National Ilan University
國立宜蘭大學工程學刊第 8 期 29-41 頁，2012 年 12 月
Bulletin of College of Engineering National Ilan University No. 8, P. 29-41, December 2012
Bulletin of College of Engineering
http://engineering.niu.edu.tw/main.php

以廚餘堆肥化之液肥復育鋅污染土壤與地力回復之研究

林文經[1*] 林文修[1] 李元陞[2] 劉鎮宗[3]

1.宜蘭大學環境工程學系（所）研究生

2.宜蘭大學環境工程學系（所）教授

3.宜蘭大學環境工程學系（所）副教授

摘要

使用酸洗法處理重金屬污染之土壤是一種常見的方式；雖可移除重金屬，但也造成土壤中原有的營養元素因酸洗流失，而影響農作物之生長與生產力。本研究以廚餘液肥，作為土壤整治之清洗液來復育鋅污染土壤，過程中能將液肥所含肥力留存於土壤中減少肥分損失。以 pH 2.0 液肥清洗液清洗二次後，表土及裡土鋅的移除率分別達 45% 及 23%，可符合 600 mg Zn kg^{-1} 之食用農地管制標準。比較其肥力變化；經酸性水溶液清洗後之土壤肥力均明顯低於原土樣，而經液肥清洗後土壤肥力明顯提升；表土及裡土之有機質分別增加 5.0%及 7.5%、銨態氮分別增加 120%及 40%、有效性磷分別增加 65% 與 63%、交換性鉀分別增加 153% 與 499%。

關鍵詞：鋅、土壤肥力、廚餘液肥、土壤清洗法

***通訊作者 E-mail：linwinjen@yahoo.com.tw**

National Ilan University
國立宜蘭大學工程學刊第 8 期，29-41 頁，2012 年 12 月
Bulletin of College of Engineering National Ilan University No. 8, P. 29-41, December 2012
Bulletin of College of Engineering
http://engineering.niu.edu.tw/main.php

Reclamation of Zinc-contaminated Soil Using Dissolved Organic Matter Solution Prepared from Liquid Fertilizer of Food Waste Composting

Wen-Jing Lin[1*], Wen-hsiu Lin[1], Yuan-sheng Li[2], Cheng-Chung Liu[3]

1. Graduate Student, National Ilan University, Department of Environmental Engineering
2. Professor, National Ilan University, Department of Environmental Engineering
3. Associate Professor, National Ilan University, Department of Environmental Engineering

ABSTRACT

Soil washing using an acid solution is a common practice for removing heavy metals from contaminated soil in Taiwan. However, significant soil fertility degradation and high operation costs are the major disadvantages of soil washing. Washing soil with a dissolved organic matter (DOM) solution has been identified as a method that can moderate the loss of nutrients in the soil and enhance metal removal. Liquid fertilizer of food waste composting can be used to prepare a dissolved organic matter (DOM) solution. This study employed DOM solutions to remediate Zn-contaminated soil (with concentrations up to 992 and 757 mg kg^{-1} respectively in topsoil and subsoil) and determine the factors affecting removal of Zn, such as pH, initial concentration of DOM solution, temperature, and washing frequency. When washing with pH 2.0 and 1,500 mg L^{-1} DOM solution twice, about 45% and 23% of Zn were removed from the topsoil and subsoil at 25°C, respectively. With this treatment, the increase in organic matter content ranged from 5.0% to 7.5%; available ammonium ($N\text{-}NH_4$) content ranged from 47% to 140%; available phosphorus content ranged from 63% to 65%; and exchangeable potassium content ranged from 153% to 499%.

Keywords: Zinc, Soil fertility, Liquid fertilizer, Soil washing

***Corresponding author E-mail: linwinjen@yahoo.com.tw**

一、前言

近年來因工商業迅速發展及人類經濟的活動，不肖廠商任意將含重金屬的廢水排放到水體中，農民取用此水源灌溉時造成農地品質惡化。土壤一旦遭受破壞或污染，很難恢復原來的功能（許正一，2000）。復育受重金屬污染土壤之技術，包括 (1) 化學處理法(包括萃取法、安定化法) (2) 工程技術法(包括排土與客土法、現地淋洗土壤法、現地電熔法等)；及 (3) 生物處理法(即植生攝取法、植生綠化法等)(陳尊賢，2003)。雖然許多土壤復育技術可用於重金屬污染土壤之整治，但並不一定可將重金屬含量降低至可繼續農作之目標。淋洗法不僅可有效移除土壤重金屬，其他優點還包括有較佳之經濟效益及僅需著重於特定的粒徑，可適當的減少處理量、可循環與再利用現地物質等優點(陳尊賢，2008)。但此法對土壤性質之破壞較其他整治技術為大，造成之影響如土壤 pH 值降低時溶解大量的鐵、鋁、錳，對作物造成毒害。再者當土壤變酸時會致使磷與鐵、鋁結合形成不溶解性之磷酸鐵與磷酸鋁等化合物，有礙作物對磷之吸收，並使土壤中鈣、鉀、鎂等元素流失。此外在酸性土壤中分解有機物之放射菌及細菌、固氮菌、硝化細菌等，其繁殖活性會受阻，影響作物之生育及產量(羅秋雄，2002)。其他研究也指出，土壤以鹽酸進行淋洗後，容易造成土壤酸化及土壤組成流失，且對土壤之有機質、化學性質以及土壤微生物族群及活力會造成極大之影響，而使整治後的土壤有不適合再耕作之問題(陳尊賢，2003；Brewster et al, 1994)。因此復育之土壤若要回復於農用，有必要對原有處理技術加以改良。由於民生富裕與國人之飲食習慣，在日常生活所產生的垃圾中，含有極高比例的「廚餘」，約佔一般家庭垃圾量的二至三成，而一般廚餘的處置多以衛生掩埋、堆肥或焚化為主，造成掩埋場或焚化廠的負擔。「廚餘」若能回收再利用，不但可減輕垃圾處理壓力，並降低垃圾掩埋場臭味與滲出水之污染，以及紓緩垃圾焚化廠廢氣排放問題(行政院環境保護署，2008)，而「廚餘液肥」為廚餘回收後經前處理與發酵，成為穩定化堆肥過程中所滲出之『液肥』，目前廚餘液肥的用途除了使用於農作物之施肥及植物增強抗病蟲害能力與產能外並無其他再利用方式。先前已有研究以酒廠污泥所含之高濃度有機質進行復育重金屬污染土壤之研究，且證實以有機質吸附重金屬之機制，具有相當成效(劉鎮宗，2007；陳冠步，2010；林盈蓁，2011；林文修、林文經，2012)；研究中遂以廚餘堆肥發酵過程中所產生含高濃度有機質的之液肥，進行鋅污染農地之清洗復育試驗，為液肥的再利用途徑進行驗證。鋅(Zinc, Zn)在人體含量約佔體重的 0.003%，相當於成人體內約有 2 公克鋅。90% 的鋅都存在肌肉與骨骼中，其餘

10% 在血中扮演舉足輕重的角色。鋅缺乏會導致免疫力低下、食慾不振、生長減緩、下痢、掉髮、夜盲、前列腺肥大、男性生殖功能減退、動脈硬化、貧血等問題。鋅也是人體之必需元素，一般生物對其耐受性皆高，但攝取過量的鋅同樣會造成毒害。食入高量的鋅(300 mg 以上)會產生腸胃不適、頭痛、視覺受影響等症狀、嚴重者可能會休克(陳建民，2008)。

本研究目的為：(1) 探究液肥清洗液對鋅的移除效率 (2) 比較液肥清洗與傳統酸洗對土壤基本性質的差異(3)建立以廚餘液肥復育受重金屬污染土壤的最佳操作參數。

二、材料與方法

本研究使用的土壤樣本採集自彰化縣嚴重鋅污染且未經整治之農田場址(TMD97 座標：203594, 2661464)，採樣時以適當間距將採樣區內相距一公尺之五個不同採樣點的土壤混合，以取得區域內的平均濃度，經風乾、磨碎，過 2.0 mm 篩網後裝罐儲存，作為建立最佳試劑萃取試驗之供試土樣。經王水消化處理後測得此土壤的表土鋅濃度 992 mg Zn kg^{-1}；裡土 757 mg Zn kg^{-1}；因此整治時鋅的移除率，須分別達到表土 40% 以及裡土 21%以上，才可使其鋅含量降低至食用作物農地之管制標準(600 mg Zn kg^{-1})。

表 1. 原始廚餘液肥之化學組成與性質

pH		7.42
TOC	mg L^{-1}	7914
K	mg L^{-1}	3663
Na	mg L^{-1}	917
Ca	mg L^{-1}	16.3
Mg	mg L^{-1}	0.008
Fe	mg L^{-1}	0.079
P	mg L^{-1}	38.8

