Treatment of Chelated-Metals Containing Wastewaters by Fenton-like Process

李德倫、申永順

E-mail: 9805413@mail.dyu.edu.tw

ABSTRACT

The purpose of this study is to use Column Fenton-like Process and Cementation Process to treat wastewater of single heavy metal (Cu2+) and various chelating agents (EDTA, NTA) to study various operating factors in reaction system (initial pH of solution, zero-valent iron addition level, initial concentration of pollutant, inflow rate and H2O2 addition level), in order to understand reactant reaction behavior and removal efficiency. Through pollutant-oxidizer mass balance calculation, this study evaluated consuming efficiency of sacrificed metal and oxidizer, and analyzed through BDST column kinetic simulation, so as to select treatment performance of Advanced Oxidation Process plus Cementation Process and its optimum operating condition. When the solution containing CuEDTA or CuNTA (treated by means of Cementation Process) ran column reaction, total copper removal rate would fall with increasing initial pH of solution, decreasing zero-valent iron level, increasing initial concentration of pollutant, and higher inflow rate. In addition, the experiment on copper topography distribution during reaction in mass balance perspective showed that, after reaction, solid-state copper growth rate tended to rise with decreasing nitial pH of solution, increasing zero-valent iron level, higher initial concentration of pollutant, and lower inflow rate. In Fe0/CuEDTA system, the optimum operation condition is: initial pH of solution is 3.0, zero-valent iron level is 0.25g/L, initial concentration of CuEDTA is 5.0mM and inflow rate is 6ml/min. Total copper removal rate reached 98% after reacting 60min. After 4h, the total copper removal rate amounted to 64%. In Fe0/CuNTA system, the optimum operation condition is: initial pH of solution is 3.0, zero-valent iron level is 0.2g/L, initial concentration of CuNTA is 5.0mM and inflow rate is 6ml/min. Total copper removal rate reached 73% after reacting 2.5min; and after 4h, the total copper removal rate amounted to 28%. When the solution containing CuEDTA or CuNTA (treated by means of Fenton-like Process) ran column reaction, total copper removal rate would fall with increasing initial pH of solution, decreasing zero-valent iron level, increasing initial concentration of pollutant, higher inflow rate, and increasing H2O2 level. In addition, the experiment on copper topography distribution during reaction in mass balance perspective found that, after reaction, solid-state copper growth rate tended to increase with decreasing initial pH of solution, increasing zero-valent iron level, higher initial concentration of pollutant, lower inflow rate, and decreasing H2O2 level. In Fe0/H2O2/CuEDTA system, the optimum operation condition is: initial pH of solution is 3.0, zero-valent iron level is 0.25g/L, initial concentration of CuEDTA is 5.0mM, H2O2 level is 2.5mM and inflow rate is 6ml/min. The total copper removal rate reached 70% after reacting 2.5min; and after 4h, the total copper removal rate amounted to 15 %. In Fe0/H2O2/CuNTA system, the optimum operation condition is: initial pH of solution is 3.0, zero-valent iron level is 0.2g/L, initial concentration of CuNTA is 5.0mM, H2O2 level is 2.5mM and inflow rate is 6ml/min. The total copper removal rate reached 51% after reacting 2.5min; and after 4h, the total copper removal rate amounted to12%. Compared to other treatment processes, such as Sulfide treatment method, Chelating Ion Exchange Resin method, Bio-treatment method, Electrocoagulation-Flotation Method, Electrochemical Method and Membrane Filter Method. This study only added an appropriate amount of zero-valent iron and H2O2, and excellent total copper removing efficiency could be achieved. Therefore, it not only shortens treatment time, but is also more cost efficient.

