行政院國家科學委員會專題研究計畫 成果報告

以氣舉式生物反應器處理光電業含二甲基亞(DMSO)廢水之可行性評估

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以氣舉式生物反應器處理光電業含二甲基亞碸 (DMSO) 廢水之可行性評估

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行政院國家科學委員會專題研究計畫成果報告

以氣舉式生物反應器處理光電業含二甲基亞碸 (DMSO) 廢水之可行性評估

Treatment of dimethyl-sulfoxide (DMSO)-containing optoelectronics wastewater using airlift bioreactor with PVA-immobilized cell beads

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摘 要

二甲基亞碸 (Dimethyl sulfoxide, DMSO)，分子式為$(CH_3)_2SO$，是一種適合回收再利用的環保型溶劑，價格也較為低廉。因此 DMSO 被大量使用在各種工業，使得廢水中常含有殘留的 DMSO，若不加以處理 DMSO 又會被還原成具有惡臭的二甲基硫 (Dimethyl Sulfide, DMS)。本研究長期目標在開發一套解決光電業廢水中 DMSO 的處理技術，防止 DMS 的惡臭問題。在此，除了利用活性污泥在氣舉式反應器內做重複批次降解 DMSO 的實驗，以證明其實用性，亦利用固定化技術來加強活性污泥對惡劣環境的適應性，並找出最適的環境因子。由實驗結果得知，固定化活性污泥分解 DMSO 的可適 pH 範圍為 5.0~8.5 之間，在此範圍內其 DMSO 去除率皆可達 100%。模擬廢水中的碳源(蔗糖，sucrose)最適含量為 0~50 mg/L，此含量的碳源可幫助活性污泥抵抗 DMSO 的生物毒性且使活性污泥依然以 DMSO 作為主要碳來源並降解 DMSO；活性汙泥馴養越久則碳源多寡對其降解效率的影響越不顯著，但考慮經濟效益仍建議添加的碳源濃度在 0~50 mg/L 之間為佳。接種的菌量多寡對於降解速率也是有影響的，降解速率隨著接種菌量越多也越快速。而在氣舉式反應器的重複批次試驗中，懸浮活性污泥最快可在 10 小時內將初始濃度約 850 mg/L 的 DMSO 去除達 99%以上；固定化活性污泥則在 DMSO 負荷量增加到 1200 mg/L 時依然能於 45 小時內不受負荷增加影響，穩定地將 DMSO 降解完成，有足夠的系統穩定性。

關鍵字：活性污泥、生物降解、DMSO、固定化技術、氣舉式反應器。

Abstract

DMSO (dimethyl sulfoxide) is a useful and inexpensive environment benign solvent easy to recycle. Its tremendous adoption in the industry has revealed a odorous problem caused by its decomposition product, DMS (dimethyl sulfide). Our research goal is to develop a feasible biological treatment technology to effectively treat the DMSO into oxidative pathway instead of going to the DMS pathway. We has adopted a right source of activated sludge (from a wastewater treatment plant of DMSO production chemical company) as bacterial inoculums to decompose the DMSO into DMSO2 pathway. In this year, we focus on the research results from the immobilization technology, the repeated process and the sucrose effect. Finally, we found that the best pH range in biodegradation of DMSO using a PVA immobilized cell beads is 5.0-8.5. The best dosage of sucrose is 0-50 mg/L that help bacteria to tolerate the toxicity of DMSO. From the repeated process, we found the sucrose help improve the treatment efficiency for the raw activated sludge rather than the acclimated sludge. In airlift test, the PVA-immobilized cell beads can degrade the 1200-mg/L DMSO within 45 h, in comparison to the 10 h for the free cell system in decomposition of 850-mg/L DMSO.

一、前言

1.1 DMSO 簡介

二甲基亞碸 (Dimethyl Sulfoxide, DMSO)，分子式為$(CH_3)_2SO$。具有高極性、高吸濕性、高沸點及可燃性，熱穩定性也佳，不但能溶於水，也能溶於一些特定的有機溶劑，近年來廣為各種工業所使用。在半導體

或液晶螢幕製造業中，DMSO 被用來作為洗滌劑或光阻剝離劑，造成大量含 DMSO 的廢水從洗滌或漂洗程序中排出。廢水中的 DMSO 可區分為高低兩種濃度，高濃度的 DMSO (超過 1000 mg/L)，主要來自於光阻剝離劑的使用，常經濃縮技術來加以回收再利用。而低濃度 DMSO (10~1000 mg/L)的廢水，主要來自液晶顯示器與半導體的洗淨製程中。DMSO 的廢水是屬於較難處理的，DMSO 對生物具有毒性，且廢水中的 DMSO 經過長時間累積會在自然環境中造成污染 (Murakami *et al.*, 2002)。而且在自然環境中經過部分厭氧生物途徑會還原成二甲基硫 (Dimethyl Sulfide, DMS)等有毒的惡臭化合物(Lomans *et al.*, 2002)，DMS 即使在低濃度也極為容易超過臭味的標準(Leonardos *et al.*, 1969)。

1.2 DMSO 對環境與身體的影響

由於 DMSO 使用量日益增多，而且對環境及人體均有不良影響，以目前法規來說，美國環保署允許廢水中的 DMSO 濃度為 0.05 mg/L，或以 TOC 濃度作為 DMSO 之參考濃度時，允許的範圍是 100~200 mg TOC/L (Muratani T, 1999)。

根據 Material Safety Data Sheet (MSDS)指出，短時間吸入 DMSO 容易造成刺痛感、噁心、嘔吐、頭痛，暈眩。長時間的吸入 DMSO 可能會危害人體生命安全。而皮膚接觸 DMSO 則會出現過敏、水泡、熱反應(皮膚沾有水時)、噁心、暈眩、嘔吐。且 DMSO 對眼部具有刺激性，並造成視線模糊。若短期的攝取 DMSO 會造成噁心、嘔吐、腹瀉、胃痛、昏睡等症狀。另外，在二甲基硫 (Dimethyl Sulfide, DMS)的方面，勞工安全衛生研究所物質安全資料表指出，DMS 除具有易燃性與反應性外，對人體會嚴重刺激眼睛、呼吸道及皮膚，造成灼傷。長期暴露可能造成肺水腫、損害心臟、肝、胃、甚至致命；亦為一種致癌物質。(物質安全資料表，勞工安全衛生研究所)

1.3 光電業製程中 DMSO 來源與處理方法

截至目前為止，國內有關的電子產業，其製程中所排放廢氣中的 DMS 之含量，以及其生物處理廢水系統對 DMSO 的處理能力等相關的資料仍相當匱乏，僅得知製程廢水中 DMSO 含量大約為 500~800 mg/L 左右。

平面顯示器產業在 2002 年全球景氣衰退下仍然逆勢成長，其中 LCD 監視器取代 CRT 監視器發揮了極大的效應。工研院產經中心調查預估 2005 年的產值可達 202 億美元。因此，隨著平面顯示器等光電產業的發達，DMSO 經常會出現在清洗與清除製程的廢水中。一般平面液晶顯示器業在 ARRAY 流程所排放之主要污染物列於 Table 1 (工業技術研究院，2004)。

而 TFT-LCD (薄膜電晶體液晶顯示器)製程也明顯指出，製程的廢水中主要污染物，顯影液、剝離液、清洗液中所含的 DMSO、MEA (單乙醇胺，mono-ethanol amine)、BDG (butyl diglycol)及 TMAH (氫氧化四甲基銨，tetramethylammonium hydroxide)、IPA(異丙醇，isopropyl alcohol)等，大多為有機氮、硫類物質，大部分光電廠均使用生物處理來去除以上有機物。有關一般平面液晶顯示器業者常用廢水處理技術整理如下 Table 2。(工業技術研究院，2004)。

1.4 氣舉式反應器

自 1940 年來，對於好氧發酵製程之生物反應器具有良好的氣-液質傳效果。氣舉式反應器於任何製程上皆能提供高的混合與質傳效果、高流體循環速率、混合時間短以及低剪應力(shear)等優點；其氣舉式反應器運用的領域相當廣泛，如有機物的合成、廢水生物處理以及發酵生產(啤酒、醋、檸檬酸與抗生素等)(Hinks *et al.*, 1996、Adinarayana *et al.*, 2004)。

氣舉式反應器主要是由上升區域(riser)、下降區域(downcomer)、氣-液分離區(gas-liquid separater)及基底(base)等四個部份所構成。這四個區域將反應器區分成向上及向下流動兩部份，以產生循環迴路。通常輸入氣體的區域稱為上升區域，在此區域內氣-液向上同向流動，造成較大的氣體滯留量，且為氣-液質傳效果最佳的地方。當流體離開上升區域的頂端，即進入氣-液分離區。然後，藉由上升區域與下降區域之平均密度差或靜壓力差(Shimizu *et al.*, 2001)，而使得流體流入下降區域。當流體到達底端時，隨即通過基底再進入上升區域。因此，在反應器中會產生連續循環的流動現象，其循環及混合效果佳，無機械攪拌，可減少動力輸入外，其剪應力也較小；而剪應力較小，也比較不會對微生物與固定化顆粒造成影響。一般氣舉式反應器的分類，依循環方式主要分為內部循環式以及外部循環式等兩種類型。

Znad *et al.* (2006)利用氣舉式反應器在好氧條件下批次實驗中，以懸浮活性污泥與固定化活性污泥來降解除草劑(S-ethyl dipropylthiocarbamate, EPTC)。在活性污泥濃度為 2,184 ppm、曝氣速率為 3.5 L/min 時，觀察到固定化活性污泥因為可以抵抗除草劑的毒害，所以降解速率高於懸浮活性污泥。(Znad *et al.*, 2006)

1.5 微生物固定化方法簡介及其材料

微生物或酵素固定化技術之應用，早在 80 年代即已普遍應用於生物技術相關產業上。固定化微生物細胞係指將具有活性的微生物細胞固定於擔體材料的表面或內部，使細胞聚集在有限的空間中。固定化方法大致可分為：(1)自然吸附固定化法(self-attachment immobilization)與(2)人工固定化法(artificial immobilization) (Cohen *et al.*, 2001)。

自然吸附固定化法是指在人為提供的適當環境下，微生物細胞自然附著或凝結於擔體表面上或於多孔擔體內部中生長，進而形成生物膜。人工固定化法則包括：共價鍵結法(covalent bonding)、共價交聯法(covalent crosslinking)、微膠囊包覆法(microencapsulation)及包埋法(entrapment)等；其中又以包埋法最為常用。

包埋法固定化材料可分為天然與人工合成高分子物質兩類。天然物質如褐藻膠(alginate)與紅藻膠(κ-carrageenan)，主要由海藻中取得。天然聚合物一般藉由冷卻與/或含不同離子聚合溶液混合接觸作用，以引起凝膠化成固定化聚合物。已有相關研究指出天然聚合物機械強度較脆弱，易破裂，不適合長期操作使用，但擴散性卻較人工合成聚合物好 (Leenen *et al.*, 1996)。到目前為止，已有相關研究利用許多人工合成物質以包埋微生物，如聚丙烯醯胺(polyacrylamide, PAA)、聚乙烯醇(polyvinyl alcohol, PVA)、聚丙二醇(polypropylene glycol, PPG)等。

由於天然聚合物之物理穩定性較人工合成聚合物低，因此本研究考慮利用人工合成聚合物-PVA，以包埋微生物作為處理 DMSO 之固定化材料。

二、材料與方法

2.1 汙泥來源

活性污泥選自取自於台灣長春化工公司廢水處理廠好氧底泥，之後定期添加培養基 DMSO 作為碳源。

2.2 馴養可降解 DMSO 之活性汙泥培養基

馴養可降解 DMSO 之活性汙泥培養基摘自 Yang *et al.*所發表的報告，成分如 Table 3 所示 (Yang *et al.*, 2003)。

2.3 DMSO 之分析方法

為得知分析時所採集樣品的實際 DMSO 與 $DMSO_2$ (二甲基碸，Dimethyl sulfone, $DMSO_2$)濃度，因此需要將高效能液相層析儀(High-performance Liquid Chromatography, HPLC)所偵測得到的 DMSO (或 $DMSO_2$)波峰面積值與實際配製的液相 DMSO 標準品濃度值建立成檢量線，方法描述如下：

參考 Murakami (2002)的分析方法以進行 DMSO (或 $DMSO_2$)的檢測，將懸浮液以 0.22 μm 的薄膜進行過濾，接著以高效能液相層析儀 (HPLC, Acme 9000, YOUNG LIN INSTRUMENT, Korea) 進行檢測。層析用的管柱為 Hypersil ODS (5μL, 250×4.6mm, , England)，UV detector 則將波長設定成 225 nm，詳見 Table 4。

2.4 樣品取樣分析方法

利用 HPLC 分析液相樣品中 DMSO 含量，將樣品置入 2 ml 離心管中，再以 10,000 rpm 轉速離心 10 分鐘。抽取離心管中上澄液，將懸浮液以 0.22 μm 的薄膜進行過濾，再以 HPLC 進行分析，把所得 DMSO 波峰面積值代入液相 DMSO 檢量線中，經由換算以獲得液相 DMSO 濃度值。

2.5 硫酸根離子 (sulfate ion) 之分析方法

將 50 mL 的液體樣品分裝至兩個 25 mL 的玻璃試管，其中一組加入硫酸根試劑(sulfate reagent cat. 12065-99, HACH)的白色粉末，搖晃瓶身使其內部混合均勻，即靜置等待 5 分鐘反應時間，產生白色混濁，再利用分光光度計 (UV-VIS spectrophotometer) DR/4000U (HACH, Colorado, USA)分析。將未加粉末的組別做為背景值歸零，再將另一組放入光度計中讀取硫酸根濃度，檢測範圍為 0~70 mg/L，若超過範圍則將樣品稀釋再測。

2.6 PVA 固定化菌體顆粒製備方法

利用本實驗室自行開發的 PVA 磷酸酯化法將接續馴養已有降解 DMSO 能力之活性污泥予以包埋。首先，將 9.5%的 PVA 加熱溶於水中，待其冷卻至室溫後，以等比例

之濃縮活性污泥均勻混合後放入硼酸-磷酸溶液中製備成固定化菌體顆粒。

2.7 不同菌種降解 DMSO 之比較

將國內化工產業工廠中的廢水處理單元所取之汙泥，在經過馴養後，與同一來源但未經馴養之活性汙泥分別以有或沒有添加蔗糖作為額外碳的來源，分為 4 個組別做降解 DMSO 之比較。

在 4 組 500 mL 三角錐形瓶之中分別裝填 300 mL 的模擬廢水(含有 200 mg DMSO/L)，並分別接種 30 mL 的懸浮活性污泥。各組配製如 Table 5。之後所有實驗使用之菌種和 A 菌來源相同。

2.8 不同環境因子對活性污泥分解 DMSO 的影響探討

比較(1)不同的起始 pH 濃度(2)不同碳源含量(3)不同接菌量，三種條件對固定化活性汙泥降解 DMSO 之影響。

實驗條件：DMSO 初始濃度均為 100 mg/L；pH 分為 3、5、7、8.5 和 10，配製方式詳見 Table 6。蔗糖 (sucrose) 起始濃度設定如 Table 7 所示。接菌量多寡影響實驗各組設定為 0 g、15 g、30 g、45 g 及 60g 。

2.9 反應器及其週邊設備

本研究之設備如 Fig.1 所示。氣舉式反應器裝置為一塔高約 47cm，工作體積(working volume)為 3.2 L 之壓克力製反應器，內徑 11 cm；拖曳管高 33.5 cm，內徑為 5 cm，縱橫比大約為 1：6.6。而空氣由槽體下方進入，利用電磁隔膜式空氣泵(Hiblow, Sun Mines, Taipei County, Taiwan) 經由流量計控制流量，打入反應器中。氣流速率為 10L/min。

三、結果與討論

3.1 不同菌種對固定化活性污泥降解 DMSO 之影響探討

以不同菌種分為 4 組個別降解 300 mL 的搖瓶實驗結果如 Fig. 2 所示。由 Fig. 2 可明顯看出，初始 DMSO 濃度同為 200 mg/L DMSO 的降解速率，馴養過之 A 菌種降解速率遠快於 B 菌種，且是否添加蔗糖對其之影響並不明顯。反觀同一汙泥來源卻未經馴養之 B 菌種，除降解速率緩慢許多，蔗糖之添加影響也甚鉅。探討其原因可能為，蔗糖相較於 DMSO 屬於較易分解使用的碳來源，故活性汙泥會先分解使用蔗糖才開始降解 DMSO，使 DMSO 降解初期有一段啟動期。而此時已可約略看出經過長期馴養之 A 菌種降解 DMSO 速率對於碳源添加與否影響不大。之後所有實驗皆使用和 A 菌種相同之汙泥來源。

3.2 不同環境因子對固定化活性污泥降解 DMSO 之影響探討

3.2.1 不同起始 pH 值對活性汙泥分解 DMSO 能力的影響

根據 Eckenfelder 的研究指出，大多數的微生物無法生存在 pH 值低於 4.0 或高於 10.0 時之環境中，當環境 pH 值小於 4.0 時，過多的氫離子(H^+)會導致微生物體內酵素蛋白質的變性，而僅有少數的硫酸鹽氧化菌類可存活。當 pH 值大於 10.0 時，對微生物之存活亦具有毒性。故一般而言，對微生物存活之最佳 pH 值範圍應介於 6.5~8.0 之間 (Eckenfelder, 1967)。

對固定化活性汙泥進行不同起始 pH 值的實驗結果如 Fig. 3、4 所示。Fig.3 可看出經過 72 小時的降解，pH 5~pH 8.5 間活性污泥的去除效率分別可達到 92.8%、100%以及 71.7%。而 Fig. 4 中 pH 7.0 的組別更在 48 小時即完成降解 DMSO，除 pH 3.0、pH 10.0 兩組其餘皆在 56 小時降解完成。且發現在初始 pH 5.0 至 8.5 之間的環境下培養，DMSO 的降解速率最為迅速，反應進行約 56 小時內 DMSO 即可達到 90%以上的去除率。