本研究使用之廚餘堆肥化液肥取自宜蘭縣羅東鎮有機廢棄物處理廠，其廚餘經分選、破碎、脫水、添加木屑做為介質後，再經前發酵、後發酵過程，在穩定化堆肥過程中所滲出之『液肥』，由其化學組成與性質(表 1)中得知廚餘液肥含有高濃度的有機質及氮、磷、鉀等營養元素，但其中的鈣與鎂含量則偏低。液肥原液的總有機碳(Total organic carbon, TOC)為 7914 mg L^{-1}，在適度稀釋後作為土壤重金屬污染復育之清洗液。由土壤清洗之預備實驗分別確認出具最佳移除效率之 pH、有機質濃度、固液比、時間、溫度等之清洗條件。經預備實驗得知，當液肥濃度 TOC＞1500 mg L^{-1} 以上時，移除率無明顯提升，因此在考慮液肥萃取液稀釋用量之經濟性以及可達管制標準移除率之先決條件下，將污染物最佳移除效率萃取試驗條件確立為：TOC 1500 mg L^{-1}、反應萃取時間 30 min、固液比(S / L) 1：40、反應溫度 25℃，調整 pH 並分別比較液肥清洗液及水溶液之移除效率與清洗後各項土壤肥力的變化。

研究中以不同萃取液種類比較污染土壤中鋅的移除率：將 3.0 g 受鋅污染之土壤置入 250 ml 血清瓶內，分別加入表 2 中所列之萃取液，置於往復式振盪機反應(150 rpm)及離心過濾處理(Whatman No. 42 濾紙)後，以火焰式原子吸收光譜儀(機型 GBC 932 plus)測定濾液鋅含量，並以清洗液中的鋅含量來推算重金屬移除率。確認清洗效率後，依據相同清洗條件製備清洗後肥力分析土樣，再將土樣利用酒精清除土樣孔隙中多餘的離子後，進行處理前、後的土壤肥力變化分析，項目包括：pH、有機質(Organic matter, OM)、陽離子交換容量(Cation exchange capacity, CEC)、電導度(EC)、有效性磷(P)、交換性鉀(K)、交換性鈉(Na)、鈣/鎂比等。各項肥力分析項目及方法如表 3 所示。

表 2. 清洗液種類

類別	清洗液內容
A	pH 2.0~12.0 之水溶液
B	pH 2.0~12.0 之液肥清洗液(1500 mg L^{-1})

萃取條件: S/L= 1:40，Temperature= 25℃，rpm=150，Time= 30 min

表 3. 土壤肥力檢測項目及方法

分析項目	測定方法
土壤質地	吸管法
pH	電極法(NIEA S410.62C)
有機質(Organic matter)	濕氧法-中華土壤肥料協會-土壤與肥料分析手冊
陽離子交換容量(CEC)	醋酸鈉法(NIEA S202.60A)
電導度(EC)	電導度計法(NIEA S203.51B)
有效性磷(P)	白雷氏第一法-中華土壤肥料協會-土壤與肥料分析手冊
交換性鉀(K)	中性醋酸銨(1M)萃取法-土壤與肥料分析手冊
交換性鈉(Na)	中性醋酸銨(1M)萃取法-土壤與肥料分析手冊
鈣/鎂比	中性醋酸銨(1M)萃取法-土壤與肥料分析手冊

三、 結果與討論

本研究中以廚餘液肥做為處理鋅污染土壤之清洗液，其處理機制是利用液肥高含量有機質做為螯合劑，萃取吸附於土壤粒子上的鋅，而液肥中所含之有機質的羧基是其吸附重金屬最重要的官能基 (劉鎮宗，2007)，並且有機物質可作為載體並形成有機金屬化合物，促使金屬從土壤中移轉出來(Lamy et al, 1993)。

由圖 1 顯示液肥清洗液之紅外線光譜位於 3383 cm^{-1} 間寬廣吸收帶是由水的官能基(－OH)所致，1637cm^{-1} 附近的強吸收是由羰基和 COO^- 振動共軛之雙鍵對稱性的伸縮所造成，其中位於 1152 cm^{-1} 可能為為典型醣類連結的 C－C，C－OH，C－O－C，多醣類 C－O 伸縮之明顯吸收帶，在 1093 cm^{-1} 附近的吸收帶則可能與微生物細胞壁上的幾丁質、甲殼素或蛋白質中 C－N 之伸縮運動有關，在 1402 cm^{-1} 之吸收為羧基(－COOH)、酚基(phenolic OH)等官能基所致。

其中羧基(－COOH)、酚基(phenolic OH)等官能基之產生能對金屬離子產生吸附作用(林永鴻，2008)。並有文獻指出胺基(－NH_2)和羥基(－OH)，可利用於物理或化學吸附上；此外藉由胺基其孤對電子和過渡金屬離子產生配位共價鍵，對金屬離子具有螯合功用 (Aly et al.,1997)，也佐證了液肥清洗液所含之有機物質確有萃取土壤中重金屬離子的作用。

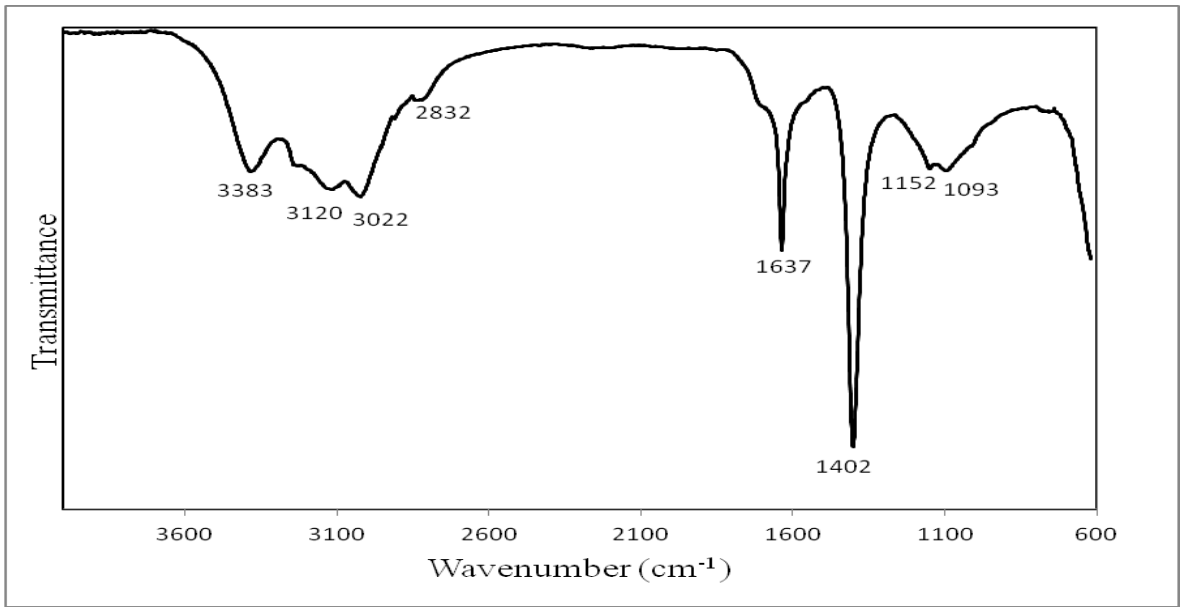


圖 1. 液肥清洗液之 FT-IR 傅立葉轉換紅外線光譜

表 4. FT-IR 傅立葉轉換紅外線光譜主要吸收峰之鑑識

波 數 cm^{-1}	波 長 μm	官 能 基 鑑 識
3400～3300	3.94～3.03	OH 和 N－H 的伸縮
3380	2.950	氫鍵的 OH
2985	3.35	CH_3 和 CH_2 的伸縮
2940～2900	3.40～3.44	脂肪族 C－H 的伸縮
1725～1720	5.79～5.81	COOH 官能基中 C＝O 的伸縮
1650～1630	6.00～6.10	第一級胺中 C＝O 的伸縮，芳香族 C＝C，H 鍵結之 C＝O，與羰基和 COO^- 振動共軛之雙鍵
1650～1613	6.00～6.19	COO^- 對稱性的伸縮
1460	6.85	脂肪族的 C－H，CC-H_3
1440	6.95	甲基中之 CH 的伸縮
1435	6.97	C－H 彎曲
1400	7.14	COO^- 非對稱性的伸縮
1390	7.20	COOH 的鹽類
1280～1230	7.80～8.10	C－O 伸縮，芳香族的 C-O，酯類的 C-O，以及酚類的 C－OH
1170～950	8.50～10.5	典型醣類連結的 C－C，C－OH，C－O－C。Si－O 不純物，多醣類 C－O 伸縮
1035	9.67	O－CH_3 的振動
840	11.9	芳香族 C－H 的振動