Keywords : Fenton-like process、Cementation Process、heavy metal、chelating agent

Table of Contents

REFERENCES

1.經濟部工業局，「電鍍業減廢回收與污染防治」 (1997)。 2.施英隆，「環境化學」，五南圖書出版中心 (2000)。 3.經濟部工業局，「電鍍業資源化應用技術手冊」 (2002)。 4.李敏華譯著，「水質化學」，復漢出版社印行 (2003)。 5.經濟部工業局，「廢水物化處理技術彙編」 (2004)。 6.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)。 7.環保署環境保護人員訓練所，「毒性污染物質處理」 (2007)。 8.中華民國行政院環境保護署公佈之放流水標準，網址 http://w3.epa.gov.tw/epalaw/index.aspx (2007)。 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.吳明晃，「以化學置換程序處理水溶液中含鎘、汞離子之研究」，國立台灣科技大學化學工程研究所碩士論文 (2000)。 11.龐熙華，「利用電聚浮除法處理廢水中Cu-EDTA之研究」，淡江大學水資源及環境工程學系研究所碩士論文 (2001)。 12.吳嘉偉，「結合化學置換法及Fenton-like程序處理含重金屬及有機混合溶液之反應行為研究」，大葉大學環境工程研究所碩士論文 (2004)。 13.賴志青，「利用研磨鐵粉廢棄物處理含染料廢水之資源化應用研究-Fenton氧化程序」，國立高雄第一科技大學環境與安全衛生工程系碩士論文 (2004)。 14.張博荀，「H2O2/Fe2+化學氧化法處理反應性染料-Black B之研究」，國立成功大學化學工程研究所碩士論文 (2004)。 15.楊偉崙，「Fenton-like氧化反應中污染物競爭氫氧自由基之效應」，國立屏東科技大學環境工程與科學系碩士論文 (2005)。 16.許啟裕，「Fenton-like氧化法中NAPL型態污染物之氧化與氫氧自由基二階反應係數」，國立屏東科技大學環境工程與科學系碩士論文 (2005)。 17.梁書豪，「以Fenton-like氧化處理受燃料油污染之土壤」，國立中山大學環境工程研究所碩士論文 (2006)。 18.李思亮，「台灣南部地區之土壤環境因子對天然鐵氧礦物催化Fenton-like氧化效率之影響」，國立屏東科技大學環境工程與科學系碩

