Recycling techniques of wastewater in polyvinyl chloride manufacturing process

黃健榮、彭元興

E-mail: 321855@mail.dyu.edu.tw

ABSTRACT

Production of polyvinyl chloride (PVC) using either a suspension or a emulsification method entails producing large quantities of wastewater. The suspension method produces effluent at a 4.0 m3/tonne PVC rate. Because the effluent has lower amounts of SS and COD, there were many research and case studies of its reclaimation. However, since the PVC particles in the effluent are not biodegradable and they tend to plug membrane pores causing fouling, hence it has a relative low reclaimation rate and high treatment cost problem needing resolution. The emulsification method produces ca. 2.5 m3/tonne PVC. Due to the high SS and COD concentration, however, there is a lack of announced successful treatment case that can provide reference to the trade. In this study, we engaged the effluent from a PVC mill in Taiwan and proceeded to treat it for reclaimation purpose. The study was conducted in 3 stages. In the first stage, the PVC effluents were mixed at a fixed ratio (suspension method 22% vs. emulsification method 78%) and fed to a ColOX bioreactor and a sand filtration unit for the preliminary treatment. The treatment variable studied was hydraulic retention time (HRT) effects on the removal efficacies of COD, PVA particles and SS. In the 2nd stage, the discharge from the ColOX unit was respectively treated with granular activated carbon, and ozone/UV irradiation (O3/UV) processes to allow recycling of the effluent. In the activated carbon experiments, effects of the absorbent on the adsorption of organic compounds and determination of the saturation point were examined. In the O3/UV process, the ozone infusion rate, and oxidation time on the removal efficiency of the organics were examined. In the 3rd stage, the potential for using the reclaimed water as makeup water for cooling tower was investigated. Treatment efficiency of different approaches were analyzed and compared. The first stage ColOX study results indicated that an HRT of 2 h provided the best removal efficacy. Thus, we 've set the flow rate to 31.2 L/min, and HRT of 2.0 h for a persistent trial run. After the ColOX unit, effluent COD decreased from an average of 104 to 35 mg/L, with a COD removal rate of 66.6%. The 2nd stage activated carbon study showed that by setting an inflow rate of 4 L/min and continuously operated for 3 mo, until the activated carbon failed, the average influx COD of 34 mg/L was reduced to 13 mg/L, with removal rate of 62%; and the activated carbon granules lasted for 64 d (ca. 2 mo), afterward their performance gradually declined. Thus, activated carbon granules should be replaced or subjected to regeneration every 2 months. The O3/UV treatment entailed an ozone dosage of 100 g/h influsion rate and 6 sets of UV irradiation conditions. The results indicated that after 4 min of oxidation, the effluent COD reduced from 38 mg/L to 17 mg/L, with a removal rate of 56%. In the 3rd stage, we conducted a model mill cooling tower makeup water test using the treated effluents. A fixed ratio of 65.7% reclaimed water and 34.3% waters of other sources was used, and dispersant, corrosion inhibitor, and microbial dispersant were preadded, and the pH adjusted to 7.8~8.2, residual chlorine set to 0.2~0.5 mg/L. After 14 d of operation, we found that on-line deposition meter showed a cleanliness of 99.8%, a caron steel coupon corrosion rate of 0.299 MPY (< 2 MPY demanded by the standard); a copper coupon corrosion rate of 0.017 MPY (< 0.5 MPY demanded by the standard). Thus, indicating that the reclaimed water for cooling tower makeup water did not cause scaling of the heat exchange tube array and deposition or corrosion of the system. Furthermore, even concentrating the cooling water 6-fold, the water still met the limitations, confirming that the reclaimed effluent could serve as makeup water for cooling tower. Upon evaluating the treatment efficiency, capital cost and problems caused by solid wastes of PVC effluent systems, we deemed that a treatment flow of ColOX + sand filtration unit + O3/UV was superior to a system employing ColOX + sand filtration unit + activated carbon for treating PVC process effluents.