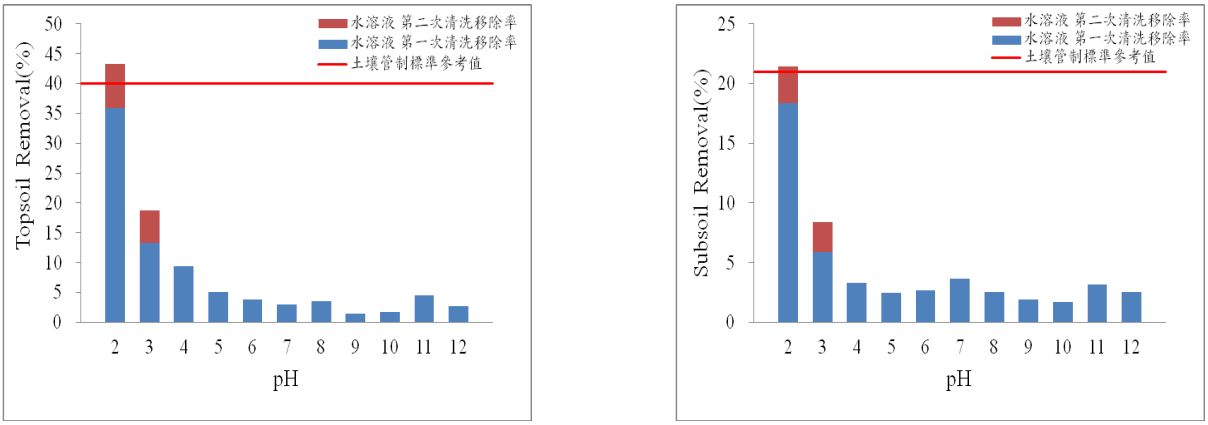
(Tan, 1994; Stevenson, 1994)

比較以相同 pH 2.0 的液肥清洗液(表 2A)與水溶液(表 2B)，清洗復育鋅污染土壤樣本，經第一次清洗時，水溶液處理之移除率表土為 36 %，裡土為 18 % (圖 2)；經液肥清洗液處理之移除率表土為 37 %，裡土為 20 % (圖 3)，均未能達到食用農地管制標準(表土 40 %、裡土 21 %)，遂再以相同萃取條件進行第二次清洗，經第二次清洗後水溶液累計之總移除率，表土為 43 %，裡土為 21 %；液肥清洗液累計之總移除率，表土為 45 %、裡土為 23 %。顯示經二次清洗後，液肥與水溶液萃取液之移除率皆可符合管制標準，且液肥清洗液之總移除率皆高於水溶液。而以 pH 3.0 以上的液肥清洗液與水溶液進行清洗，則土壤中鋅的移除率皆無法降至管制標準以下。

檢視液肥與水溶液清洗液在 pH 2 ~ 12 各區段之移除率 (圖 2 和 圖 3)，均以 pH 2.0 之清洗效果最佳，但移除率隨 pH 的上升而下降，尤其以水溶液之移除率在 pH 3.0 以上的下降趨勢最為明顯；其餘 pH 2 ~ 5 與 pH 8 ~ 12 之區段，液肥清洗液之移除效率皆較水溶液為佳。值得注意的是，水溶液在 pH 3 ~ 4 之移除率甚至急遽下降到不到液肥清洗液的一半，也證實了液肥在酸性環境下有強化移除率的貢獻。而堆肥液肥對重金屬之吸附機制為其富含之有機質中的腐植酸具有羧基碳結構，因表面帶負電而可吸附帶正電之重金屬離子(林永鴻，2008)；其中－COO^-及－COOH 與重金屬離子發生錯合作用的機制如下(劉鎮宗，2007)：

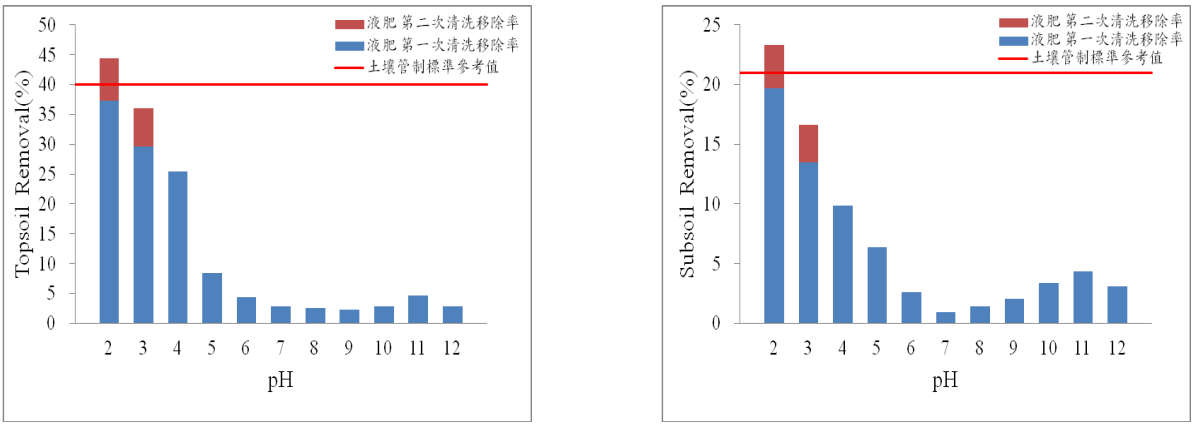
$$R－COO^- + Zn^{2+} \rightarrow R－COO\ Zn^{2+}$$

$$R－NH_2 + Zn^{2+} \rightarrow Zn\ (R－NH_2)^{2+}$$



(a) 表土　　(b) 裡土

圖 2. 不同 pH 水溶液對中鋅之移除率(S/L=1:40，Tamperture=25℃，rpm=150，Time=30min)



（a）表土　　（b）裡土

圖 3. 不同 pH 液肥清洗液對中鋅之移除率(TOC= 1500 mg L^{-1}，S/L=1:40，Tamperture= 25℃，rpm= 150，Time= 30 min)

表 5. 廚餘堆肥化液肥-清洗(表土層)後的土壤性質及肥力變化(1500 mg L^{-1}, 25℃, 30 min, S/L 1:40)

表土	Unit	Original soil	pH 2 /液肥	pH 2 /Water	pH 3 /液肥	pH3 /Water
Zn (1st washing)	mg kg^{-1}	992	622	636	698	698
Zn (2nd washing)	mg kg^{-1}	---	550	563	634	644
pH		5.4	4.1	3.4	4.8	4.3
Organic matter	%	6.2	6.5	5.3	6.9	5.3
CEC	$cmol_c$ kg^{-1}	13.4	11.7	11.0	12.9	11.3
$EC_{1:5}$	dS m^{-1}	0.15	0.10	0.06	0.08	0.02
NH_4^+-N	%	0.05	0.11	0.01	0.14	0.02
Available P	mg kg^{-1}	3.77	6.21	2.70	8.05	3.31
Exchangeable K	mg kg^{-1}	580	1470	150	1660	218
Exchangeable Na	mg kg^{-1}	155	97	56	122	79
Exchangeable Ca	$cmol_c$ kg^{-1}	3.13	0.85	1.59	0.3	0.45
Exchangeable Mg	$cmol_c$ kg^{-1}	0.66	0.35	0.39	0.16	0.32
Ca^{2+}/Mg^{2+}		4.7:1	2.4:1	4.1:1	1.98:1	1.4:1
ESP	%	2.17	1.33	1.31	1.57	1.43

食用作物農地管制標準 600 mg Zn kg^{-1}

表 6. 廚餘堆肥化液肥-清洗(裡土層)後的土壤性質及肥力變化(1500 mg L^{-1}, 25℃, 30 min, S/L 1:40)