士論文 (2006)。 19.徐立科，「以離子交換程序處理含多成份重金屬離子及螯合物混合廢水反應行為之研究」，大葉大學環境工程研究所碩士論文 (2006)。 20.郭敬聖，「結合化學置換法及Fenton-like程序處理含重金屬及有機物混合溶液之反應行為研究」，大葉大學環境工程研究所碩士論文 (2007)。 21.顏偉盛，「以Fenton-like程序處理含螯合重金屬廢水反應行為之研究」，大葉大學環境工程研究所碩士論文 (2008)。 22.Anuradha, R., and Santhiti, T.,“ Batch-mixed iron treatment of high arsenic water ”, Water Research, Vol. 35, pp. 4474-4479 (2001). 23.Anotai, J., Lu, M.C., and Chewpreecha, P.,“ Kinetics of aniline degradation by Fenton and electro-Fenton processes ”, Water Research, Vol. 40, pp. 1841-1847 (2006). 24.Argun, M.E., and Dursun, S.,“ A new approach to modification of natural adsorbent for heavy metal adsorption ”, Bioresource Technology, Vol. 99, pp. 2516-2527 (2008). 25.Baeza, C., Rossner, A., Jardim, W.F., Litter, M.I., and Mansilla, H.D.,“ Removal of EDTA by UV-C/Hydrogen Peroxide ”, Environmental Technology, Vol. 10, pp. 1277-1281 (2003). 26.Burbano, A.A., Dionysiou, D.D., Suidan, M.T., and Richardson, T.L.,“ Oxidation kinetics and effect of pH on the degradation of MTBE with Fenton reagent ”, Water Research, Vol. 39, pp. 107-118 (2005). 27.Bissey, L.L., Smith, J.L., and Watts, R.J.,“ Soil organic matter-hydrogen peroxide dynamics in the treatment of contaminated soils and groundwater using catalyzed H2O2 propagations (modified Fenton ’s reagent) ”, Water Research, Vol. 40, pp. 2477-2484 (2006). 28.Barreiro, J.C., Capelato, M.D., Martin-Neto, L., and Hansen, H.C.B.,“ Oxidative decomposition of atrazine by a Fenton-like reaction in a H2O2/ferrihydrite system ”, Water Research, Vol. 41, pp. 55-62 (2007). 29.Behnajady, M.A., Modirshahla, N., and Ghanbary, F.,“ A kinetic model for the decolorization of C.I. Acid Yellow 23 by Fenton process ”, Journal of Hazardous Materials, Vol. 148, pp. 98-102 (2007). 30.Chen, P.H., and Watts, R.J.,“ Determination of rates of hydroxyl radical generation in mineral-catalyzed Fenton-like oxidation ”, Journal of the Chinese Institute of Environmental Engineering, Vol. 10, pp. 201-208 (2000). 31.Chitra, S., Paramasivan, K., Sinha, P.K., and Lal, K.B.,“ Ultrasonic treatment of liquid waste containing EDTA ”, Journal of Cleaner Production, Vol. 12, No.4, pp. 429-435 (2004). 32.Chang, F.C., Lo, S.L., and Ko, C.H.,“ Recovery of copper and chelating agents from sludge extracting solutions ”, Separation and Purification Technology, Vol. 53, pp. 49-56 (2007). 33.Chen, S., Sun, D., and Chung, J.S.,“ Treatment of pesticide wastewater by moving-bed biofilm reactor combined with Fenton-coagulation pretreatment ”, Journal of Hazardous Materials, Vol. 144, pp. 577-584 (2007). 34.Chu, W., Chan, K.H., Kwan, C.Y., and Choi, K.Y.,“ Degradation of atrazine by modified stepwise-Fenton ’s processes ”, Chemosphere, Vol. 67, pp. 755-761 (2007). 35.Deng, Y., and Englehardt, J.D.,“ Treatment of landfill leachate by the Fenton process ”, Water Research, Vol. 40, pp. 3683-3694 (2006). 36.Du, Y., Zhou, M., and Lei, L.,“ Kinetic model of 4-CP degradation by Fenton/O2 system ”, Water Research, Vol. 41, pp. 1121-1133 (2007). 37.Duran, A., and Monteagudo, J.M.,“ Solar photocatalytic degradation of reactive blue 4 using a Fresnel lens ”, Water Research, Vol. 41, pp. 690-698 (2007). 38.Evgenidou, E., Konstantinou, I., Fytianos, K., and Poulios, I.,“ Oxidation of two organophosphorous insecticides by the photo-assisted Fenton reaction ”, Water Research, Vol. 41, pp. 2015-2027 (2007). 39.Fouad, O.A., and Abdel-Basir, S.M.,“ Cementation-induced recovery of self-assembled ultrafine copper powders from spent etching solutions of printed circuit boards ”, Powder Technology, Vol. 159, pp. 127-134 (2005). 