

行政院國家科學委員會專題研究計畫 成果報告

發展超音電解聯用系統處理五氯酚污染土壤 研究成果報告(精簡版)

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計畫主持人：吳庭年

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發展超音電解聯用系統處理五氯酚污染土壤

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執行單位：崑山科技大學 環境工程系

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計畫參與人員：王志偉 崑山科技大學環境工程系

一、摘要

五氯酚(Pentachlorophenol,PCP)常被使用於殺蟲劑、木材防腐劑等用途，歷經數十年來的大量廣泛使用，普遍存在於自然環境中，且因生物分解五氯酚的速率極為緩慢，因而成為土壤及地下水的指標性污染物。電解氧化技術可利用電化學反應來氧化污染物，此技術已成功應用於去除廢水中許多難分解污染物。此外，電化學技術亦為一項高靈敏度、快速測定的工具。本研究提出之構想為一多年期計畫，發展結合超音電解處理程序整治高污染五氯酚土壤，利用超音波萃取機制先將污染土壤中五氯酚自土壤吸附相萃取至水溶相，藉由超過濾機制將土壤與溶液分離，分離出之溶液於電解系統中應用電催化機制將五氯酚脫氯，並進一步氧化降解，而達到無害化程度。惟受限於計畫經費與期程，現階段的研究主要專注於電化學技術的應用，做為水中氯酚化合物的偵測工具，及使用於電還原脫氯的應用。

電偵測實驗部分，以三極式白金電極系統，使用電化學分析儀，以線性掃描伏安法(LSV)測定水中微量氯酚化合物，使用的掃描速度為0.3V/s、電解質0.1M Na₂SO₄及電壓掃描範圍-1.50V至+1.80V，極譜圖中4-氯酚、2,4-二氯酚及五氯酚氧化波峰分別出現在1.228V、1.120V及1.037V左右，測定之三種氯酚化合物濃度與其對應之波峰電流值成良好線性關係， r^2 值為介於0.9964與0.9978之間。實驗品管分析作業包括重複分析及標準品查核分析之結果良好，4-氯酚、2,4-二氯酚、及五氯酚之偵測極限值可達0.13 mg/L、0.24 mg/L及0.09 mg/L。由實驗結果驗證，電化學分析可做為水中微量氯酚化合物之快速測定方法。

電還原脫氯實驗部分，使用三極式白金電極系統，在0.1M Na₂SO₄電解質條件下，操作不同電壓對五氯酚進行還原脫氯實驗。比較降解電壓0.2 V、0.3 V與0.4V之操作，電解60 min後五氯酚降解率

分別為37%、56%與7%，脫氯率則達20%、56%及10%。由實驗結果可初步判定以0.3V之操作電壓降解效果最佳，且降解的五氯酚可達完全脫氯的情況。

關鍵詞：五氯酚(PCP)、白金電極、電偵測、電還原、脫氯

Abstract

Pentachlorophenol (PCP) is widely used as pesticide and wood preservative. After broadly applied in a great quantity for several decades, PCP can be found in most natural environments. Thus, PCP becomes one of most prevalent underground contaminants due to its slow rate of biodegradation. Electrochemical oxidation has been applied as a remedy scheme for many refractory compounds such as pesticides and chlorinated phenols. Besides, electrochemical technology can be applied as a tool for highly sensitive and rapid measurement. The original objective of this research is to develop an associated scheme of ultrasonic extraction and electrochemical oxidation for removing PCP from soil. First, the mechanism of ultrasonic extraction is utilized to partition PCP from soil matrix to the slurry solution. The extract is further filtered through ultra-filtration (UF) membrane and sequentially subjected to electrochemical oxidation for the purpose of de-chlorination and degradation of PCP. However, the presented study is focused on the application of electrochemical technology as a detection tool and/or as a dechlorination scheme for chlorophenols due to the limitation of budget and time.

In the experiments of electrochemical measurement, a tri-electrode system used a platinum (Pt) electrode as working electrode, a Pt wire as counter electrode, and a saturated Ag/AgCl electrode as reference electrode. Electrochemical analyzer is operated in a linear sweep voltammetric (LSV) mode: scan rate 0.3 V/s, 0.1M Na₂SO₄ as electrolyte, and

scan range -1.5 to 1.8 V. The oxidative peaks of 4-chlorophenol (4-MCP), 2,4-dichlorophenol (2,4-DCP), and PCP occur at 1.228V, 1.120V, and 1.037V in the cyclic voltammogram. A linear relationship between concentration and peak current exists based on r^2 values ranging 0.9964 and 0.9978, and this linearity can be employed as calibration curve to measure the concentrations of chlorophenols. The results of QA/QC including duplication and standard check are satisfied, and the detection limits are 0.13 mg/L for 4-MCP, 0.24 mg/L for 2,4-DCP, and 0.09 mg/L for PCP. Consequently, electrochemical analysis can be employed as a detection tool for trace chlorophenols in water.

In the experiments of electrochemical dechlorination, the tri-electrode system was also employed to compare the effect of PCP degradation and dechlorination under various operating potentials. The reaction cell was fed with 0.1M Na_2SO_4 as electrolyte, and installed a Pt electrode as working electrode, a Pt wire as counter electrode, and a saturated Ag/AgCl electrode as reference electrode. The degradation of PCP was found 37 %, 56%, and 7 % after 60mins under 0.2, 0.3, and 0.4 V, respectively; meanwhile, the dechlorination of PCP was 20 % for 0.2V, 56% for 0.3V, and 10% for 0.4V. The result showed that 0.3 V could be the optimum potential for PCP degradation and dechlorination, and the degraded PCP was found completely dechlorinated.

Keywords : Pentachlorophenol (PCP), Platinum electrode, Electrochemical Detection, Electrochemical Reduction, Dechlorination

二、前言

自 1930 年代經人造合成製造出五氯酚以來，五氯酚即被廣泛使用，早期常做為木材防腐劑、除草劑、滅菌劑及消毒劑等用途，歷經數十年來的大量使用，五氯酚普遍存在於自然環境中，且因生物分解五氯酚的速率極為緩慢，致使五氯酚常為污染土壤及地下水的來源之一。台灣地區發現五氯酚污染土壤及地下水的案例，以中石化安順廠最具代表性，該廠 1970 年代為五氯酚鈉製造工廠，雖於 1982 年工廠停工關閉，但現場仍遺留下五氯酚、戴奧辛及汞污染的問題尚待解決，自 1990 年代中期廠方陸續進行局部污染調查及整治先期試驗，並設置活性碳塔吸附處理地下水中五氯酚，對於地下水五氯酚污染擴散雖達到初步的控制，但對於高污染土壤（含五氯酚及戴奧辛）目前僅進行挖除暫存處置，

現場暫存區內放置的污染土壤超過 10,000m³。現今廠方已無能力負擔龐大的污染清除處理費用，且目前土污基金已支應該場址污染調查及清除費用近億元之譜，因此有迫切之需要尋求經濟且有效的方式處理現場暫存的大量污染土壤。

三、研究目的

本研究之主要目的為發展結合超音電解處理程序整治高污染五氯酚土壤，一般整治方式之設計以現地處理方式優先考慮，但因台灣土壤/地下水污染管制場址中已安置數量可觀的五氯酚污染土壤，因此本研究提出之結合程序處理系統係針對已挖除之五氯酚高污染土壤進行處理研究。依處理程序流程為利用超音波萃取機制，於污染土壤懸浮液中使五氯酚自土壤吸附相分配至水溶相，接續利用超過濾機制進行土壤與水溶液分離，萃取之五氯酚溶液則利用電解氧化技術進行處理，使五氯酚進行脫氯反應，接續進行降解反應。由於結合處理程序設計上較為繁複，關連因素之探討也較多，現階段研究受限於計畫經費與期程，研究主題專注於電化學技術的應用，如做為水中氯酚化合物的偵測工具，及使用於電還原脫氯的應用。因此調整階段工作目標如下：

- (1) 建立電化學偵測水中氯酚化合物的技術。
- (2) 確認氯酚化合物濃度的測定範圍。
- (3) 驗證電化學偵測水中氯酚化合物的品管要求。
- (4) 選擇合適的電極進行五氯酚脫氯降解反應。
- (5) 確認五氯酚脫氯降解的程度。
- (6) 建立五氯酚脫氯降解最佳操作參數。

四、文獻探討

針對電化學偵測應用的部分，氯酚化合物之檢測方法不少，可利用氣相層析儀/火焰離子測器 (GC/FID)、氣相層析儀/電子捕捉偵測器 (GC/ECD)、氣相層析儀/質譜儀 (GC/MS)、高效能液相層析儀 (HPLC)、電化分析儀等儀器來進行測定分析。國內相關研究曾利用 GC/FID 測定土壤五氯酚，測定濃度 50~600 $\mu\text{g/g}$ ，回收率為 105.8% [廖淑秋, 2002]；及利用 GC/ECD 測定五氯酚溶液 [曾聖倫, 2004]。亦有相關研究使用正己烷萃五氯酚溶液後，利用 GC/MS 分析測定，其回收率為

96.5±0.7%[曾聖倫, 2004]。HPLC亦被應用於200mg/kg的酸性及鹼性土壤之五氯酚測定分析,其回收率分別為58.93%與53.71%[邱瑞斌, 2002]。至於使用電化學分析儀做為分析工具的案例甚少,僅有本團隊應用電化學技術偵測水中微量氯酚化合物的報導[吳庭年等人, 2006; 吳庭年和王志偉, 2006]。

針對電化學脫氯降解的部分,國內針對水中氯酚類污染物處理方法之研究較為豐富,包括生物降解、濕式氧化、臭氧處理、紫外線二氧化鈦程序、超臨界二氧化碳萃取等方式,對於五氯酚污染土壤處理方法之研究則有生物復育、電動力復育、電動力-Fenton法、化學氧化法、微波脫附處理等方式。電解氧化技術亦可利用電化學反應來氧化污染物,此技術已成功應用於去除廢水中氯酚類[Torres et al., 2003; Comninellis et al., 1995]、多氯聯苯[Chiarenzelli et al., 2001]、2,4-D[Brillas et al., 2000]、其他有機氯類農藥[Brillas et al., 2003; Ventura et al., 2003]等。電解氧化技術除具有高級氧化處理技術所具備的優點,更可利用其電催化功能將污染物選擇性降解至某一特定階段,使污染物無毒化或降低毒性後,可接續利用生物處理技術將中間產物礦化至二氧化碳,此乃電解氧化技術最具吸引力與挑戰性之處。