由於緩衝溶液的不同，pH 3.0、5.0、7.0 和 pH8.5、10.0 在水中溶氧量(DO)差別極大。pH 3.0、5.0、7.0 等組別因緩衝溶液含有大量的檸檬酸 (citric acid，分子式 $C_6H_8O_7$，又稱枸櫞酸)，除在實驗經 24 小時後即有白色混濁產生，長出懸浮菌體，溶液中檸檬酸含量越多也越顯混濁，導致 DO 迅速下降，甚至到 0 mg/L。反之含硼酸 (boric acid，分子式 H_3BO_3) 的組別 pH 8.5、pH 10.0，一直到降解實驗後期才有些微混濁產生，而因硼酸的存在也使活性汙泥顆粒摸起來變得更為有彈性。

3.2.2 不同起始碳含量對活性汙泥分解 DMSO 能力的影響

根據 Yang *et al.*的研究指出，在相同環境條件下比較有添加或是沒有添加 50 mg/L 蔗糖的 DMSO 降解。添加蔗糖的部分，DMSO 的 TOC 由 80~84%上升至 92-95%。額外添加的蔗糖可作為附加碳源程序而提升微生物對毒性有機物 (DMSO) 分解能力，並與所謂的共代謝程序相當類似 (Rittmann

and McCarty, 2001)。依據其研究成果顯示，在此處理程序中，某些化合物沒有被微生物利用作為能源來生物分解這些化合物。然而，必要的酵素可以在簡單的可生物分解化合物中產生，如蔗糖，可以用來使某些具有毒性且不容易被自然生物分解的化合物 (如 DMSO) 被完整的生物分解。

在 Yang *et al.*的實驗中，若無另外添加蔗糖作為碳源，則 DMSO 無法完全的被生物分解去除 (80~84%)，在添加後，去除效率增加至 92~95%。由此可知，額外添加蔗糖 (sucrose) 可以提供生物降解 DMSO 時進行共代謝所需之碳源 (Yang *et al.*, 2003)。

對固定化活性汙泥進行不同起始碳源(蔗糖) 含量的實驗，較低濃度的結果如 Fig. 5、6、7 所示；Fig. 5 可以看出經過 45 小時的降解，蔗糖 (sucrose) 濃度在 0~200 mg/L 間活性污泥的去除效率分別為 73%、100%、76%及 79%，蔗糖濃度為 300 mg/L 則降解較慢僅有 44%。且發現在蔗糖濃度偏高如 100 mg/L、200 mg/L 及 300mg/L 的初始降解速度均比 0 mg/L 及 50 mg/L 快，但之後降解速度即漸趨平緩。反之，活性汙泥在蔗糖初始濃度 0~50 mg/L 之間的環境下培養，DMSO 的去除雖然一開始較為緩慢，但經約 30 小時啟動期後即開始迅速降解 DMSO，降解速率遠快於蔗糖濃度偏高的組別，反應進行在 50 小時內 DMSO 即可達到 90%以上的去除率。

經過不斷地重複批次降解 DMSO 後，固定化活性汙泥顆粒降解 DMSO 的速率大幅提升。Fig. 7 為經過三個月馴養之後，所有組別的固定化活性汙泥顆粒將 100 mg/L 的 DMSO 降解完成皆僅需 12 小時。觀察重複批次實驗結果可發現，固定化活性汙泥顆粒經過反覆的降解 DMSO 之後，除了降解完成所需時間隨著批次增加而縮短，蔗糖濃度多寡對於活性汙泥顆粒降解 DMSO 之影響也越薄弱，由 Fig. 7、8 可看出在蔗糖濃度為 0~500 mg/L 之間降解速率時間幾乎相同，僅 12 小時即可將 DMSO 降解完畢。

另外，較高濃度蔗糖的實驗結果如 Fig. 8 所示，固定化活性污泥顆粒經過持續的馴養後，蔗糖濃度為 0、50、500 mg/L 的組別皆可在 12 小時內將 100 mg/L DMSO 降解完畢，蔗糖濃度 1000 及 1500 mg/L 的組別也能在 28 及 32 小時降解完成，所有組別的去除率均可達到 100%，且隨著蔗糖濃度越高，降解時間也較久。由此可知，蔗糖濃度在超過 1,000 mg/L 後對於活性污泥降解 DMSO 是有影響的。

3.2.3 不同接菌量對分解能力之影響

一般而言，活性污泥降解 DMSO 之速率變快有兩種原因：菌體降解活性增加或菌量增多。不同接菌量降解 DMSO 之重複批次結果如 Fig. 9、10。

由圖可看出降解速率並未如預想之菌量越多降解速率越快。每批次 DMSO 降解完成後皆將固定化顆粒集中，並以滅菌過之模擬廢水洗淨顆粒表面，再重新分裝各 30 g 到 5 個三角錐瓶進行下一批次試驗，故各三角錐瓶中菌體顆粒的狀態及活性應是平均且一致的，因此降解速率的最大影響因素以菌量多寡為主。由實驗結果可知降解速率約為 30 g、45 g 快於 15 g、60 g，若僅比較 15 g、30 g 及 45 g 三組之降解速率，則能有菌量越多降解速率也越快現象之呈現。探討接菌量為 60 g 時降解速率不高之原因，可能因三角錐瓶中置入 300 mL 模擬廢水及 60g 菌體顆粒，僅以 120 rpm 震盪培養，因空間狹小造成混合不均勻且阻礙質傳，造成降解速率變慢的主因。反之，若具備足夠的空間及良好的環境條件，則降解速率將隨著接菌量越多而提高。

3.3 氣舉式反應器重複批次實驗

3.3.1 搖瓶中活性汙泥在 DMSO 的生長

當懸浮活性汙泥培養於包含 200 mg/L DMSO 模擬廢水的三角錐形瓶時，DMSO 在 17 小時內被降解，且 DMSO 轉換為硫酸鹽離子並直接地累積在模擬廢水中；培養基中懸浮活性汙泥濃度也隨著 DMSO 降解而升高，顯示活性汙泥能藉由降解 DMSO 而生長，實驗結果如 Fig. 11。

3.3.2 DMSO 曝氣逸散背景實驗

為了測試 DMSO 是否因培養基沈積造成濃度下降或是因為曝氣而造成 DMSO 逸散至空氣中，將含有 700 mg/L DMSO 的模擬廢水置入反應器中進行空白試驗，並逐時採樣檢測 DMSO 濃度，注入反應器的氣流速率為 10 L/min。

由試驗結果發現在常溫 25℃的培養條件並以 10 L/min 的氣流速率進行曝氣的環境中，在前 24 小時起始濃度 700 mg/L 的 DMSO 模擬廢水因培養基吸附，以及因曝氣而逸散的 DMSO 濃度少於 10 mg/L，從 40 小時開始則因曝氣造成水氣蒸發而使濃度開始上升，如 Fig. 12。因此在常溫 25℃，

氣流量 10 L/min 的培養條件下 DMSO 逸散至空氣中的濃度變化幾乎可以忽略。

3.3.3 活性污泥於氣舉式反應器重複批次降解 DMSO 試驗

為了解活性污泥經過長時間的操作後是否仍能穩定性的分解去除 DMSO，以作為是否可應用於實廠操作之判斷依據。本試驗於最適培養條件下進行重複批次培養試驗，觀察其對菌體活性及 DMSO 分解速率之影響。

（1）懸浮活性污泥反應器重複批次試驗

懸浮活性汙泥在氣舉式反應器重複批次降解 DMSO 的實驗結果如 Fig. 13。由 Fig. 13 可知懸浮活性污泥最終可在 10 小時內將負荷量為 850 mg/L 的 DMSO 去除近 99%，相較於 Muratani (1999) 所發表降解 600 mg/L DMSO 需 15 小時以上，以及 Yang and Myint (2003) 發表 600 mg/L DMSO 在 6.66 小時的水力停留時間達到 95% TOC 去除率為佳。

（2）固定化活性污泥反應器重複批次試驗

固定化活性汙泥在氣舉式反應器重複批次降解 DMSO 的實驗結果如 Fig. 14。由 Fig. 14 可知固定化活性污泥最終可在 45 小時內將負荷量 1200 mg/L DMSO 降解完成，處理 800 mg/L DMSO 的負荷量也僅需 21 小時即完成。以倍數提高 DMSO 進料濃度並未影響固定化活性汙泥的降解活性，在 1200 mg/L 的 DMSO 負荷量下活性汙泥仍能不受影響穩定的降解 DMSO。由此可看出固定化活性汙泥對於 DMSO 負荷量的增加是具有忍受及處理能力的，系統穩定性也足夠。

四、結論

4.1 結論

本研究主要是探討利用活性污泥在氣舉式反應器進行一連串分解 DMSO 之批次試驗，並利用固定化技術加強活性污泥對環境的適應性。分別探討環境及環境操作因子(包括 pH 值、蔗糖濃度及接菌量多寡) 對活性污泥分解 DMSO 的影響以及連續批次 DMSO 進料對活性污泥負荷的影響。

本研究所得知的結論，茲分述如下：

1. 固定化活性污泥顆粒分解 DMSO 的最佳 pH 值範圍為 5.0 至 7.0 之間，在 pH 為 8.5 的起始條件下分解較緩慢，但依然能順利完成降解 DMSO。而在較低之 pH 3.0 及較高之 pH10.0 環境中，固定化活性污泥對 DMSO 進行分解雖受到阻礙，但在 pH 3.0 的環境下降解能力仍優於 pH 10.0。
2. 不同蔗糖濃度之影響試驗結果顯示，於濃度為 0~50 mg/L 之間較為適當，也較符合經濟效益成本。若濃度太高將使活性污泥偏向以蔗糖為主要碳源，而降低其分解 DMSO 之能力，且高濃度蔗糖後期的降解速率漸趨平緩原因可能是因葡萄糖產生造成抑制活性污泥降解 DMSO。
3. 由懸浮污泥反應器重複批次試驗結果顯示，於初始 DMSO 濃度負荷量範圍為 100 ~850 mg/L 時，活性汙泥可完全降解 DMSO，去除率皆可達到 100 %。
4. 由固定化活性污泥反應器重複批次試驗結果顯示，系統於初始 DMSO 濃度負荷量範圍為 100 ~1200 mg/L 時，固定化活性汙泥顆粒可完全降解 DMSO，去除率皆可達到 100 %，且添加較高濃度的 DMSO 並未影響活性污泥顆粒穩定降解 DMSO。
5. 對活性污泥顆粒在氣舉式反應器中進行連續批次試驗結果顯示，DMSO 分解速率會隨著重複批次次數增加而逐漸增加。此外，在變更 DMSO 進料濃度時沒有影響分解速率情形發生，顯示活性污泥顆粒具有不錯的 DMSO 濃度變化忍受能力，系統具穩定性足夠。此對於應用於往後連續或實務操作之可能性具有相當高的發展潛力。

4.2 建議

1. 欲分解之目標物 DMSO 降解後會生成酸性物質(sulfate)而導致 pH 值下降，影響懸浮污泥的活性而導致去除效果不佳。因此，於連續處理 DMSO 的情況下，需適當地維持其 pH 值，使 pH 值不至於降到會影響污泥活性的程度。
2. 透過固定化技術除了降低 pH 對污泥直接性的影響，固定化顆粒也方便收集控管且易維持內部菌體的穩定性，具有往後應用到實廠操作的價值。
3. 活性污泥顆粒經過長期馴養後具有不錯的 DMSO 分解能力以及 DMSO 濃度變化忍受能力，系統具有穩定性。此對於應用於往後生物反應器連續操作之可能性具有相當高的發展潛力。具有發展以生物反應器處理 DMSO 的研究價值。

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附 錄

Table 1、ARRAY 流程所排放之主要污染物

空氣污染排放物	廢水污染排放物	廢棄物污染排放物
異丙醇、丙酮、聚亞醯胺、氟氣、磷酸、氯化氫、硝酸、矽甲烷、氫氟酸、硫酸、磷化氫、乙醇、乙酸正丁酯…等。	異丙醇、丙酮、光阻劑、顯影液、蝕刻液、剝離液、磷酸、乙醇、硝酸、氫氟酸、硫酸、磷化氫、二甲亞碸、四甲基氨氫氧化物…等。	集塵灰、汞燈、氟化鈣污泥…等

工業研究院執行經濟部工業局九十三年度專案計畫-平面顯示器產業環境建構計畫, 2004

Table 2、平面液晶顯示器業者常用廢水處理技術(工業研究院執行經濟部工業局九十三年度專案計畫-平面顯示器產業環境建構計畫, 2004)

污染防治設備		處理容量範圍(CMD)
廢水處理設備	物化處理法	300~900
	生物處理法	900~1700
	厭氧－好氧薄膜生物處理	700~1500
	厭氧反應槽	600~1200

Table 3、Composition of DMSO degradation medium.

Component	Quantity	Company
DMSO	280-997mg/L (半導體廢水為600mg/L)	SIGMA-ALDRICH CO.
Sucrose	50 mg / L	SIGMA-ALDRICH CO.
$CaCl_2$	1.82 mg / L	SIGMA-ALDRICH CO.
$(NH_4)_2SO_4$	120 mg / L	Merck
$FeCl_3•6H_2O$	0.15 mg / L	Merck
$MnSO_4•H_2O$	2.5 mg / L	Merck
$MgSO_4•7H_2O$	25 mg / L	WAKO PURE CHEMICAL INDUSTRES. LTD.
KH_2PO_4	2.72 g / L	聯工製藥
K_2HPO_4	5.225 g / L	聯工製藥
其他使用之藥品均為試藥級或以上等級藥品。		

Table 4、高效能液相層析儀之操作條件

HPLC 型號	YOUNGLIN INSTRUMENT Acme 9000	備註
層析管規格	Hypersil ODS (5μL, 250×4.6 mm)	
移動相1	0.1 mol/L 丙酮 (acetone)	UV&移動相1僅可測DMSO ($DMSO_2$ 訊號太弱)
移動相2	0.025% /L 硫酸 (sulfuric acid)	RI&移動相2可測得 DMSO、$DMSO_2$
流速	1.0 mL/min	
UV detector檢測波長	225nm	

Table 5、不同菌種降解 DMSO 之比較組別

組別 1	組別 2	組別 3	組別 4
A 菌種含 50 mg/L sucrose	A 菌種無 sucrose	B 菌種含 50 mg/L sucrose	B 菌種無 sucrose

Table 6、緩衝溶液配製表[Dawson *et al.*, 1968]

pH	緩衝溶液種類	所需含量(mL)	配製方法
3	0.1 M citric acid	238.35	兩者混合即可，總體積為300mL。
	0.2 M Na_2HPO_4	61.65	
5	0.1 M citric acid	145.50	
	0.2 M Na_2HPO_4	154.50	
7	0.1 M citric acid	52.95	
	0.2 M Na_2HPO_4	247.05	
8.5	0.1 M KCl + H_3BO_3	150	混合後以蒸餾水稀釋至 300 mL。
	0.1 M NaOH	30.3	
10	0.1 M KCl + H_3BO_3	150	
	0.1 M NaOH	131.1	

Table 7、不同碳源含量對分解能力之影響實驗組別

蔗糖含量 (mg/L)	組別1 控制組(無菌)	組別2、30g菌	組別3、30g菌	組別4、30g菌	組別5、30g菌	組別6、30g菌
低濃度	50 mg	0 mg	50 mg	100 mg	200 mg	300 mg
高濃度	50 mg	0 mg	50 mg	500 mg	1000 mg	1500 mg

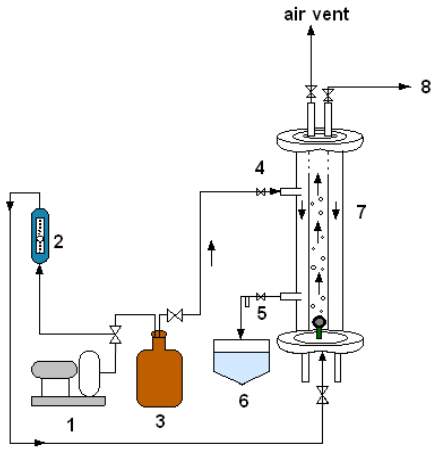


Fig. 1、Set-up of air-lift system:
(1) diaphragm air pump; (2) rotameter; (3) DMSO reservoir; (4) feeding port; (5) liquid sampling port; (6) settler; (7) airlift; (8) gas sampling port for DMS using Tedlar bags.