裡土	Unit	Original soil	pH 2 /液肥	pH 2 /Water	pH 3 /液肥	pH3 /Water
Zn (1st washing)	mg kg^{-1}	757	608	618	655	655
Zn (2nd washing)	mg kg^{-1}	---	580	594	631	636
pH		5.2	4.2	3.6	4.6	4.4
Organic matter	%	4.0	4.3	3.1	4.8	3.7
CEC	C mol_c kg^{-1}	11.5	11.2	10.0	13.5	10.1
$EC_{1:5}$	dS m^{-1}	0.08	0.06	0.05	0.07	0.02
NH_4^+-N	%	0.05	0.07	0.03	0.08	0.05
Available P	mg kg^{-1}	3.16	5.15	2.55	6.98	2.85
Exchangeable K	mg kg^{-1}	242	1450	155	1620	177
Exchangeable Na	mg kg^{-1}	168	90	83	116	93
Exchangeable Ca	$cmol_c$ kg^{-1}	3.07	1.07	1.25	0.33	0.58
Exchangeable Mg	$cmol_c$ kg^{-1}	0.72	0.32	0.34	0.1	0.22
Ca_2^+/Mg_2^+		4.3:1	3.3:1	3.7:1	3.3:1	2.6:1
ESP	%	2.35	1.51	1.04	1.57	1.35

食用作物農地管制標準 600 mg Zn kg^{-1}

比較以 pH 2.0 液肥及水溶液復育後土壤地力變化之結果，分別詳見於表 5 與表 6。液肥清洗後：銨態氮表土增加了 1.2 倍，裡土增加 0.4 倍；有效性磷表土增加 0.65 倍，裡土增加了 0.63 倍；交換性鉀表土則增加 1.53 倍；裡土增加 4.99 倍；僅交換性鈉及鈣、鎂則有部分流失；交換性鈉表土減少 0.4 倍，裡土則減少 0.46 倍；鈣鎂比表土減少 0.49 倍，裡土則減少 0.13 倍。其鈣鎂比減少原因，推測為清洗過程中土粒上的 Ca^{2+}和 Mg^{2+}被大量的析出、脫附所致；而液肥清洗後之土壤其 Ca^{2+}和 Mg^{2+}無法提升的原因，可能為液肥原液中所含之 Ca^{2+}和 Mg^{2+}不足之因素所致。而另外比較以 pH 2.0 水溶液清洗後之土壤肥力：銨態氮表土降低了 0.8 倍，裡土降低 0.4 倍；有效性磷表土降低 0.28 倍，裡土降低了 0.19 倍；交換性鉀表土則降低 0.9 倍；裡土降低了 0.36 倍；交換性鈉表土減少 0.67 倍，裡土則減少 0.51 倍；鈣鎂比表土減少 0.23 倍，裡土則減少 0.14 倍。另外鈉飽和度（Exchangeable Sodium Percentage，簡稱 ESP）是指土壤溶液中鈉離子佔總陽離子之當量濃度的百分比。鈉可使土粒分散，並可能使土壤結構緊密，造成透水性降低，導致排水不良等，土壤中鈉飽和度愈大，愈易使土壤趨向於鹼性反應。當鈉飽和度大於 15 就可視為鹼土，因此鈉離子含量增多對土壤有害 (謝兆申、王明果，1995；Brady, 2002)。淋洗後土壤中的 Na^+離子因酸洗而流失，因此鈉飽和度皆有降低：表土降低 0.39

倍，裡土降低 0.36 倍；而以水溶液酸洗者尤其嚴重分別降低了 0.4 倍及 0.56 倍。另外以 pH 3.0 液肥及水溶液清洗後土壤中的鋅含量雖均未能達到管制標準，但其各項土壤肥力以 pH 3.0 溶液清洗皆較以 pH 2.0 溶液清洗者為高；其中以水溶液清洗者其表土與裡土：有機質高出 0～22%；銨態氮高出 67～100%；有效性磷高出 23～120%；交換性鉀高出 14～45%；交換性鈉則高出 12～41%；而以液肥清洗者其表土與裡土之有機質高出 6～13%、銨態氮高出 14～27%、有效性磷高出 30～36%；交換性鉀高出 12～13%；交換性鈉則高出 26～29%；顯示以 pH 越低的清洗液清洗者，其土壤肥力流失情形愈嚴重。以上結果顯示，以水溶液清洗後土樣各項肥力都有大量流失情形；而以液肥清洗之土壤肥力流失情形則有明顯改善，僅在交換性鈉及鈣、鎂略有流失，其他肥力如銨態氮、有效性磷、交換性鉀等含量則皆有顯著提升。證實使用經液肥溶液清洗後，可將土壤鋅濃度降至管制值標準，並有助於土壤肥力之維持。

四、 結 論

本研究在妥善復育受鋅污染土壤的前提下，驗證了經二次的液肥溶液（pH 2.0）清洗後，表土及裡土層中鋅含量最後分別降至 550 mg kg^{-1} 及 580 mg kg^{-1}，符合食用農地管制標準，也證實了廚餘液肥在清洗時，可利用其富含之有機質中的羧基碳結構及羥基與胺基等官能基，對金屬離子產生螯合、吸附作用，有效的萃取土壤中的重金屬離子；在清洗後也能將所富含的有機質與營養元素留存於土壤中，避免傳統酸洗中土壤肥力的損失，有效降低整治後地力回復之經濟及時間成本。本研究之成果也為廚餘液肥之再利用形式開啟嶄新的方向。

雖然土壤中的鈣鎂有所流失但已較單純以水溶液酸洗者為少，為了解清洗復育後之土壤直接施用於農業行為之可行性，未來可在清洗後之土壤進行盆栽試驗及模擬雨季淋洗之土柱淋洗試驗；藉以分析其土壤肥力變化並實際調查對作物生長情形之影響，用以評估田間再利用之可行性。進而由嘗試加入各項營養元素來改良液肥成份，期能更加精確調控土壤中各項肥力含量，有效提高復育後農作物之產量。

致謝

感謝【國立宜蘭大學土壤環境科學實驗室】，林文修同學之殷切指導與協助。

參考文獻

中華土壤肥料協會，**土壤分析手冊**，行政院農業委員會，台北，台灣。

林永鴻，2008，“不同堆肥的腐植酸之光譜特性及對鋁的吸附行為研究”，**行政院農委會高雄區農業改良場研**究彙報，第 19 卷第一期，第 46-56 頁。

林盈蓁，2011，“以酒廠污泥備製之可溶性有機碳溶液複合 EDTA、Citric Acid 復育銅污染土壤之研究”， **環教永續低碳城市建構暨資源與環境學術研討會**。

林文修、林文經，2012，“以可溶性有機質溶液復育鉛污染土壤之研究”，**海峽兩岸土壤肥料學術研討會**，第九屆。

行政院環境保護署，2008，**廚餘回收再利用操作管理參考手冊**，台北，台灣。

許正一，2000，“台灣環境教育中不可缺席的一環：土壤環境生態教育”，**環境教育季刊**，第 42 期，第 59-66 頁。

陳尊賢，2003，“受重金屬污染農地土壤之整治技術與相關問題分析”，**台灣土壤及地下水環境保護協會簡訊**，第九期，第 2 - 9 頁。

陳尊賢、蘇紹瑋，2008，“土壤清洗法整治重金屬污染土壤 國內外最新研究與整治案例之回顧“，**台灣土壤及地下水環境保護協會簡訊**，第 42 期，第 4-12 頁，台北，台灣。

陳建民，2008，**環境毒物學 金屬篇**，新文京開發出版有限公司，台北，台灣。

陳冠步，2010，“以酒廠污泥備製之可溶性有機碳溶液復育鎘污染土壤之研究”，**海峽兩岸土壤肥料學術研討會**，第八屆。

劉鎮宗，2007，**以酒廠污泥移除水中鉻銅鋅鎳之研究**，博士論文，農業化學研究所， 國立臺灣大學，台北，台灣。

謝兆申、王明果，1995，**土壤調查技術手冊**，國立中興大學土壤調查試驗中心，台中，台灣。

羅秋雄，2002，**強酸性土壤改良**，桃園區農業改良場，桃園，台灣。

Aly, A.S., Jeon, B.D., Park, Y.H., *Preparation and evalutation of thechitin derivatives for wastewater treatments*, John Wiley & Sons Incorporated, 1997.

Brady, N.C., Weil, R.R., *The Nature and Properties of Soils*, Upper Saddle River, America, New Jersey, 2002.