五、研究方法

5.1 實驗藥品

本研究使用之藥品包括4-氯酚(4-chlorophenol, 4-MCP)購自日本試藥工業株式會社、2,4-二氯酚(2,4-dichlorophenol, DCP; 純度99.90%)購自日本試藥工業株式會社、五氯酚鈉(Sodium Pentachlorophenate, PCP)為分析級藥品購自J.T.Baker、硫酸鈉(Sodium Sulfate, 純度99.00%)購自關東化學株式會社、乙晴(Acetonitrile, 純度99.8%)、甲醇(Methanol, 純度99.9%)為液相層析級藥品購自UNI-WARD CORP, 實驗所需之溶液皆以二段水(電阻值達18.0 MΩ-cm)來配製,二段水取自於Milli-Q system (Millipore, Tk-10, USA)。

5.2 實驗儀器設備

實驗系統裝置如圖5-1所示,為非分離式反應槽,其容積為50 ml,以磁石攪拌器加以攪拌,並以恆溫循環水槽控溫,工作電極(working electrode, WE)選用白金電極,輔助電極(counter electrode, CE)為白金絲,參考電極(reference

electrode, RE)為銀/氯化銀參考電極(saturated Ag/AgCl electrode, SSE);工作電極之電位由電化學分析儀(BioAnalytical System BAS100B/W)供給,電流變化由6位半精密高階數位電表(Keithley 2000 Multimeter)量測。

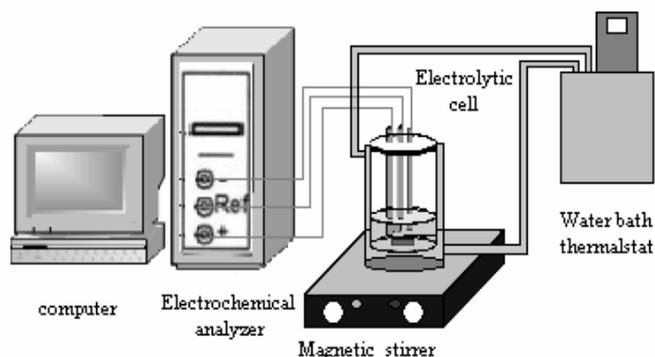


圖 5-1 實驗裝置示意圖

5.3 研究方法

5.3.1 電化學偵測實驗

線性掃描伏安法(LSV)為在一定的電極面積與分析物的濃度下,施加電位後由LSV極譜圖中找出其氧化電位。本研究待測物質氯酚化合物溶於水中後,置入三極式系統反應器,反應槽內溶液含0.1 M Na₂SO₄做為電解質,以不同的掃描速度進行電位掃描,找出適合的掃描的速度後,再以不同濃度的氯酚化合物溶液進行測試,觀察濃度與其電流的變化,由濃度與電流間的線性關係做為濃度測定之推算依據。

5.3.2 電化學脫氯降解實驗

配製5 mg/L PCP溶液添加濃度0.1 M電解質,以利電解氧化實驗進行,操作條件採用定電壓電解,工作電極電位由電化學分析儀控制,再並聯6位半精密高階數位電表量測實驗進行中電流的變化,操作電壓範圍介於0.20~0.40 V之間,每組實驗反應時間為60 min,前15 min時每5 min取樣一次,接續每15 min取樣一次,採集0.2 mL液體樣品稀釋至2 mL,分別提供離子層析儀(IC)及液相層析儀(HPLC)分析之用。

5.3.2 分析方法

PCP濃度以液相層析儀(HPLC, HITACHI)進行分析,層析管柱為MIGHTYSIL RP-18 GP 5 μm 250 × 4.60 mm。分析條件為:流速:1 mL/min,注射量:20 μL;移動相:乙晴/超純水(75% /25%),紫外光偵測器波長:228 nm。

氯離子的測定以離子層析儀(DIONEX Model DX-100)進行分析測定，層析管柱為陰離子層析管柱AS12A與AG4A。分析條件：流速：1.5mL/min，注射量：1mL，移動相：Na₂CO₃/NaHCO₃。

六、結果與討論

6-1 氯酚化合物測定分析

分別配製濃度 0.8mg/L 4-氯酚、2,4-二氯酚及五氯酚溶液，使用電解質為 0.1 M Na₂SO₄，操作電壓範圍為 -1.60 V 至 1.60 V，以電化學分析儀進行 CV 掃描，圖 6-1 極譜圖中顯示 4-氯酚、2,4-二氯酚及五氯酚出現之氧化波峰電位分別為 1.228 V、1.120 V 及 1.037 V 左右，含氯數較高之氯酚化合物呈現之波峰電流值較小，可能原因推測為含氯數較高之氯酚化合物一般較難以氧化所致。

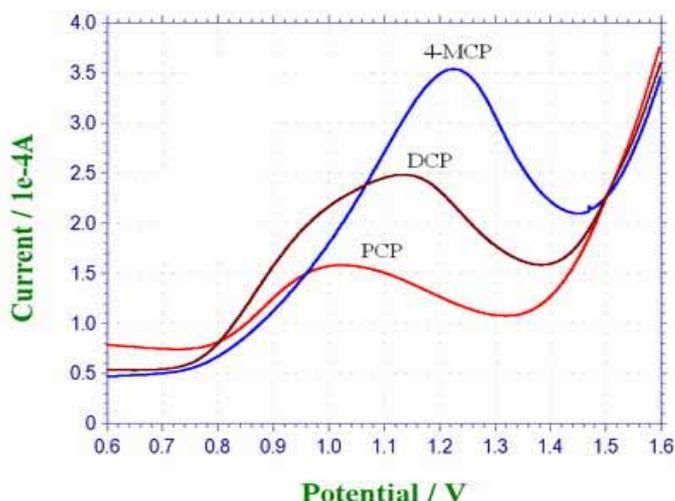


圖 6-1 氯酚化合物線性掃描伏安圖(2,4-二氯酚(DCP)、4-氯酚(4-MCP)及五氯酚(PCP)，濃度：0.8 mg/l)

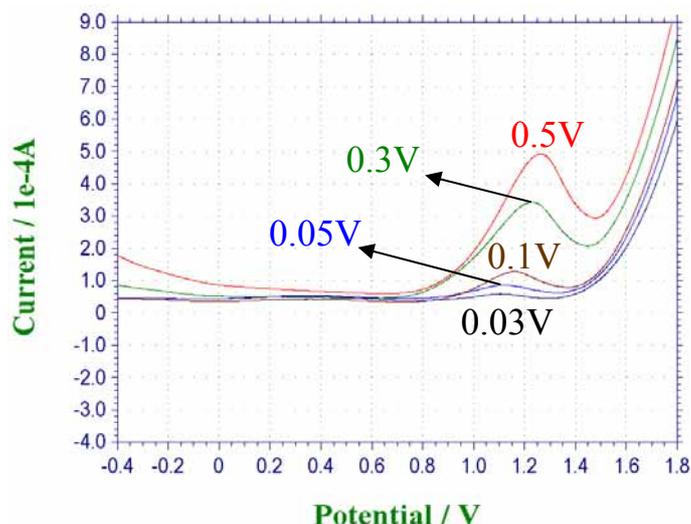


圖 6-2 4-氯酚不同掃描速度之線性掃描伏安圖(0.03V~0.5V，濃度 0.8mg/L)

續以 0.03 至 0.5 V/s 的掃描速度進行 LSV 掃描，圖 6-2 顯示使用較高的掃描速度可得到較高的電流值，但卻會造成圖譜失真的情形，本研究選定可顯現明顯且穩定的氧化波峰之掃描速度做為測定條件，設定 0.3V/s 為本實驗之固定掃描速度。

以 LSV 進行氯酚化合物分析測定，設定條件為電解質 0.1 M Na₂SO₄、掃描速度 0.3V/s 及電壓範圍 -1.50V 至 +1.80V。圖 6-3 為 0.2-8mg/L 4-氯酚之 LSV 測定結果，當測定濃度高於 1mg/L 易氧化物在陽極產生沈澱，降低電流訊號使波峰電流與電位呈現不規則性的改變。當 4-氯酚濃度低於 1mg/L 則訊號值明顯呈規律變化，取線性範圍內之測定濃度與其對應之波峰電流值進行回歸分析，線性係數 r^2 為 0.9971。

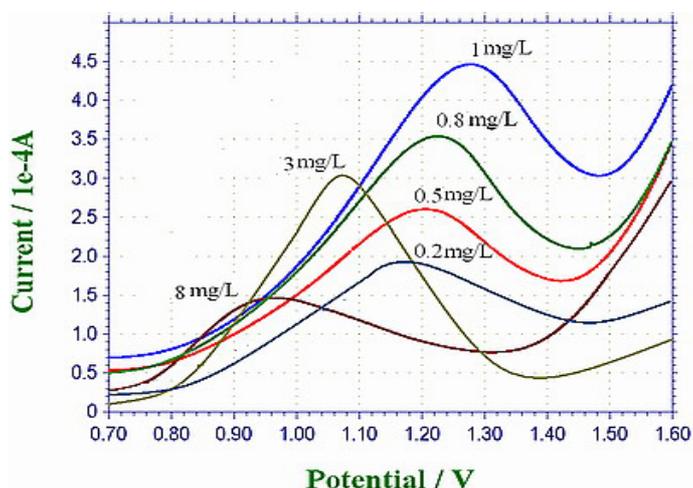


圖 6-3 不同濃度 4-氯酚之現性掃描伏安圖(濃度 =0.2-8mg/L)

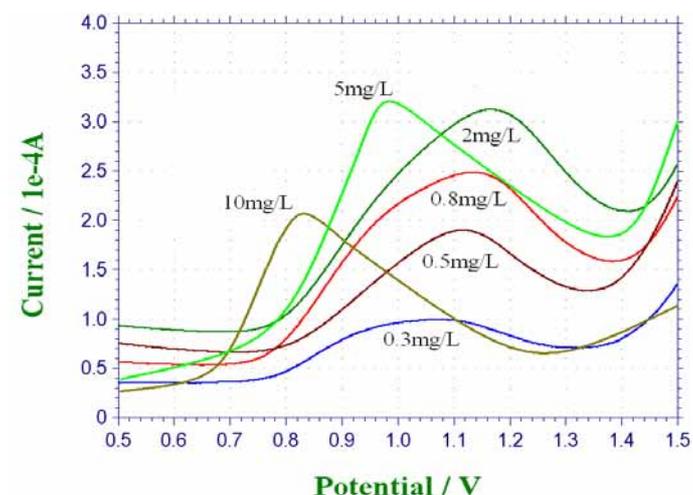


圖 6-4 不同濃度 2,4-二氯酚之現性掃描伏安圖(濃度=0.3-10mg/L)