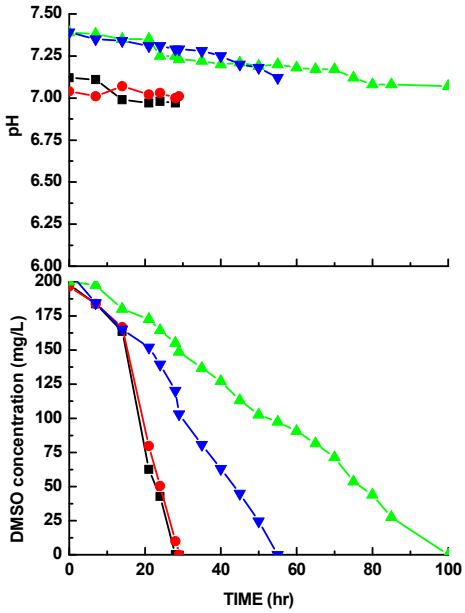


Fig. 2、Effect of acclimation and addition of sucrose by DMSO or other on dimethyl sulfoxide degradation. conditions: Temp.: 30°C; the rotational speed: 120 rpm; initial pH: 7.0; sucrose: 50 mg/L
(—■—) A operated with addition of 50 mg/l of sucrose;
(—●—) A operated without addition of 50 mg/l of sucrose;
(—▲—) B operated with addition of 50 mg/l of sucrose;
(—▼—) B operated without addition of 50 mg/l of sucrose

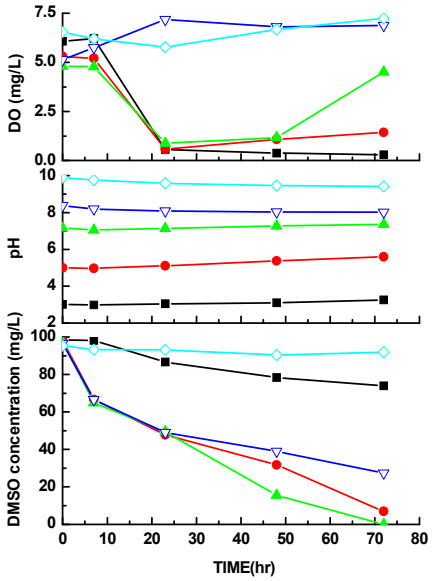


Fig. 3、Effect of pH value on DMSO degradation using the immobilized cells of activated sludge. Operational conditions: Temp.:30°C; the rotational speed: 120 rpm. Various initial pH value:
(—■—)pH3.0; (—●—)pH5.0; (—▲—)pH7.0; (—▽—)pH8.5; (—◇—)pH10.0

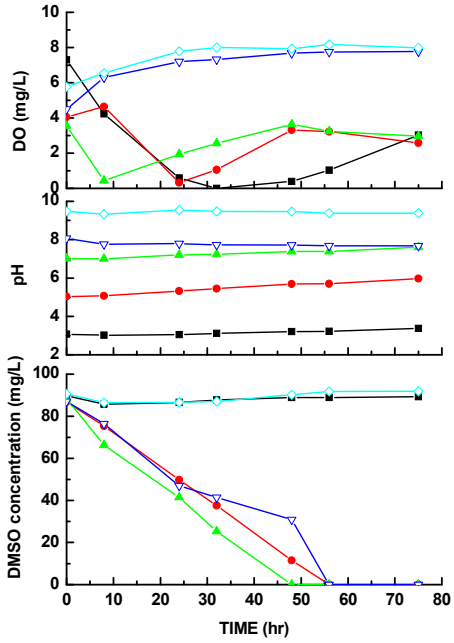


Fig. 4、Effect of pH value on DMSO degradation using the immobilized cells of activated sludge. Operational conditions: Temp.:30°C; the rotational speed: 120 rpm. Various initial pH value:
(—■—)pH3.0; (—●—)pH5.0; (—▲—)pH7.0; (—▽—)pH8.5; (—◇—)pH10.0

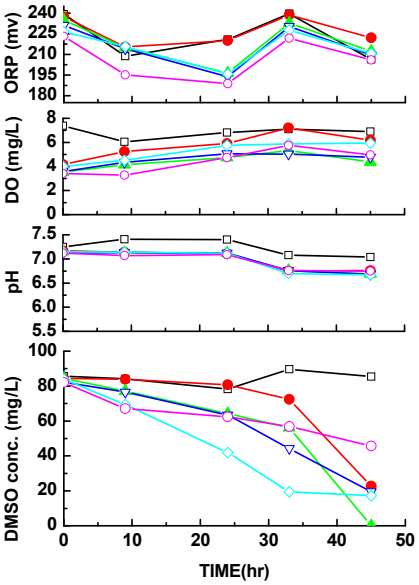


Fig.5、Effect of initial sucrose concentration on DMSO degradation using the immobilized cells of activated sludge. Operational conditions: Temp.:30°C; the rotational speed:120 rpm; initial pH : 7.0; initial sucrose concentration:
(—□—)control:50mg/L; (—●—)0mg/L
(—▲—)50mg/L; (—▽—)100mg/L
(—◇—)200mg/L; (—○—)300mg/L

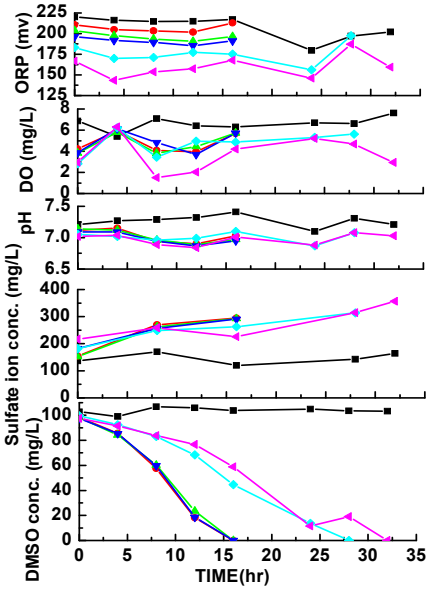


Fig.6、Effect of initial sucrose concentration on DMSO degradation using the immobilized cells of activated sludge. Operational conditions: Temp.:30°C; the rotational speed: 120 rpm; initial pH: 7.0; initial sucrose concentration:
(—■—)control: 50mg/L; (—●—)0mg/L;
(—▲—)50mg/L; (—▼—)100mg/L;
(—◆—)200mg/L; (—◄—)300mg/L

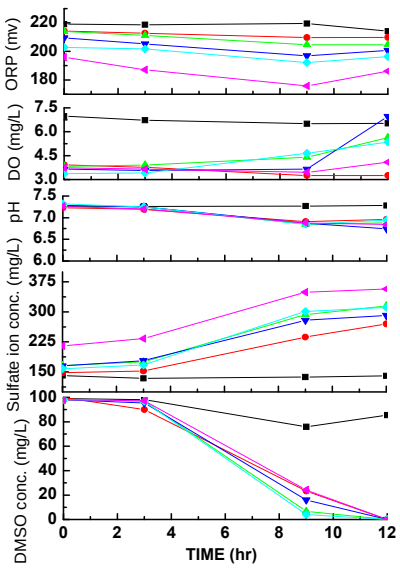


Fig.7、Effect of initial sucrose concentration on DMSO degradation using the immobilized cells of activated sludge. Operational conditions: Temp.:30°C; the rotational speed: 120 rpm; initial pH: 7.0; initial sucrose concentration:
(—■—)control: 50mg/L; (—●—)0mg/L;
(—▲—)50mg/L; (—▼—)100mg/L;
(—◆—)200mg/L; (—◄—)300mg/L

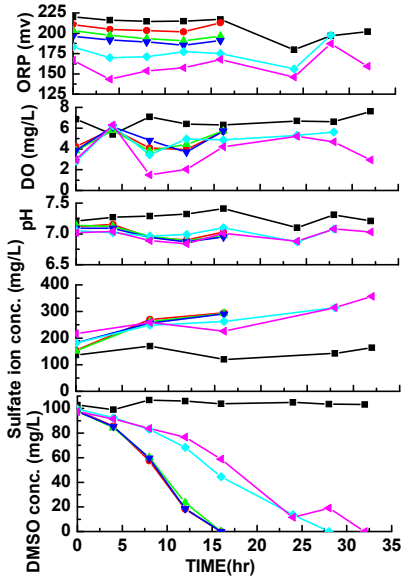


Fig.8、Effect of initial sucrose concentration on DMSO degradation using the immobilized cells of activated sludge. Operational conditions: Temp.: 30°C; the rotational speed: 120 rpm; initial pH: 7.0; initial sucrose concentration:
(—■—)control: 50mg/L; (—●—)0mg/L;
(—▲—)50mg/L; (—▼—)500mg/L;
(—◆—)1000mg/L; (—◄—)1500mg/L

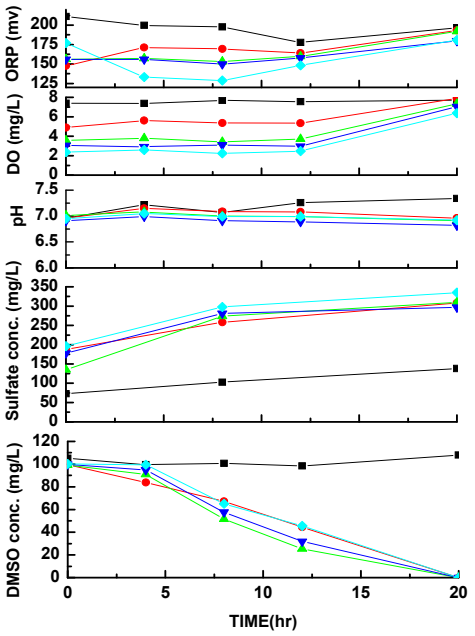


Fig. 9、Effect of biomass on DMSO degradation using the immobilized cells of activated sludge. Operational conditions: Temp.:30°C; the rotational speed: 120 rpm; initial pH : 7.0; biomass:
(—■—)0g; (—●—)15g; (—▲—)30g; (—▼—)45g; (—◆—)60g

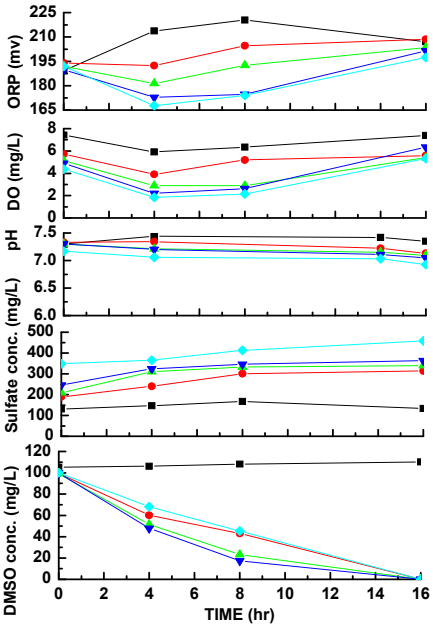


Fig. 10、Effect of biomass on DMSO degradation using the immobilized cells of activated sludge. Operational conditions: Temp.:30°C; the rotational speed: 120 rpm; initial pH : 7.0; biomass:
(—■—)0g; (—●—)15g; (—▲—)30g; (—▼—)45g; (—◆—)60g

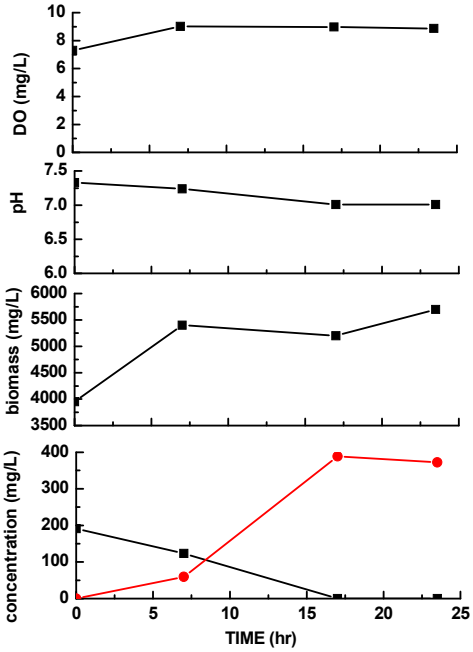


Fig. 11、Degradation of 200 mg/L DMSO by the suspended activated sludge as the sole source of carbon. Operational conditions: initial pH: 7.0± 0.2 Temp.:30°C ;the rotational speed:120 rpm;
(—■—)DMSO; (—●—)Sulfate ion.

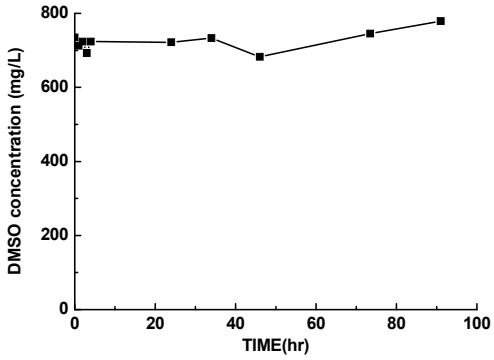


Fig.12、Effect of dimethyl sulfoxide (DMSO) concentration on adsorption of medium and aeration using air. Operational conditions: initial pH:7.0± 0.2; Temp.:30°C; the rotational speed:120 rpm; Initial DMSO concentration: 700 mg/L

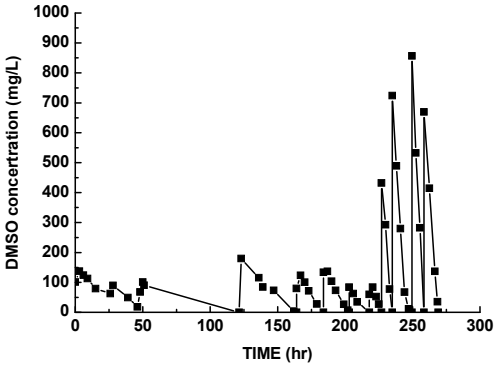


Fig. 13、DMSO biodegradation in airlift bioreactor under repeated-batch mode. Operational conditions: initial pH: 7.0± 0.2; Temp.: 30°C; air rate: 10 L/min

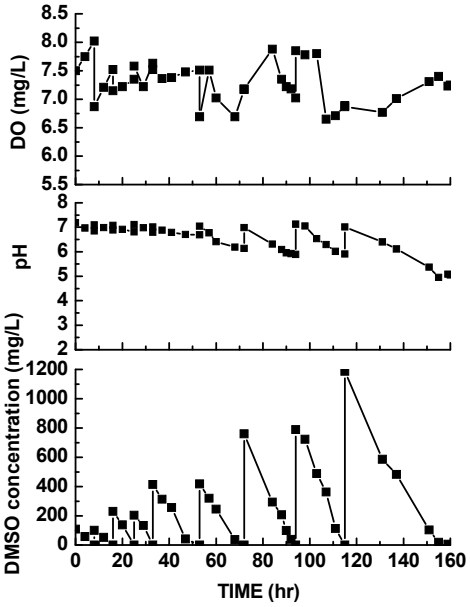


Fig. 14、Repeated batch on DMSO degradation using the immobilized cells of activated sludge. Operational conditions: Temp.: 30°C; initial pH: 7.0± 0.2; air rate: 10L/min.

出席國際學術會議心得報告

97 年 7 月 23 日

報告人姓名	黃思蓴	系所職稱	土木與工程資訊學系教授
時間 會議 地點	97 年 6 月 24 日~6 月 27 日 美國波特蘭	本校核定補助字號	
會議名稱	(中文) 空氣與廢棄物管理第 101 屆研討會與展示 (英文) A&WMA's 101st Annual Conference & Exhibition		
發表論文題目	1. Slurry-phase biological treatment of acetone waste gases using an airlift with the PAA-entrapped *T. pantotropha* cell beads. 2. Restaurant Indoor Air Quality in Hsinchu County, Taiwan. 3. Evaluation of Indoor Air Quality at Taipei City Hospital by Indoor CO_2 Concentration.		

參加會議經過

1. 於開會的第一天到達會場，完成報到手續，如照片 1、照片 2。依規定於第二天早上在展示場的 LOBBY 將 POSTER 張貼完成，照片 3、照片 4。於 6 月 26 日早上 9 點 40 分在第 B119 會場第一場次 (AE-2a) 的第三篇進行報告。會議資料，如附件二冊。
2. 在展示場有收集資料及照一些教學用圖片，如照片 5、照片 6 及照片 7。

與會心得

1. 生物濾床技術在空氣領域已經愈來愈少人投入。生物濾床領域文章發表最多的單位，辛辛納提大學環工系，發表如何加入界面活性劑來改善捕捉疏水性有機污染物的效率。好學校伊利諾香檳分校的環工系則發表，活性碳做為前處理可以緩衝突來的高負荷。第 4 篇是環保設備公司所發表的實務模廠級設備於具毒性酚醛樹脂的處理。第 5 篇是好學校德州奧斯汀分校陳 Lily (Li-Jung) 所發表的乙醇能源工廠的乙醇排氣處理。
2. 以上所發表的內容，大都是生物濾床非主流的實驗內容，過去或許在正規實驗中會發現的歧異現象，現在可能因為沒有題目可以做，只好再做進一步的研究。例如界面活性劑及緩衝進流濃度。而乙醇工廠則是因為最近能源的事件而讓此題目變得新奇而已。最後，有公司嘗試將生物濾床用於毒性物質。

建議

1. 有關生物處理臭味的問題，也許可以找個研討會，例如生化工程等研討會，直接看有沒有更精進的技術可以利用。

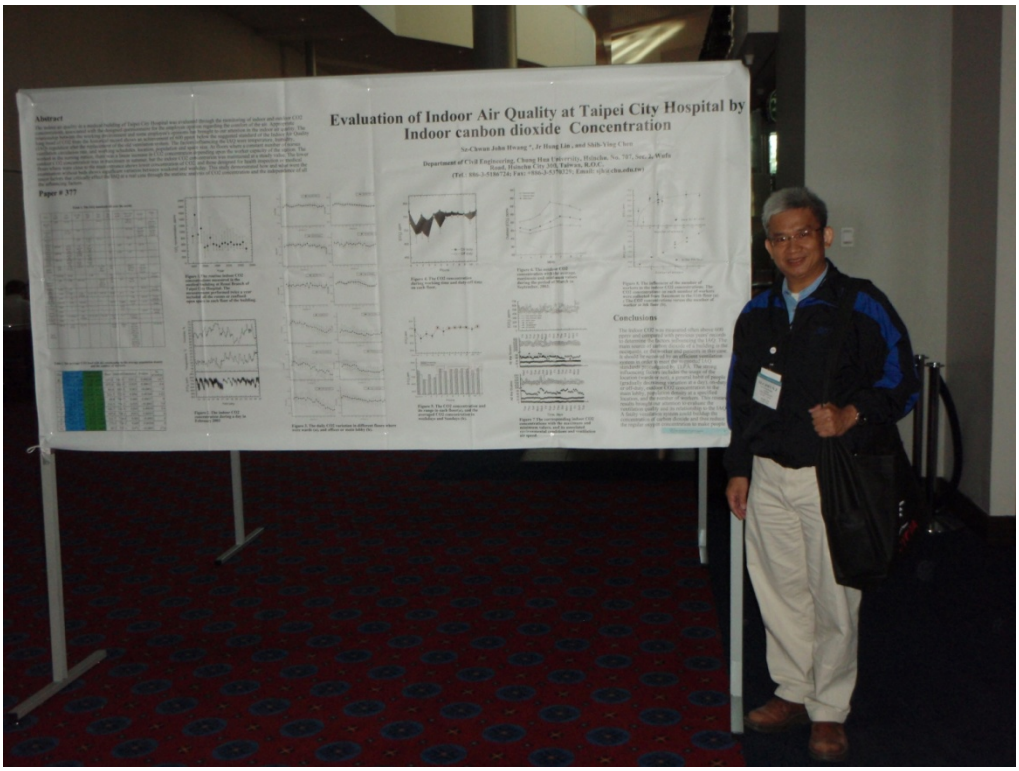
攜回資料名稱及內容

1. 帶回美國環保署一些 CD 資料，(1) US EPA Selected NCER Publications (Links)；(2)Sustainable reuse and revitalization of potentially contaminated sites; (3)Green City partnerships; (4)Interactive abandoned mine lands workshop series; (5)Integrated science assessment for oxides of nitrogen and sulfur- ecological criteria; (6)Air quality criteria for lead; (7)Air quality for monoxide; (8)Earth science reference handbook and data products handbooks vol. 1 & 2.
2. 帶回廠商 CD，Tisch Environment.

