

以電聚浮除法處理含多成分重金屬螯合物混合廢水反應行為之研究

陳胤璋、申永順

E-mail: 9607865@mail.dyu.edu.tw

摘要

本研究旨在探討以電聚浮除程序處理含單成分及多成分之螯合重金屬水溶液之反應行為，針對不同的反應條件進行探討，以瞭解污染物去除效率與反應行為之影響，並進行螯合重金屬於水溶液中之反應動力行為之探討，以及各因子下之螯合重金屬之去除型態，作為未來應用研究之參考。本研究以內循環批式反應系統進行實驗，分別探討螯合劑種類及濃度、重金屬種類及濃度、水溶液之pH值、電流密度、電極板數目、電極板材質等不同實驗因子下的重金屬及螯合劑之去除率，並與添加H₂O₂的電解Fenton法程序處理效果進行比較，以了解添加H₂O₂對去除的影響。本研究提出二種螯合重金屬之電膠凝反應去除模式：(1)以螯合重金屬分子型態去除及(2)螯合重金屬先經斷鍵，重金屬再以自由離子型態被氫氧根離子沉澱；並經由重金屬與螯合劑二者之去除情形，加以描述整體反應中兩種去除模式的傾向與比例。另針對本實驗反應時所消耗的電能以及去除量的計算分析，以探討各反應因子下之最小耗能參數。以電聚浮除程序處理含單一重金屬溶液時，三種重金屬的去除率大小分別為Zn²⁺ > Cu²⁺ > Ni²⁺，在含有螯合劑的情況下，Zn²⁺和Cu²⁺的去除率會減少，而Ni²⁺的去除率會略微增加。針對螯合劑而言，在本程序中若是其單純存在，則去除率甚微，但在添加重金屬的情況下，去除率約可達到30%左右。整體重金屬去除行為推估大多都以斷鍵去除型態的比例較多，以螯合重金屬分子型態直接去除的比例佔少數。以電聚浮除程序處理含混合重金屬溶液時，三種重金屬的去除率大小與單成份反應時有所不同，分別為Cu²⁺ > Zn²⁺ > Ni²⁺，經發現Zn²⁺的去除率比單成份反應時差，顯示水中若同時存在Cu²⁺或Ni²⁺時，會對Zn²⁺去除率造成競爭反應。螯合劑的去除率跟單一重金屬時的情況相差不大，去除形式的判斷大多都為斷鍵去除的比例較多。而經由單一重金屬的實驗結果得知，三種螯合重金屬的斷鍵去除比例大小依次為Zn²⁺ > Cu²⁺ > Ni²⁺。以電解Fenton程序處理含混合螯合重金屬之溶液時，在三種不同的重金屬中，Cu²⁺之去除率隨著添加H₂O₂的量而減少，Zn²⁺則變化不大，Ni²⁺在H₂O₂使用的濃度為螯合重金屬的一倍時，去除率會增加，但在添加更高劑量時則無影響，而COD的去除率則會隨著H₂O₂的添加量增加而減少。