40.Fingar, N., and Letan, D.,“ Advanced Oxidation for Treatment of Aqueous Extracts from EDTA Extraction of Pb and Zn Contaminated Soil ”, J. Envir. Engrg., Vol. 132, No.10, pp. 1376-1380 (2006). 41.Gallard, H., and De, L.J.,“ Kinetic modeling of Fe(III)/H2O2 oxidation reactions in dilute aqueous solution using atrazine as a model organic compound ”, Water Research, Vol. 34, pp. 3107-3116 (2000). 42.Gulkaya, I., Surucu, G.A., and Dilek, F.B.,“ Importance of H2O2/Fe2+ rate in Fenton ’s treatment of a carpet dyeing wastewater ”, Journal of Hazardous Materials, Vol. 136, pp. 763-769 (2006). 43.Georgi, A., Schierz, A., Trommler, U., Horwitz, C.P., Collins, T.J., and Kopinke, F.D.,“ Humic acid modified Fenton reagent for enhancement of the working pH range ”, Applied Catalysis B: Environmental, Vol. 72, pp. 26-36 (2007) 44.Gros, F., Baup, S., and Aurousseau, M.,“ Intensified recovery of copper in solution: Cementation onto iron in fixed or fluidized bed under electromagnetic field ”, Chemical Engineering and Processing, Vol. 47, pp. 295-302 (2008). 45.Guinea, E., Arias, C., Cabot, P.L., Garrido, J.A., Rodriguez, R.M., Centellas, F., and Brillas, E.,“ Mineralization of salicylic acid in acidic aqueous medium by electrochemical advanced oxidation processes using platinum and boron-doped diamond as anode and cathodically generated hydrogen peroxide ”, Water Research, Vol. 42, pp. 499-511 (2008). 46.Guo, H., Stuben, D., Berner, Z., and Kramar, U.,“ Adsorption of arsenic species from water using activated siderite-hematite column filters ”, Journal of Hazardous Materials, Vol. 151, pp. 628-635 (2008). 47.Hong, S., Zhang, H., Duttweiler, C.M., and Lemley, A.T.,“ Degradation of methyl tertiary-butyl ether (MTBE) by anodic Fenton treatment ”, Journal of Hazardous Materials, Vol. 144, pp. 29-40 (2007). 48.Hrvoje, K., Ana, L.B., and Natalija, K.,“ Fenton type processes for minimization of organic content in coloured wastewaters: Part I: Processes optimization ”, Dyes and Pigments, Vol. 74, pp. 380-387 (2007). 49.Hsing, H.J., Chiang, P.C., Chang, E.E., and Chen, M.Y.,“ The decolorization and mineralization of Acid Orange 6 azo dye in aqueous solution by advanced oxidation processes: A comparative study ”, Journal of Hazardous Materials, Vol. 141, pp. 8-16 (2007). 50.Juang, R.S., and Shiau, L.D.,“ Ion exchange equilibria of metal chelates of ethylenediaminetetra-acetic acid with Amberlite IRA-68 ”, American Chemical Society, Vol. 37, pp. 555-571 (1998). 51.Jeong, J., and Yoon, J.,“ pH effect on OH radical production in photo/ferrioxalate system ”, Water Research, Vol. 39, pp. 2893-2900 (2005). 52.Kavitha, V., and Palanivelu, K.,“ Destruction of cresols by Fenton oxidation process ”, Water Research, Vol. 39, pp. 3062-3072 (2005). 53.Kurt, U., Avsar, Y., and Gonullu, M.T.,“ Treatability of water-based paint wastewater with Fenton process in different reactor types ”, Chemosphere, Vol. 64, pp. 1536-1540 (2006). 54.Lai, C.C., and Ku, Y.,“ The mass transfer and kinetic behavior of chelated copper solution: effect of species distribution ”, Electrochimica Acta, Vol. 37, pp. 2497-2502 (1992). 55.Lin, S.S., and Gurol, M.D.,“ Catalytic decomposition of hydrogen mechanism and implications ”, Environmental Science and Technology, Vol. 32, pp. 1417-1423 (1998). 56.Liou, M.J., and Lu, M.C.,“ Catalytic degradation of nitroaromatic explosives with Fenton ’s reagent ”, Journal of Molecular Catalysis A: Chemical, Vol. 277, pp. 155-163 (2007). 57.Liu, R., Chiu, H.M., Shiau, C.S., Yeh, R.Y.L., and Hung, Y.T.,“ Degradation and sludge production of textile dyes by Fenton and