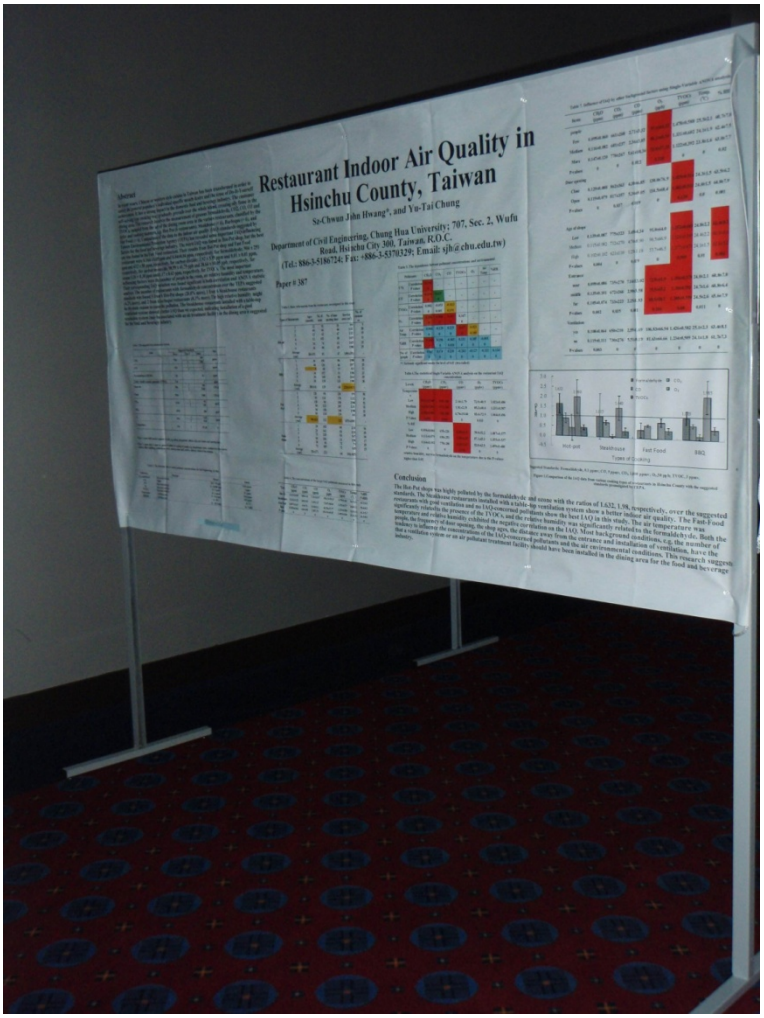
照片 1、會場外觀

照片 2、會場內觀

照片 3、張貼海報論文：Evaluation of Indoor Air Quality at Taipei CityHospital by Indoor CO2 Concentration

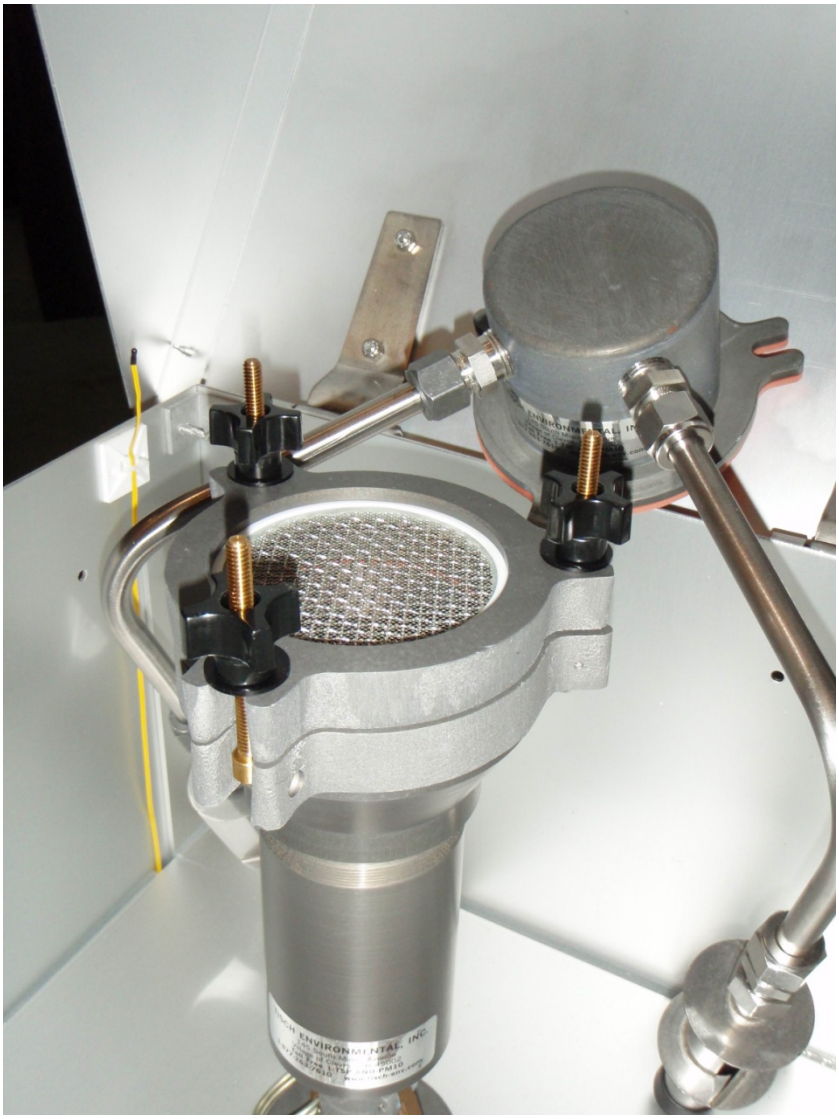


照片 4、張貼海報論文：Restaurant Indoor Air Quality in Hsinchu County, Taiwan



照片 5、攜回 PM_{10} 設備照片，教學用。

照片 6、攜回 Cascade Impactor 教學用照片二張之一。



照片 7、攜回 Cascade Impactor 教學用照片二張之二。

Biological Treatment of Acetone Waste Gases Using a Slurry-Phase Airlift with the PAA-entrapped *T. pantotropha* Cell Beads

Paper # 372

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[2] Energy & Environment Laboratories, Industrial Technology Research Institute, Bldg. 64, 195, Sec. 4, Chung Hsing Rd., Chutung, Hsinchu 310, Taiwan, R.O.C.

Abstract

Acetone is the most commonly used solvent in the Hsinchu Science Park, Taiwan. The innovative air-lift bioreactor embedded with the polyacrylic-amide (PAA) entrapped *Thiosphaera pantotropha* cell beads (2 l) was employed to treat this acetone-contaminated air stream (10 l min^{-1}; 100-1000 ppmv). The 41-l medium solution circulated for more than 9 months was originally used to absorb acetone, which was then degraded by the PAA-entrapped cell beads, and became slurry after 85 days operation. During the first phase operation, the average removal rate is about 79 % for 300 ppmv of acetone in average in the influent air stream. The capacity of the airlift to treat acetone is 109.6 g m^{-3} h^{-1} under the loading of 137.5 g m^{-3} h^{-1}. The maximum COD:N ratio of 100:2.9 is achieved and a balanced nutrient state was indicated by the ORP measurement. The pH of the system was maintained at neutral because of the strong buffer intensity added in the medium (final $\beta=1.18 \times 10^{-2}$ mole l^{-1}). The dissolved oxygen was gradually down to the 2 mg l^{-1}. The conductivity and ionic strength were 4.5-5.6 mS cm^{-1} and 0.1 M, respectively. The PAA-entrapped cell beads provided the best inoculum source to keep the system steadily operated.

Introduction

The Taiwan combined IC production value of the semi-conductor industry, which is one of the most important industries in Taiwan, rated top 3 high all over the world, fully supporting Taiwan economics and social prosperity. However, the high-tech industries use a lot solvent such as acetone, isopropyl alcohol, ethyl diol, butadiene, toluene, xylene as cleaner in the film development, itch, and vapor deposition processes. Many volatile organic compounds (VOCs) were emitted [Khan and Ghoshal, 2000]. Chang and Chang [1999] and Chang and Lu [2003] have reported that the acetone was the most frequently found compounds contributing 50-80% of total VOCs to the Hsinchu Science Park (HSP) of Taiwan. Since the acetone embedded airstream often contains high boiling-point compounds, many treatment facilities couldn't maintain its high treatment efficiency as the new one can promise. For the long period of time, many VOCs, e.g. acetone and isopropyl alcohol which would further be degraded to acetone, go into the residential area adjacent to HSP. People's health and safety were seriously concerned.

VOCs are often treated by adsorption, condensation, absorption, incineration, and biofiltration [Khan and Ghoshal, 2000; Chang and Lu, 2003]. Biofiltration is the most cost-effective method but it

encounters many operational problems such as compaction, drying of filter media, aging and acidification. The alternative process, biotrickling filter, is able to solve most of the problems, but it still clogs in a period of time. Bioscrubber has a less efficiency than the other two processes mentioned above. Also, it needs an additional large treatment facility to treat the circulation liquid, which contains a high concentration of BOD requiring a long operation time for bacteria to degrade it before recirculation.

Airlift that possesses a very good mass transfer efficiency in between gas and liquid phases is a well known bioprocess often used in biochemical engineering. Now the gaseous acetone can be expected to be well dissolved into the liquid phase of the airlift. However, acetone is very toxic to microorganisms; therefore, the protection of microorganisms using an immobilization technique is necessary for the biodegradation. Many articles also demonstrated that the PAA-immobilization system where microorganism is entrapped into the cell beads is a very stable process and its bare leakage of microorganisms continuously provides a source of pure culture. Thus, this study is probably the first report dealing with the three-phase (acetone gas, liquid medium and PAA) airlift bioprocess treating the waste gases containing acetone.

According to our previous reports, acetone can be degraded by *Thiosphaera pantotropha* in a shake-flask culture [Ru, 2003; Lu, 2004] and in a 2.5-m high airlift bioreactor, in which the airlift design and hydrodynamics properties were thoroughly investigated [Chen, 2006]. In this study, the optimal treatment capacity in treatment of the acetone-containing gas stream was evaluated, and kinetics data were modeled under certain assumptions.

experimental methods

Chemicals

Acrylamide Monomer and N,N,N',N'-tetra- methylethylenediamine (TEMED) were purchased from Acros organics (as a part of Fisher Scientific) (Belgium). N,N'-methylenebisacrylamide (BIS) was obtained from Tokyo Kasei. BCA analysis kit was purchased from Pierce company (Thermo Fisher Scientific Inc). Acetone was purchased from Union Chemical Company (Taiwan). All the other chemicals were of reagent grade.

Microorganisms

T. pantotropha (also named as *Paracoccus pantotrophus*) ATCC 35512 was purchased from Bioresource Collection and Research Center (BCRC), Taiwan. The storage of microorganism was annually manipulated at -78 ^{o}C, but subculture was done every month. The composition of medium used for airlift is shown as Table 2-1.

Table 2-1. The composition of acetone biodegradation working medium

Components	**Quantity**	**Company**

Na_2HPO_4	4.2 g	**Shimakyu, Japan**
KH_2PO_4	1.5 g	**Union Chemicals, Taiwan**
$MgSO_4 \cdot 7\ H_20$	0.1 g	**Union Chemicals, Taiwan**
$NaNO_3$	0.1 g	**Union Chemicals, Taiwan**
Tap water	**Fill to 1.0 L**	**Union Chemicals, Taiwan**

Free cell was measured by an optical density, OD_{600nm}, and dry cell weight (105 ^oC for 12 h). Immobilized cell concentration was determined by the protein content of the cell beads using the BCA Protein Assay kit [Pierce chemical company, 1997].

Polyacrylicamide (PAA) Cell Beads

Acrylicamide monomer, crosslinker BIS and accelerator TEMED were added into aseptic distillated water under a constant proportion at 4 ^oC and mixed thoroughly. On the other side, the settled centrifuged culture (20%, v/v) mixed with sodium alginate (0.5%, w/v) at 4 ^oC. Next, the polymer solution and the culture solution were instantaneously mixed into a small syringe by a peristaltic pump before ejected into the calcium chloride solution (0.3%，w/v). The calcium and alginate will immediately form a very stable complex, helping the fast formation of cell beads in a 0.5-1.0 h. When the cell beads were solidified, they were screened and moved to the potassium phosphate solution (pH 7.8) to remove the calcium alginate. At the meantime, the polyacrylic amide (PAA) cell beads were formed. The size of cell beads can be controlled by the needle size of the syringe used.

Acetone Analysis

Acetone gaseous and liquid concentrations were analyzed by a Gas Chromatograph (GC) (China Chromatography 8900, Taipei County, Taiwan) equipped with a flame ionized detector (FID). A 15-m long 0.53-mm ID Supelco, SPB-5 capillary column with a fused thickness of 3.0 μm was used. Nitrogen carrier gas of GC is used. The oven, injector and detector temperature were 150, 180 and 200 ^oC, respectively.

Gaseous acetone calibration was prepared by placing 1, 2, 3, 4 and 5 μl of acetone solvent into five 10-liter SKC Tedlar air sample bags, respectively, and measuring them after the bags were placed into an oven at 70 ^oC for 1 minute and then cooled down to room temperature.

Standard liquid acetone solution was prepared using a 250-ml brown bottle with a gas-tight rubber/Teflon stopper. The bottles containing different amount of acetone were placed in a water bath at 150 rpm and 30 ^oC for 30 minutes. The samples were mixed with 0.5% propyl alcohol as an inner standard in a proportion of 1:1 (v/v). of The 2-ml sample was centrifuged at 6,000 rpm for 10 minutes and then 0.5 μl supernatant was withdrawn into GC/FID for analysis.

Airlift Bioreactor

The airlift bioreactor is depicted in Table 2-1. The column of the airlift was made of acrylic, 2.5 m high and 19 cm ID with a total working volume of 41 l. It was divided by a flat plate of 127 cm long × 19 cm wide into two sections, i.e. the drag tube and downcomer. This configuration with a diameter-to-height ratio of 1:9 is very suitable for gas transfer into the liquid. The gaseous acetone at 10 l min^{-1} came into the reactor through the bottom gas distributor. The Dissolved oxygen, pH and ORP sensors were installed for monitoring the performance of system.

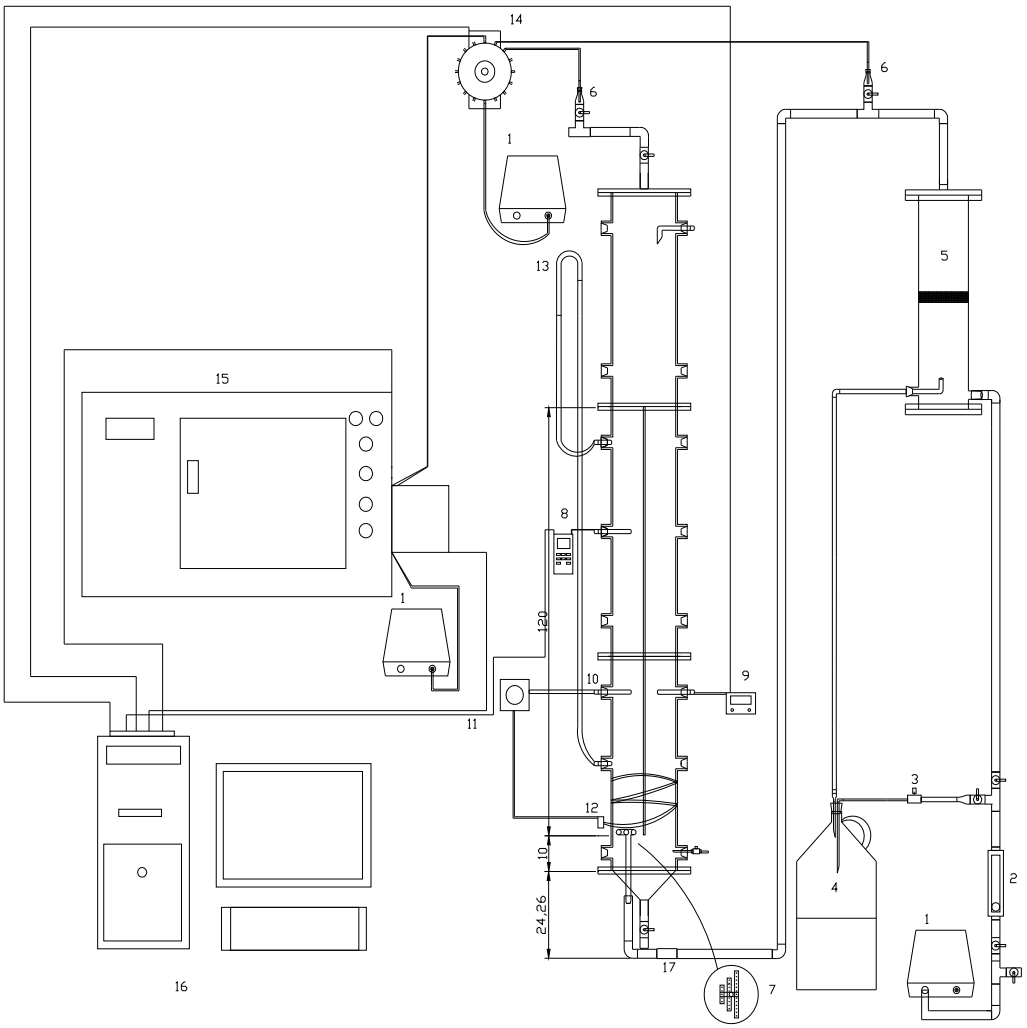

Figure 2-1. The airlift bioreactor. (1) Diaphragm air pump, (2) rotameter, (3) needle valve, (4) VOC bottles, (5) equalization basin, (6) sampling port, (7) gas distributor, (8) D.O. meter, (9) pH meter, (10) temperature sensor, (11) temperature control relay, (12) heating ribbon, (13) U-shape manometer, (14) auto-sampler, (15) GC, (16) computer, (17) check valve.