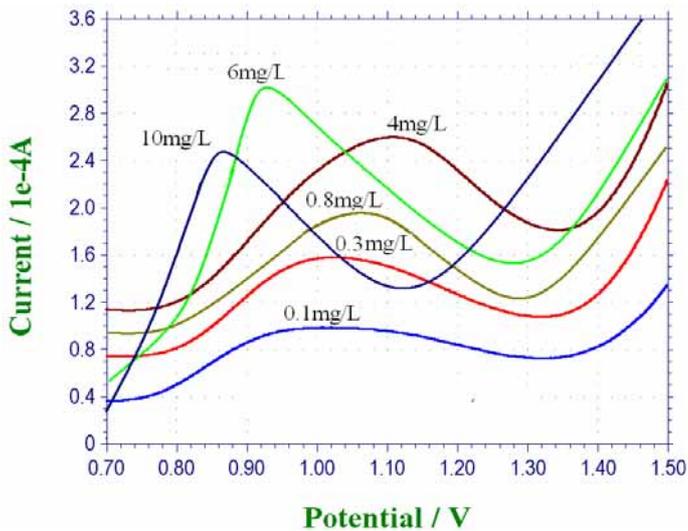


圖 6-5 不同濃度五氯酚之現性掃描伏安圖(濃度=0.1-6mg/L)

表 6-1 氯酚化合物測定之偵測極限及品管分析

	RSD	Recovery	MDL
4-MCP	±3.78%	94.70%	0.13 mg/L
DCP	±4.36%	95.20%	0.24 mg/L
PCP	±3.44%	95.60%	0.091 mg/L

圖 6-4 及圖 6-5 分別為 0.3-2mg/L 2,4-二氯酚及 0.1-4mg/L 五氯酚之 LSV 測定結果，當 2,4-二氯酚濃度超過 2mg/L 及五氯酚濃度超 4mg/L 時，電流訊號值並不隨著濃度之增加而增加，其濃度線性範圍分別為 0.3-2mg/L 及 0.1-4mg/L，線性係數 r^2 為 0.9964 及 0.9978，皆滿足減量線 $r \geq 0.995$ 之規範要求。

表 6-1 為進行重複分析、查核分析及偵測極限等品管之測定結果，重複分析為將重複樣品依相同處理及分析步驟進行檢測，三種測定之氯酚化合物重複分析差異率(RSD)皆小於±5%。查核分析使用不同來源之標準品製備查核樣品，三種測定之氯酚化合物查核回收率達 94.7%-95.6%。偵測極限以 7 個低濃度之相同樣品進行測定，依檢量線換算濃度，分別計算 7 個測定濃度的標準偏差 S_A ，重複測定 7 個相同樣品計算標準偏差 S_B 值，以 S_A^2 與 S_B^2 計算 F 值，再計算其共同標準偏差 S_{pooled} 值，最後以 $3S_{pooled}$ 求得偵測極限值，4-MCP、DCP 與 PCP 之偵測極限分別為 0.13mg/L、0.24mg/L 及 0.09mg/L。

6.2 五氯酚脫氯降解

探討白金電極對於電解氧化水中五氯酚，在不同電解電壓條件下對五氯酚進行電解破壞去除以及了解氯離子釋放量之情形。配製 5mg/L 的五氯酚溶液，在電解質 0.1 M Na_2SO_4 、電壓範圍：1.80 V 至 -1.20V 的條件下，以電化學分析儀進行循環伏安法(Cyclic Voltammrtey,CV)測定，其結果如圖 6-6 所示。由圖 6-6 得知，極譜圖中出現氧化及還原反應的波峰，由於白金電極屬於還原性電極，因此本研究實驗選擇還原電位 0.3 V 附近做為電解實驗之操作電壓。在工作電極為白金電極的系統中，比較不同電解電壓操作之五氯酚移除效果於圖 6-7。由圖 6-7 得知，以使用電解電壓 0.30 V(vs. Ag/AgCl)，電解質為 0.1 M Na_2SO_4 為最佳的操作條件，電解 60 min 後五氯酚可達到 56 % 的移除效率；而使用電解電壓 0.2 V 及 0.4 V(vs. Ag/AgCl)之實驗組對五氯酚的移除效率分別為 37 % 及 7%。由此可知，施予的電壓提高並無法提升去除效率，反而使五氯酚的去除效率受到限制。於實驗過程中同時採樣分析溶液中氯離子的濃度變化，並計算五氯酚脫氯效率。由圖 6-8 得知，在電解電壓 0.30V (vs. Ag/AgCl)，電解質為 0.1 M Na_2SO_4 條件下，電解 60min 後五氯酚溶液中氯離子的釋放率可達 56%；而使用電解電壓 0.2 V 及 0.4 V(vs. Ag/AgCl)之實驗組在電解 60min 後，其氯離子的釋放率分別為 20% 及 10%。對比五氯酚之降解率與脫氯率的數據，於電解電壓 0.30V (vs. Ag/AgCl) 之操作條件，發現降解效率與脫氯率相當，此結果暗示降解之五氯酚可以達到完全脫氯的效果。

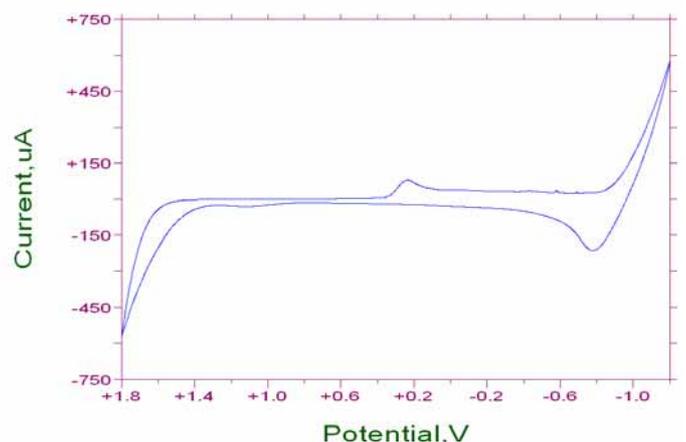


圖 6-6 白金電極之循環伏安圖(電壓掃描範圍：-1.20~1.80V(vs.Ag/AgCl)；PCP 濃度：5 mg/L；電解質：0.1M Na_2SO_4)

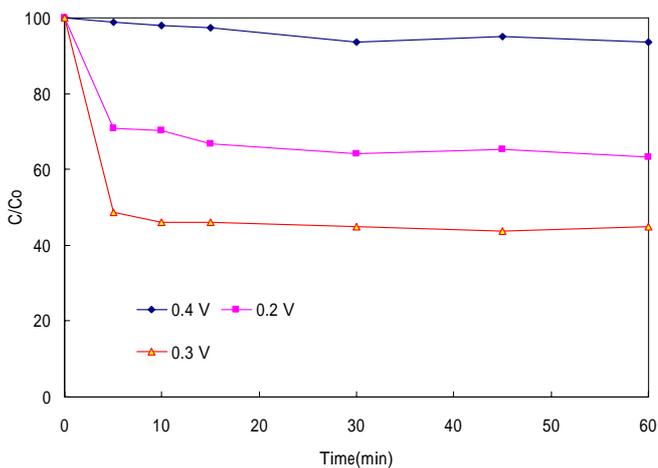


圖 6-7 不同電解電壓對 PCP 殘餘率之影響 (PCP 濃度：5 mg/L；電壓：0.2、0.3 及 0.4 V(vs. Ag/AgCl)；電解質：0.1 M Na₂SO₄)

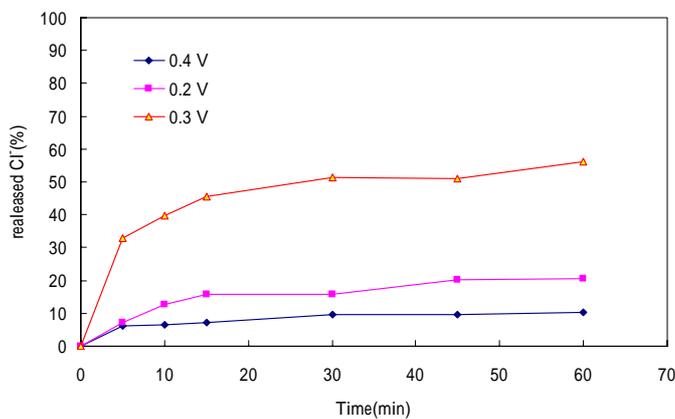


圖 6-8 不同電解電壓中五氯酚氯離子釋放率(PCP 濃度：5 mg/L；電壓：0.2、0.3 及 0.4 V(vs. Ag/AgCl)；電解質：0.1 M Na₂SO₄)

七、計畫成果自評

本研究計畫結果證實，應用電化學技術不僅可以用以測定水中微量的氯酚化合物，也可以應用在水中五氯酚的降解脫氯，實驗中測試的白金電極在較佳的操作條件下，對五氯酚的降解效率與脫氯效率皆可達 56%。

本研究計畫支持 1 位碩士研究生進行其碩士論文研究，部分成果已陸續發表於國內研討會[參考文獻 8]或兩岸研討會[參考文獻 7]，研究成果仍將彙整投稿於國際研討會或期刊。

