

Studies on Biodegradation Capacity and Inhibitory Effects of Heavy Metals for Methyl Tertiary Butyl Ether-Degrading Cult

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ABSTRACT

The thesis was focused on obtaining MTBE-degrading cultures through acclimation by a laboratory-scale biotrickling filter. Removal of MTBE vapors from air streams in a biotrickling filter was studied under various operating conditions including inlet MTBE concentration, air residence time, liquid recirculation rate, liquid temperature, and flow direction of air-to-liquid. Additionally, the MTBE-degrading pure culture isolated from a biotrickling filter was employed to study the inhibitory effects of heavy metals on the biodegradation of MTBE, and the kinetic characteristics for the pure culture were examined by a batch experiment. With the several months' acclimation period, the mixed culture was capable of degrading MTBE with the removal rate of 1—3 mg-MTBE/g-cell h under suspended growth or attached growth conditions. It was also found that the removal efficiency was up to 77.7%, and the volume elimination capacity was 14.1 g-MTBE/m³ h in the biotrickling filter. Therefore, it is believed the developed biotrickling filter can be used as a pollution control device for treating MTBE-contaminated air. For the operating conditions investigation, MTBE vapor was found to volatilize to air from liquid phase when the liquid recirculation rate was high. However, MTBE removal increases to 90% when temporarily stop the recirculation liquid feeding. Results of the experiment also indicate that to increase the air residence time will increase the MTBE removal rate, under both co-flow and counter-flow conditions for the air-liquid contact. Of these, operating in co-flow condition was found to give a better MTBE removal. Because the temperature effect on MTBE removal was significant in high temperature operation condition compared to low temperature operation condition, it should be operated in an appropriate temperature environment for the field application. For the aerobic condition of the batch experiment, it was found that MTBE can be degraded completely in ten hours by the pure culture (i.e., 74.5 mg-MTBE/g-cell h). The kinetic parameters for maximum specific growth rate, the half saturation constant, and inhibitory coefficient were 0.0613 hr⁻¹, 4.95 mg/L, and 158-816 mg/L, respectively. The inhibitory effect of several selected metals on the rate of MTBE degradation under aerobic conditions was tested. The metals considered were Cr³⁺, Cu²⁺, Mn²⁺, Pb²⁺, and Zn²⁺. The MTBE degradation was carried out in batch liquid culture with MTBE being introduced in combination with each of the metals. Results showed: (1)inhibitory effect of Cu²⁺ on MTBE degradation was occurred at low concentration, and MTBE was unable to be degraded at Cu²⁺ concentration greater than 10 mg/L; (2)the presence of Cr³⁺, Mn²⁺, Pb²⁺, and Zn²⁺ had no effect on MTBE degradation at their concentrations of 1 mg/L; however, the presence of Cr³⁺, Pb²⁺, and Zn²⁺ had inhibitory effect on MTBE degradation at their concentrations of 10 mg/L; (3)the presence of Mn²⁺ had no effect on MTBE degradation until concentration as high as 50 mg/L; (4) the magnitude of inhibitory effect follows the pattern of Cu²⁺ > Cr³⁺ > Zn²⁺ > Pb²⁺ > Mn²⁺.