One ml of gaseous acetone was automatically sampled by using a Valco 16-port stream selector and a Valco 10-port 2-position injector. All the relay control signal and the GC analysis signal were transmitted from or to the personal computer, respectively, through a NI-DAQ card (NI-6024, National Instrument, Austin). All the liquid samples were withdrawn from the top surface of bioreactor using a siphon tube.

Results and Discussion

Our new innovative artificial-cell-bead-embedded airlift bioreactor requires external nutrition sources; for example, nitrogen. Once using this bioreactor to treat waste VOC gases was feasible, the stability (pH, conductivity, dissolved oxygen and redox potential, duration and maximum treatment capacity were the most interested issues to be investigated.

Microbial Characteristics

The characteristics of *T. pantotropha* has thoroughly been studied in a shake flask culture [Lyuu, 2003]. *T. pantotropha* is a nitrogen requiring bacterium. In the previous study, various organic nitrogen sources: i.e. yeast extract, monosodium L-glutamate and Urea, and inorganic sources: sodium nitrate and ammonium chloride were chosen for evaluating the efficiency of acetone biodegradation. We found that using the nitrate as a nitrogen nutrient is the best results in biodegradation of acetone. Only 12 h was needed for 90% acetone removal; 20 h for completely biodegradation of acetone (data not shown). In addition, it has the advantages of less biomass produced and lower cost for nitrate purchase. The optimal loading of 1 g l^{-1} was chosen for the rest of experiment.

The acetone biodegradation activity was seriously inhibited when the liquid acetone concentration was more than 700 mg l^{-1}. The acetone removal efficiency was then decreased from 100% to 57%. However, this microbial toxicity could be prevented by using an immobilization technique, to have the microorganisms entrapped into the PAA cell beads. The acetone removal efficiency could maintain 91% (data not shown).

Treatment of Gaseous Acetone in Airlift

The acetone-containing gas stream was treated by the airlift with the PAA-immobilized *T. pantotropha* entrapped -cell beads. The 85-day performance data are shown in the Figure 4-1. The average input and output concentration of gaseous acetone were about 300 ppmv and 63 ppmv, respectively. The removal efficiency was around 79%. The accumulated liquid acetone concentration was 25 mg l^{-1} in average.

During day 24-35, the gas auto-sampler for GC/FID was clogged. Because less quantity of acetone shown in the computer screen, the opening of VOCs valve was turned to the maximum, leading to the real acetone input concentration more than 631 ppmv. The gaseous and liquid acetone concentrations were 97 ppmv and 23 mg l^{-1}, respectively. Since the removal efficiency was more than 85%, it demonstrated that the liquid water can provide a large load-buffering intensity in equalization of the capacity; i.e. absorption of the peak acetone gas stream immediately.

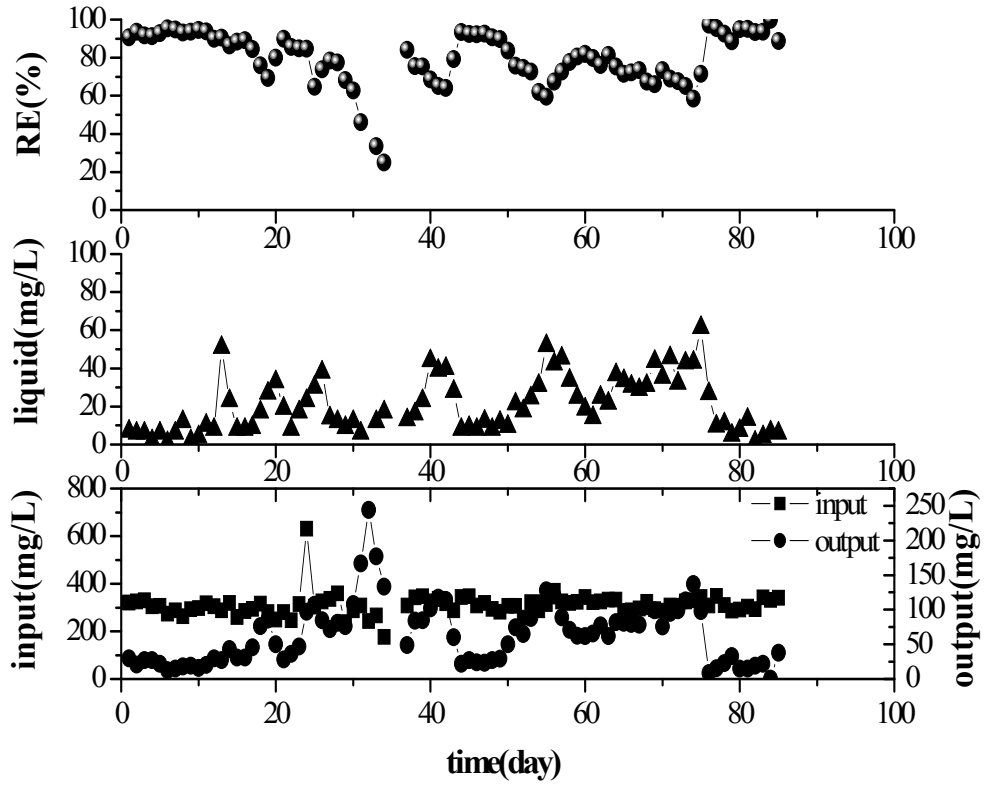

Figure 4-1. The time course profile of acetone biodegradation by the airlift with 2-l PAA-immobilized cell beads in treatment of the gas stream containing 300 ppmv of acetone at 10 l min^{-1}.

The Nutrition Demand

In the reality, we need the absorption solvent to capture acetone, but we couldn't use the enrichment medium to carry the PAA cell-entrapped gel beads due to the high cost of chemicals. Therefore, only a constant amount of tap water (41 l) with HCMM medium (Hwang et al., 2003) containing 1-g l^{-1} sodium nitrate was used as a cell bead carrier. The result of acetone biodegradation is shown in Figure 4-2. However, the system couldn't start up unless our adding 100 mg l^{-1} of sodium nitrate to the tap water. An additional amount of sodium nitrate was further required 5 times to maintain a stable treatment efficiency when the removal efficiency of 300-ppmv gaseous acetone decreased down to below 60% or the liquid acetone concentration increased to above 30 -50 mg l^{-1}.

For example, at day 19, the acetone removal efficiency of 90% decreased down to 69% which was corresponding to the rising of liquid acetone concentration to 27 mg l^{-1}. Day 20 after the addition of 25 mg l^{-1} sodium nitrate, the removal efficiency increased from 69% to 80% with the further duration of 11 days. Except the period of day 24-35 when GC gas auto sampler was clogged; otherwise, the trend of coming down and then going up in the gaseous acetone concentration was kept for a couple of weeks until at day 74, the liquid acetone concentration was over 50 mg l^{-1}. Therefore, 5-times dosage of 125-mg l^{-1} sodium nitrate was added to the system. The apparent improvement in the liquid acetone concentration was observed. In fact, the system was not added any nitrogen source for a year (data not shown).

In calculation of nitrogen dosage, the results are shown in Table 4-1. For the first 19 days, the COD: N ratio was maintained at 100:10.5, if both the initial 1 g l^{-1} of sodium nitrate and its external addition of 100 mg l^{-1} were taken into account. As seen in Table 4-1, the COD:N ratio becomes less and less. Eventually, no more nitrogen source was added to the system after day-74 addition. The system was run for almost one year until it became too slurry. This trend of COD:N also provides a good information regarding how to feed the nutrition for this type of artificial cell-entrapped gel beads. In other words, it is economically feasible.

Table 4-1. The COD:N ratio during the acetone biodegradation

Day	Addition of nitrate, mg l^{-1}	Accumulation of nitrate, mg l^{-1}	g-N day^{-1}	g-C day^{-1}	g-COD day^{-1}	COD: N 100: N
0	100	1,100	2.37	6.35	22.57	10.5
19	25	1,125	1.49	6.35	22.57	6.6
31	25	1,150	1.12	6.35	22.57	5.0
42	25	1,175	0.88	6.35	22.57	3.9
55	25	1,200	0.66	6.35	22.57	2.9
74	125	1,325				

*: The conversion factor of g-acetone to g-COD and to g-C are 2.2 (=128/58) g-COD/g acetone and 0.62 (=36/58), respectively; the 10 lpm of 300-ppmv acetone gas stream gives the mass flow rate of 10.2 g-acetone/day.

Generally, the ratio of COD:N:P in a biological treatment plant was suggested to be 100:5:1 in textbook. Brauer [1986], and Johnson and Scow [1999] suggested the C:N:P ratio should be 100:5:1 in order to prevent the limit of Nitrogen nutrient and to maintain the microbial activity in biodegradation. Acuna et al. [2002] reported the type of nutrient sources and its concentration were also very important in treatment of toluene. Brar and Gupta [2000] used the same *T. pantotropha* to metabolize the TCE at the optimal C:N ratio of 100:20 that was in the range of our C:N ratios (37.4-10.5) calculated from Table 4-1.

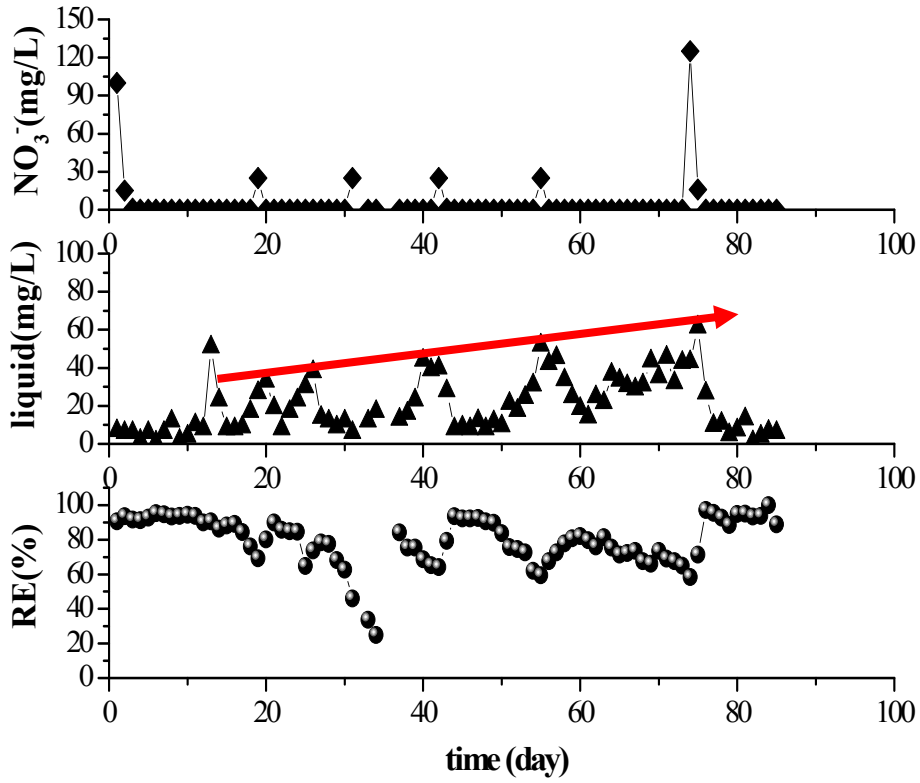

Figure 4-2. The time course profile of nitrogen nutrient in acetone biodegradation by the airlift with 2-l PAA-immobilized cell beads in treatment of the gas stream containing 300 ppmv of acetone at 10 l min^{-1}.

The Stability of the Airlift System

1. pH

Most bacteria cannot survive in the environments where the pH is below 5 or above 9. In our previous study, free *T. pantotropha* could only metabolize the acetone at pH 7 and 8.5, not at pH below 5.5 or above 10. In this study, the pH was maintained in between 7.10-7.25, indicating the system had a strong buffering intensity to neutralize the carbonaceous acid. Thus, the culture medium was used for one-year operation without any blow-down operation. The phosphate buffering intensity, β, was finally determined to be 1.18×10^{-2} initially and 1.50×10^{-3} mole L^{-1} at day 85. Although the buffering intensity is still available, the PAA cell beads normally will provide a good environment for pH change by altering the distribution of hydrogen ions through the formation of hydrogen-bond in its matrix.

Optical density for free cell growth in the liquid

The growth of suspended cell in the liquid phase can be evaluated by optical density (OD). In this study, the OD value increased from 0.3 (absorbance) in the beginning of the operation to 1.5 finally. It took first 10 days to achieve the OD value of 1.2, and then increased slowly to 1.5 at day 85. Bailey et al. [1986] reported that the biomass in the fed-batch bioreactor usually attained to a steady state where the microorganisms were under stationary phase due to the limit of other nutrient supply. According to the results of acetone concentration modeling, the removal of acetone was gradually dependent upon the biomass existing in the liquid phase instead of those in the PAA cell beads. This result demonstrates that the PAA entrapped-cell beads could provide an initial source for the dominant microorganism.

Conductivity

Conductivity was used to analyze the electrolyte content of the liquid water in the airlift. At day 85, the conductivity value and ionic strength were 4.5-5.6 mS cm^{-1} and 0.072-0.089 M, respectively. According to the water body classification standard in Taiwan, Class 1 used for water supply and swimming should contain the conductivity and ionic strength of below 750 μS cm^{-1} @25℃ and 0.012 M, respectively. An IC foundry uses a pure water met with the standard of the conductivity and ionic strength of below 0.0556 μS cm^{-1} @25℃ and 8.9×10-7 M, respectively. The reverse osmosis for drinking purpose gives a water with the conductivity and ionic strength of 0.0625 μS cm^{-1} @25℃ and 1.0×10^{-6} M, respectively. A fresh activated sludge and anaerobic digested sludge obtained from the Chang Chun PetroChemical Co., LTD. had the conductivity of 2.53 and 3.40 mS cm^{-1} and ionic strength of 0.041與0.054 M, respectively. Obviously, our liquid water had the similar property with the sludge.

Normally, the microorganisms couldn't survive under the ionic strength more than 0.1 M which was corresponding to the conductivity of 6.3 mS cm^{-1}. Our liquid water had the ionic strength close to 0.1 M but the system could continuously metabolize acetone without any inhibition, indicating the immobilized cell beads could provide a barrier for high salinity gradient.

Dissolved oxygen

Dissolved oxygen can reflect the aerobic microbial activity in degradation of acetone. Figure 4-3 shows the time course of dissolved oxygen in biodegradation of acetone in an airlift bioreactor. During the period of 85-day operation, the dissolved oxygen decreased from 8.5 to 4.6 mg O_2 l^{-1}, with the average value of 6.3 mg O_2 l^{-1}. The decreasing trend indicates the more biological activity produced in the liquid water. The maximum dissolved oxygen in pure water is 9.07 mg but its value

decreased down to 2-3 mg O_2 l^{-1} in the aerated basin in a full-scale activated sludge system. Therefore, our designed system could provide enough oxygen for microbial degradation.

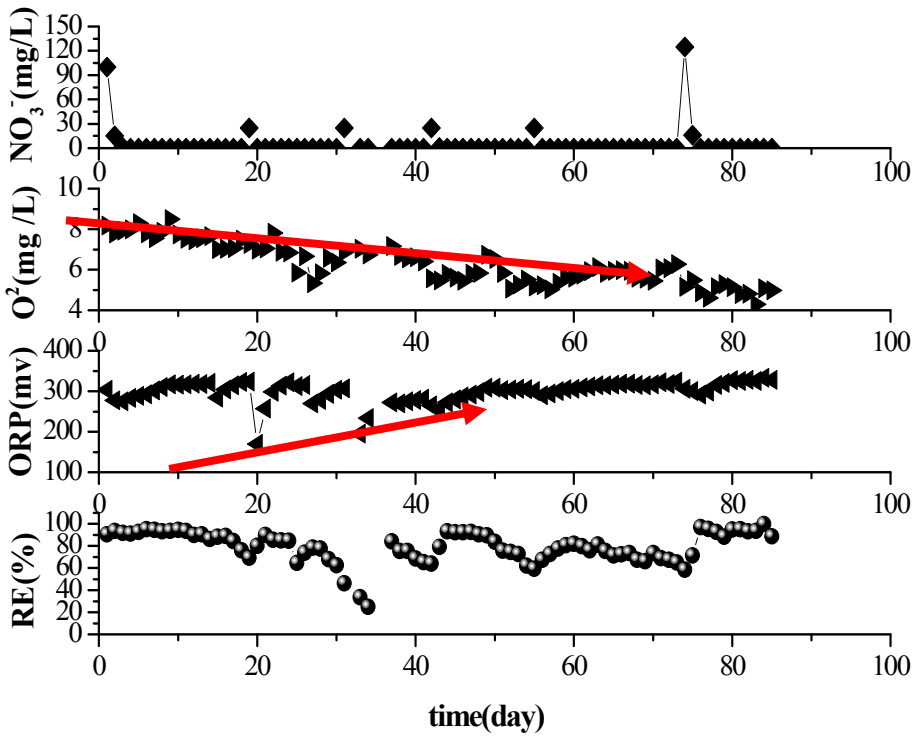

Figure 4-3. The time course profile of dissolved oxygen and redox potential in acetone biodegradation by the airlift with 2-l PAA-immobilized cell beads in treatment of the gas stream containing 300 ppmv of acetone at 10 l min^{-1}.

Implication of Nutrient Demand and the Redox Potential

Both the dissolved oxygen and the redox potential can provide the information whether the system is in the aerobic or anaerobic condition. The redox potential change also provides the information of the oxygenic compound composition variation in the water and the biological activity increase. From the Figure 4-3, the shock loading of sodium nitrate caused the pulse change of redox potential. The peak ORP value became less and less significant in the course of the operation time. Since no nitrogen nutrient was needed after day 85, this redox potential could further be used as an indicator for determining whether the system was in a steady-state condition.

The gradually decrease of peak change in redox potential could be redrawn in Figure 4-4. The ORP values were between 170-332 mV, with the average of 299 mV. We can see the response of the ORP values after adding the sodium nitrate from Figure 4-4. In the beginning of operation, the microbial activity had not achieved a stable condition, so the redox potential decreased immediately when the nitrate was reduced to nitrogen, and recovered right away after some oxygenate compounds were formed by the culture. The peak change became less and less when the microorganisms were more and more active in the last two addition of nitrate. Eventually, the addition of oxygenate nitrate and depreciation of oxygen balanced in the course of time. Hsu [2002] reported that the fast increase of

redox potential corresponded to a better aerobic activity; but the decrease corresponded to a better anaerobic activity. Wang [2002] reported that the removal efficiency in tetra-chloro-ethylene became the best while the ORP value anaerobically changed from -250 mV to -350 mV.