photo-Fenton processes ” , Dyes and Pigments, Vol. 73, pp. 1-6 (2007). 58.Lodha, B., and Chaudhari, S., “ Optimization of Fenton-biological treatment scheme for the treatment of aqueous dye solutions ” , Journal of Hazardous Materials, Vol. 148, pp. 459-466 (2007). 59.Lucas, M.S., Dias, A.A., Sampaio, A., Amaral, C., and Peres, J.A., “ Degradation of a textile reactive Azo dye by a combined chemical-biological process: Fenton ’ s reagent-yeast ” , Water Research, Vol. 41, pp. 1103-1109 (2007). 60.Liou, M.J., and Lu, M.C., “ Catalytic degradation of explosives with goethite and hydrogen peroxide ” , Journal of Hazardous Materials, Vol. 151, pp. 540-546 (2008). 61.Monahan, M.J., Teel, A.L., and Watts, R.J., “ Displacement of five metals sorbed on kaolinite during treatment with modified Fenton ’ s reagent ” , Water Research, Vol. 39, pp. 2955-2963 (2005). 62.Modrzejewska, B., Guwy, A.J., Dinsdale, R., and Hawkes, D.L., “ Measurement of hydrogen peroxide in an advanced oxidation process using an automated biosensor ” , Water Research, Vol. 41, pp. 260-268 (2007). 63.Morgan, B., and Lahav, O., “ The effect of pH on the kinetics of spontaneous Fe(II) oxidation by O2 in aqueous solution-basic principles and a simple heuristic description ” , Chemosphere, Vol. 68, pp. 2080-2084 (2007). 64.Peralta-Hernandez, J.M., Meas-Vong, Y., Rodriguez, F.J., Chapman, T.W., Maldonado, M.I., and Godinez, L.A., “ In situ electrochemical and photo-electrochemical generation of the Fenton reagent: A potentially important new water treatment technology ” , Water Research, Vol. 40, pp. 1754-1762 (2006). 65.Pirkanniemi, K., Metsarinne, S., and Sillanpaa, M., “ Degradation od EDTA and novel complexing agents in pulp and paper mill process and waste water by Fenton ’ s reagent ” , Journal of Hazardous Materials, Vol. 147, pp. 556-561 (2007). 66.Rangsivek, R., and Jekel, M.R., “ Removal of dissolved metals by zero-valent iron (ZVI): Kinetics, equilibria, processes and implications for stormwater runoff treatment ” , Water Research, Vol. 39, pp. 4153-4163 (2005). 67.Saritha, P., Aparna, C., Himabindu, V., and Anjaneyulu, Y., “ Comparison of various advanced oxidation processes for the degradation of 4-chloro-2 nitrophenol ” , Journal of Hazardous Materials, Vol. 149, pp. 609-614 (2007). 68.Siedlecka, E.M., Wieckowska, A., and Stepnowski, P., “ Influence of inorganic ions on MTBE degradation by Fenton ’ s reagent ” , Journal of Hazardous Materials, Vol. 147, pp. 497-502 (2007). 69.Sun, J.H., Sun, S.P., Fan, M.H., Guo, H.Q., Qiao, L.P., and Sun, R.X., “ A kinetic study on the degradation of p-nitroaniline by Fenton oxidation process ” , Journal of Hazardous Materials, Vol. 148, pp. 172-177 (2007). 70.Shen, Y., Lei, L., Zhang, X., Zhou, M., and Zhang, Y., “ Effect of various gases and chemical catalysts on phenol degradation pathways by pulsed electrical discharges ” , Journal of Hazardous Materials, Vol. 150, pp. 713-722 (2008). 71.Son, H.S., Im, J.K., and Zoh, K.D., “ A Fenton-like degradation mechanism for 1,4-dioxane using zero-valent iron (Fe0) and UV light ” , Water Research, Vol. 01, pp. 1-7 (2009). 72.Tokumura, M., Ohta, A., Znad, H.T., and Kawase, Y., “ UV light assisted decolorization of dark brown colored coffee effluent by photo-Fenton reaction ” , Water Research, Vol. 40, pp. 3775-3784 (2006). 73.Walling, C., and Coose, A., “ Mechanism of the ferric ion catalyzed decomposition of hydrogen peroxide effect of organic substrates ” , J. American Chem. Soc., Vol. 95, pp. 2987-2991 (1973). 74.Watts, R.J., Udell, M.D., and Rauch, D.A., “ Treatment of pentachlorophenol contaminated soil using Fenton ’ s reagent ” , Hazardous Waste and Hazardous Materials, Vol. 7, pp. 335-345 (1990). 75.Wang, Z., Chen, D., and Chen, L., “ Gold cementation from thiocyanate solutions by iron powder ” , Minerals Engineering, Vol. 20, pp. 581-590 (2007). 76.Wang, S., “ A Comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater ” , Dye and Pigments, Vol. 76, pp. 714-720 (2008). 77.Yu, G., Zhu, W.P., and Yang, Z.H., “ Pretreatment and biodegradability enhancement of DSD acid manufacturing wastewater ” , Chemophere, Vol. 37, pp. 487-494 (1998). 78.Yaping, Z., and Jiangyong, H., “ Photo-Fenton degradation of 17 β -estradiol in presence of α -FeOOHR and H2O2 ” , Applied Catalysis B: Environmental, Vol. 78, pp. 250-258 (2008). 79.Yetilmezsoy, K., and Sakar, S., “ Improvement of COD and color removal from UASB treated poultry manure wastewater using Fenton ’ s oxidation ” , Journal of Hazardous Materials, Vol. 151, pp. 547-558 (2008). 80.Zhang, H., Choi, H.J., and Huang, C.P., “ Treatment of landfill leachate by Fenton ’ s reagent in a continuous stirred tank reactor ” , Journal of Hazardous Materials, Vol. 136, pp. 618-623 (2006). 81.Zheng, H., Pan, Y., and Xiang, X., “ Oxidation of acidic dye Eosin Y by the solar photo-Fenton processes ” , Journal of Hazardous Materials, Vol. 141, pp. 457-464 (2007). 82.Zelmanov, G., and Semiat, R., “ Iron(3) oxide-based nanoparticles as catalysts in advanced organic aqueous oxidation ” , Water Research, Vol. 42, pp. 492-498 (2008).