Keywords : MTBE ; biotrickling filter ; heavy metals ; kinetic parameter

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REFERENCES

- Francois, A., H. Mathis, D. Godefroy, P. Piveteau, F. Fayolle, F. Monot,(2002), " degradation of Methyl tert-Butyl Ether and Other Fuel Oxygenates by a New Strain, *Mycobacterium austroafricanum* IFP 2012 ", *Appl. Environ. Microbiol.*, 68: 2754-2762 Fayolle, F., J.-P. Vandecasteele, F. Monot,(2001), " Microbial degradation and fate in the environment of methyl tert-butyl ether and related fuel oxygenates " *Appl. Microbiol. Biotechnol.* 56: 339-349 Keller, A. et al., 1998, " Health and environmental assessment of MTBE, " Report to the governor and legislature of the state of California as sponsored by SB 521. Duffy, J. S., J. A. Pup, and J. J. Kneiss, 1992, " Toxicological evaluation of MTBE testing performed under TSCA consent agreement, " *Journal of Soil Contamination*, 1, p27-37. Sorial, G.A. F.L. Smith, P. Biswas, and R.C. Brenner, 1993, " Development of aerobic biofilter design criteria for treating VOCs, " *Proceedings of the 86th Annual Meeting & Exhibition of the Air & Waste Management Association*, Denver, CO, USA. Hernandez-Perez, G., F. Fayolle, J.-P. Vandecasteele,(2001), " Biodegradation of ethyl t-butyl ether (ETBE), methyl t-butyl ether (MTBE) and t-amyl methyl ether (TAME) by *Gordonia terrae* " *Appl. Microbiol. Biotechnol.* 55: 117-121 Hardison, L. K., S. S. Curry, L. M. Ciuffetti, M. R. Hyman,(1997), " Metabolism of Diethyl Ether and Cometabolism of Methyl tert-Butyl Ether by a Filamentous Fungus, a *Graphium* sp. " , *Appl. Environ. Microbiol.*, 63: 3059-3067 Garnier, P. M., R. Auria, C. Augur, S. Revah,(1999), " Cometabolic biodegradation of methyl t-butyl ether by *Pseudomonas aeruginosa* grown on pentane " *Appl. Microbiol. Biotechnol.* 51: 498-503 Steffan, R.J., McClay, K., Vaiberg, S., Condee, C.W., Zhang, D., 1997, " Biodegradation of the gasoline oxygenates Methyl tert-Butyl Ether, Ethyl tert-Butyl Ether, tert-Amyl Ethyl Ether by propane-oxidizing bacteria, " *Applied Environ. Microbiology*, 63: 4216-4222. Mo, K., Lora, C.O., Wanken, A.E., Javanmardian, M., Yang, N., Kulpa, C.F., 1997, " Biodegradation of ethyl tert-Butyl Ether by pure bacterial cultures, " *Appl. Microbiol. Biotechnol.*, 47:69-72. Salanitro, J.P., Diaz, L.A., Williams, M.P., Wisniewski, H.L., 1994, "Isolation of a bacterial culture that degrades MTBE, " *Applied Environ. Microbiology*, 60:2593-2596. Park, K. and R. Cowan, (1997), Effects of oxygen and temperature on the biodegradation of MTBE. *Proceedings of the 213th ACS National Meeting: Division of Environmental Chemistry*, San Francisco, CA, April 13-17. Stoffels, M., R. Amann, W. Ludwig, D. Hekmat, and K.-H. Schleife. (1998) " Bacterial Community dynamics during start-up of a Trickle-bed Bioreactor degrading Aromatic Compounds " , *Appl. Environ. Microbiol.* 64: 930-939 Mpanias, C. J., B. C. Baltzis . (1998) " Biocatalytic removal of mono-Chlorobenzene vapor in trickling filters " , *Catalysis Today*. 40: 113-120 Findlay G. Edwards and N. Nirmalakhandan. (1996) " Biological Treatment of Airstreams Contaminated with VOCs:an Overview " . *Wat. Sci. Tech.* 34: 565-571 Fortin , N. Y., M. A. Deshusses . (1999) " Treatment of Methyl tert-Butyl Ether Vapors in Biotrickling Filters. 1. Reactor Steady —State Performance, and Culture Characteristics " , *Environ. Sci. Technol.* 33: 2980-2986 Sa, C. S. A., R. A. R. Boaventura. (2001) " Biodegradation of phenol by

Pseudomonas putida DSM 548 in a trickling bed reactor ”, *Biochem. Eng.* 9: 211-219 Den, W., M. Pirbazari, C. C. Huang, K. P. Shen. (1998)