關鍵詞：電聚浮除程序；螯合重金屬廢水；電流密度

目錄

第一章 前言.....	1	1.1 研究動機.....	1	1.2 研究目的及內容.....	2
第二章 理論背景及文獻回顧.....	4	2.1 重金屬廢水特性簡介.....	4	2.1.1. 重金屬廢水之特性.....	7
		2.1.2. 重金屬廢水之危害性.....	9	2.1.3. 一般重金屬廢水處理技術.....	10
		2.2 螯合重金屬於水溶液中平衡探討.....	11	2.2.1. 螯合劑之型式.....	12
		2.2.2. 重金屬離子在水中與氫氧根離子之錯合及沉澱反應.....	13	2.2.3. 重金屬離子與螯合劑之螯合反應.....	14
		2.2.4. 水溶液中螯合劑與氫離子之水解反應.....	15	2.2.5. 化學平衡之理論計算結果.....	16
		2.2.6. 螯合重金屬與其他相關之pC-pH圖.....	19	2.3 電化學處理.....	25
		2.3.1 電膠凝法.....	26	2.3.2 電聚浮除法.....	33
		2.3.3 電解Fenton法.....	45	2.3.4 電化學處理方法之研究文獻.....	67
第三章 研究目的與架構.....	86	第四章 實驗程序與設備.....	89	4.1 實驗設備與儀器.....	89
		4.2 實驗藥品.....	91	4.3 實驗裝置.....	93
		4.4 實驗步驟.....	94	4.4.1. 電聚浮除程序處理單一重金屬與螯合劑廢水 反應實驗.....	97
		4.4.2. 電聚浮除程序處理混合重金屬與螯合劑廢水 反應實驗.....	98	4.4.3. 電解Fenton法程序處理混合重金屬與螯合劑 廢水反應實驗.....	99
		4.5 分析測定方法.....	101	第五章 結果與討論.....	110
		5.1 探討模式.....	110	5.2 背景實驗.....	115
		5.3 電聚浮除程序處理單一重金屬與螯合劑廢水反應 實驗.....	118	5.3.1. 銅螯合劑系統.....	118
		5.3.2. 鎳螯合劑系統.....	165	5.3.3. 鋅螯合劑系統.....	211
		5.4 電聚浮除程序處理混合重金屬與螯合劑廢水反應 實驗.....	257	5.4.1. 濃度效應.....	257
		5.4.2. pH效應.....	267	5.4.3. 電流密度效應.....	277
		5.4.4. 電板數目效應.....	287	5.4.5. 電板材質效應.....	297
		5.4.6. 比例效應.....	306	5.4.7. 螯合劑種類效應.....	315
		5.4.8. 綜合比較.....	324	5.5 電聚Fenton法程序處理混合重金屬與螯合劑廢水 反應實驗.....	328
第六章 結論與建議.....	334	6.1 結論.....	334	6.2 建議.....	339
參考文獻.....	341				

參考文獻

1. Adhoum, N., and Monser, L., "Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation", *Chemical Engineering and Processing*, Vol. 43, pp. 1281-1287 (2003).

2. Adhoum, N., Monser, L., Bellakhal, N., and Belgaied, J.E., "Treatment of electroplating wastewater containing Cu²⁺, Zn²⁺ and Cr(VI) by electrocoagulation", *Journal of Hazardous Materials*, Vol. B112, pp. 207-213 (2004).

3. Balmer, L.M., and Foulds, A.W., "Separating Oil from Oil-in-Water Emulsions by Electrocoagulation/Electroflotation", *Filtration & Separation*, pp. 366-370 (1986).

4. Bigda, R.J., "Consider Fenton's Chemistry for Wastewater Treatment", *Environmental Science and Technology*, Vol. 91, No. 12, pp. 62-66 (1995).

5. Brillas, E., and Mur, E., "Iron (II) Catalysis of the Mineralization of Aniline Using a Carbon-PTFE O₂-Fed Cathode", *Journal of Electrochemical Society Letters*, Vol. 143, No. 3, pp. L49-L53 (1996).

6. Gao, P., Chen, X., Shen, F., and Chen, G., "Removal of chromium(VI) from wastewater by combined electrocoagulation – electroflotation without a filter", *Separation and Purification Technology*, Vol. 43, pp. 117-123 (2005).

7. George, C., Radovan, I., and Pitulice, V.L., "Correlation between organic component and electrode material: consequences on removal of surfactants from wastewater", *Electrochimica Acta*, Vol. 46, pp. 297-303 (1984).

8. Chou, T.C., and Lee, H. C., "Electrocoagulation of Wastewater", *Fifth International Symposium on Electrochemistry*, NCKU, pp. 39-58 (1985).

9. Hansen, H., Nuñez K., and Grandon, P.R., "Electrocoagulation as a remediation tool for wastewaters containing arsenic", *Minerals Engineering*, Vol. 19, pp. 521-524 (2006).