Brewster, M., Peters, R., Patton, T., Martino L., 1994, “Treatability study for evaluating treatment of metals-contaminated soil,” Paper presented at the *Industrial and Engineering Chemistry Special Symposium on Emerging Technologies in Hazardous*

National Ilan University
國立宜蘭大學工程學刊第8期，61-77頁，2012年12月
Bulletin of College of Engineering National Ilan University No. 8, P. 61-77, December 2012
Bulletin of College of Engineering
http://engineering.niu.edu.tw/main.php

厭氧廢水處理氯化脂肪族化合物臨界負載率之估計

邱應志[1] Richard E. Speece[2]

1. 國立宜蘭大學環境工程學系（所）教授
2. 美國范德堡大學土木與環境工程系研究所教授

摘要

在生物轉化工業廢水之優先管制污染物過程中，厭氧反應器具備有相當的應用潛力。經過適當的馴化後，氯化脂肪族化合物可與乙酸或丙酸以顯著的速率同時被分解轉化。依據宿命模式推估顯示，在乙酸或丙酸的反應器中，生物轉化在移除氯化脂肪族化合物上為主要機制，佔了移除率的67%至99%；而揮發則為次要機制，可貢獻0.2% 至33%的移除率。特定氯化脂肪族化合物之臨界負載率，定義為主要基質利用率因受氯化脂肪族化合物影響而降為原值50%時之負載率。代謝丙酸時，氯化脂肪族化合物之臨界負載率介於0.4與24 mg/g cell-day；而代謝乙酸時，此臨界負載率介於0.1與21mg/g cell-day。而氯化脂肪族烯烴類比氯化鏈烷烴類可以較快的速率被厭氧微生物轉化。若不超過此臨界負載率，厭氧處理程序可以穩定地同時將主要基質伴同氯化脂肪族化合物一起生物轉化。

關鍵詞：氯化脂肪族化合物、甲烷菌、揮發有機性化合物、可處理性

***通訊作者E-mail：ycchiu@niu.edu.tw**

National Ilan University
國立宜蘭大學工程學刊第8期，61-77頁，2012年12月
Bulletin of College of Engineering National Ilan University No. 8, P. 61-77, December..2012
Bulletin of College of Engineering
http://engineering.niu.edu.tw/main.php

Estimation of Chlorinated Aliphatics Critical Loading Rates for Anaerobic Wastewater Treatments

Ying-Chih Chiu[1], Richard E. Speece[2]

1. Professor, Department of Environmental Engineering, National Ilan University
2. Professor, Department of Civil and Environmental Engineering, Vanderbilt University

ABSTRACT

Anaerobic reactors have considerable potential of biotransforming priority pollutantsfrom industrial wastewaters. With proper acclimation, selected chlorinated aliphatics were transformed simultaneously with acetic acid or propionic acid at significant rates. Based on fate model estimation. Biotransformation, accounted for from 67% to 99% of the total removal, was the major mechanism of chlorinated aliphatics removal; while volatilization, ranged from 0.2% to 33% of removal, was the secondary one for reactors supplied with either HPr or HAc. The critical loading rate was defined as the loading rate of a specific chlorinated aliphatic which resulted in reduction of the primary substrate utilization to 50%. The chlorinated aliphatics critical loading rates for the microbes metabolizing HPr were from 0.4 to 24 mg/g cell-day, while those rates for the microbes metabolizing HAc ranged from 0.1 to 21 mg/g cell-day. On the other hand, anaerobic microorganisms biotransformed chlorinated aliphatic alkenes at a higher rate than those of alkanes. Under the critical loading, an anaerobic wastewater treatment process could stably and simultaneously biotransform primary substrate along with chlorinated aliphatics.

Keywords: Chlorinated aliphatics, Methanogen, VOCs, Treatability.

***Corresponding author E-mail: ycchiu@niu.edu.tw**

1. INTRODUCTION

Halogenated aliphatic compounds are used in industrial processes and are prevalent groundwater contaminants and significant components of hazardous wastes and landfill leachates (Chaudhry and Chapalamadugu, 1991; Zhang and Bennett, 2005). They are also the high-risk chemicals found in drinking water in the United States (Crouch et al., 1983). Many halogenated compounds are highly toxic, and because they are often recalcitrant or insoluble, they escape degradation. However, microbes exposed to these synthetic chemicals have developed the ability to utilize some of the halogenated compounds (Chaudhry and Chapalamadugu, 1991). Field and Sierra-Alvarez (2004) also reported chlorinated compounds are also degraded under anaerobicconditions in which they are utilized as an electron donor and carbon source. Cometabolism occurs when a compound, a co-metabolite, is not metabolized as a source of carbon or energy but is incidentally transformed by organisms using another primary substrate (Kobayashi and Rittmann, 1982; Liu, 1986). Acclimation plays a key role in such biodegradation of inhibitory compounds.

The objective of this study was to evaluate the treatability of an anaerobic treatment process, such as used in industrial wastewater treatment, to biotransform seven chlorinated apliphatics, while simultaneously converting the primary substrate to methane. Acetic acid (HAc) and propionic acid (HPr) were used as the primary substrates because they represented key intermediates in anaerobic digestion of organic pollutants. The critical loading rate of chlorinated aliphatic which reduced the utilization rate of the primary substrate to 50% of a control was also evaluated.

2. MATERIALS AND METHODS

Methylene chloride (MC; CH_2Cl_2), chloroform (CF; $CHCl_3$), carbon tetrachloride (CT; CCl_4), 1,1-dichloroethylene (1,1-DCE; CCl_2CH_2), trichloroethylene (TCE; CCl_2CHCl), tetrachloroethylene (PCE; CCl_2CCl_2), and 1,1,1-trichloroethane (1,1,1-TCA; CCl_3CH_3), as common industrial solvents, were assayed.

A continuous flow stirred-tank reactor (CSTR) with high concentrations of suspended-growth biomass was used. Fourteen reactors were used for testing the 7 chlorinated aliphatic compounds, with each of the 2 primary substrates, HPr or HAc. A 2 L, wide-mouth Pyrex glass bottle was used as the reactor for each compound. The chlorinated organics were

delivered through Teflon tubing. A pH electrode entered the reactor through the top mouth of the bottle. To evaluate the removal of chlorinated compounds by volatilization, gas productions and contents were daily recorded and analyzed. The selected substrate was added into each reactor through a glass tubing. All materials that contacted with chlorinated compounds were glass, Teflon, or stainless steel to eliminate the possibility of adsorption. All reactors were incubated at a temperature of $35 \pm 2\ ^{o}C$. To eliminate the effects of photodegradation (Glaze et al., 1993), the incubation room was always kept dark, except when sampling and recording. A syringe pump driven by a stepping motor was used to add chlorinated compounds into the reactor.

A computer controlled pH-Stat system was used to carry out this study. A computer read the pH signal once per 45 seconds, then compared it with a default value to set the on/off of the primary substrate injection pump. The pH probes were calibrated by an off-line pH meter daily. In this way, the pH value in the reactor was automatically kept at 6.8 ± 0.1. Since the primary substrate (HPr or HAc) was acids, maintenance of a nearly constant pH, coupled with a controlled alkalinity, resulted in maintenance of nearly constant primary substrate concentrations. In this system, with an alkalinity of $1{,}200 \pm 200$ mg $CaCO_3$/L, the HAcs in reactors were from 1,500 to 2,500 mg/L, and the HPrs in reactors ranged between 500 and 1,500 mg/L. For single reactor, the HPr or HAc concentration variation was less than 100 mg/L.

Based on half-velocity constant (K_S)= 40 mg/L (Costello et al., 1991), the HPr concentrations of 500~1,500 mg/L resulted in 93% to 97% of the maximum substrate utilization rate during operation. While for K_S = 400 mg/L (Takashima and Speece, 1989), the HAc concentrations of 1,500~2,500 mg/L resulted in 79% to 86% of the maximum substrate utilization rate during operation. Hence, a primary substrate-unlimited and pH-Stat environment were automatically maintained by computerized control. Therefore, these variations in substrate utilization were interpreted as being principally related to inhibition by the injected specific chlorinated aliphatic and not to primary substrate variation.

The solid retention time (SRT) of 20 days was controlled by wasting 1/20 of the mixed contents daily and replacement with an equal volume inorganic basal media shown in Table 1. The pH of basal media was about 8 with 6,000 mg/l $NaHCO_3$ as a buffer. To avoid sudden drops in pH during the feeding of primary substrates, the concentrated organic acids were diluted to 10% and 40% concentration for HPr and HAc, respectively. A trace metal solution was added daily into each reactor (5 mg Fe/L, 1 mg Ni/L, and 1 mg Co/L of reactor-day) to promote predomination of a high-rate *Methanosarcina* enrichment vs. the low rate

Methanothrix (*Methanosaeta*). This procedure was described in detail by Takashima and Speece (1989).

Fate Model

Biotransformation, biomass adsorption, abiotic transformation, and volatilization are the major mechanisms for the removal of chlorinated aliphatics (inhibitors) during wastewater treatment. A model was developed to clarify the contributions of these mechanisms in the system.