“ Technology review for vapor phase biofiltration part : Technological development and applications “ *Journal of the Chinese Institute of Environmental Engineering.* 8: 159-179 Cox, H. H. J., and M. A. Deshusses. ,(2002), “ Co-treatment of H₂S and toluene in a biotrickling filter ”, *Chem. Engine. Journal* ,87:101-110 Hekmat, D., A. Linn, M. Stephan, and D. Vortmeyer. ,(1997), “ Biodegradation dynamics of aromatic compounds from waste air in a trickl-bed reactor ” *Appl. Microbiol.Biotechnol.* 48: 129-134 Langwaldt, J. H. and J. A. puhakka., (2000), “ On-site biological remediation of contaminated groundwater: a review “ *Environmental Pollution.*107: 187-197 Cox, H. H. J., T. T. Nguyen, M. A. Deshusses., (2000), “ Toluene degradation in the recycle liquid of biotrickling filters for air pollution control ” *Appl. Microbiol.Biotechnol.* 54: 133-137 Converse, B. and E. D. Schroeder, (1999), “ Biodegradation of Methyl Tertiary Butyl Ether (MTBE) Using a Granular Activated Carbon Trickling Filter, ” *Proceedings of the 92nd Annual Meeting & Exhibition of the Air & Waste Management Association, St Louis, Missouri, USA.*