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行政院國家科學委員會補助國內專家學者

出席國際學術會議報告

94 年 11 月 25 日

報告人姓名	吳庭年	服務機構 及職稱	崑山科技大學環境工程系 助理教授
時間 會議 地點	民國 94 年 11 月 7 日至 11 日，韓國 濟州島	本會核定 補助文號	NSC 94-2211-E-168-008
會議 名稱	(中文)國際水質協會水回收專家群研討會-廢水回收及永續利用 (英文)IWA Water Reuse Specialty Group Symposium on Wastewater Reclamation & Reuse for Sustainability		
發表 論文 題目	(中文)以白金電極利用電化學機制移除水中納乃得 (英文)Electrochemical Detoxification of Methomyl in Water with Pt Electrodes		
<p>報告內容應包括下列各項：</p> <p>一、參加會議經過</p> <p>得知國際水質協會水回收專家群國際研討會於 2005 年 11 月 7-11 日在韓國 濟州島 RAMADA 飯店舉行後，即積極準備投稿準備工作，本研討會主要邀請世界各國大學教授、科學家、工程師及相關議題執業人員共同參與，特別是希望世界各國之專家有機會可齊聚一堂，並對於水質回收及再利用相關議題進行探討。</p> <p>本屆會議蒐集世界各國學者專家口頭發表及張貼海報之論文約 600 篇，與會人員來自世界各國。會議議題涵蓋(1)Biofilm and Membrane Bio Reactor (MBR) (2)Filtration Technology (Membrane, GAC/PAC, Sand, etc.) (3)Natural System Technology (SAT, Lake/River Bank Filtration) (4)Micropollutants Measurement and Control (5)Disinfection and Oxidation for Pathogens (6)Health and Risk Assessment (7)Treatment Process Monitoring (8)Regulation, Policies, and Planning (9)Case Studies and (10)Desalination。</p> <p>於 2005 年 3 月將年度內執行國科會計畫相關研究之成果整理為論文摘要投稿，5 月接獲通知審查結果被選定為口頭發表，6 月底完成論文全文繳交，發表之題目為：以白金電極利用電化學機制移除水中納乃得 (Electrochemical Detoxification of Methomyl in Water with Pt Electrodes)。</p>			

11月與會時，始得知本論文報告被安排在特別專題時段(Environmental Nano and Bio-Technology)，並吸引多方關注。

二、與會心得

於11月10日在「Environmental Nano and Bio-Technology」之 Special Section (Room B)會場進行口頭發表，發表後並蒙會場主持人 Joan Rose (U.S.)及邀請演講者 Nosang Myung (U.S.)提問討論，在場之學者專家一致給予本論文成果相當正面的肯定。此外，筆者亦於會議期間積極聆聽各場次之發表，尤其對於環境奈米技術議題之相關論文更感興趣，不但對相關研究課題之開發有更進一步的想法，亦吸收其他不同領域議題之技術與應用，收穫頗為豐富。

在各場次休息的茶點時間，並與多位外國專家學者就相關議題持續討論，彼此交換意見。在歡送晚宴上，更認識許多各國與會代表，不僅瞭解各國的研究發展，對於各國的風俗習慣藉由交談亦有初步認識，吸收不少新知，並增廣許多見聞。

三、考察參觀活動(無是項活動者省略)

略。

四、建議

參加國際研討會與各國專家學者進行學術交流，確實令人受益良多。本年度幸蒙國科會於核定計畫(NSC 94-2211-E-168-008)項下同意補助出席國際研討會之相關費用，本人深表感謝。惟本人近2年已出席3次國際會議(辛巴威、希臘、韓國)及2次兩岸會議(西安)，亦連續2年向國科會申請專家出席國際會議補助，但皆獲得“經費受限，歉難同意”的回答，深感申請補助的困難，尤其是那些沒有國科會計畫的學者專家。若欲學者提升研究水平及拓展國際交流，鼓勵學者專家多出席國際研討會是必要的，因此，在經費預算許可的情況下，應多提供申請者補助的機會，尤其是那些沒有資源又有心研究的專家學者(如私立科大、技術學院等)。

五、攜回資料名稱及內容

本次國際研討會會議成果相當豐碩，攜回之資料計有論文摘要乙冊、會議議程、及論文全文光碟一片。資料名稱為“WRRS2005: Wastewater Reclamation & Reuse for Sustainability”。

六、其他

略。

Electrochemical Detoxification of Methomyl in Water with Pt Electrodes

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ABSTRACT

In this study, electrochemical oxidation was proposed as a remediation method for aqueous methomyl. Lab data showed that electrolyte species instead of its concentration could significantly affect the extent and rate of oxidation. Comparing with NaCl and KCl, use of Na₂SO₄ as the electrolyte causes the low-efficiency oxidation for methomyl. Electrochemical experiments showed that the degradation of methomyl was less than 20 % at 1.2V of oxidizing potential, and it implied that 1.2V of oxidizing potential was not sufficient for continuous generation of radicals or strong oxidants in great amounts. Under the strong oxidizing potentials (above 2.4 V), the chain electrochemical reactions can be triggered to produce more radicals or strong oxidants and thus lead to a complete degradation of methomyl. During the process of electrochemical oxidation, methomyl can be successfully mineralized to carbon dioxide and water without the remaining of intermediates or by-products based upon the examination of HPLC-MS. In addition, the extent and rate of methomyl degradation appeared relatively slow at the presence of calcium. Different levels of calcium concentrations (150 mg/L and 300 mg/L) showed a similar degree of depression on methomyl degradation. Calcium ion can be reduced and adsorbed on the surface of electrode, and thus the formed electrode deposit could reduce the current efficiency and lead to the depression of methomyl degradation.

Keywords

Electrochemical oxidation, methomyl, oxidizing potential, electrode deposit

INTRODUCTION

Methomyl, one of carbamate pesticides, is widely used in agricultural applications for crop protection. The annual usage of methomyl is estimated over a thousand ton in Taiwan, and its applications cover the bug control for vegetables, tobacco, or corn. Methomyl is able to induce pesticide poisoning or fatalities, and sometimes, it is involved in suicides or homicides. For example, methomyl has been intentionally misused in a seafood-poisoning incident to injure over one hundred people at Kaohsiung (Taiwan) in 2002. Besides, pesticide residual on the vegetables is another concern for methomyl uptake via the intake of vegetables. The uptake of methomyl can induce acute poisoning by inhibiting acetylcholinesterase (AChE) activity reversibly with a subsequent accumulation of acetylcholine at peripheral and central nervous systems (WHO, 1996). Symptoms of poisoning include excessive salivation, accelerated excretion in the respiratory tract, seizures, and even death due to paralysis of the respiratory muscles (Ecobichon, 1996; Moriya and Hashimoto, 2005).

Because of their toxic characteristics, pesticides are not easily biodegradable on a regular basis. There are various innovative methodologies proposed as an alternative for the decontamination of pesticides in water such as photocatalytic oxidation, ultrasonic radiation, bioremediation, thermal desorption...etc. (Arapoglou et al., 2003).

The employment of electrochemical treatment for recalcitrant toxics is especially drawing much attention recently (Vlyssides et al., 2005). Electrochemical oxidation has the advantage of high sensitivity, easy control and without secondary pollution, and also it has been successfully applied as a remedy scheme for many refractory pesticides (Brillas et al., 2000; Ventura et al., 2002) and chlorinated phenols (Brillas et al., 2003; Torres et al., 2003). Besides, electrochemical oxidation can selectively degrade contaminants to certain extent by the mechanism of electro-catalysis.

Based on wide application of electrochemical treatment, this work was aimed at developing the electrochemical methodology to solve the potential problem regarding aqueous micropollutants, such as methomyl. In this study, the treatment of aqueous methomyl by electrochemical oxidation was examined in a bench-scale cell using a Pt cathode and a Pt anode. The objective of lab work was to show the effectiveness and efficiency of methomyl removal through electrochemical treatment, and also existing lab data could be useful enough for those who intend to develop electrochemical treatment as an alternative for water purification.

MATERIALS AND METHODS

Chemicals

Methomyl powder (>90%) obtained from local agrochemical supplier (Taiwan) was used to prepare stock solution, and analytical standard of methomyl (99.9%) was purchased from Riedel-de Haen Co. Stock solutions of methomyl was made in a small aliquot of methanol and subsequently diluted with de-ionized water for immediate use. Potassium chloride (99% KCl) was obtained from Shimakyu Chemical Co. (Japan), and sodium chloride (99.5% NaCl) was obtained from Wako Chemical Co. (Japan). Sodium sulfate (99% Na₂SO₄) was obtained from Kanto Chemical Co. (Japan), and calcium carbonate (99.95% CaCO₃) was obtained from Merck Co. All reagents were prepared with de-ionized water, which was made by Mili-Q system (Millipore TK-10, USA).

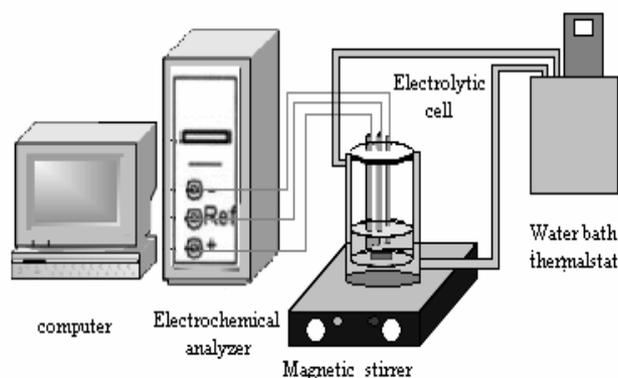


Fig.1. Experimental setup of the electrochemical treatment system

Experimental Set-up

As shown in Fig 1, a bench-scale electrochemical treatment system was utilized for the oxidation of methomyl in experiments. The electrochemical treatment system is

composed of an electrochemical analyzer, an electrolytic cell, a magnetic stirrer and a thermostatic water bath. The volume of the electrolytic cell is only 14 ml, in which the cathode and the anode are placed in the same compartment. The electrolytic cell was equipped with a Pt electrode as working electrode (WE), a Pt wire as counter electrode (CE) and a saturated Ag/AgCl electrode as reference electrode (RE). The voltage source was supplied and precisely controlled by a BAS 100B Electrochemical Analyzer. During the experiment, the liquor of the reactor was completely mixed with a mini stirrer and the reaction temperature was controlled by the recycle of cooling water from the thermostatic water bath.