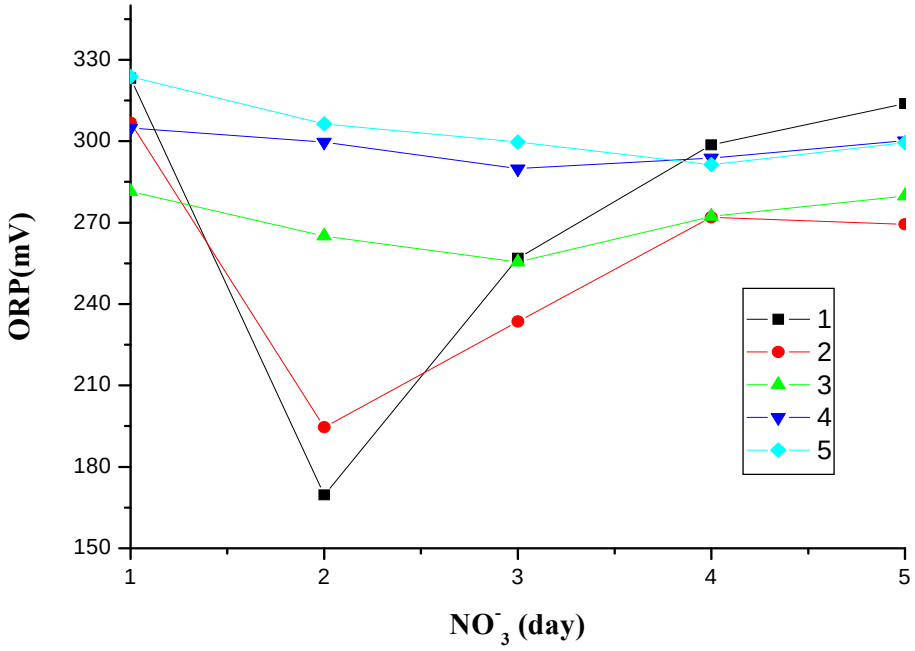

Figure 4-4. The redox potential during the 5 days after addition of nitrate into the system in acetone biodegradation by the airlift with 2-l PAA-immobilized cell beads in treatment of the gas stream containing 300 ppmv of acetone at 10 l min^{-1}.

Elimination Capacity of Acetone

The elimination capacity (EC) versus acetone loading is drawn in Figure 4-5. The acetone-carbon elimination capacity of 109.6 g-C $m^{-3}h^{-1}$ when the carbon loading was 137.5 g-C m^{-3} h^{-1}. Chang and Lu [2003] reported that the treatment capacity of isopropyl alcohol and acetone in their biofilters were 80 and 53 g-Cm^{-3} h^{-1}, respectively, when the influent concentration was between 75-300 ppmv with 90% removal efficiency. Obviously, our system using liquid water as a media can provide a better treatment capacity but less removal efficiency.

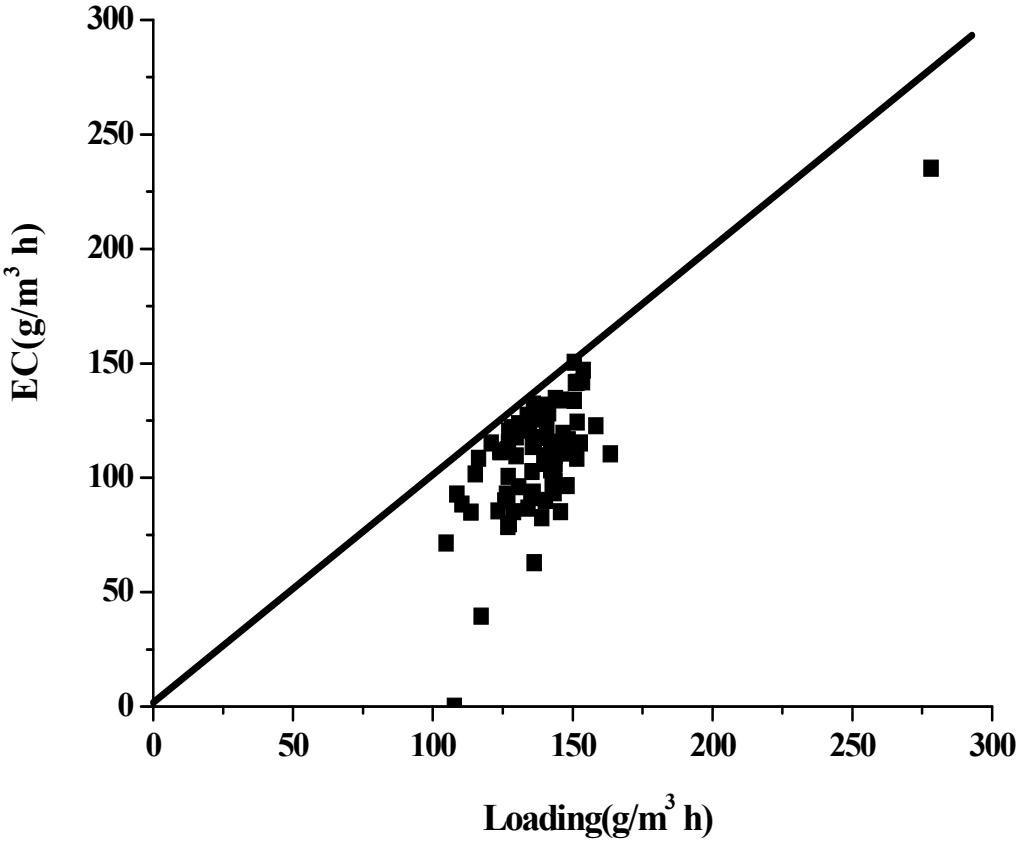

Figure 4-5. The elimination capacity versus acetone loading in acetone biodegradation by the airlift with 2-l PAA-immobilized cell beads in treatment of the gas stream containing 300 ppmv of acetone at 10 l min^{-1}.

Summary

The innovation of the PAA entrapped-cell beads embedded in the airlift for acetone waste gas treatment made the system become a three-phase bioreactor. The elimination capacity of 300-ppm acetone was 109.6 g-C $m^{-3}h^{-1}$ with 79% removal efficiency. It is higher than the data reported for biofiltration. In the nutrition issue, the gradually increasing COD:N ratio demonstrated the nitrogen cycle in the bioreactor was eventually formed. The maximum COD:N ratio was 100:3. The sudden decrease of the redox potential could be used to detect if the system requires more nitrogen nutrient or to show the denitrification phenomenon.

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Keywords: Acetone, airlift bioreactor, immobilization, *Thiosphaera pantotropha*

出席國際學術會議心得報告會議報告

97 年 7 月 23 日

報告人姓名	黃思蓴	系所 職稱	土木與工程資訊學系教授
時間 會議 地點	97 年 6 月 24 日~6 月 27 日 美國波特蘭	本校核定 補助字號	
會議 名稱	(中文) 空氣與廢棄物管理第 101 屆研討會與展示 (英文) A&WMA's 101st Annual Conference & Exhibition		
發表 論文 題目	1. Slurry-phase biological treatment of acetone waste gases using an airlift with the PAA-entrapped T. pantotropha cell beads. 2. Restaurant Indoor Air Quality in Hsinchu County, Taiwan. 3. Evaluation of Indoor Air Quality at Taipei CityHospital by Indoor CO2 Concentration.		

參加會議經過

1. 於開會的第一天到達會場，完成報到手續，如照片 1、照片 2。依規定於第二天早上在展示場的 LOBBY 將 POSTER 張貼完成，照片 3、照片 4。於 6 月 26 日早上 9 點 40 分在第 B119 會場第一場次 (AE-2a) 的第三篇進行報告。會議資料，如附件二冊。
2. 在展示場有收集資料及照一些教學用圖片，如照片 5、照片 6及照片 7。

與會心得

1. 生物濾床技術在空氣領域已經愈來愈少人投入。生物濾床領域文章發表最多的單位，辛辛納提大學環工系，發表如何加入界面活性劑來改善捕捉疏水性有機污染物的效率。好學校伊利諾香檳分校的環工系則發表，活性碳做為前處理可以緩衝突來的高負荷。第 4 篇是環保設備公司所發表的實務模廠級設備於具毒性酚醛樹脂的處理。第 5 篇是好學校德州奧斯汀分校陳 Lily (Li-Jung) 所發表的乙醇能源工廠的乙醇排氣處理。
2. 以上所發表的內容，大都是生物濾床非主流的實驗內容，過去或許在正規實驗中會發現的歧異現象，現在可能因為沒有題目可以做，只好再做進一步的研究。例如界面活性劑及緩衝進流濃度。而乙醇工廠則是因為最近能源的事件而讓此題目變得新奇而已。最後，有公司嘗試將生物濾床用於毒性物質。

建議

1. 有關生物處理臭味的問題，也許可以找個研討會，例如生化工程等研討會，直接看有沒有更精進的技術可以利用。

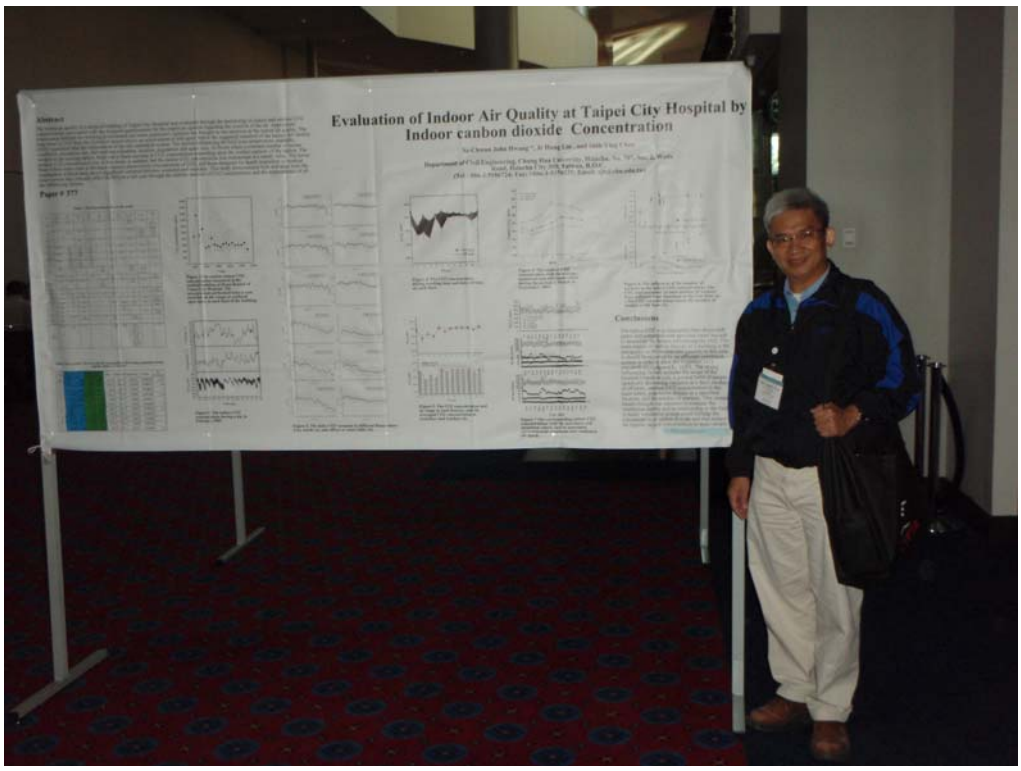
攜回資料名稱及內容

1. 帶回美國環保署一些 CD 資料，(1) US EPA Selected NCER Publications (Links)；(2)Sustainable reuse and revitalization of potentially contaminated sites; (3)Green City partnerships; (4)Interactive abandoned mine lands workshop series; (5)Integrated science assessment for oxides of nitrogen and sulfur- ecological criteria; (6)Air quality criteria for lead; (7)Air quality for monoxide; (8)Earth science reference handbook and data products handbooks vol. 1 & 2.
2. 帶回廠商 CD，Tisch Environment.

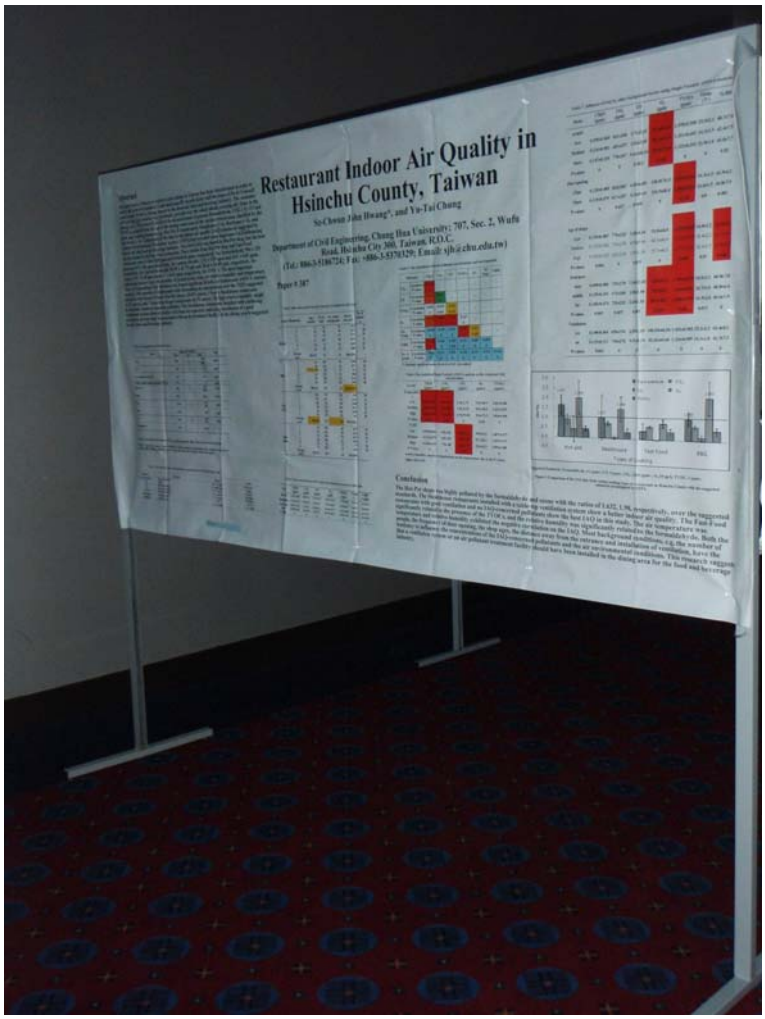
照片 1、會場外觀

照片 2、會場內觀

照片 3、張貼海報論文：Evaluation of Indoor Air Quality at Taipei CityHospital by Indoor CO2 Concentration

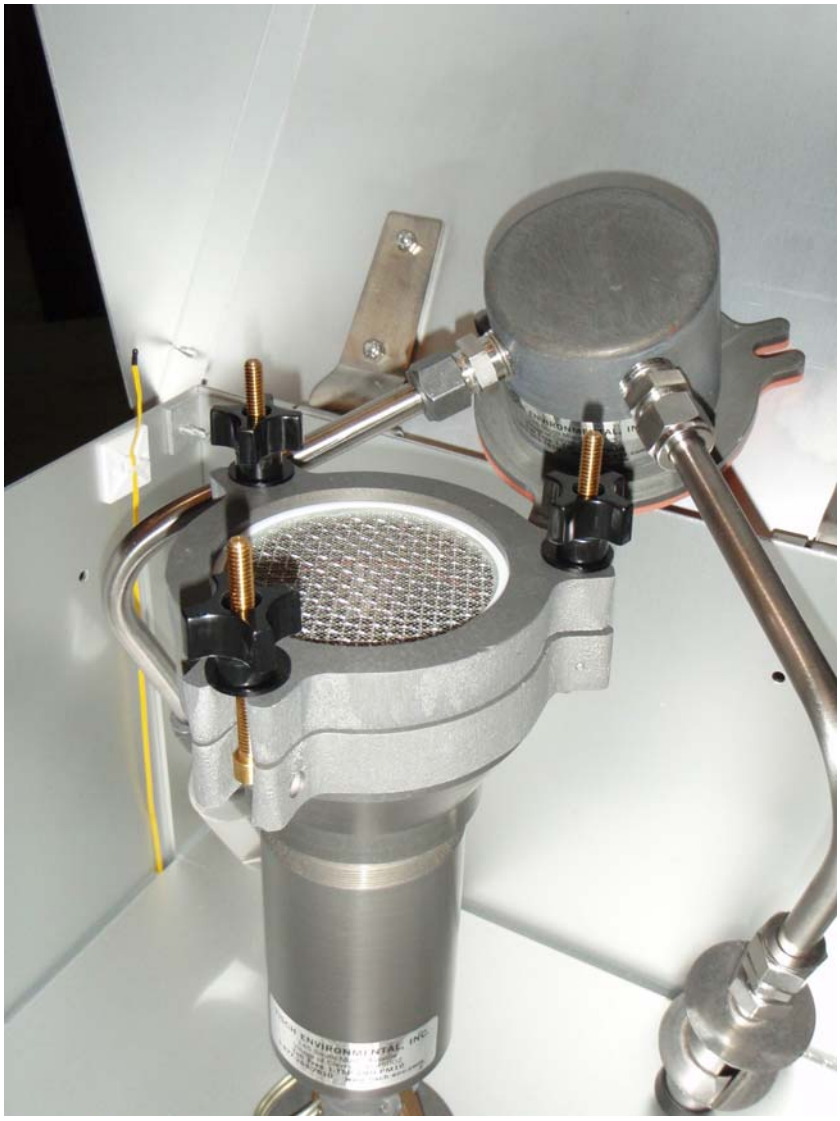


照片 4、張貼海報論文：Restaurant Indoor Air Quality in Hsinchu County, Taiwan



照片 5、攜回 PM_{10} 設備照片，教學用。

照片 6、攜回 Cascade Impactor 教學用照片二張之一。



照片 7、攜回 Cascade Impactor 教學用照片二張之二。

Biological Treatment of Acetone Waste Gases Using a Slurry-Phase Airlift with the PAA-entrapped *T. pantotropha* Cell Beads

Paper # 372

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Abstract

Acetone is the most commonly used solvent in the Hsinchu Science Park, Taiwan. The innovative air-lift bioreactor embedded with the polyacrylic-amide (PAA) entrapped *Thiosphaera pantotropha* cell beads (2 l) was employed to treat this acetone-contaminated air stream (10 l min^{-1}; 100-1000 ppmv). The 41-l medium solution circulated for more than 9 months was originally used to absorb acetone, which was then degraded by the PAA-entrapped cell beads, and became slurry after 85 days operation. During the first phase operation, the average removal rate is about 79 % for 300 ppmv of acetone in average in the influent air stream. The capacity of the airlift to treat acetone is 109.6 g m^{-3} h^{-1} under the loading of 137.5 g m^{-3} h^{-1}. The maximum COD:N ratio of 100:2.9 is achieved and a balanced nutrient state was indicated by the ORP measurement. The pH of the system was maintained at neutral because of the strong buffer intensity added in the medium (final $\beta=1.18 \times 10^{-2}$ mole l^{-1}). The dissolved oxygen was gradually down to the 2 mg l^{-1}. The conductivity and ionic strength were 4.5-5.6 mS cm^{-1} and 0.1 M, respectively. The PAA-entrapped cell beads provided the best inoculum source to keep the system steadily operated.

