Photoreduction of Cr(VI) in Aqueous Solution by UV/TiO2 Process

張琮祐、申永順

E-mail: 9708076@mail.dyu.edu.tw

ABSTRACT

ABSTRACT UV/TiO2 photo-reduction process was used to treat the reaction of wastewater with hexavalent chromium in this study. The impact on removal efficiency and reaction behavior of hexavalent chromium from such effects as solutions with different pH, the dosages of titanium dioxide, the initial concentration of reactant, homogeneous trivalent iron, the category and dosages of organic compound (so-called hole-scavenger) were aimed at, and then the compositional distribution patterns of hexavalent chromium in water solution, the reaction kinetic model and reaction pathway selectivity were built, to assess the efficiency and reaction channels of photo-reduction system, which were the basis for deciding the effectiveness and operating conditions for the reduction process. When UV/TiO2 photo-reduction process was used to treat the solution with hexavalent chromium and do the batch reactions, as the pH value increased, the constant of removal efficiency for hexavalent chromium decreased, and the main affecting factor were the differences of reducing potential difference, hydrogen ion concentration and electrical charge on material surface in solutions with different pH. In addition, in view of mass balance to discuss the distribution patterns of chromium during reaction, it is found that the total chromium concentration in solution was decreased after reaction; however, there was no chromic oxide precipitation in the solution with pH value of 3.0, therefore, trivalent chromium might be further reduced to zero-valent chromium through capturing electrons, it was speculated that this was the second-order reduction reaction. When UV/TiO2/EDTA photo-reduction process was used to treat the solution with hexavalent chromium and do the batch reactions, the photo-reduction reaction of hexavalent chromium was promoted by organic matter EDTA added, because EDTA could capture holes effectively to avoid combination between electrons and holes; moreover, it could increase the adsorptive capacity of hexavalent chromium on titanium dioxide surface. Under the condition of the solution with pH of 3.0, the amount of titanium dioxide was 1.0 g/L, the initial concentration of hexavalent chromium was 20 mg/L and the dosages of EDTA was 0.768 mM, hexavalent chromium could be removed completely after 50 minutes of reaction time. When UV/TiO2/Fe3+ photo-reduction process was used to treat the solution with hexavalent chromium and do the batch reactions, the photo-reduction reaction of hexavalent chromium was promoted by adding an appropriate amount of iron ions, because the iron ions could capture electrons rapidly to become ferrous iron ions, so there were oxidation-reduction reactions between ferrous iron and hexavalent chromium; but if the concentration of iron ions was too high, the production of hydrogen-oxygen free radicals would increase, thus inhibited the photo-reduction reaction. When UV/TiO2/EDTA/Fe3+ photo-reduction process was used to treat the solution with hexavalent chromium and do the batch reactions, the reduction efficiency for hexavalent chromium of each reaction system was compared, and the optimal reduction efficiency for hexavalent chromium was gained in UV/TiO2/Cr6+/EDTA/Fe3+ system. The results showed that, when the organic matter and iron ions were added at the same time, there would be a additive effect for reduction of hexavalent chromium. When analyzed the titanium dioxide powder before and after the reaction through EDS and XRD, the existence of chromium could not be detected effectively. According to the actual diagrams for titanium dioxide powder of each system before and after reaction, in UV/TiO2/Cr6+ and UV/TiO2/Cr6+/EDTA systems, the white titanium dioxide powder before reaction was changed to light green after reaction, this phenomenon shown that, partial hexavalent chromium was reduced to solid chromium. In UV/TiO2/Cr6+/Fe3+ and UV/TiO2/Cr6+/EDTA/Fe3+ systems, it could find rust sediments. In contrast to the traditional chemical precipitation, this study only added appropriate amount of organic hole-scavenger and trivalent iron ion, and a good reduction efficiency of hexavalent chromium was gained, not only could reduce the using amount of reducer and alkali agent to reduce sludge, but could also reduce the treating time to make it more cost-effective, thus increased the practicality of photo-catalyst reactor.

Keywords : hexavalent chromium, organic hole-scavenger, UV/TiO2 photo-catalysis process, photo-reduction