Oxidation Experiments

Lab works were focused on the technical feasibility and performance of electrochemical oxidation of methomyl at a bench-scale reactor. The initial concentration of 100 mg/l methomyl (about 0.617mM) was prepared in solute to simulate pesticide contamination of potable water each run. For the ease of electrochemical reaction, three electrolytes including KCl, NaCl and Na₂SO₄ were employed in batch experiments. The oxidation of methomyl was investigated under various electrolytes and also compared at different electrolyte concentrations. Only single electrolyte was used each run and its concentration was maintained at least 0.1 mol/l in the electrolytic cell. Oxidation experiments were carried out at a constant operating voltage in the range of 1.2 V and 3.0 V. Before each oxidation experiment, working electrode was cleaned with tiny 0.05 μ m aluminum powder by remittently wet-polishing to rub out adsorbed deposits on the electrode surface. Reference electrode was immersed in 3 mol/l KCl solution to maintain its saturated status while not in use. Each run was lasted for 120 minutes and sampled with a syringe every 30 minutes. The sampled liquor was instantly subjected to the analysis of high performance liquid chromatography (HPLC) for the determination of methomyl concentration. Based on HPLC chromatogram, several selected samples were further analyzed by high performance liquid chromatography/ mass spectrometry (HPLC/MS) to identify byproducts or intermediates of methomyl degradation.

Sample Analysis

Following Taiwan EPA standard analysis method NIEA W633.50A (Taiwan EPA, 1994), the analysis of methomyl was implemented by reverse-phase high performance liquid chromatography with UV detection (HPLC-UV). The HPLC-UV system was mainly composed of a Hitachi L-7100 LC pumping module, a Hitachi L-7420 UV diode array detector and a Mightysil 5 μ m-C18, 4.6mm × 250mm RP column. The detector wavelength was set at 254nm as reference. The mobile-phase composition was maintained at a 25 / 75 ratio of methanol and water, and the mobile-phase flow was controlled at 1 ml/min. Under these analytical operations, the retention time of methomyl occurred at 8.5 min on the HPLC chromatogram. Methomyl standard solutions were prepared in water in a concentration range of 0.5 mg/l and 120mg/l.

RESULTS AND DISCUSSION

Effect of Electrolyte Concentration

Platinum electrodes were concurrently used as both cathode and anode in the proposed electrochemical reactor. As using a high oxygen overvoltage anode,

hydroxyl radical can be generated through the oxidation of water (Panizza et al., 2000). The electrogenerated hydroxyl radical was first absorbed on the active sites of the electrode surface, and the absorbed hydroxyl radical was subsequently released to oxidize aqueous pollutant in solute (Vlyssides et al., 2005). The occurring electrochemical reactions within the electrolytic cell are complicated and not entirely known. According to the result of HPLC/MS analysis, there was no aqueous intermediate identified during the electrolysis of methomyl. The complete mineralization of methomyl was logically assumed, in other word, the oxidation products of methomyl are carbon dioxide, nitrate and sulfate. Thus, the mechanism of direct oxidation of methomyl was proposed as follows:



Based on the analysis of cyclic voltammetry, electrochemical experiments were performed at a constant oxidizing potential of 1.2 V in order to conduct the oxidation of water. As using three levels of electrolyte concentrations, the degradation of methomyl during electrochemical experiments was compared in Fig 2. It is clear that a slow degradation of methomyl can be achieved under all electrolyte concentrations, however the removal efficiency is more significant when using 1.0 mol/l KCl as electrolyte. Therefore, the electrolyte concentration had better to maintain at least 1,000 times larger than the pollutant level for supporting effective electron transfer in aqueous solution. As observed in Fig 2, the limited degradation of methomyl seems to point to the inadequacy of oxidizing potential during electrochemical experiments. Under oxidizing potential of 1.2 V, the oxidation of water generates oxygen instead of hydroxyl radical as shown in reaction (3). Oxygen, as an oxidant, can diffuse away from the electrode to carry on indirect oxidation of methomyl in solute.

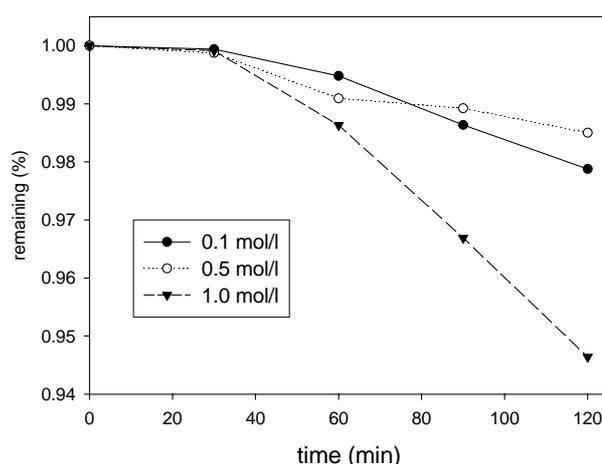
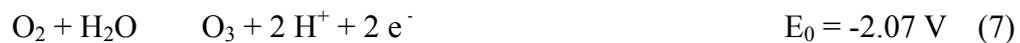
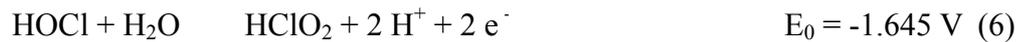


Fig.2 Degradation of methomyl under various electrolyte concentrations during electrochemical oxidation (Operation condition : potential = 1.2 V, electrolyte : 0.1 mol/l KCl, 0.5 mol/l KCl or 1.0 mol/l KCl)

Effect of Oxidizing Potential

As can be seen in Fig 3, the degradation of methomyl is greatly enhanced as the

supplied potential reaching 1.8V or above. At the presence of chloride ion, the involved electrochemical reactions can produce strong oxidants (such as Cl₂, HOCl, HClO₂ and O₃) to oxidize aqueous methomyl. Because these electrogenerated oxidants have stronger oxidizing potentials than oxygen, the observed degradation of methomyl was greatly improved as operating potential above 1.8V. These involved electrochemical reactions may be giving by the following:



As using 0.1 mol/l KCl as electrolyte, a complete degradation of methomyl was observed after 2 hours of electrochemical oxidation under oxidizing potential of 2.4V. However, a continual increase of oxidizing potential to 3.0V did not result in a rapid degradation rate during electrochemical oxidation in Fig 3a. The possible deduction is that the oxidation of water may produce hydroxyl radical under oxidizing potential of 3.0V as the mechanism of reaction (1) and simultaneously induce the generation of other oxidants as the mechanism of reaction (3) to reaction (7), however the self-scavenging reaction can be triggered around the electrode to consume the electrogenerated oxidants due to the strong oxidizing potential of hydroxyl radical.

In Fig3b, the ascending trend of methomyl degradation is obvious with intensifying oxidizing potential of electrochemical oxidation. The optimum oxidizing potential was found around 2.4V for attaining satisfied removal efficiency through electrochemical oxidation. Under this optimum oxidizing potential (2.4V), complete degradation of methomyl can be achieved for both cases of concentrated electrolyte (1.0 mol/l KCl) and diluted electrolyte (0.1 mol/l KCl). As shown in Fig 4, an intensive specific degradation rate of methomyl is correspondent to the case using concentrated electrolyte and vice versa. This observation indicated that concentrated electrolyte can support the undergoing of electrochemical oxidation but oxidizing potential is the determining factor for the success of the proposed treatment system.

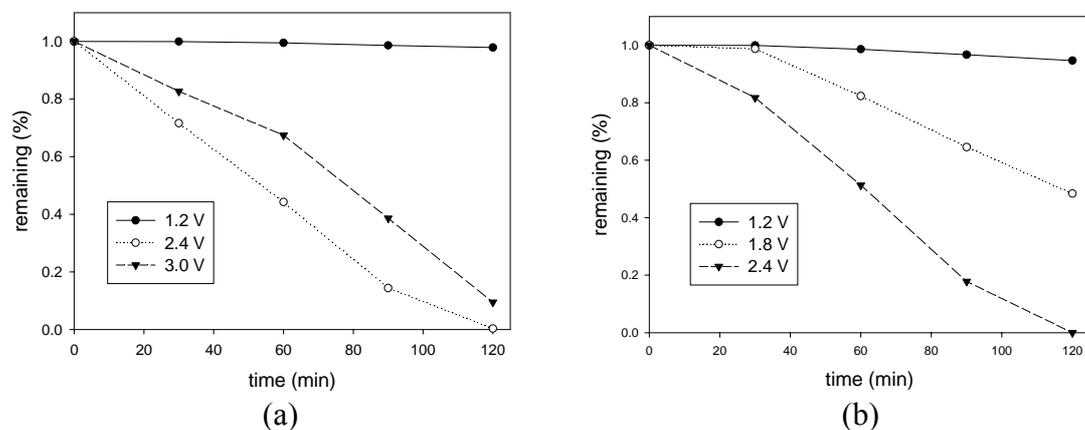


Fig.3 Degradation of methomyl under various voltage supplies during electrochemical

oxidation (Operation condition : (a)potential = 1.2 V, 2.4 V or 3.0 V, electrolyte : 0.1 mol/l KCl; (b) potential = 1.2 V, 1.8 V or 2.4 V, electrolyte : 1.0 mol/l KCl)

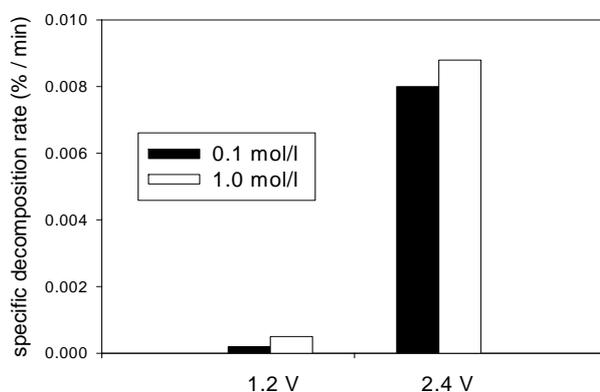


Fig.4 Comparison of specific degradation rate of methomyl under various voltage supplies and electrolyte levels

Effect of Electrolyte Species

In this study, three common electrolytes including KCl, NaCl and Na₂SO₄ were tested under the optimum oxidizing potential. As it is observed from Fig 5, there was no remaining methomyl detected in the both cases of KCl and NaCl. In the case of Na₂SO₄, the performance of methomyl removal was very poor. As mentioned previously, KCl and NaCl can initiate the mediated reactions to produce strong oxidants Cl₂, HOCl and HClO₂ that play a crucial role in electrochemical oxidation of methomyl. Comparing with Na₂SO₄, use of KCl or NaCl as electrolyte was appropriate for the cleanup of aqueous methomyl via electrochemical oxidation.