Table 1. Composition of basal inorganic nutrients used in the reactor

Constituent	Concentration in Reactor (mg/L)
NH_4Cl	1,200
$MgSO_4 . 7H_2O$	400
KCl	400
$Na_2S . 9H_2O$	300
$CaCl_2 . 2H_2O$	50
$(NH_4)_2HPO_4$	80
$FeCl_2 . 4H_2O$	40
$CoCl_2 . 6H_2O$	10
KI	10
$(NaPO_3)_6$	10
$MnCl_2 . 4H_2O$	0.5
NH_4VO_3	0.5
$CuCl_2 . 2H_2O$	0.5
$ZnCl_2$	0.5
$AlCl_3 . 6H_2O$	0.5
$NaMoO_4 . 2H_2O$	0.5
H_3BO_3	0.5
$NiCl_2 . 6H_2O$	0.5
$NaWO_4 . 2H_2O$	0.5
Na_2SeO_3	0.5
Cysteine	10
$NaHCO_3$	6,000

Biotransformation. Biotransformation of a chlorinated aliphatic can be expressed by Monod kinetics. Corapcioglu and Hossain (1991) concluded that a first-order rate expression could be satisfactorily quantified for biotransformation processes of chlorinated aliphatic

hydrocarbons under methanogenic conditions. When individual compounds were biodegraded through a secondary utilization mechanism, the concentration of active microorganisms could be approximated as the total active biomass in the reactor (Namkung and Rittmann, 1987). Therefore, the Monod equation can be re-arranged as:

$$R_{bio} = - k_1 X_a S_I V \quad (1)$$

Where

R_{bio} = Rate of chlorinated compound removed by biotransformation, mg/day.

k_1 = Pseudo first-order biological reaction constant, L/mg cell-day.

X_a = Concentration of active microorganisms, mg/L.

S_I = Concentration of chlorinated compound in the reactor, mg/L.

V = Volume of reactor, L.

Volatilization. In continuous stirred-tank reactors (CSTRs), the volatile compounds can be stripped out by the off-gas. For a quasi-equilibrium process, the transfer of a volatile compound between a liquid phase and a gas phase could be modeled as follows (Harrington et al., 1993; Namkung and Rittmann, 1987; Rittmannet al., 1988).

$$R_{vol} = - \frac{GH_M S_I}{RT} = - GH_c S_I \quad (2)$$

where

R_{vol} = Rate of compound removed by volatilization, mg/day.

G = Gas volumetric flow rate, L/day.

R = Universal gas constant (= 8.206×10^{-2} L-atm/^{o}K-mole).

T = Absolute temperature, ^{o}K.

H_M = Henry's Law constant, atm-m^3/mole.

H_c = Henry's Law constant, dimensionless.

However, the assumption that off gas was saturated with the chlorinated aliphatics as it left the liquid phase was doubtful. Therefore, a factor of the fractional saturation of chlorinated aliphatic in the off gas was added as Equation 3 (Matter-Muller et al., 1981; Parker et al., 1993).

$$f = 1 - \exp\left(-\frac{\alpha K_L a V}{H_c G}\right) \quad (3)$$

Where

f = Fractional saturation, dimensionless.

= Process water to clean water correction factor, dimensionless.

K_{La} = Overall mass-transfer coefficient, day $^{-1}$.

The factor for process water ranges from 0.4 to 0.8 (Metcalf and Eddy, 1991), therefore, the middle value of 0.6 was used. The values of overall mass-transfer coefficient (K_{La}) was found to be 17.28 day $^{-1}$ in the laboratory. For compounds with higher Henry's Law constant, such as PCE, CT, 1,1,1-TCA, the f-values were low at high gas production. For MC and CF, with lower Henry's Law constant, the f-values were greater than 0.7 when gas productions were less than 70 L/day.

Biomass Adsorption. Hydrophobic organic compounds were known to adsorb to organic solids, of which biological solids were a prime example. Therefore, the adsorbed chlorinated aliphatics were removed from the system when biomass was removed with the effluent (Namkung and Rittmann, 1987). The partitioning of each hydrophobic chlorinated compounds between the water phase and biomass was estimated by Equations 4 and 5 (Harrington et al., 1993; McCarty et al., 1980).

$$K_p = 3.06\times10^{-6} K_{ow}^{0.67} \quad (4)$$

$$R_{abs} = - Q X K_p S_I \quad (5)$$

Where

K_p= Partition coefficient, L/mg cell.

K_{ow} = Octanol/water partition coefficient, m^3 H_2O/m^3octanol

R_{ads}= Rate of chlorinated compound removed by adsorption onto biomass, mg/day.

Q = Continuous flow rate, L/day.

X = Concentration of wasted cells, mg cell/L.

Abiotic Transformation. Bouwer and McCarty (1983) reported that the transformation of the chlorinated aliphatics was the result of biological action, whereas a combination of biological and chemical processes appeared responsible for the transformations of bromoaliphatic compounds under reducing conditions. For surface waters, photolysis often controls the fate of chlorinated compounds. But in anaerobic wastewater treatment, the

digesters were always closed systems and kept dark. Therefore, photolysis should not contribute to the breakdown of chlorinated aliphatics. At constant pH, the reactions of abiotic hydrolysis or dehydrohalogenation follow first-order kinetics (Vogel, 1988). Therefore, the pseudo first-order rate constant (K_{abi}) could be derived from the half-life ($t_{½}$) as expressed by Equation 6.

$$K_{abi} = 0.69/t_{½} \quad (6)$$

Model Developed. For a CSTR system, a mass balance equation (Equation 7) was derived by combining the mechanisms discussed above:

$$\frac{dI}{dt} V = Q I_i - Q I + R_{bio} + R_{vol} + R_{ads} + R_{abi} \quad (7)$$

Where

I_i= Chlorinated compound concentration in influent, mg/L.

I= Chlorinated compound concentration in reactor, mg/L.

Due to dynamic change in the system, the finite difference method was used for analysis. The data at time $t+\Delta t$ were derived from data at time t based on the change during the time interval Δt. Based on analytical data, the Δt of 1 day was used in this model. Table 2 listed the values of the parameters used in the model to estimate the contributions.

Analytical Method and Procedures

A gas chromatography (Shimadzu GC-6AM) equipped with FID was found suitable for analyzing higher concentrations of chlorinated compounds. Nitrogen gas (40 mL/min) served as the carrier of the injected samples. An 1.7 m glass column, packed with 0.3% Carbowax 20M/0.1% H_3PO_4, 60/80 Carbopack-C (Supelco, Inc., Bellefonte, PA) was used. After receiving a 10.0 mL sample from the liquid phase of the reactor, the 15 mL vial was capped with a Teflon septum, then was shaken for 3 minutes and followed by standing stilly for 1 minute to reach gas-liquid equilibrium. Next, a 50.0 μL aliquot from the head space was injected into the gas chromatography column for analysis. The practical quantification range was found to be from 0.25 to 50 mg/L, when temperatures of detector and oven were 200 ^{o}C and 120 ^{o}C, respectively. Acetic acid and propionic acid were also measured by the Schimadzu GC-6AM. The sample from reactor was prepared by centrifugation at 4,000 rpm for 10

minutes. A supernatant of 1.0 mL was acidified (pH<3) by 10% formic acid, then a 1.0 μL aliquot from the liquid mixture was injected into the column for analysis. The practical quantification range was found to be from 50 to 1,000 mg/L. The procedures in Standard Methods (APHA,1998) were followed for determining the mixed liquor suspended solids(Method 2540D) and the mixed liquor volatile suspended solid (MLVSS)(Method 2540E).

3. RESULTS AND DISCUSSION

Acclimation and start-up were carried out simultaneously. During this period, an amount of 0.1 mg/L-day of a specific chlorinated compound was injected daily into each reactor to allow contact with the microbes for acclimation. Due to interacting with different substrates and chlorinated compounds, each reactor reached a specific stable substrate utilization rate and biomass concentration after 6 months, under unlimited primary substrate supplement. For reactors fed with HPr, the propionate utilization rates (PURs) ranged form 2.2 to 4 g HPr/g cell-day, with biomass concentrations of 2,000 to 5,000 mg/L. While reactors fed HAc, the acetate utilization rates (AURs) were from 3 to 6 g HAc/g cell-day, with biomass concentrations of 4,500 to 11,000 mg/L. The reactors using HAc as primary substrates were injected daily with additional 200 mg-$NaHCO_3$/ L of reactor to maintain stable alkalinities (1,200 ± 200 mg as $CaCO_3$/L). The reactors using HPr as primary substrates always maintained stable alkalinities with the basal media.

Biotransformation, biomass adsorption, abiotic transformation, and volatilization were the major mechanisms for the removal of chlorinated aliphatics. The contributions of the various mechanisms were the results of competition. The developed model (Equation 7) was used to clarify the contributions of these mechanisms in the system. The biotransformation constants (k_1) of the pseudo-first-order reaction were retrieved from the previous experiment used the same system (see Table 2). The estimated contribution of each mechanism was summarized in Table 3.