INTRODUCTION

The Taiwan combined IC production value of the semi-conductor industry, which is one of the most important industries in Taiwan, rated top 3 high all over the world, fully supporting Taiwan economics and social prosperity. However, the high-tech industries use a lot solvent such as acetone, isopropyl alcohol, ethyl diol, butadiene, toluene, xylene as cleaner in the film development, itch, and vapor deposition processes. Many volatile organic compounds (VOCs) were emitted [Khan and Ghoshal, 2000]. Chang and Chang [1999] and Chang and Lu [2003] have reported that the acetone was the most frequently found compounds contributing 50-80% of total VOCs to the Hsinchu Science Park (HSP) of Taiwan. Since the acetone embedded airstream often contains high boiling-point compounds, many treatment facilities couldn't maintain its high treatment efficiency as the new one can promise. For the long period of time, many VOCs, e.g. acetone and isopropyl alcohol which would further be degraded to acetone, go into the residential area adjacent to HSP. People's health and safety were seriously concerned.

VOCs are often treated by adsorption, condensation, absorption, incineration, and biofiltration [Khan and Ghoshal, 2000; Chang and Lu, 2003]. Biofiltration is the most cost-effective method but

it encounters many operational problems such as compaction, drying of filter media, aging and acidification. The alternative process, biotrickling filter, is able to solve most of the problems, but it still clogs in a period of time. Bioscrubber has a less efficiency than the other two processes mentioned above. Also, it needs an additional large treatment facility to treat the circulation liquid, which contains a high concentration of BOD requiring a long operation time for bacteria to degrade it before recirculation.

Airlift that possesses a very good mass transfer efficiency in between gas and liquid phases is a well known bioprocess often used in biochemical engineering. Now the gaseous acetone can be expected to be well dissolved into the liquid phase of the airlift. However, acetone is very toxic to microorganisms; therefore, the protection of microorganisms using an immobilization technique is necessary for the biodegradation. Many articles also demonstrated that the PAA-immobilization system where microorganism is entrapped into the cell beads is a very stable process and its bare leakage of microorganisms continuously provides a source of pure culture. Thus, this study is probably the first report dealing with the three-phase (acetone gas, liquid medium and PAA) airlift bioprocess treating the waste gases containing acetone.

According to our previous reports, acetone can be degraded by *Thiosphaera pantotropha* in a shake-flask culture [Ru, 2003; Lu, 2004] and in a 2.5-m high airlift bioreactor, in which the airlift design and hydrodynamics properties were thoroughly investigated [Chen, 2006]. In this study, the optimal treatment capacity in treatment of the acetone-containing gas stream was evaluated, and kinetics data were modeled under certain assumptions.

EXPERIMENTAL METHODS

Chemicals

Acrylamide Monomer and N,N,N',N'-tetra- methylethylenediamine (TEMED) were purchased from Acros organics (as a part of Fisher Scientific) (Belgium). N,N'-methylenebisacrylamide (BIS) was obtained from Tokyo Kasei. BCA analysis kit was purchased from Pierce company (Thermo Fisher Scientific Inc). Acetone was purchased from Union Chemical Company (Taiwan). All the other chemicals were of reagent grade.

Microorganisms

T. pantotropha (also named as *Paracoccus pantotrophus*) ATCC 35512 was purchased from Bioresource Collection and Research Center (BCRC), Taiwan. The storage of microorganism was annually manipulated at -78 ^{o}C, but subculture was done every month. The composition of medium used for airlift is shown as Table 2-1.

Table 2-1. The composition of acetone biodegradation working medium

Components	Quantity	Company
Na_2HPO_4	4.2 g	Shimakyu, Japan
KH_2PO_4	1.5 g	Union Chemicals, Taiwan
$MgSO_4 \cdot 7\ H_20$	0.1 g	Union Chemicals, Taiwan
$NaNO_3$	0.1 g	Union Chemicals, Taiwan
Tap water	Fill to 1.0 L	Union Chemicals, Taiwan

Free cell was measured by an optical density, OD_{600nm}, and dry cell weight (105 ^oC for 12 h). Immobilized cell concentration was determined by the protein content of the cell beads using the BCA Protein Assay kit [Pierce chemical company, 1997].

Polyacrylicamide (PAA) Cell Beads

Acrylicamide monomer, crosslinker BIS and accelerator TEMED were added into aseptic distillated water under a constant proportion at 4 ^oC and mixed thoroughly. On the other side, the settled centrifuged culture (20%, v/v) mixed with sodium alginate (0.5%, w/v) at 4 ^oC. Next, the polymer solution and the culture solution were instantaneously mixed into a small syringe by a peristaltic pump before ejected into the calcium chloride solution (0.3%，w/v). The calcium and alginate will immediately form a very stable complex, helping the fast formation of cell beads in a 0.5-1.0 h. When the cell beads were solidified, they were screened and moved to the potassium phosphate solution (pH 7.8) to remove the calcium alginate. At the meantime, the polyacrylic amide (PAA) cell beads were formed. The size of cell beads can be controlled by the needle size of the syringe used.

Acetone Analysis

Acetone gaseous and liquid concentrations were analyzed by a Gas Chromatograph (GC) (China Chromatography 8900, Taipei County, Taiwan) equipped with a flame ionized detector (FID). A 15-m long 0.53-mm ID Supelco, SPB-5 capillary column with a fused thickness of 3.0 μm was used. Nitrogen carrier gas of GC is used. The oven, injector and detector temperature were 150, 180 and 200 ^oC, respectively.

Gaseous acetone calibration was prepared by placing 1, 2, 3, 4 and 5 μl of acetone solvent into five 10-liter SKC Tedlar air sample bags, respectively, and measuring them after the bags were placed into an oven at 70 ^oC for 1 minute and then cooled down to room temperature.

Standard liquid acetone solution was prepared using a 250-ml brown bottle with a gas-tight rubber/Teflon stopper. The bottles containing different amount of acetone were placed in a water

bath at 150 rpm and 30 ^{o}C for 30 minutes. The samples were mixed with 0.5% propyl alcohol as an inner standard in a proportion of 1:1 (v/v). of The 2-ml sample was centrifuged at 6,000 rpm for 10 minutes and then 0.5 µl supernatant was withdrawn into GC/FID for analysis.

Airlift Bioreactor

The airlift bioreactor is depicted in Table 2-1. The column of the airlift was made of acrylic, 2.5 m high and 19 cm ID with a total working volume of 41 l. It was divided by a flat plate of 127 cm long × 19 cm wide into two sections, i.e. the drag tube and downcomer. This configuration with a diameter-to-height ratio of 1:9 is very suitable for gas transfer into the liquid. The gaseous acetone at 10 l min^{-1} came into the reactor through the bottom gas distributor. The Dissolved oxygen, pH and ORP sensors were installed for monitoring the performance of system.

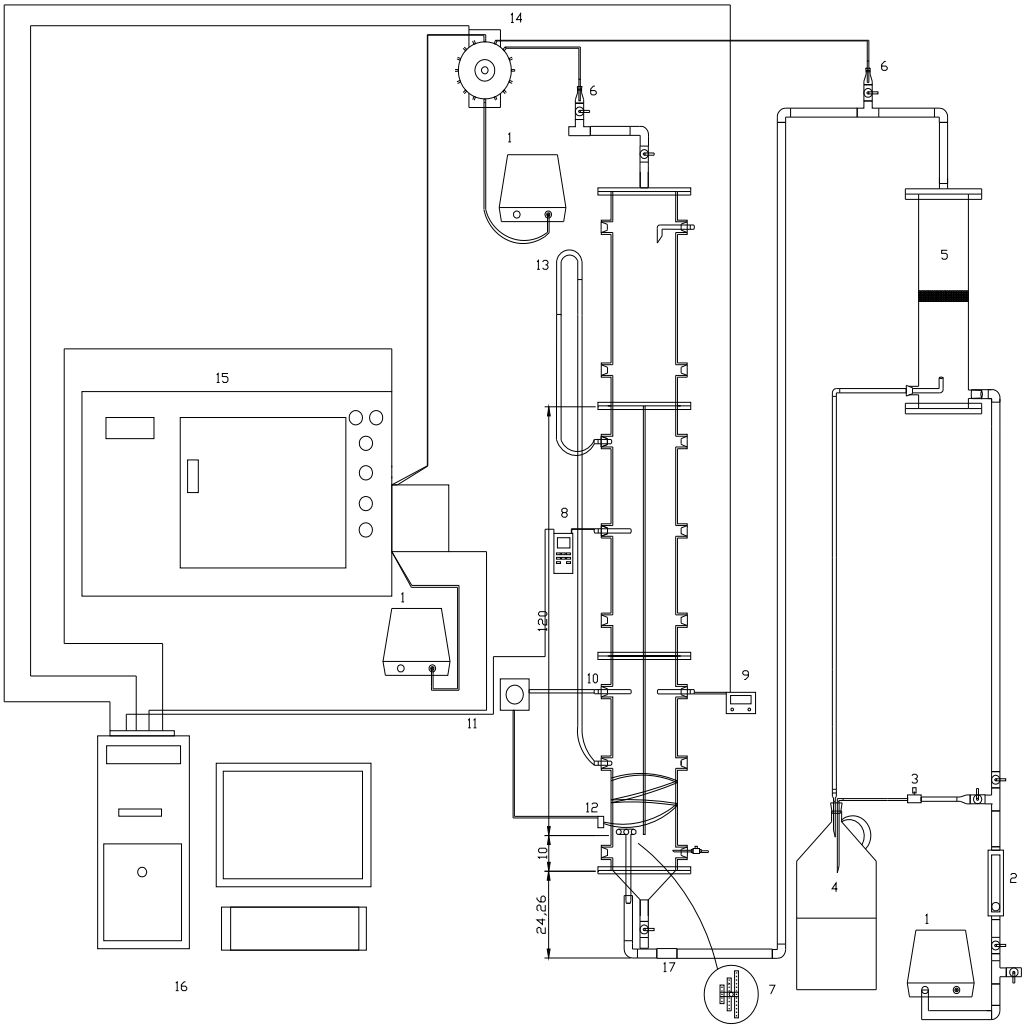

Figure 2-1. The airlift bioreactor. (1) Diaphragm air pump, (2) rotameter, (3) needle valve, (4) VOC bottles, (5) equalization basin, (6) sampling port, (7) gas distributor, (8) D.O. meter, (9) pH meter, (10) temperature sensor, (11) temperature control relay, (12) heating ribbon, (13) U-shape manometer, (14) auto-sampler, (15) GC, (16) computer, (17) check valve.

One ml of gaseous acetone was automatically sampled by using a Valco 16-port stream selector and a Valco 10-port 2-position injector. All the relay control signal and the GC analysis signal were transmitted from or to the personal computer, respectively, through a NI-DAQ card (NI-6024, National Instrument, Austin). All the liquid samples were withdrawn from the top surface of bioreactor using a siphon tube.

RESULTS AND DISCUSSION

Our new innovative artificial-cell-bead-embedded airlift bioreactor requires external nutrition sources; for example, nitrogen. Once using this bioreactor to treat waste VOC gases was feasible, the stability (pH, conductivity, dissolved oxygen and redox potential, duration and maximum treatment capacity were the most interested issues to be investigated.

Microbial Characteristics

The characteristics of *T. pantotropha* has thoroughly been studied in a shake flask culture [Lyuu, 2003]. *T. pantotropha* is a nitrogen requiring bacterium. In the previous study, various organic nitrogen sources: i.e. yeast extract, monosodium L-glutamate and Urea, and inorganic sources: sodium nitrate and ammonium chloride were chosen for evaluating the efficiency of acetone biodegradation. We found that using the nitrate as a nitrogen nutrient is the best results in biodegradation of acetone. Only 12 h was needed for 90% acetone removal; 20 h for completely biodegradation of acetone (data not shown). In addition, it has the advantages of less biomass produced and lower cost for nitrate purchase. The optimal loading of 1 g l^{-1} was chosen for the rest of experiment.

The acetone biodegradation activity was seriously inhibited when the liquid acetone concentration was more than 700 mg l^{-1}. The acetone removal efficiency was then decreased from 100% to 57%. However, this microbial toxicity could be prevented by using an immobilization technique, to have the microorganisms entrapped into the PAA cell beads. The acetone removal efficiency could maintain 91% (data not shown).

Treatment of Gaseous Acetone in Airlift

The acetone-containing gas stream was treated by the airlift with the PAA-immobilized *T. pantotropha* entrapped -cell beads. The 85-day performance data are shown in the Figure 4-1. The average input and output concentration of gaseous acetone were about 300 ppmv and 63 ppmv, respectively. The removal efficiency was around 79%. The accumulated liquid acetone concentration was 25 mg l^{-1} in average.

During day 24-35, the gas auto-sampler for GC/FID was clogged. Because less quantity of acetone shown in the computer screen, the opening of VOCs valve was turned to the maximum, leading to the real acetone input concentration more than 631 ppmv. The gaseous and liquid acetone concentrations were 97 ppmv and 23 mg l^{-1}, respectively. Since the removal efficiency was more than 85%, it demonstrated that the liquid water can provide a large load-buffering intensity in equalization of the capacity; i.e. absorption of the peak acetone gas stream immediately.

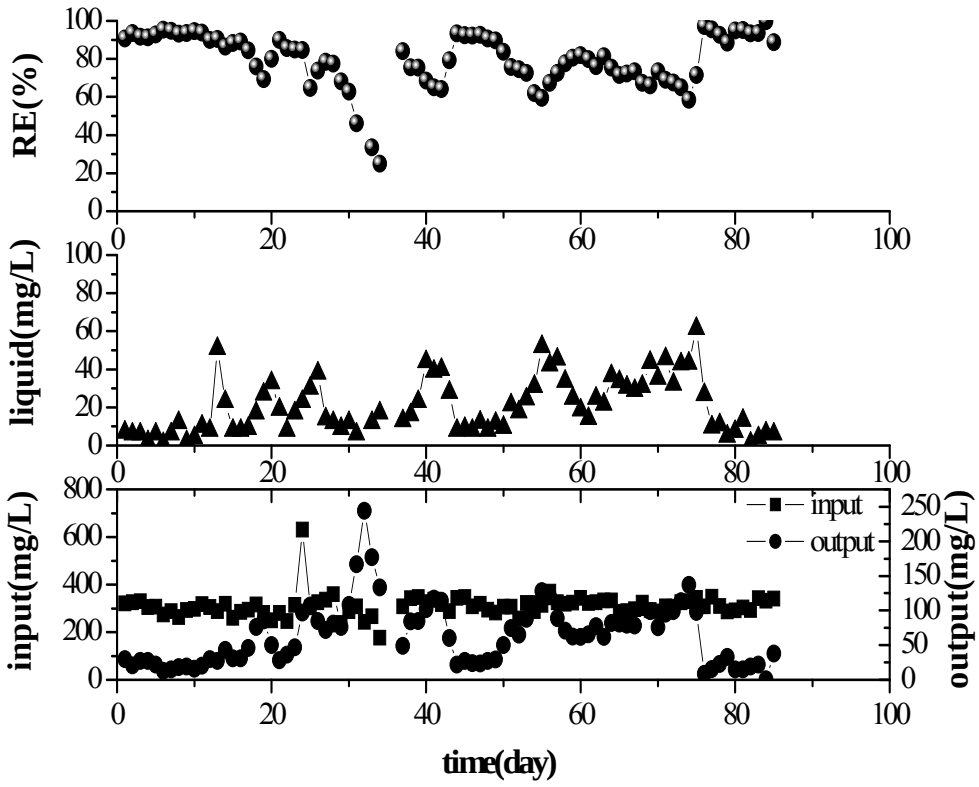

Figure 4-1. The time course profile of acetone biodegradation by the airlift with 2-l PAA-immobilized cell beads in treatment of the gas stream containing 300 ppmv of acetone at 10 l min^{-1}.

The Nutrition Demand

In the reality, we need the absorption solvent to capture acetone, but we couldn't use the enrichment medium to carry the PAA cell-entrapped gel beads due to the high cost of chemicals. Therefore, only a constant amount of tap water (41 l) with HCMM medium (Hwang et al., 2003) containing 1-g l^{-1} sodium nitrate was used as a cell bead carrier. The result of acetone biodegradation is shown in Figure 4-2. However, the system couldn't start up unless our adding 100 mg l^{-1} of sodium nitrate to the tap water. An additional amount of sodium nitrate was further required 5 times to maintain a stable treatment efficiency when the removal efficiency of 300-ppmv gaseous acetone decreased down to below 60% or the liquid acetone concentration increased to above 30 -50 mg l^{-1}.

For example, at day 19, the acetone removal efficiency of 90% decreased down to 69% which was corresponding to the rising of liquid acetone concentration to 27 mg l^{-1}. Day 20 after the addition of 25 mg l^{-1} sodium nitrate, the removal efficiency increased from 69% to 80% with the further duration of 11 days. Except the period of day 24-35 when GC gas auto sampler was clogged; otherwise, the trend of coming down and then going up in the gaseous acetone concentration was kept for a couple of weeks until at day 74, the liquid acetone concentration was over 50 mg l^{-1}. Therefore, 5-times dosage of 125-mg l^{-1} sodium nitrate was added to the system. The apparent

improvement in the liquid acetone concentration was observed. In fact, the system was not added any nitrogen source for a year (data not shown).