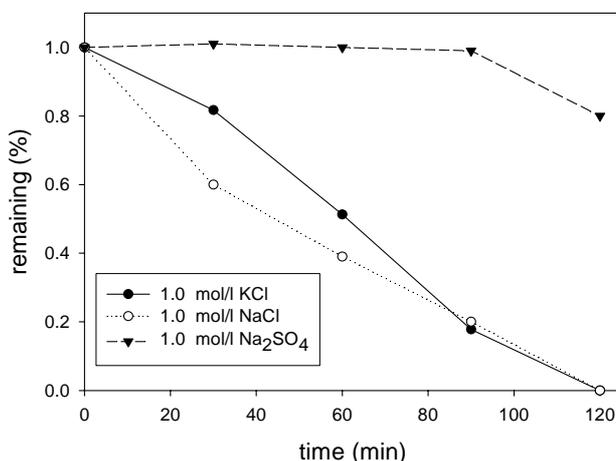


Fig.5 Degradation of methomyl using various electrolyte species during electrochemical oxidation (Operation condition : potential = 2.4 V, electrolyte : 1.0 mol/l KCl, 1.0 mol/l NaCl or 1.0 mol/l Na₂SO₄)

Effect of Aqueous Hardness

Calcium carbonate was used to prepare hard water for investigating the influence of aqueous hardness on the electrochemical oxidation of methomyl. The simulated conditions of 150 mg/l and 300 mg/l as CaCO₃ as well as the blank were used in electrochemical experiments. As shown in Fig 6, an equivalent extent of inhibition

effect on methomyl oxidation was observed in both cases of 150 mg/l and 300 mg/l as CaCO_3 . Under the environment of hard water, the observed inhibition effect can induce 30% depression of methomyl removal in Fig 6. The inhibition effect may result from the competition of methomyl and calcium ion to react with electrogenerated oxidants or the complicated chemical chain reactions with calcium. Calcium ion can be reduced and adsorbed on the electrode surface, and the fact of surface deposit on the electrode was testified from experimental observations. Besides, the absorbed deposit on the electrode can block electron transfer and reduce current efficiency, for that reason the removal of methomyl from hard water becomes more difficult via electrochemical oxidation.

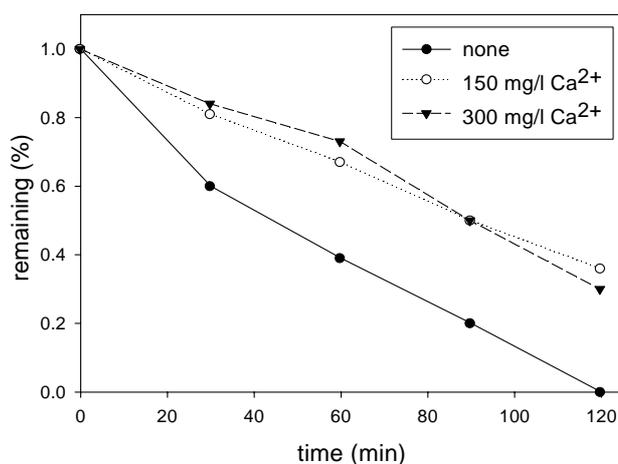


Fig.6 Degradation of methomyl in the hard water environment during electrochemical oxidation (Operation condition : potential = 2.4 V, electrolyte : 1.0 mol/l NaCl, Ca^{2+} concentration : none, 150 mg/l Ca^{2+} or 300 mg/l Ca^{2+})

CONCLUSIONS

This work studied the technical feasibility and performance of electrochemical oxidation on the Pt electrode for the treatment of aqueous methomyl. Based on the results of electrochemical experiments, several concluding remarks were summarized as follows:

- The degradation of methomyl is favorable as using concentrated electrolyte (1.0 mol/l) in the process of electrochemical treatment. The concentration of electrolyte is suggested to maintain at least 1,000 times larger than the pollutant level for attaining the efficient removal, especially operating under an insufficient oxidizing potential.
- Oxidizing potential is the determining factor for the success of the electrochemical treatment system. Different levels of oxidizing potential not only offer graded intensity of electron transfer but also initiate diverse electrochemical reactions to generate radicals and strong oxidants. In this work, the full removal of methomyl can be accomplished with the optimum oxidizing potential of 2.4V through electrochemical oxidation.
- KCl and NaCl are superior to Na_2SO_4 to serve as electrolyte for electrochemical oxidation of methomyl. Due to the participation of chloride ion in chained electrochemical reaction, electrogenerated strong oxidants (such as Cl_2 , HOCl ,

and HClO₂) can quickly oxidize aqueous methomyl and consequently improve removal efficiency.

- Under the environment of hard water, the inhibition effect on the degradation of methomyl was found about 30% reduction of removal efficiency. At the presence of calcium carbonate, the absorbed deposit could take place on the working electrode.
- Electrochemical oxidation with Pt electrodes can be successfully applied as a treatment process for the removal of aqueous methomyl. The degradation of methomyl was mainly relied on electrogenerated radicals or strong oxidants via the oxidation of water.

ACKNOWLEDGEMENTS

The partial financial support from National Science Council, Taiwan, R.O.C. under a contract No. NSC 93-2211-E-168-001 is gratefully acknowledged.

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行政院國家科學委員會補助國內專家學者出席國際學術會議報告

94 年 11 月 25 日

附件三

報告人姓名	吳庭年	服務機構 及職稱	崑山科技大學環境工程系 助理教授
時間 會議 地點	民國 94 年 11 月 7 日至 11 日，韓國 濟州島	本會核定 補助文號	NSC 94-2211-E-168-008
會議 名稱	(中文)國際水質協會水回收專家群研討會-廢水回收及永續利用 (英文)IWA Water Reuse Specialty Group Symposium on Wastewater Reclamation & Reuse for Sustainability		
發表 論文 題目	(中文)以白金電極利用電化學機制移除水中納乃得 (英文)Electrochemical Detoxification of Methomyl in Water with Pt Electrodes		
報告內容應包括下列各項： 一、參加會議經過 得知國際水質協會水回收專家群國際研討會於 2005 年 11 月 7-11 日在 韓國 濟州島 RAMADA 飯店舉行後，即積極準備投稿準備工作，本研討 會主要邀請世界各國大學教授、科學家、工程師及相關議題執業人員共同 參與，特別是希望世界各國之專家有機會可齊聚一堂，並對於水質回收及 再利用相關議題進行探討。 本屆會議蒐集世界各國學者專家口頭發表及張貼海報之論文約 600 篇，與會人員來自世界各國。會議議題涵蓋(1)Biofilm and Membrane Bio Reactor (MBR) (2)Filtration Technology (Membrane, GAC/PAC, Sand, etc.) (3)Natural System Technology (SAT, Lake/River Bank Filtration) (4)Micropollutants Measurement and Control (5)Disinfection and Oxidation for Pathogens (6)Health and Risk Assessment (7)Treatment Process Monitoring (8)Regulation, Policies, and Planning (9)Case Studies and (10)Desalination。 於 2005 年 3 月將年度內執行國科會計畫相關研究之成果整理為論文摘 要投稿，5 月接獲通知審查結果被選定為口頭發表，6 月底完成論文全文繳 交，發表之題目為：以白金電極利用電化學機制移除水中納乃得 (Electrochemical Detoxification of Methomyl in Water with Pt Electrodes)。11 月與會時，始得知本論文報告被安排在特別專題時段(Environmental Nano and Bio-Technology)，並吸引多方關注。			

二、與會心得

於 11 月 10 日在「Environmental Nano and Bio-Technology」之 Special Section (Room B) 會場進行口頭發表，發表後並蒙會場主持人 Joan Rose (U.S.) 及邀請演講者 Nosang Myung (U.S.) 提問討論，在場之學者專家一致給予本論文成果相當正面的肯定。此外，筆者亦於會議期間積極聆聽各場次之發表，尤其對於環境奈米技術議題之相關論文更感興趣，不但對相關研究課題之開發有更進一步的想法，亦吸收其他不同領域議題之技術與應用，收穫頗為豐富。

在各場次休息的茶點時間，並與多位外國專家學者就相關議題持續討論，彼此交換意見。在歡送晚宴上，更認識許多各國與會代表，不僅瞭解各國的研究發展，對於各國的風俗習慣藉由交談亦有初步認識，吸收不少新知，並增廣許多見聞。

三、考察參觀活動(無是項活動者省略)

略。

四、建議

參加國際研討會與各國專家學者進行學術交流，確實令人受益良多。本年度幸蒙國科會於核定計畫(NSC 94-2211-E-168-008)項下同意補助出席國際研討會之相關費用，本人深表感謝。惟本人近 2 年已出席 3 次國際會議(辛巴威、希臘、韓國)及 2 次兩岸會議(西安)，亦連續 2 年向國科會申請專家出席國際會議補助，但皆獲得”經費受限，歉難同意”的回答，深感申請補助的困難，尤其是那些沒有國科會計畫的學者專家。若欲學者提升研究水平及拓展國際交流，鼓勵學者專家多出席國際研討會是必要的，因此，在經費預算許可的情況下，應多提供申請者補助的機會，尤其是那些沒有資源又有心研究的專家學者(如私立科大、技術學院等)。

五、攜回資料名稱及內容

本次國際研討會會議成果相當豐碩，攜回之資料計有論文摘要乙冊、會議議程、及論文全文光碟一片。資料名稱為”WRRS2005: Wastewater Reclamation & Reuse for Sustainability”。

六、其他

略。

Electrochemical Detoxification of Methomyl in Water with Pt Electrodes

Ting Nien Wu*

*Department of Environmental Engineering, Kun Shan University, Yung-Kang City, Tainan Hsien 710, Taiwan, R.O.C. (E-mail: wutn@mail.ksut.edu.tw)

Abstract

In this study, electrochemical oxidation was proposed as a remediation method for aqueous methomyl. Lab data showed that electrolyte species instead of its concentration could significantly affect the extent and rate of oxidation. Comparing with NaCl and KCl, use of Na₂SO₄ as the electrolyte causes the low-efficiency oxidation for methomyl. Electrochemical experiments showed that the degradation of methomyl was less than 20 % at 1.2V of oxidizing potential, and it implied that 1.2V of oxidizing potential was not sufficient for continuous generation of radicals or strong oxidants in great amounts. Under the strong oxidizing potentials (above 2.4 V), the chain electrochemical reactions can be triggered to produce more radicals or strong oxidants and thus lead to a complete degradation of methomyl. During the process of electrochemical oxidation, methomyl can be successfully mineralized to carbon dioxide and water without the remaining of intermediates or by-products based upon the examination of HPLC-MS. In addition, the extent and rate of methomyl degradation appeared relatively slow at the presence of calcium. Different levels of calcium concentrations (150 mg/L and 300 mg/L) showed a similar degree of depression on methomyl degradation. Calcium ion can be reduced and adsorbed on the surface of electrode, and thus the formed electrode deposit could reduce the current efficiency and lead to the depression of methomyl degradation.