Gas productions from reactors supplied with HAc (5 to 15 L gas/L of reactor-day) were generally higher than in those reactors supplied with HPr (less than 5 L gas/L of reactor-day). Higher gas production could enhance the chlorinated compounds removals by volatilization. However, those reactors supplied with HAc always supported more biomass, which encouraged biotransformation. Based on the model result, biotransformation was the major

mechanism of chlorinated aliphatics removal for reactors supplied with either HPr or HAc. For these compounds, biotransformation accounted for from 67% to 99% of the total removal, while removal by volatilization ranged from 0.2% to 33%. Since CT had the highest Henry's Law constant, CT with HAc had the highest volatilization contribution. On the other hand, biomass adsorption did not significantly affect the transformation of chlorinated aliphatics (less than 0.12%).The effect of abiotic transformation on removal of chlorinated aliphatics was almost negligible.

During the experiment period, a new loading of a specific chlorinated compound could immediately reduce the substrate utilization rate (PUR or AUR). However, with a continuous loading at the same level, the substrate utilization rate might partially recover and stay stable. Sometimes, the loading was too torrential to recover the substrate utilization rate, and then the loading was terminated. A lighter loading was applied after the system retrieving the normal substrate utilization rate. All the responses of substrate utilizations resulted from different loadings of chlorinated aliphatics were recorded to establish dose-response cures. The carbon tetrachloride loading and PUR response was used as an example, and illustrated in Figure 1. The critical loading rate was estimated from the 50% PUR of the regressed line. Exponential regression was found to give better correlation than linear regression. Table 4 summarized the estimated critical loading rates of the chlorinated aliphatics for cultures fed with HPr or HAc.

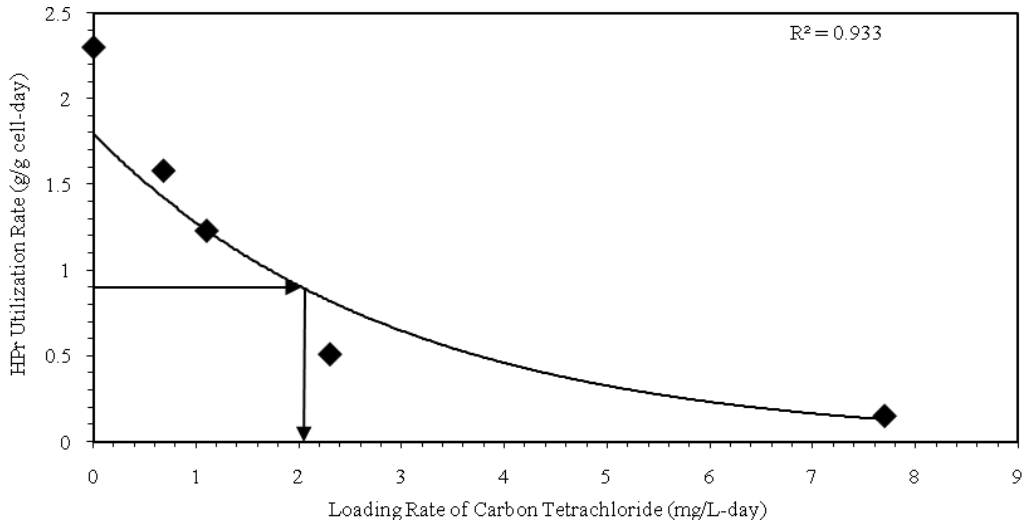


Figure 1. Carbon tetrachloride loading and toxicity response when propionic acid was the Primary Substrate.

Based on reactor volume, the critical loading rates of chlorinated alkenes (1,1-DCE, TCE, and PCE) ranged from 8 to 130 mg/L of reactor-day (0.01 to 0.1 mmole/g cells-day).

Chlorinated alkanes (MC, CF, CT, and 1,1,1-TCA) lowered those values to the levels between 1 to 4.5 mg/L of reactor-day (0.001 to 0.007 mmole/g cells-day). The response of TCE could be loaded at higher dose for cultures fed with HPr and HAc than both CF and TCA. Therefore, compounds with 3 chlorines but containing a double bond could get faster biotransformation.

For the cultures fed with HAc as the primary substrate, the more chlorinated the alkene, the higher the critical loading rate. However, the chlorinated alkanes fed with HAc did not present the same result. Blum and Speece (1991) reported the inhibitory concentration of 50% (IC_{50}) of chlorinated aliphatics for unacclimated methanogens, fed with acetate, was in the order of PCE > TCE > DCE > MC >CT. This order was identical with the critical loading results of this study. Therefore, for the acclimated cultures fed HAc, the critical loading rate loading rate was still correlated to the toxicity of chlorinated aliphatic to the unacclimated methanogens. In the experiment period, due to a pH probe failure, the microbes in reactor receiving CF were lifeless. Therefore, the culture was replaced by biomass that had been acclimated to MC for 1 year. The inter-acclimated culture resulted in prompt biotransformations of CF and the intermediate MC. The mechanism needs further study to explore. For the cultures fed HPr, the critical loading rates of chlorinated aliphatics were in the same order of PCE > TCE > MC > CT > CF as fed HAc, when based on biomass.

Comparing the ratios of primary substrates utilized to chlorinated aliphatic biotransformed, the reactors supplied with HPr always had a higher values than the reactors supplied with HAc. During anaerobic fermentation, HPr can be converted to hydrogen and acetate, then to methane and carbon dioxide, while HAc is directly converted into methane and carbon dioxide. Hydrogen might be the electron donor used directly for dechlorination (Maymo-Gatell et al., 1997).Therefore, the dechlorination of chlorinated aliphatics might be enhanced by the presence of hydrogen. These results were consistent with those of DiStefano et al. (1992). Since all chlorinated aliphatics could be biotranformed using HAc as the primary substrate, which produced no hydrogen intermediate. Therefore, dechlorination of chlorinated aliphatics by hydrogen might not be the only path.

4. CONCLUSIONS

Anaerobic reactors for the removal of organic pollutants from industrial wastewaters had significant potential for biotransformation of some priority pollutants. With proper acclimation, the anaerobic treatment process had a considerable potential for simultaneous biodegradation

of toxic chlorinated aliphatics during conversion of the primary substrate to methane. These critical loading rates gave ranges for stable anaerobic wastewater treatment while biodegrading chlorinated aliphatics. Based on biomass, the chlorinated aliphatics critical loading rates for the microbes metabolizing HPr were from 0.4 to 24 mg/g cell-day, while those rates for the microbes metabolizing HAc ranged from 0.1 to 21 mg/g cell-day. Anaerobic microorganisms biotransformed chlorinated aliphatic alkenes at a higher rate than those of alkanes.

Table 2. The values of the parameters used in the fate model

Compound	Primary Substrate	k_1 [a] (L/mg cell-day)	H_c [b] (Dimensionless, 35 °C)	log K_{ow} [c] (L/mg cell-day)	$t_{1/2}$ [d] (year)
Methylene Chloride (MC)	HPr	2×10^{-2}	0.129	1.30	1.5
	HAc	0.8×10^{-2}			
Chloroform (CF)	HPr	4×10^{-2}	0.223	1.90	1.3
	HAc	1×10^{-2}			
Carbon Tetrachloride (CT)	HPr	2×10^{-2}	1.823	2.73	7000
	HAc	1×10^{-2}			
1,1,1-Trichloroethane (1,1,1-TCA)	HPr	4×10^{-2}	0.987	2.18	0.5
	HAc	2×10^{-2}			
1,1-Dichloroethylene (1,1-DCE)	HPr	1×10^{-2}	0.83 [c]	2.13	1.5 [e]
	HAc	0.9×10^{-2}			
Trichloroethylene (TCE)	HPr	3×10^{-2}	0.591	2.53	0.9
	HAc	2×10^{-2}			
Tetrachloroethylene (PCE)	HPr	1×10^{-2}	1.116	2.88	0.7
	HAc	0.8×10^{-2}			

a: Rhee, 1990. b: Gossett, 1987. c: Montgomery and Welkom, 1990. d: Vogel et al., 1987. e: Dilling et al., 1975. .