Keywords: polyvinyl chloride (PVC), polyvinyl alcohol (PVA), ColOX bioreactor, sand filtration unit, activated carbon, ozone, UV light

Table of Contents

封面內頁 簽名頁 授權書 iii 中文摘要 iv ABSTRACT vi 誌謝 viii 目錄 ix 圖目錄 xiii 表目錄 xv 第一章 前言 1 1.1 研究動機 1 1.2 研究目的 2 第二章 背景資料 3 2.1 PVC聚合方法及製程廢水特性 3 2.1.1 PVC聚合方法 3 2.1.2 PVC製程廢水特性 4 2.2 懸浮法PVC廢水處理及回收案例之探討 5 2.2.1 現況PVC廢水回收再利用方式 5 2.2.2 PVC廢水及再生處理研究之回顧 9 2.3 乳化法PVC廢水處理案例之探討 18 第三章 文獻回顧 19 3.1 廢水生物膜法處理之技術研究 19 3.1.1 生物膜法基本原理 19 3.1.2 影響固定式生物膜反應器處理效果之因素 19 3.1.3 ColOX 生物反應系統 21 3.2 活性碳吸附法技術研究 23 3.2.1 活性碳介紹 23 3.2.2 活性碳吸附理論 23 3.2.3 影響活性碳吸附因子 24 3.2.4 脫附原理 25 3.3 臭氧高級氧化處理技術研究 26 3.3.1 臭

氧(O3)氧化法 28 3.3.2 臭氧/紫外光(O3/UV)法 29 3.3.3 臭氧/雙氧水(O3/H2O2) 30 3.3.4 臭氧/活性碳 30 第四章 實驗設計與方法 31 4.1 實驗流程 31 4.2 實驗設備 33 4.2.1 廢水再生處理模廠測試系統 33 4.2.2 冷卻水塔模廠測試系統 37 4.3 實驗方法與步驟 39 4.3.1 水質調查及再生用水標準之建立 39 4.3.2 ColOX測試方法 40 4.3.3 活性碳吸附測試之方法 40 4.3.4 臭氧處理系統運轉操作及測試方法 41 4.3.5 冷卻水塔模廠測試之方法 42 4.4 分析項目與方法 44 4.4.1 分析項目 44 4.4.2 廢水中PVA含量之檢測 45 第五章 實驗結果與討論 47 5.1 廢水處理系統之試驗結果 47 5.1.1 ColOX最適水力停留時間之探討 47 5.1.2 ColOX連續運轉測試 50 5.2 廢水再生系統之試驗結果 53 5.2.1 活性碳吸附系統 53 5.2.2 臭氧處理系統 56 5.3 冷卻水塔模廠測試結果 59 5.3.1 補充水量摻混比例設定 60 5.3.2 冷卻水塔模廠測試結果 60 5.4 經濟效益評估與討論 63 5.4.1 操作成本分析64 5.4.2 投資成本分析 65 5.4.3 投資回收年限評估66 第六章 結論與建議 70 6.1 結論 70 6.2 建議 71 參考文獻 73 附錄 78