10. Huang, C.P., Shu, C.S., Chen, C.W., and Dong, C., "Electrochemically Generated Fenton's Reagent for the Removal of Chlorophenols in Water", *Proceedings of the 1st Workshop on Drinking Water Management and Treatment Technologies*, Taipei, pp. 1-25 (1992).

11. Hu, C.Y., Lo, S.L., and Kuan, W.H., "Effects of the molar ratio of hydroxide and fluoride to Al(III) on fluoride removal by coagulation and electrocoagulation", *Journal of Colloid and Interface Science*, Vol. 283, pp. 472-476 (2005).

12. Irdemez, S.A., Demircioglu, N., and Yildiz, Y.S., "The effects of pH on phosphate removal from wastewater by electrocoagulation with iron plate electrodes", *Journal of Hazardous Materials*, Vol. B137, pp. 1231-1235 (2006).

13. Kiwi, J., Pulgarin, C., and Peringer, P., "Effect of Fenton and Photo-Fenton Reactions on the Degradation and Biogradability of 2 and 4-nitro-phenols in Water Treatment", *Applied Catalysis*, Vol. 3, pp. 335-350 (1994).

14. Kuo, W.G., "Decolorizing Dye Wastewater with Fenton's Reagent", *Water Research*, Vol. 26, No. 7, pp. 881-886 (1992).

15. Lai, C.L., and Lin, S.H., "Treatment of chemical mechanical polishing wastewater by electrocoagulation: system performances and sludge settling characteristics", *Chemosphere*, Vol. 54, pp. 235-242 (2004).

16. Lai, C.L., and Lin, S.H., "Electrocoagulation of chemical mechanical polishing (CMP) wastewater from semiconductor fabrication", *Chemical Engineering Journal*, Vol. 95, pp. 205-211 (2003).

17. Lai, C.L., and Lin, K.S., "Sludge conditioning characteristics of copper chemical mechanical polishing wastewaters treated by electrocoagulation", *Journal of Hazardous Materials*, Vol. B136, pp. 183-187 (2006).

18. Matsue, T., Fujihira, M., and Osa, T., "Oxidation of Alkylbenzenes by Electrogenerated Hydroxyl Radical", *Journal of Electrochemical Society*, Vol. 28, No. 12, pp. 2565-2569 (1981).

19. Meunier, N., Drogui, P., Montané, C., Hausler, R., Mercier, G., and Blais, J.F., "Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate", *Journal of Hazardous Materials*, Vol. B137, pp. 581-590 (2006).

20. Miwa, D.W., Malpass, G.R.P., Machado, S.A.S., and Motheo, A.J., "Electrochemical degradation of carbaryl on oxide electrodes", *Water Research*, Vol. 40, pp. 3281-3289 (2006).

21. Mollah, M.Y.A., Morkovsky, P., Gomes, J.A.G., Kesmez, M., Parga, J., and Cocke, D.L., "Fundamentals, present and future perspectives of electrocoagulation", *Journal of Hazardous Materials*, Vol. B114, pp. 199-210 (2004).

22. Moon, D.K., Maruyama, T., Osakada, K., and Yamamoto, T., "Chemical Oxidation of Polyaniline by Radical Generating Reagents, O₂, H₂O₂-FeCl₃ Catalyst, and Dibenzoyl Peroxide", *Soviet Journal of Water Chemistry and Technology*, Vol. 11, No. 2, pp. 115-118 (1991).

23. Oloman, C., and Watkinson, A.P., "The Electroreduction of Oxygen to Hydrogen Peroxide on Fluidized Cathodes", *The Canadian Journal of Chemical Engineering*, Vol. 53, pp. 268-273 (1975).

24. Oloman, C., and Watkinson, A.P., "The Electroreduction of Oxygen to Hydrogen Peroxide on Fixed Bed Cathodes", *The Canadian Journal of Chemical Engineering*, Vol. 54, pp. 312-318 (1976).