Keywords

Electrochemical oxidation, methomyl, oxidizing potential, electrode deposit

INTRODUCTION

Methomyl, one of carbamate pesticides, is widely used in agricultural applications for crop protection. The annual usage of methomyl is estimated over a thousand ton in Taiwan, and its applications cover the bug control for vegetables, tobacco, or corn. Methomyl is able to induce pesticide poisoning or fatalities, and sometimes, it is involved in suicides or homicides. For example, methomyl has been intentionally misused in a seafood-poisoning incident to injure over one hundred people at Kaohsiung (Taiwan) in 2002. Besides, pesticide residual on the vegetables is another concern for methomyl uptake via the intake of vegetables. The uptake of methomyl can induce acute poisoning by inhibiting acetylcholinesterase (AChE) activity reversibly with a subsequent accumulation of acetylcholine at peripheral and central nervous systems (WHO, 1996). Symptoms of poisoning include excessive salivation, accelerated excretion in the respiratory tract, seizures, and even death due to paralysis of the respiratory muscles (Ecobichon, 1996; Moriya and Hashimoto, 2005).

Because of their toxic characteristics, pesticides are not easily biodegradable on a regular basis. There are various innovative methodologies proposed as an alternative for the decontamination of pesticides in water such as photocatalytic oxidation, ultrasonic radiation, bioremediation, thermal desorption...etc. (Arapoglou et al., 2003). The employment of electrochemical treatment for recalcitrant toxics is especially drawing much attention recently (Vlyssides et al., 2005). Electrochemical oxidation has the advantage of high sensitivity, easy control and without secondary pollution, and also it has been successfully applied as a remedy scheme for many refractory pesticides (Brillas et al., 2000; Ventura et al., 2002) and chlorinated phenols (Brillas et al., 2003; Torres et al., 2003). Besides, electrochemical oxidation can selectively degrade contaminants to certain extent by the mechanism of electro-catalysis.

Based on wide application of electrochemical treatment, this work was aimed at developing the electrochemical methodology to solve the potential problem regarding aqueous micropollutants, such as methomyl. In this study, the treatment of aqueous methomyl by electrochemical oxidation was examined in a bench-scale cell using a Pt cathode and a Pt anode. The objective of lab work was to show the effectiveness and efficiency of methomyl removal through electrochemical treatment, and also existing lab data could be useful enough for those who intend to develop electrochemical treatment as an alternative for water purification.

MATERIALS AND METHODS

Chemicals

Methomyl powder (>90%) obtained from local agrochemical supplier (Taiwan) was used to prepare stock solution, and analytical standard of methomyl (99.9%) was purchased from Riedel-de Haen Co. Stock solutions of methomyl was made in a small aliquot of methanol and subsequently diluted with de-ionized water for immediate use. Potassium chloride (99% KCl) was obtained from Shimadzu Chemical Co. (Japan), and sodium chloride (99.5% NaCl) was obtained from Wako Chemical Co. (Japan). Sodium sulfate (99% Na₂SO₄) was obtained from Kanto Chemical Co. (Japan), and calcium carbonate (99.95% CaCO₃) was obtained from Merck Co. All reagents were prepared with de-ionized water, which was made by Mili-Q system (Millipore TK-10, USA).

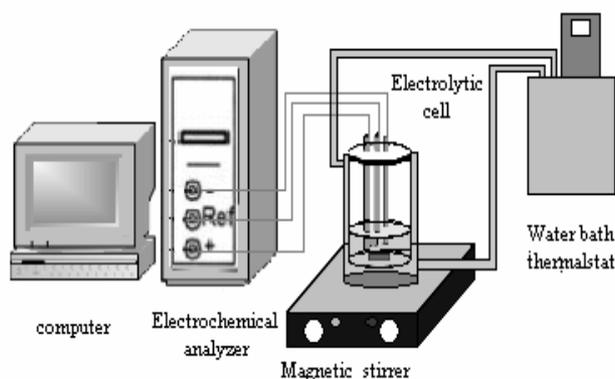


Fig.1. Experimental setup of the electrochemical treatment system

Experimental Set-up

As shown in Fig 1, a bench-scale electrochemical treatment system was utilized for the oxidation of methomyl in experiments. The electrochemical treatment system is composed of an electrochemical analyzer, an electrolytic cell, a magnetic stirrer and a thermostatic water bath. The volume of the electrolytic cell is only 14 ml, in which the cathode and the anode are placed in the same compartment. The electrolytic cell was equipped with a Pt electrode as working electrode (WE), a Pt wire as counter electrode (CE) and a saturated Ag/AgCl electrode as reference electrode (RE). The voltage source was supplied and precisely controlled by a BAS 100B Electrochemical Analyzer. During the experiment, the liquor of the reactor was completely mixed with a mini stirrer and the reaction temperature was controlled by the recycle of cooling water from the thermostatic water bath.

Oxidation Experiments

Lab works were focused on the technical feasibility and performance of electrochemical oxidation of methomyl at a bench-scale reactor. The initial concentration of 100 mg/l methomyl (about 0.617mM) was prepared in solute to simulate pesticide contamination of potable water each run.

For the ease of electrochemical reaction, three electrolytes including KCl, NaCl and Na₂SO₄ were employed in batch experiments. The oxidation of methomyl was investigated under various electrolytes and also compared at different electrolyte concentrations. Only single electrolyte was used each run and its concentration was maintained at least 0.1 mol/l in the electrolytic cell. Oxidation experiments were carried out at a constant operating voltage in the range of 1.2 V and 3.0 V. Before each oxidation experiment, working electrode was cleaned with tiny 0.05 μm aluminum powder by remittently wet-polishing to rub out adsorbed deposits on the electrode surface. Reference electrode was immersed in 3 mol/l KCl solution to maintain its saturated status while not in use. Each run was lasted for 120 minutes and sampled with a syringe every 30 minutes. The sampled liquor was instantly subjected to the analysis of high performance liquid chromatography (HPLC) for the determination of methomyl concentration. Based on HPLC chromatogram, several selected samples were further analyzed by high performance liquid chromatography/ mass spectrometry (HPLC/MS) to identify byproducts or intermediates of methomyl degradation.

Sample Analysis

Following Taiwan EPA standard analysis method NIEA W633.50A (Taiwan EPA, 1994), the analysis of methomyl was implemented by reverse-phase high performance liquid chromatography with UV detection (HPLC-UV). The HPLC-UV system was mainly composed of a Hitachi L-7100 LC pumping module, a Hitachi L-7420 UV diode array detector and a Mightysil 5 μm-C18, 4.6mm × 250mm RP column. The detector wavelength was set at 254nm as reference. The mobile-phase composition was maintained at a 25 / 75 ratio of methanol and water, and the mobile-phase flow was controlled at 1 ml/min. Under these analytical operations, the retention time of methomyl occurred at 8.5 min on the HPLC chromatogram. Methomyl standard solutions were prepared in water in a concentration range of 0.5 mg/l and 120mg/l.

RESULTS AND DISCUSSION

Effect of Electrolyte Concentration

Platinum electrodes were concurrently used as both cathode and anode in the proposed electrochemical reactor. As using a high oxygen overvoltage anode, hydroxyl radical can be generated through the oxidation of water (Panizza et al., 2000). The electrogenerated hydroxyl radical was first absorbed on the active sites of the electrode surface, and the absorbed hydroxyl radical was subsequently released to oxidize aqueous pollutant in solute (Vlyssides et al., 2005). The occurring electrochemical reactions within the electrolytic cell are complicated and not entirely known. According to the result of HPLC/MS analysis, there was no aqueous intermediate identified during the electrolysis of methomyl. The complete mineralization of methomyl was logically assumed, in other word, the oxidation products of methomyl are carbon dioxide, nitrate and sulfate.

Thus, the mechanism of direct oxidation of methomyl was proposed as follows:



Based on the analysis of cyclic voltammetry, electrochemical experiments were performed at a constant oxidizing potential of 1.2 V in order to conduct the oxidation of water. As using three levels of electrolyte concentrations, the degradation of methomyl during electrochemical experiments was compared in Fig 2. It is clear that a slow degradation of methomyl can be achieved under all electrolyte concentrations, however the removal efficiency is more significant when using 1.0 mol/l KCl as electrolyte. Therefore, the electrolyte concentration had better to maintain at least 1,000 times larger than the pollutant level for supporting effective electron transfer in aqueous

solution. As observed in Fig 2, the limited degradation of methomyl seems to point to the inadequacy of oxidizing potential during electrochemical experiments. Under oxidizing potential of 1.2 V, the oxidation of water generates oxygen instead of hydroxyl radical as shown in reaction (3). Oxygen, as an oxidant, can diffuse away from the electrode to carry on indirect oxidation of methomyl in solute.