REFERENCES

1.王樹成,2009,聚氯乙烯離心母液的雙膜法處理及回用,中國氯?臐A7:41~44。2.王權,2001,臭氧氧化法在聚氯乙烯離心母液處理 中的應用,中國氯?臐A5:42~43。 3.王權、劉志鵬,2007,生物接觸氧化法在懸浮法聚氯乙烯母液處理中的應用,聚氯乙烯,12:43~45 。 4.王欣澤、王寶貞、王琳,2001,臭氧 - 紫外線深度氧化去除水中有機污染物的研究哈爾濱建築大學學報,34(2):70~73。 5.代莎莎、 劉建廣、宋武昌,2007,臭氧氧化法在深度處理難降解有機廢水中的應用,水科學與工程技術,17(7):24。 6.呂志昇,2008,PVC製程 廢水中微量PVA處理方法,長春石化公司苗栗廠研究報告。 7.李雪輝,2002,油田採出水過濾器的原理與應用,石油機械,30(11): 56~58。 8.李茂雙、張龍、田正菊、呂軍, 2001, 聚氯乙烯廢水處理及回用研究, 齊魯石油化工, 29(3):211~214。 9.李宗憲, 1998, 缺 氧/好氧生物濾床法去除汙水中氮磷之研究,淡江大學水資源及環境工程研究所碩士論文,台北淡水。 10.李靜、劉國榮,2007,臭氧高 級氧化技術在廢水處理中的應用,污染防治技術,20(6):55~57。 11.余素林,2003,厭氧-好氧組合工藝處理PVC化工離心母液廢水的試 驗研究,南開大學環境科學與工程管理學院碩士論文,天津。 12.林正芳,1993,工業污染防治技術手冊 - 工業廢水活性碳處理,中國 技術服務社,台北。13.周?Q,2004,內循環式好氧生物膜反應器處理PVC化工心母液試驗研究,南開大學環境科學與工程管理學院碩 士論文,天津。 14.周長波、李永定、張振家,2005,聚氯乙烯離心母液的處理及回用,中國給水排水,21(4):82~84。 15.吳振昇,1985 ,以熱與化學處理法再生活性碳之技術研究,國立台灣大學環境工程學研究所碩士論文,台北。 16.唐受印、戴友芝、汪大翬等人 , 2004, 廢水處理工程(第二版), 化學工業出版社, 北京。 17.馬立民, 2009, PVC離心母液膜法回收利用技術, 聚氯乙烯, 37(7):41~43 。 18.高衛平,2004,膜生物反應器(MBR)處理聚氯乙烯工業廢水的研究,華東理工大學化工所碩士論文,上海。 19.高潔,2002,光化 學氧化技術去除水中有機污染物的試驗研究,環境污染與防治,24:272 273。 20.黃國強,2001,應用固定式生物膜反應器處理煉油廢 水之研究,高雄第一科技大學環境與安全衛生工程系碩士論文,高雄。 21.陳文、熊正為、婁金生、黃仕元,2003,臭氧在水處理中副 產物的論述,懷化學院學報,22(2):37~40。 22.華兆哲,曹揚,陳堅,2006,Fenton法氧化降解聚乙烯醇的機制,化工環保,26(1):1~4。 23.喬彤森,1997,?"瑋N和電解氧化技術在廢水處理中的應用,環境保護,15(4):265~268。24.張彭義,2002,臭氧高級氧化技術在廢 水處理中的研究進展,石油技術與應用,20(4):278~280。 25.蔡銘祥,2003,好氧生物氧化系統技術介紹,台灣環保產業雙月刊 ,17:6~7。 26.潘祖仁、邱文豹、王貴恆主編,1999,塑料工業手冊 - 聚氯乙烯,化學工業出版社,北京。 27.劉勇先、耿宏霞、王廷英 ,2009,膜法處理PVC離心母液水在生產中的應用,聚氯乙烯,37(7):45~46。 28.劉安東,2010,生化法處理並回用PVC離心母液技術 ,聚氯乙烯,38(2):40~42。 29.劉輝堂,2004,臭氧製造與應用簡報,愛樹科技公司。 30.歐陽嶠暉,1980,旋轉生物原板法污泥特性, 中國文化學院實業計劃(工學組)研究所博士論文,台北。31.薛衛東、董前程,2008,母液水的處理和利用,聚氯乙烯,36(11):42~44。 32.謝坤龍,2008,Jelcleer廢水處理系統操作手冊,美商奇異台灣分公司。 33.鐘離,胡孫林,詹懷字,2000,氯乙烯污水AOPs過程及其 反應動力學.化工科技,8(5):20~22。 34.行政院環保署網站, http://www.niea.gov.tw/analysis/method/ListMethod.asp,環境檢驗所,桃 園中壢, 2010。 35.Eckenfelder, W.W., Argaman, Y., Miller, E., 1989, Process selection criteria for the biological treatment of industrial waste water, Environmental Progress, 8(1):40~45. 36.Friedman B.A., 1969, Structure of excellular polymers and their relationship to bacterial flocculation, Journal Bacterial, 98:1238 ~ 1334. 37. Feng J. and Johnson D.C., 1994, Electrocatalysis of anodic oxygen- transfer reactions: evolution of ozone, Electrochemical Society, 141(10):2708 38. Huang. J.C., Batees, V.T., 1980, Comparative performance of rotating biological contactors using air and pure oxygen, Journal of the Water Pollution Control Federation, 52(11):2686~2703. 39. Mulder M., 1996, Basic principles of membrane technology, 2 nd, Kluwer Academic Publishers, Dordrecht. 40.Rittmann, B.E., McCarty, P. L., 1981, Substrate flux into biofilm of any thickness, Journal of the Environmental Engineering, 107(4):831~849. 41. Sotelo J.L., Beltran F.J., 1989, Henry's law constant for the ozone-water system, Water Research, 23:1239~1246. 42. 宮本靖, 2001, 生分解性 ?堇琝瑋N,(株) 出版,東 京