25. Oloman, C., and Watkinson, A.P., "Hydrogen Peroxide Production in Trickle Bed Electrochemical Reactors", *Journal of Applied Electrochemistry*, Vol. 9, pp. 117-121 (1979).

26. Parga, J. R., Cocke, D. L., Valenzuela, J.L., Gomes, J.A., Kesmez, M., Irwin, G., Moreno, H., and Weir, M., "Arsenic removal via electrocoagulation from heavy metal contaminated groundwater in La Comarca Lagunera México", *Journal of Hazardous Materials*, Vol. B124, pp. 247-254 (2005).

27. Pletcher, "Industrial Electrochemistry", Chapman & Hall Ltd, U.S.A., 1st ed., Chap. 11, pp. 292-298 (1982).

28. PurChas, D.B., "Solid/Liquid Separation Equipment Scale-Up", Chap. 6, England, pp. 188-197 (1977).

29. Ramirez, E.R., "Comparative Physicochemical Study of Industrial Wastewater Treatment by Electrolytic Dispersed Air and Dissolved Air Flotation Technologies", *Proc. 34th Ind. Waste Conference*, Purdue University, pp. 699-709 (1979).

30. Solozhenko, E. T., Soboleva, N.M., and Goncharuk, V.V., "Decolourization of Azodye Solutions by Fenton's Oxidation", *Water Research*, Vol. 29, No. 9, pp. 2206-2210 (1995).

31. Sudoh, M., Kodera, T., Sakai, K., Zhang, J.Q., and Koide, K., "Oxidative Degradation of Aqueous Phenol Effluent with Electrogenerated Fenton's Reagent", *Journal of Chemical Engineering of Japan*, Vol. 19, No. 6, pp. 513-518 (1986).

32. Sudoh, M., Kodera, T., Hino, H., and Shimamura, H., "Effect of Anodic and Cathodic Reactions on Oxidative Degradation of Phenol in an Undivided Bipolar Electrolyzer", *Journal of Chemical Engineering of Japan*, Vol. 21, No. 2, pp. 198-203 (1988).

33. Sudoh, M., Kodera, T., Hino, H., and Shimamura, H., "Oxidative Degradation Rate of Phenol in an Undivided Bipolar Electrolyzer", *Journal of Chemical Engineering of Japan*, Vol. 21, No. 5, pp. 536-538 (1988).

34. Sudoh, M., Kitaguchi, H., and Koide, K., "Polarization Characteristics of Packed Bed Electrode Reactor for Electroreduction of Oxygen to Hydrogen Peroxide", *Journal of Chemical Engineering of Japan*, Vol. 18, No. 4, pp. 364-371 (1985).

35. Sudoh, M., Kodera, T., and Ichino, T., "Effect of Oxygen parging into Packed-Bed Electrode on Production Rate of Hydrogen Peroxide", *Journal of Chemical Engineering of Japan*, Vol. 24, No. 2, pp. 165-170 (1991).

36. Sudoh, M., Minamoto, K., Makino, T., and Hakamada, H., "Production of Hydrogen Peroxide in Acidic Solutions by Electrolysis of Peroxide Ions Generated by Electroreduction of Oxygen in Alkaline Solutions",