In calculation of nitrogen dosage, the results are shown in Table 4-1. For the first 19 days, the COD: N ratio was maintained at 100:10.5, if both the initial 1 g l^{-1} of sodium nitrate and its external addition of 100 mg l^{-1} were taken into account. As seen in Table 4-1, the COD:N ratio becomes less and less. Eventually, no more nitrogen source was added to the system after day-74 addition. The system was run for almost one year until it became too slurry. This trend of COD:N also provides a good information regarding how to feed the nutrition for this type of artificial cell-entrapped gel beads. In other words, it is economically feasible.

Table 4-1. The COD:N ratio during the acetone biodegradation

Day	Addition of nitrate, mg l^{-1}	Accumulation of nitrate, mg l^{-1}	g-N day^{-1}	g-C day^{-1}	g-COD day^{-1}	COD:N 100:N
0	100	1,100	2.37	6.35	22.57	10.5
19	25	1,125	1.49	6.35	22.57	6.6
31	25	1,150	1.12	6.35	22.57	5.0
42	25	1,175	0.88	6.35	22.57	3.9
55	25	1,200	0.66	6.35	22.57	2.9
74	125	1,325				

*: The conversion factor of g-acetone to g-COD and to g-C are 2.2 (=128/58) g-COD/g acetone and 0.62 (=36/58), respectively; the 10 lpm of 300-ppmv acetone gas stream gives the mass flow rate of 10.2 g-acetone/day.

Generally, the ratio of COD:N:P in a biological treatment plant was suggested to be 100:5:1 in textbook. Brauer [1986], and Johnson and Scow [1999] suggested the C:N:P ratio should be 100:5:1 in order to prevent the limit of Nitrogen nutrient and to maintain the microbial activity in biodegradation. Acuna et al. [2002] reported the type of nutrient sources and its concentration were also very important in treatment of toluene. Brar and Gupta [2000] used the same *T. pantotropha* to metabolize the TCE at the optimal C:N ratio of 100:20 that was in the range of our C:N ratios (37.4-10.5) calculated from Table 4-1.

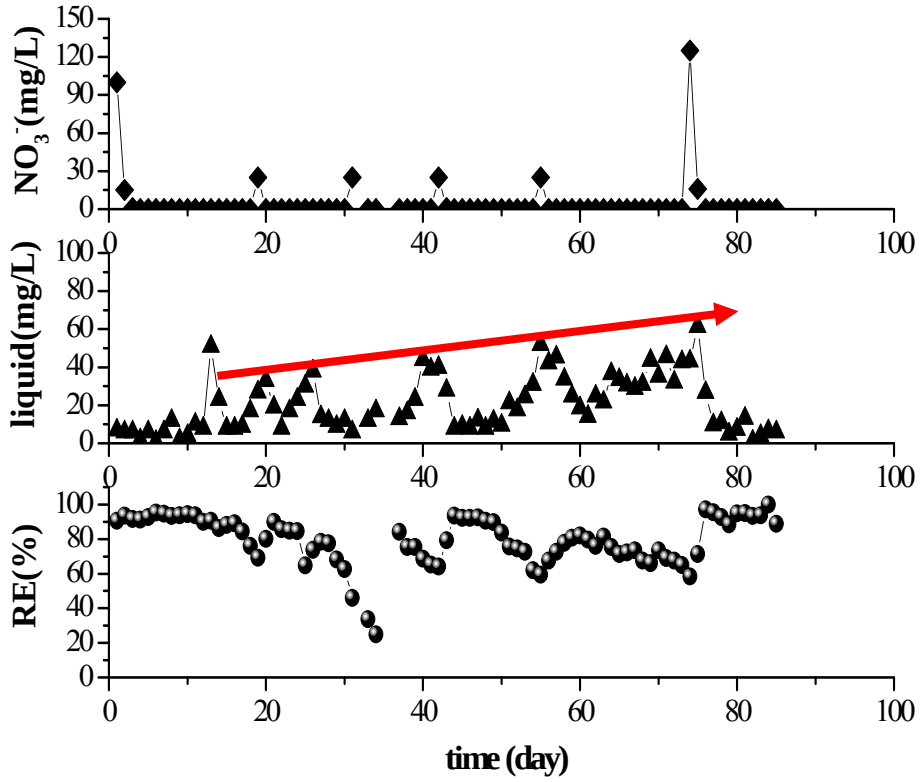

Figure 4-2. The time course profile of nitrogen nutrient in acetone biodegradation by the airlift with 2-l PAA-immobilized cell beads in treatment of the gas stream containing 300 ppmv of acetone at 10 l min^{-1}.

The Stability of the Airlift System

1. pH

Most bacteria cannot survive in the environments where the pH is below 5 or above 9. In our previous study, free *T. pantotropha* could only metabolize the acetone at pH 7 and 8.5, not at pH below 5.5 or above 10. In this study, the pH was maintained in between 7.10-7.25, indicating the system had a strong buffering intensity to neutralize the carbonaceous acid. Thus, the culture medium was used for one-year operation without any blow-down operation. The phosphate buffering intensity, β, was finally determined to be 1.18×10^{-2} initially and 1.50×10^{-3} mole L^{-1} at day 85. Although the buffering intensity is still available, the PAA cell beads normally will provide a good environment for pH change by altering the distribution of hydrogen ions through the formation of hydrogen-bond in its matrix.

Optical density for free cell growth in the liquid

The growth of suspended cell in the liquid phase can be evaluated by optical density (OD). In this study, the OD value increased from 0.3 (absorbance) in the beginning of the operation to 1.5 finally. It took first 10 days to achieve the OD value of 1.2, and then increased slowly to 1.5 at day 85. Bailey et al. [1986] reported that the biomass in the fed-batch bioreactor usually attained to a steady state where the microorganisms were under stationary phase due to the limit of other nutrient supply.

According to the results of acetone concentration modeling, the removal of acetone was gradually dependent upon the biomass existing in the liquid phase instead of those in the PAA cell beads. This result demonstrates that the PAA entrapped-cell beads could provide an initial source for the dominant microorganism.

Conductivity

Conductivity was used to analyze the electrolyte content of the liquid water in the airlift. At day 85, the conductivity value and ionic strength were 4.5-5.6 mS cm^{-1} and 0.072-0.089 M, respectively. According to the water body classification standard in Taiwan, Class 1 used for water supply and swimming should contain the conductivity and ionic strength of below 750 μS cm^{-1} @25℃ and 0.012 M, respectively. An IC foundry uses a pure water met with the standard of the conductivity and ionic strength of below 0.0556 μS cm^{-1} @25℃ and 8.9×10-7 M, respectively. The reverse osmosis for drinking purpose gives a water with the conductivity and ionic strength of 0.0625 μS cm^{-1} @25℃ and 1.0×10^{-6} M, respectively. A fresh activated sludge and anaerobic digested sludge obtained from the Chang Chun PetroChemical Co., LTD. had the conductivity of 2.53 and 3.40 mS cm^{-1} and ionic strength of 0.041與0.054 M, respectively. Obviously, our liquid water had the similar property with the sludge.

Normally, the microorganisms couldn't survive under the ionic strength more than 0.1 M which was corresponding to the conductivity of 6.3 mS cm^{-1}. Our liquid water had the ionic strength close to 0.1 M but the system could continuously metabolize acetone without any inhibition, indicating the immobilized cell beads could provide a barrier for high salinity gradient.

Dissolved oxygen

Dissolved oxygen can reflect the aerobic microbial activity in degradation of acetone. Figure 4-3 shows the time course of dissolved oxygen in biodegradation of acetone in an airlift bioreactor. During the period of 85-day operation, the dissolved oxygen decreased from 8.5 to 4.6 mg O_2 l^{-1}, with the average value of 6.3 mg O_2 l^{-1}. The decreasing trend indicates the more biological activity produced in the liquid water. The maximum dissolved oxygen in pure water is 9.07 mg but its value decreased down to 2-3 mg O_2 l^{-1} in the aerated basin in a full-scale activated sludge system. Therefore, our designed system could provide enough oxygen for microbial degradation.

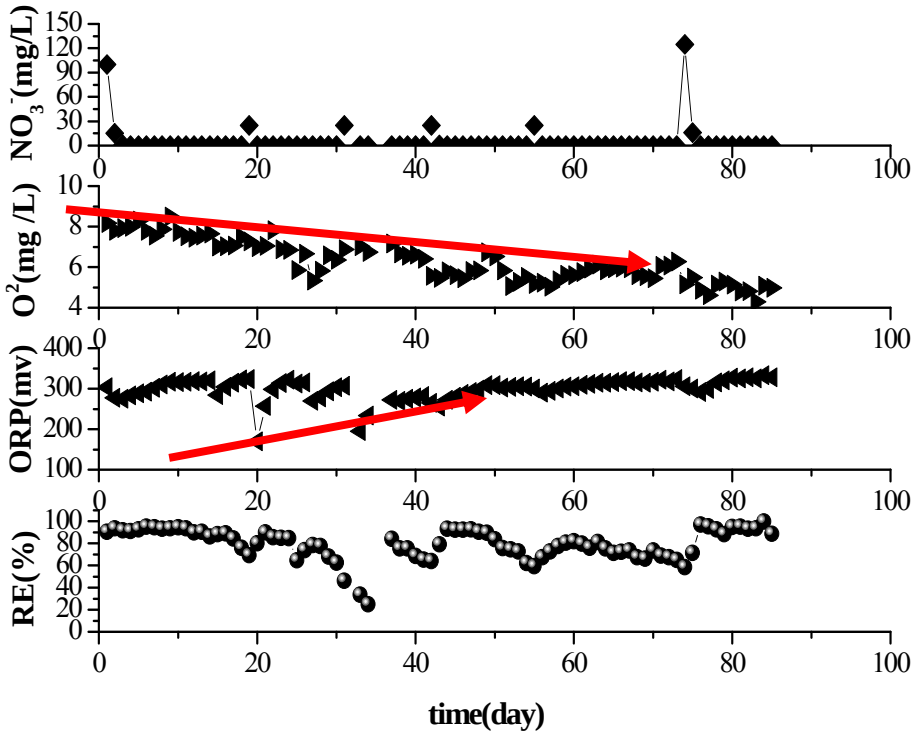

Figure 4-3. The time course profile of dissolved oxygen and redox potential in acetone biodegradation by the airlift with 2-l PAA-immobilized cell beads in treatment of the gas stream containing 300 ppmv of acetone at 10 l min^{-1}.

Implication of Nutrient Demand and the Redox Potential

Both the dissolved oxygen and the redox potential can provide the information whether the system is in the aerobic or anaerobic condition. The redox potential change also provides the information of the oxygenic compound composition variation in the water and the biological activity increase. From the Figure 4-3, the shock loading of sodium nitrate caused the pulse change of redox potential. The peak ORP value became less and less significant in the course of the operation time. Since no nitrogen nutrient was needed after day 85, this redox potential could further be used as an indicator for determining whether the system was in a steady-state condition.

The gradually decrease of peak change in redox potential could be redrawn in Figure 4-4. The ORP values were between 170-332 mV, with the average of 299 mV. We can see the response of the ORP values after adding the sodium nitrate from Figure 4-4. In the beginning of operation, the microbial activity had not achieved a stable condition, so the redox potential decreased immediately when the nitrate was reduced to nitrogen, and recovered right away after some oxygenate compounds were formed by the culture. The peak change became less and less when the microorganisms were more and more active in the last two addition of nitrate. Eventually, the addition of oxygenate nitrate and depreciation of oxygen balanced in the course of time. Hsu [2002] reported that the fast increase of redox potential corresponded to a better aerobic activity; but the decrease corresponded to a better anaerobic activity. Wang [2002] reported that the removal

efficiency in tetra-chloro-ethylene became the best while the ORP value anaerobically changed from -250 mV to -350 mV.

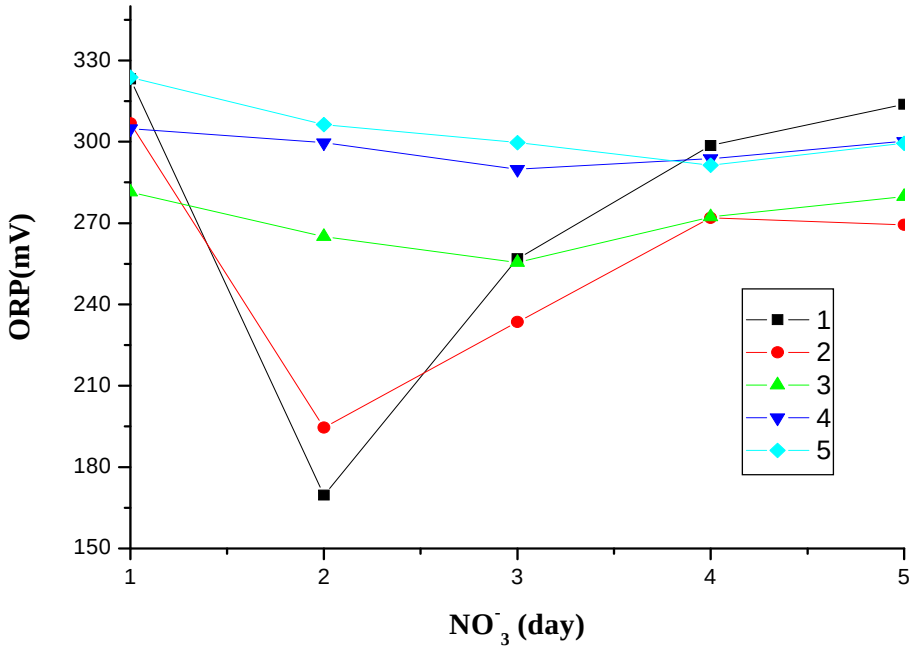

Figure 4-4. The redox potential during the 5 days after addition of nitrate into the system in acetone biodegradation by the airlift with 2-l PAA-immobilized cell beads in treatment of the gas stream containing 300 ppmv of acetone at 10 l min^{-1}.

Elimination Capacity of Acetone

The elimination capacity (EC) versus acetone loading is drawn in Figure 4-5. The acetone-carbon elimination capacity of 109.6 g-C $m^{-3}h^{-1}$ when the carbon loading was 137.5 g-C m^{-3} h^{-1}. Chang and Lu [2003] reported that the treatment capacity of isopropyl alcohol and acetone in their biofilters were 80 and 53 g-Cm^{-3} h^{-1}, respectively, when the influent concentration was between 75-300 ppmv with 90% removal efficiency. Obviously, our system using liquid water as a media can provide a better treatment capacity but less removal efficiency.

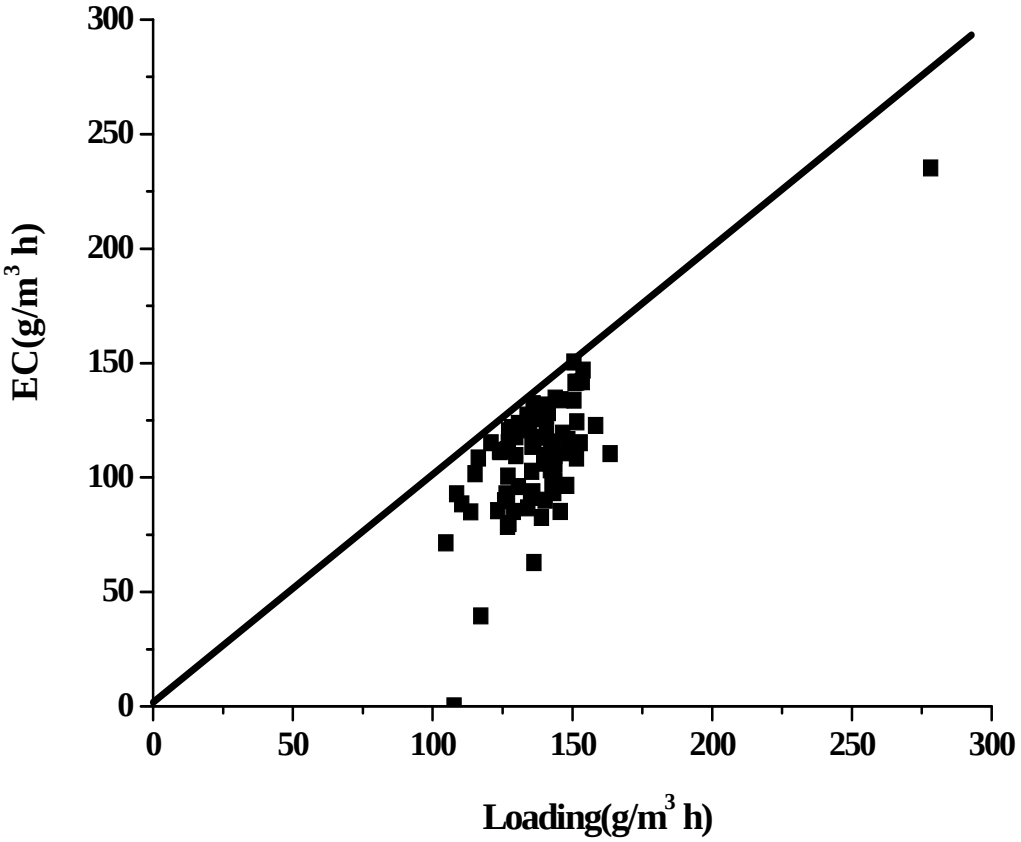

Figure 4-5. The elimination capacity versus acetone loading in acetone biodegradation by the airlift with 2-l PAA-immobilized cell beads in treatment of the gas stream containing 300 ppmv of acetone at 10 l min^{-1}.

SUMMARY

The innovation of the PAA entrapped-cell beads embedded in the airlift for acetone waste gas treatment made the system become a three-phase bioreactor. The elimination capacity of 300-ppm acetone was 109.6 g-C $m^{-3}h^{-1}$ with 79% removal efficiency. It is higher than the data reported for biofiltration. In the nutrition issue, the gradually increasing COD:N ratio demonstrated the nitrogen cycle in the bioreactor was eventually formed. The maximum COD:N ratio was 100:3. The sudden decrease of the redox potential could be used to detect if the system requires more nitrogen nutrient or to show the denitrification phenomenon.

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