulfation submitted before or after the calcination process, in the cyclohexene isomerization reaction ”, Journal of Molecular Catalysis A: Chemical, Vol.135, No. 2, pp.155-162(1998). 31. Obee, T. N. and Hay, S.O.,“ Effects of Moisture and Temperature on the Photooxidation of Ethylene on Titania ”, Environ. Sci. Technol., Vol.31, pp.2034 -2038(1997). 32. Park, E.H., Jung, J. and Chung, H.H.,“ Simultaneous oxidation of EDTA and reduction of metal ions in mixed Cu(II)/Fe(III)-EDTA system by TiO2 photocatalysis ”, Chemosphere Vol. 64, pp.432-436 (2006). 33. Papadam, T., Xekoukoulotakis, N. P., Poulios, I. and Mantzavions, D.,“ Photocatalytic transformation of acid orange 20 and Cr(VI) in aqueous TiO2 suspensions ”, Journal of Photochemistry and Photobiology A: Chemistry Vol. 186, pp.308-315 (2007). 34. Pralrie, M. R., Evans, L. R., Stange, B. M. and Martinez, S. L.,“ An Investigation of TiO2 Photocatalysis for the Treatment of Water Contaminated with Metals and Organic Chemicals ”, Environ. Sci. Technol. Vol. 27, pp.1776-1782 (1993). 35. Sopyan, I., Watanabe, M., Murasawa, S., Hashimoto, K. and Fujishima, A.,“ An efficient TiO2 thin-film photocatalyst: photocatalytic properties in gas-phase acetaldehyde degradation ”, Journal of Photochemistry and Photobiology A: Chemistry, Vol. 98, No.1, pp. 79-86(8) (1996) 36. Shifu, C. and Gengyu, C,“ Study on the photocatalytic reduction of dichromate and photocatalytic oxidation of dichlorvos ”, Chemosphere Vol.60, pp.1308-1315 (2005). 37. Schrank, S.G., Jose, H.J. and Moreira, R.F.P.M.,“ Simultaneous photocatalytic Cr(VI) reduction and dye oxidation in a TiO2 slurry reactor ”, Journal of Photochemistry and Photobiology A: Chemistry Vol. 147, pp.71-76 (2002). 38. Tan, T., Beydoun, D. and Amal, R.“ Effects of organic hole scavengers on the photocatalytic reduction of selenium anions ”, Journal of Photochemistry and Photobiology A: Chemistry, Vol. 159, pp.273-280 (2003). 39. Tuprakay, S. and Liengcharernsit, W.,“ Lifetime and regeneration of immobilized titania for photocatalytic removal of aqueous hexavalent chromium ”, Jouurnal of Hazardous Materials Vol.124, pp.53-58 (2005). 40. Wang, X., Pehkonen, S. O. and Ray, A. K.,“ Photocatalytic reduction of Hg(II) on two commercial TiO2 catalysts ”, Electrochimica Acta, Vol. 49, pp.1435 – 1444 (2004). 41. Xie, B., Zhang, H., Cai, P., Qiu, R. and Xiong, Y.,“ Simultaneous photocatalytic reduction of Cr(VI) and oxidation of phenol over monoclinic BiVO4 under visible light irradiation ”, Chemosphere Vol. 63, pp.956-963 (2006). 42. Yang, J.K. and Lee, S.M.,“ Removal of Cr(VI) and humic acid by using TiO2 photocatalysis ”, Chemosphere, Vol. 63, pp.1677-1684 (2006).