Journal of Chemical Engineering of Japan, Vol.24, No.4, pp. 465-471 (1991) . 37.Sun, Y., and Pignatello, J.J., “ Photochemical Reactions Involved in the Total Mineralization of 2,4-D by Fe³⁺/H₂O₂/UV ” , Environmental Science and Technology, Vol.27, pp. 304-310 (1993) . 38.Town, R.M., and Powell, H.K.J., “ Elimination of Adsorption Effects in Gel Permeation Chromatography of Humic Substances ” ,Analytica Chimica Acta, Vol. 256, pp. 81-86 (1992) . 39.Vik, E.A., “ Small Water Treatment Plants Using Electroagulation 4th Asia Pacific Regional Water Supply Conference & Exhibition ST. III-3 ” . (1983) . 40.Yilmaz, A.E., Boncukcuoglu, R., Kocakerim, M.M., and Keskinler, B., “ The investigation of parameters affecting boron removal by electrocoagulation method ” , Journal of Hazardous Materials, Vol. B125 , pp. 160-165 (2005) . 41.方鴻源, 「金屬資源化回收電鍍沸水中Ni、Cr回收再利用可行性之研究」, 永續性產品與產業管理研討會論文集 (2005)。 42.行政院環保署放流水標準, 網址 <http://www.epa.gov.tw/main/index.asp> , (2006)。 43.李宗哲, 「利用電聚浮除法處理染料廢水能力之研究」, 淡江大學水資源與環境工程研究所 (1997)。 44.沈筱菁, 「電聚浮除結合活性污泥法處理都市垃圾焚化底渣水洗廢水之研究」, 淡江大學水資源與環境工程研究所碩士論文 (2002)。 45.吳宗南, 「電解Fenton法處理染料染整廢水之可行性研究」, 國立中央大學環境工程研究所碩士論文 (1996)。 46.林秀玲, 「利用電聚浮除法處理焚化飛灰水洗穩定廢水」, 淡江大學水資源與環境工程研究所碩士論文 (2003)。 47.施英隆, 「環境化學」, 五南圖書出版中心 (1999)。 48.范文彬, 「利用電聚浮除法處理半導體業CMP廢水之研究」, 淡江大學水資源與環境工程研究所碩士論文 (2001)。 49.高思懷, 張子蕙, 「利用電聚浮除法處理生活污水能力之探討」, 第二十三屆廢水處理技術研討會論文集, pp. 358-365 (1995)。 50.財團法人環保科技中心-電聚浮除系統網站, 網址 <http://ECsys.myweb.hinet.net/> , (2006) 51.陳威揚, 「銅離子在電聚浮除處理中之現象與其受陰離子之影響」, 淡江大學水資源與環境工程研究所碩士論文 (2000)。 52.陳重男, 「無機陰離子影響Fenton's Reagent氧化能力之探討」, 第二屆海峽兩岸環境保護學術研討會論文集, pp.140-148 (1993)。 53.曾迪華, 「電鍍廢水化學沉降處理法之比較」, 經濟部廢水物化處理技術彙編, 24期 (2004)。 54.黃富世, 「台灣中部地區電鍍業毒性化學物質之運作量調查與風險評估」, 逢甲大學土木及水利工程研究所碩士論文 (1999)。 55.黃順興, 「電聚浮除法處理氯苯之探討」, 淡江大學水資源與環境工程研究所碩士論文 (2000)。 56.張子蕙, 「利用電聚浮除法處理生活污水能力之探討」, 淡江大學水資源與環境工程研究所 (1998)。 57.張志銘, 「電聚浮除配合逆滲透法處理石化廢水之研究」, 淡江大學水資源與環境工程研究所碩士論文 (2000)。 58.張芳淑, 「Fenton反應之最適化控制因子探討」, 私立淡江大學水資源及環境工程研究所博士論文 (1995)。 59.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/msds.htm> , (2005)。 60.鄧婉妤, 「以Feton法結合Ferrite process 處理含EDTA與重金屬廢水」, 中山大學環境工程研究所博士論文(2004)。 61.劉世濤, 「電聚浮除法處理受污染感潮河段河水之能力」, 淡江大學水資源與環境工程研究所碩士論文 (2000)。 62.劉冠池, 「利用電聚浮除釋鐵量之推估探討垃圾焚化廠廢水處理之最適條件」, 淡江大學水資源與環境工程研究所碩士論文 (2001)。 63.龐熙華, 「利用電聚浮除法處理廢水中Cu-EDTA之研究」, 淡江大學水資源與環境工程研究所碩士論文 (2001)。 64.蘇拾生, 「EC電聚浮除處理技術介紹」, 工業污染防治, 第62期, pp. 168-183 (1997)。 65.顧洋, 「廢水高級氧化處理技術」, 廢水處理新技術研習會論文集, pp. (4-1) - (4-43) (1992)。