Table of Contents

REFERENCES

參考文獻 1.經濟部工業局，「廢水物化處理技術彙編」(2004)。 2.施英隆，「環境化學」，五南圖書出版中心 (2000)。 3.行政院環保署放流水標準， http://www.epa.gov.tw/main/index.asp. (2007)。 4.呂宗昕，「圖解奈米科技與光觸媒」，商周出版 (2003)。 5.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)。 6.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)。 7.經濟部工業局，「電鍍業資源化應用技術手冊」(2002)。 8.楊萬發，「水及廢水處理化學」，茂昌圖書有限公司 (1987)。 9.環保署環境檢驗所，「水中銀、鎘、鉻、銅、鐵、錳、鎳、鉛及鋅檢測方法—火焰式原子吸收光譜儀」，http://www.niea.gov.tw (2005)。 10.田福助，電化學—理論與應用，高立圖書有限公司 (1987)。 11.前台灣省建設廳水污染防治所，「台灣省電鍍廢水解決方案之研究」(1981)。 12.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)。 13.王文裕，「二氧化鈦光電特性及染料於光觸媒反應器之分解效率」，國立台灣科技大學化學工程研究所博士論文 (2006)。 14.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)。 15.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) 16.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)。 17.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)。 18.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)。 19.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)。 20.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)。 21.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)。 22.Aarthi, T., Madras, G. “ Photocatalytic reduction of metals in presence of combustion synthesized nano-TiO2 ”, Catalysis Communications, Vol. 9, pp.630-634 (2008). 23.Bouzazam, A., 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). 24.Cie ’ sla, P., Karocki, A., Stasicka, Z., “ Photoredox behaviour of the Cr – EDTA complex and its environmental aspects ”, Journal of Photochemistry and Photobiology A: Chemistry, Vol. 162, pp.537-544 (2004). 25.Cho,Y., Kyung, H., Choi,W., “ Visible light activity of TiO2 for the photoreduction of CCl4 and Cr(VI) in the presence of nonionic surfactant (Brij) ”, Applied Catalysis B: Environmental, Vol. 52, pp.23-32 (2004). 26.Chen, S. and Cao, G., “ Study on the Photocatalytic reduction of dichromate and photocatalytic oxidation of dichlorvos ”, Chemosphere, Vol. 60, pp.1308-1315 (2005). 27.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). 28.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). 29.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). 30.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) 31.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) 32.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). 33.Iwata, T., Ishikawa, M., Ichino, R, and Okido, M., “ Photocatalytic reduction of Cr(VI)on TiO2 film formed by anodizing ”, Surface and Coatings Technology, pp169-170 (2003). 34.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). 35.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). 36.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). 37.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). 38.Khalil, L.B., Rophael, M.W.and Mourad, W.E., “ The removal of the toxic Hg(II) salts from water by photocatalysis ”, Applied Catalysis B: Environmental Vol. 36, pp.125-130 (2002). 39.Kocot, P., Szaci?owski, K. and Stasicka, Z., “ Photochemistry of the [FeIII(edta)(H2O)]-and[FeIII(edta)(OH)2-complexes in presence of environmentally relevant species ”, Journal of Photochemistry and Photobiology A: Chemistry Vol. 188, pp.128-134 (2007). 40.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). 41.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). 42.Mansilla,H.D., Bravo,C., Ferreyra, R., Litter, M.I., Jardim, W.F., Lizama, F., Freer , J., Fern ’ andez, J., “ Photocatalytic EDTA degradation on suspended and immobilized TiO2 ”, Journal of Photochemistry and Photobiology A: Chemical, Vol. 181, pp.188-194(2006). 43.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). 44.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). 45.Nguyen, V.N.H., Beydoun, D., Amal, R., “ Photocatalytic reduction of selenium ions using different TiO2 photocatalysts ”, Chemical Engineering Science, Vol.60, pp.5759-5769(2005). 46.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). 47.Nguyen, V.N.H., Beydoun, D., Amal, R., “ Photocatalytic reduction of selenite and selenate using TiO2 photocatalyst ”, Journal of Photochemistry and Photobiology A: Chemical, Vol.171, pp.113-120(2005). 48.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). 49.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). 50.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). 51.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). 52.Rengaraj ,S., Venkataraj, S., Yeon, J.W., Kim ,Y. , Li ,X.Z., Pang ,G.K.H., “ Preparation, characterization and application of Nd – TiO2 photocatalyst for the reduction of Cr(VI) under UV light illumination ”, Applied Catalysis B: Environmental. Vol. 77, pp.157-165 (2007). 53.Rodenas, L.A.G., Weisz, A.D., Magaz, G.E., Blesa, M.A., “ Effect of Light on the Electrokinetic Behavior of TiO2 Particles in Contact with Cr(VI) Aqueous Solutions ”, Journal of Colloid and Interface Science ,Vol.230,pp.181 – 185 (2000). 54.Siemon, U., Bahnemann, D., Testa, J.J., Rodr ’ ?guez, D., Litter, M.I., Bruno, N., “ Heterogeneous photocatalytic reactions comparing TiO2 and Pt/TiO2 ”, Journal of Photochemistry and Photobiology A: Chemistry, Vol. 148, pp. 247 – 255 (2002). 55.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) 56.Shifu, C. and Gengyu, C, “ Study on the photocatalytic reduction of dichromate and photocatalytic oxidation of dichlorvos ”, Chemosphere Vol.60, pp.1308-1315 (2005). 57.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). 58.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). 59.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). 60.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). 61.Wang, X., Pehkonen, S.O., Ray, A.K., “ Photocatalytic reduction of Hg(II) on two commercial TiO2 catalysts ”, Electrochimica Acta Vol. 49, pp.1435-1444 (2004). 62.Wang, L., Wang, N., Zhu, L., Yu , H. and Tang, H., “ Photocatalytic reduction of Cr(VI) over different TiO2 photocatalysts and the effects of dissolved organic species ”, Hazardous Materials, Vol. 153, pp.93-99(2008). 63.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). 64.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).