Diks R.M.M. and S.P.P. Ottengraf, (1991), “ Verification studies of a simplified model for the removal of dichloromethane from waste gases using a biological trickling filter, ” *Bioprocess engineering,* 6:93-99. Eweis, J.B., N. Watanabe, E. D. Schroeder, D. P.Y. Chang, K. M. Scow, (1998), “ MTBE biodegradation in the presence of other gasoline compounds ” *National Ground Water Association Conference on MTBE and Perchlorate, Anaheim, CA, June 3-4.* Mo, K., Lora, C.O., Wanken, A.E., Javanmardian, M., Yang, N., Kulpa, C.F., (1997), “ Biodegradation of ethyl tert-Butyl Ether by pure bacterial cultures, ” *Appl. Microbiol. Biotechnol.,* 47:69-72. Abbas, A. S., and C. Edwards,(1990), “ Effects of Metals on *Streptomyces coelicolor* Growth and Actinorhodin Production ” , *Appl. Environ. Microbiol.*56: 675-680 Tyagi, R. D., D. Couillard, J. P. Villeneuve,(1986), “ Functional Design of Activated Sludge Processes with Heavy Metal Inhibition ” , *The Canadian Journal of Chemical Engineering* , 64: 632-638 Said, W. A. and D. L. Lewis,(1991), “ Quantitative Assessment of the Effects og Metals on Microbial Degradation of Organic Chemicals ” ,*Appl. Environ. Microbiol.*57: 1498-1503 Baldrian, P., C. Wiesche, J. Gabriel, F. Nerud, F. Zadrazil,(2000), “ Influence of Cadmium and Mercury on Activities of Lignolytic Enzymes and Degradation of Polycyclic Aromatic Hydrocarbons by *Pleurotus ostreatus* in Soil ” , *Appl. Environ. Microbiol.*66: 2471-2478 Cabrero, A., S. Fernandez, F. Mirada, J. Garcia,(1998), “ Effects of Copper and Zinc on the Activated Sludge Bacteria Growth Kinetics ” , *Wat. Res.*,32: 1355-1362 Codina, J. C., M. A. Munoz, F. M. Cazorla, A. P-Garcia, M. A. Morinigo, A. D. Vicenti,(1998), “ The Inhibition of Methanogenic Activity from Anaerobic Domestic Sludges as a Simple Toxicity Bioassay ” , *Wat. Res.*,32: 1338-1342 Silver, S.,(1998) “ Genes for all metals-a bacterial view of the Periodic Table The 1996 Thom Award Lecture ” , *Journal of Industrial Microbiological & Biotechnology* ,20: 1-12 林啟文、吳照雄 (1999), 「汽油添加劑MTBE之生物降解技術研究」, 期中報告, 中國石油股份有限公司。計畫編號: NSC-CPC-E-212-001 侯松男 (2002), 「含氧汽油添加劑分解菌之馴化、篩選及生長條件研究」, 大葉大學環境工程研究所碩士論文 邱創汎、王耀銘、張坦卿 (1996), 「空氣污染生物處理技術本土化之評析」, 工業污染防治, 第58期, p111-124 陳良誌 (2000), 「1.模場生物滴濾處理含異辛醇排氣之操作性能研究; 2.以實場生物滴濾塔處理合成樹脂廠排氣之操作性能研究」, 國立中山大學環境工程研究所碩士論文 朱振華 (1998), 「生物濾床法處理含BTEX廢氣程序控制之研究」, 國立中興大學環境工程研究所碩士論文 蘇佳慶 (1996), 「以生物滴濾塔處理排氣中一氧化氮之操作性能研究」, 國立中山大學環境工程研究所碩士論文 吳非隆 (1995), 「以生物滴濾塔處理排氣中甲苯成份之操作性能研究」, 國立中山大學環境工程研究所碩士論文 黃忠永 (1996), 「以生物滴濾塔及濾床處理煉油廢水場排氣中揮發性有機物之研究」, 國立中山大學環境工程研究所碩士論文 涂秀妹 (2001), 「以實場生物滴濾塔處理排氣中苯乙烯及丙烯?之操作性能研究」, 國立中山大學環境工程研究所碩士論文 王嘉禧 (2000), 「以生物滴濾塔處理排氣中氨之操作性能研究」, 國立中山大學環境工程研究所碩士論文 許宏寬 (2001), 「MTBE生物降解研究」, 雲林科技大學環境與安全工程研究所碩士論文 廖志祥、李明堂、何佳倩 (2001), 「以H₂O₂/UV並以抽取回送式處理MTBE污染地下水」, 第二十六屆廢水處理技術研討會, 國立高雄第一科技大學, 高雄市 林啟文、吳照雄 (2000), 「汽油添加劑MTBE之生物降解技術研究」, 期末報告, 中國石油股份有限公司。計畫編號: NSC-CPC-E-212-001 林啟文、張金全 (2001), 「連續批次反應系統處理含氧汽油添加劑及環狀有機物之動力特性研究(1/3)」, 行政院國科會專題研究計畫成果報告, 行政院國科會。計畫編號: NSC 89-2211-E-212-006 林啟文、張金全 (2002), 「連續批次反應系統處理含氧汽油添加劑及環狀有機物之動力特性研究(2/3)」, 行政院國科會專題研究計畫期中成果報告, 行政院國科會。計畫編號: NSC 90-2211-E-212-008 林啟文、洪士賢、陳政遠、呂珊茹 (2002), 「ETBE與TAME對甲基第三丁基醚分解菌之抑制效應研究」, 中華民國環境工程學會第二十七屆廢水處理技術研討會, 台北市 陳谷汎、陳谷汎、方韋寧、陳廷育、高志明 (2002), 「以好氧生物復育法整治受甲基第三丁基醚(MTBE)污染場址之評估」, 第一屆海峽兩岸土壤與地下水污染整治研討會, pp B179-B185 王雅玢、陳志強、謝煌麒, (2001) 「汽油油中金屬元素之特徵」, 第二十六屆廢水處理技術研討會, 高雄市 張豐藤、李俊德、李文智, (2000) 「柴油車排放廢氣中重金屬元素之特徵」, 第十七屆空氣污染控制技術研討會, 雲林縣 平成股份有限公司, 「工業區土壤及地下水質污染全面性調查工作」, 新竹市環保局委託研究計畫期末報告, 1999 李俊璋、謝佳禕, 「修車廠作業員工揮發性有機物質暴露評估」, 碩士論文, 國立成功大學環境醫學研究所, 1999 張全勝 (1994), MTBE及TAME製程與觸媒發展及其反應原料之取得, 觸媒與製成, 第三卷第三期, pp54-58 黃士軒 (1999), 「甲基第三丁基醚(MTBE)在土壤中傳輸之研究」, 台灣大學環境工程研究所碩士論文