Table 3. Processes responsible for observed removal of chlorinated aliphatic compounds

Compound	Primary Substrate	Estimated Contribution of Removal							
		Biotransformation		Biomass Adsorption		Abiotic		Volatilization	
		(%)	(mg/L-day)	(%)	(mg/L-day)	(%)	(mg/L-day)	(%)	(mg/L-day)
Methylene Chloride	Propionic Acid	99	1	0.01	0	0.01	0	0.2	0.003
	Acetic Acid	98	7	0.01	0	0	0	2	0.1
Chloroform	Propionic Acid	99	1	0.03	0	0	0	0.3	0
	Acetic Acid	95	4	0	0	0	0	5	0.2
Carbon Tetrachloride	Propionic Acid	95	2	0.1	0.002	0	0	5	0.1
	Acetic Acid	67	2	0.07	0	0	0	33	0.9
1,1,1-Trichloroethane	Propionic Acid	93	2	0.04	0	0.02	0	7	0.1
	Acetic Acid	86	2	0.04	0	0	0	14	0.4
1,1-Dichloroethylene	Propionic Acid	87	37	0.04	0.01	0	0	13	5
	Acetic Acid	82	2	0.03	0	0	0	18	0.5
Trichloroethylene	Propionic Acid	95	28	0.07	0.02	0.01	0	5	2
	Acetic Acid	86	12	0.06	0.01	0	0	14	2
Tetrachloroethylene	Propionic Acid	90	45	0.12	0.06	0	0	10	8
	Acetic Acid	94	16	0.1	0.02	0	0	6	0.8

* HRT=20 days.

Table 4. Estimated critical loading rate of chlorinated aliphatic compounds in pH-stat system (HRT=20 days)

Compound	Primary Substrate	Average Biomass (mg/L)	Substrate Utilization Rate * (g/g cells-day)	Critical Loading Rate		
				Based on Reactor Volume (mg/L of reactor-day)	Based on Biomass (mg/g cells-day)	Based on Primary Substrate Utilization (mg/g substrate)
Methylene Chloride	HPr	2,600	3.2	2.3	0.8	0.7
	HAc	10,000	5.6	4	0.4	0.2
Chloroform	HPr	5,000	2.0	2	0.4	0.4
	HAc[+]	6,000	3.0	> 4.5	> 0.8	> 0.5
Carbon Tetrachloride	HPr	2,700	1.8	1.8	0.7	0.6
	HAc	4,500	7.8	1.7	0.3	0.1
1,1,1-Trichloroethane	HPr	2,000	1.6	1.2	0.9	0.3
	HAc	11,000	3.2	1	0.1	0.04
1,1-Dichloroethylene	HPr	2,300	1.8	-	-	-
	HAc	9,000	4.0	8	1.1	0.4
Trichloroethylene	HPr	3,500	2.4	56	24	8
	HAc	8,000	3.2	90	14	5
Tetrachloroethylene	HPr	2,300	2.4	40	19	11
	HAc	10,000	2.6	130	21	6

* Based on the regressed equations.

[+]Conducted in a mix-liquor of MC and CF acclimated cultures.

- R^2 is too low to estimate.

REFERENCES

APHA, AWWA, WEF, *Standards Methods for Examination of Water and Wastewaters,* 20th ed. American Public Health Association, Washington, DC, USA, 1998.

Blum, J.W., Speece, R.E., 1991, "A database of chemical toxicity to environmental bacterial and its use in interspecies comparisons and correlations," *Research journal of the Water Pollution Control Federation*, Vol. 63(3), pp. 198–207.

Bouwer, E.J., McCarty, P.L., 1983, "Transformations of 1- and 2-carbon halogenated aliphatic organic compounds under methanogenic conditions," *Applied and Environmental Microbiology*, Vol. 45 (4), pp. 1286–1294.

Chaudhry, G.R. and Chapalamadugu, S., 1991. "Biodegradation of halogenated organic compounds," *Microbiology Reviews*, Vol. 55 (1), pp. 59–79.

Corapcioglu, M.Y., Hossain, A., 1991, "Estimating biotransformation rate constants for sequential reductive dehalogenation reactions," *Journal of Environmental Engineering*, Vol. 117(5), pp. 631–639.

Costello, D.J., Greenfield, P.E., Lee, P.L. 1991, "Dynamic modeling of a single-stage high-rate anaerobic reactor-II. Model verification," *Water Research*, Vol. 25(7), pp. 859–871.

Crouch, E.A.C., Wilson, R., Zeise, L., 1983, "The risks of drinking water," *Water Resources Research*, Vol. 19(6), pp. 1359–1375.

Dilling, W.L., Tefertiller, N.B., Kallos, G.J., 1975, "Evaporation rates and reactivities of methylene chloride, chloroform, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and other chlorinated compounds in dilute aqueous solutions," *Environmental Science Technology*, Vol. 9(9), pp. 833–838.

DiStefano, T.D., Gossett, J.M., Zinder, S.H., 1992, "Hydrogen as an electron donor for dechlorination of tetrachloroethene by an anaerobic mixed culture," *Applied and Environmental Microbiology*, Vol. 58(11), pp. 3622–3629.

Field, J.A., Sierra-Alvarez, R., 2004, "Biodegradability of chlorinated solvents and related chlorinated aliphatic compounds," *Reviews in Environmental Science and Biotechnology*, Vol. 3 (3), pp. 185–254.

Glaze, W.H., Kenneke, J. F., Ferry, J.L., 1993, "Chlorinated byproducts from the TiO_2-mediated photodegradation of trichloroethylene and tetrachloroethylene in Water," *Environmental Science Technology*, Vol. 27(1), pp. 177–184.

Gossett, J.M., 1987, "Measurement of Henry's Law constants for C_1 and C_2 chlorinated hydrocarbons," *Environmental Science Technology*, Vol. 21(2), pp. 202–208.

Harrington, J.R., Mihelcic, J.R., Planinsek, T.L., Lewis, R.A., 1993, "FATE estimates pollutant treatability," *Water Environmental Technology*, Vol. 5(3), pp. 49–53.

Kobaysahi, H., Rittmann, B.E., 1982, “Microbial removal of hazardous organic compounds,” *Environmental Science Technology*, Vol. 16(3), pp. 170A–182A.

Liu, D., Biodegradation Tests. in: G.B. Bitton, B.J. Dutka, (Eds), *Toxicity Testing Using Microorganisms*, Vol. II. CRC Press. Inc., 1986, pp. 157–173.

Matter-Muller, C., Gujer W., Giger, W., 1981, “Transfer of volatile substances from water to the atmosphere,” *Water Research*, Vol. 15, pp. 1271–1279.

Maymo-Gatell, X., Chien, Y-t., Gossett, J.M., Zinder, S.H., 1997, “Isolation of a Bacterium That reductively DechlorinatesTetrachloroethene to Ethene,” *Science*, Vol. 276, pp. 1568–1571.

McCarty, P.L., Rittmann, B.E., Reinhard, M., 1980, “Processes affecting the movement and fate of trace organics in the subsurface environment,” *Proceedings of Wastewater Reuse for Groundwater Recharge*, pp. 93–117.

Metcalf & Eddy, Inc., *Wastewater Engineering: Treatment, Disposal, Reuse*, 3rd ed., McGraw-Hill Company, 1991.

Montgomery, J.H., Welkom, L.M., *Groundwater Chemicals Desk Reference*, Lewis Publishers, Inc., 1990.

Namkung, E., Rittmann, B.E., 1987, “Estimating volatile organic compound emissions from publicly owned treatment works,” *Journal of the Water Pollution Control Federation*, Vol. 59(7), pp. 670–678.

Parker, W.J., Thompson, D.J., Bell, J.P., Melcer, H., 1993, “Fate of volatile organic compounds in municipal activated sludge plants,” *Water Environmental Research,* Vol. 65(1), pp. 58–65.

Rhee, E., *The Response of Anaerobic Metabolism of Propionate to Process Configuration and 1,2-Carbon Chlorinated Aliphatic Compounds*, Doctor Dissertation, Drexel University, USA., 1990.

Rittmann, B.E., Jackson, D., Storck, S.L., Potential for Treatment of Hazardous Organic Chemicals with Biological Processes, in: D.L. Wise (Ed.), *Biotreatment Systems*-Vol. 3. CRC Press, 1988, pp. 15–64.

Takashima, M., Speece R.E., 1989, “Mineral nutrient requirement for high-rate methane fermentation of acetate at low SRT”, *Journal of the Water Pollution Control Federation*, Vol. 61, pp. 1645–1650.

Vogel, T.M., 1988, *Biotic and Abiotic Transformation of Halogenated Aliphatic Compounds*, Doctor Dissertation, Stanford University, USA.

Vogel, T.M., Criddle, C.S., McCarty, P.L., 1987, ”Transformations of Halogenated Aliphatic Compounds,” *Environmental Science and Technology*, Vol. 21, 8, pp. 722–736.

Zhang, C., Bennett, G.N., 2005, “Biodegradation of xenobiotics by anaerobic bacteria,” *Applied Microbiology & Biotechnology*, Vol. 67(5), pp. 600–618.