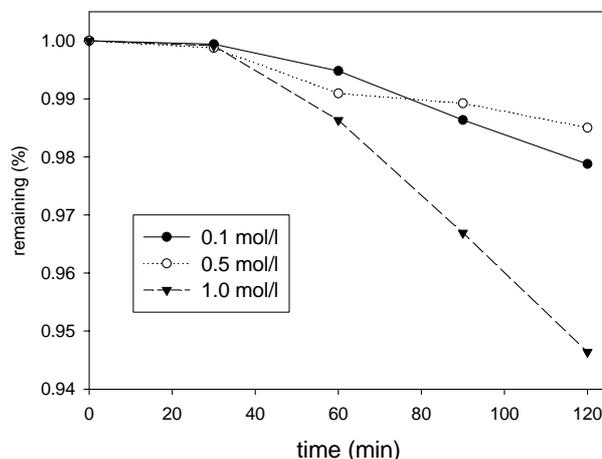


Fig.2 Degradation of methomyl under various electrolyte concentrations during electrochemical oxidation (Operation condition : potential = 1.2 V, electrolyte : 0.1 mol/l KCl, 0.5 mol/l KCl or 1.0 mol/l KCl)

Effect of Oxidizing Potential

As can be seen in Fig 3, the degradation of methomyl is greatly enhanced as the supplied potential reaching 1.8V or above. At the presence of chloride ion, the involved electrochemical reactions can produce strong oxidants (such as Cl_2 , HOCl , HClO_2 and O_3) to oxidize aqueous methomyl. Because these electrogenerated oxidants have stronger oxidizing potentials than oxygen, the observed degradation of methomyl was greatly improved as operating potential above 1.8V. These involved electrochemical reactions may be giving by the following:



As using 0.1 mol/l KCl as electrolyte, a complete degradation of methomyl was observed after 2 hours of electrochemical oxidation under oxidizing potential of 2.4V. However, a continual increase of oxidizing potential to 3.0V did not result in a rapid degradation rate during electrochemical oxidation in Fig 3a. The possible deduction is that the oxidation of water may produce hydroxyl radical under oxidizing potential of 3.0V as the mechanism of reaction (1) and simultaneously induce the generation of other oxidants as the mechanism of reaction (3) to reaction (7), however the self-scavenging reaction can be triggered around the electrode to consume the electrogenerated oxidants due to the strong oxidizing potential of hydroxyl radical.

In Fig3b, the ascending trend of methomyl degradation is obvious with intensifying oxidizing potential of electrochemical oxidation. The optimum oxidizing potential was found around 2.4V for

attaining satisfied removal efficiency through electrochemical oxidation. Under this optimum oxidizing potential (2.4V), complete degradation of methomyl can be achieved for both cases of concentrated electrolyte (1.0 mol/l KCl) and diluted electrolyte (0.1 mol/l KCl). As shown in Fig 4, an intensive specific degradation rate of methomyl is correspondent to the case using concentrated electrolyte and vice versa. This observation indicated that concentrated electrolyte can support the undergoing of electrochemical oxidation but oxidizing potential is the determining factor for the success of the proposed treatment system.

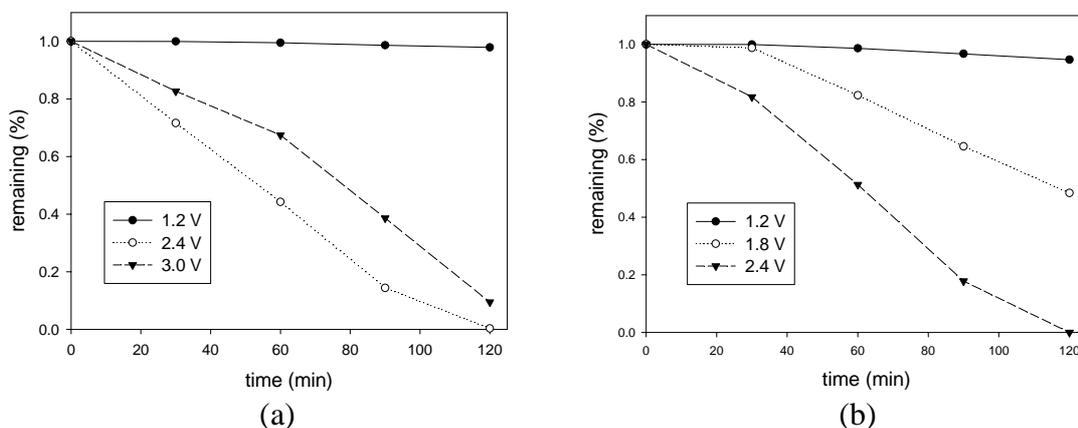


Fig.3 Degradation of methomyl under various voltage supplies during electrochemical oxidation (Operation condition : (a)potential = 1.2 V, 2.4 V or 3.0 V, electrolyte : 0.1 mol/l KCl; (b) potential = 1.2 V, 1.8 V or 2.4 V, electrolyte : 1.0 mol/l KCl)

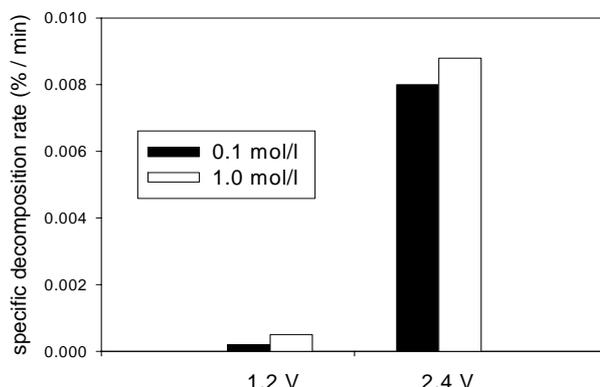


Fig.4 Comparison of specific degradation rate of methomyl under various voltage supplies and electrolyte levels

Effect of Electrolyte Species

In this study, three common electrolytes including KCl, NaCl and Na₂SO₄ were tested under the optimum oxidizing potential. As it is observed from Fig 5, there was no remaining methomyl detected in the both cases of KCl and NaCl. In the case of Na₂SO₄, the performance of methomyl removal was very poor. As mentioned previously, KCl and NaCl can initiate the mediated reactions to produce strong oxidants Cl₂, HOCl and HClO₂ that play a crucial role in electrochemical oxidation of methomyl. Comparing with Na₂SO₄, use of KCl or NaCl as electrolyte was appropriate for the cleanup of aqueous methomyl via electrochemical oxidation.

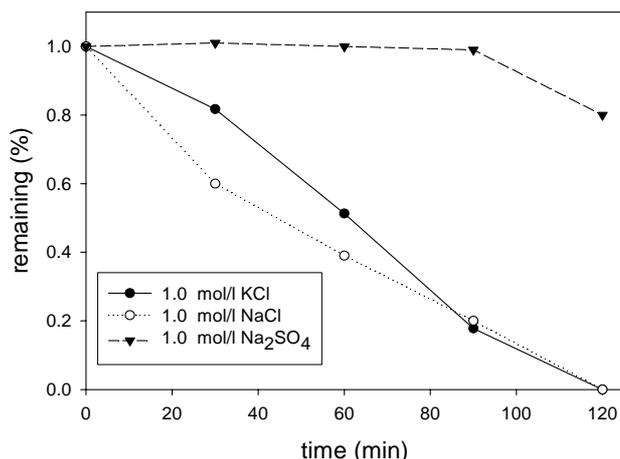


Fig.5 Degradation of methomyl using various electrolyte species during electrochemical oxidation (Operation condition : potential = 2.4 V, electrolyte : 1.0 mol/l KCl, 1.0 mol/l NaCl or 1.0 mol/l Na₂SO₄)

Effect of Aqueous Hardness

Calcium carbonate was used to prepare hard water for investigating the influence of aqueous hardness on the electrochemical oxidation of methomyl. The simulated conditions of 150 mg/l and 300 mg/l as CaCO₃ as well as the blank were used in electrochemical experiments. As shown in Fig 6, an equivalent extent of inhibition effect on methomyl oxidation was observed in both cases of 150 mg/l and 300 mg/l as CaCO₃. Under the environment of hard water, the observed inhibition effect can induce 30% depression of methomyl removal in Fig 6. The inhibition effect may result from the competition of methomyl and calcium ion to react with electrogenerated oxidants or the complicated chemical chain reactions with calcium. Calcium ion can be reduced and adsorbed on the electrode surface, and the fact of surface deposit on the electrode was testified from experimental observations. Besides, the absorbed deposit on the electrode can block electron transfer and reduce current efficiency, for that reason the removal of methomyl from hard water becomes more difficult via electrochemical oxidation.

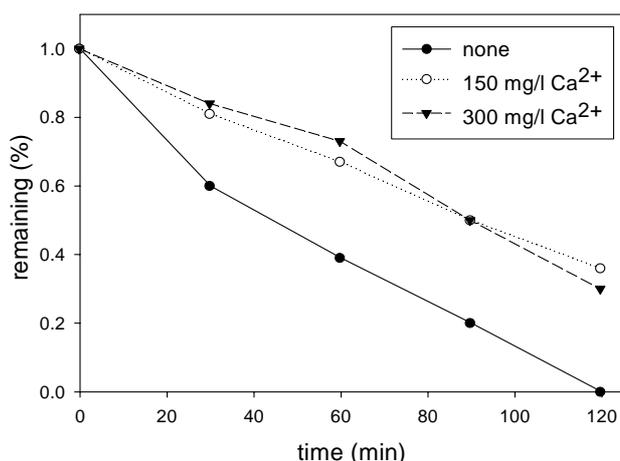


Fig.6 Degradation of methomyl in the hard water environment during electrochemical oxidation (Operation condition : potential = 2.4 V, electrolyte : 1.0 mol/l NaCl, Ca²⁺ concentration : none, 150 mg/l Ca²⁺ or 300 mg/l Ca²⁺)

CONCLUSIONS

This work studied the technical feasibility and performance of electrochemical oxidation on the Pt electrode for the treatment of aqueous methomyl. Based on the results of electrochemical experiments, several concluding remarks were summarized as follows:

- The degradation of methomyl is favorable as using concentrated electrolyte (1.0 mol/l) in the process of electrochemical treatment. The concentration of electrolyte is suggested to maintain at least 1,000 times larger than the pollutant level for attaining the efficient removal, especially operating under an insufficient oxidizing potential.
- Oxidizing potential is the determining factor for the success of the electrochemical treatment system. Different levels of oxidizing potential not only offer graded intensity of electron transfer but also initiate diverse electrochemical reactions to generate radicals and strong oxidants. In this work, the full removal of methomyl can be accomplished with the optimum oxidizing potential of 2.4V through electrochemical oxidation.
- KCl and NaCl are superior to Na₂SO₄ to serve as electrolyte for electrochemical oxidation of methomyl. Due to the participation of chloride ion in chained electrochemical reaction, electrogenerated strong oxidants (such as Cl₂, HOCl, and HClO₂) can quickly oxidize aqueous methomyl and consequently improve removal efficiency.
- Under the environment of hard water, the inhibition effect on the degradation of methomyl was found about 30% reduction of removal efficiency. At the presence of calcium carbonate, the absorbed deposit could take place on the working electrode.
- Electrochemical oxidation with Pt electrodes can be successfully applied as a treatment process for the removal of aqueous methomyl. The degradation of methomyl was mainly relied on electrogenerated radicals or strong oxidants via the oxidation of water.

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