

# Performance of a Trickled-Bed Biofilter for a MTBE-Contaminated Airstream

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## ABSTRACT

Methyl tertiary butyl ether (MTBE) with the properties of high vapor pressure and high water solubility, is an oxygenated gasoline additive. Due to its contamination to air, soil, and groundwater, MTBE is listed as the fourth category toxic chemical by Environmental Protection Administration. This study aims to improve the existing biofilter and takes advantage of high recirculation rate of the conventional trickling filter. Therefore, the developed trickled-bed biofilter can be operated in sufficient water content which prevent from growing limitation for microorganism. Overall, the objectives of the study are to construct a bench-scale biofilter, and to investigate the effects of environmental conditions on MTBE removal. The various environmental conditions include inlet MTBE concentration, liquid flow rate, and empty bed residence time (EBRT). Results of the trickled-bed biofilter removal experiments show that: (1) After 30~40 min operation, the incoming MTBE with 50 and 100 ppm was completely absorb/adsorb by the biofilter. (2) More than 80% removal efficiencies were observed with organic loading rate of MTBE below 10 g/m<sup>3</sup>.h. However, the elimination capacity approached a constant value, and removal efficiency decreased to 50% while organic loading rate increased to 28 g/m<sup>3</sup>.h. (3) MTBE removal efficiency increased from 72% to 86% as nutrient feeding rate (NFR) increased from 10 to 40ml/min, which indicates elevated nutrient feeding enhances MTBE removal. However, the removal decreases to 83% and 78% if keep increasing the NFR to 50 and 60ml/min, respectively. It is believe that too high of water content in the biofilter causes the reduction of mass transfer rate leading to the decrease of removal efficiency. (4) More than 88% and 85% removal efficiencies were achieved for inlet MTBE concentrations of 50ppm and 100ppm in EBRT of 83 seconds. However, the MTBE removal decreased to 43% as increasing MTBE concentration to 200ppm. Under inlet concentration of 200ppm, MTBE removal efficiencies were 50%, 65% and 75% for EBRT of 100, 140, and 188 seconds, respectively. Hence, MTBE removal efficiency increases while EBRT increases.

Keywords : Trickled-bed biofilter ; Biodegradation ; Organic loading ; MTBE

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## REFERENCES

- Barreto, R. D., K. A. Gray, and K. Anders, (1994) " Photocatalytic degradation of methyl-tert-butyl ether in TiO<sub>2</sub> slurries a proposed reaction scheme " Wat. Res. Vol. 29, No. 5. pp. 1243-1248 Bergendahl, J. A., and T. P. Thies, (2004) " Fenton ' s oxidation of MTBE with zero-valent iron " Wat. Res. Vol. 38, pp. 327-334 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 Church C. D., P. Tratnyek, and K. Scow (2000) " Pathways for the degradation of MTBE and other fuel oxygenates by isolate PM1 " Preprints of Extended Abstracts, Am. Chem. Soc. 40:261-263 Chung, Y., C. Huang, C. Tseng, (2001) " Biological elimination of H<sub>2</sub>S and NH<sub>3</sub> from wastegases by biofilter packed with immobilized heterotrophic bacteria " Chemosphere Vol. 43, pp. 1043-1050 Deeb R. A., and L. Alvarez-Cohen (2000) " Aerobic biotransformation of gasoline aromatics in multi-component mixtures " Biorem. J. 4: 171-179 Edwards, F. G., and N. Nirmalakhandan, (1996) " Biological treatment of airstreams contaminated with VOCs:an overview " Wat. Sci. Tech. Vol. 34, No. 3-4, pp. 565-571 Fortin, N. Y., and 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. Vol. 33, pp. 2980-2986 Francois, A., H. Mathis, D. Godefroy, P. Piveteau, F. Fayolle, and F. Monot, (2002) " Degradation of methyl tert-butyl ether and other fuel oxygenates by a New Strain, Mycobacterium austroafricanum IFP 2012 " Appl. Environ. Microbiol. Vol 68, pp. 2754-2762 Hardison L. K., S. S. Curry, L. M. Ciuffetti, and 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. 65: 4788-4792 Hanson, J. R., C. E. Ackerman, and K. M. Scow, (1999) " Biodegradation of methyl tert-butyl ether by a bacterial pure culture " Appl. Enviro. Microbiol., Nov. pp. 4788-4792 Hatazinger, P. B., K. McClay, S. Vaingerg, M. Tugusheva, C. W. Condee, and R. J. Steffan, (2001) " Biodegradation of methyl tert-butyl ether by a pure bacterial culture " Appl. Enviro. Microbiol., Dec. pp. 5601-5607 Hernandez-Perez, G., F. Fayolle, and 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. Vol. 55, pp. 117-121 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 Kharoune, M., A. Pauss, and J. M. Lebeault, (2001) " Aerobic biodegradation of an oxygenates mixture:ETBE, MTBE and TAME in an upflow fixed-bed reaction " Wat. Res. Vol. 35, No. 7, pp. 1665-1674 Kim J., (2003) " Degradation of benzene and ethylene in biofilter " Biochemistry Vol. 39, pp. 447-453 Lu, C., M. R. Lin, and C. Chu, (2002) " Effects of pH, moisture, and flow pattern on trickle-bed air biofilter performance for BTEX removal " Advances in Environmental Research 6 99-106 Mueller, J. C. (1988) " Biofiltration of gases-a mature technology for control of a wide range of air pollutants " A Report to the National Resrarch Council of Canada and the British Columbia Ministry of Advanced Education and Job Training, Project No. 2-51-797 Moe, W. M., and R. L. Irvine, (2001) " Effect of nitrogen limitation on performance of toluene degrading biofilters " Wat. Res. Vol. 35, No. 6, pp. 1407~1414 Mitani, M. M., A. A. Keller, C. A. Bunton, R. G. Rinker, and O. C. Sandall, (2002) " Kinetics and products of reactions of MTBE with ozone and ozone/hydrogen peroxide in water " Journal of Hazardous Materials B89 pp. 197-212 Nakamura D. N. (1994) " MTBE, still the best choice " Hydrocarbon Processing, 73:17 National Science and Technology Council NSTC, (1997) " Interagency Assessment of Oxygenated Fuels, Washington " , D.C. : Office of Science and Technology Policy Neal, A. B., and R. C. Loehr, (2000) " Use of biofilters and suspended-growth reactors to treat VOCs " Waste Manage. Vol. 20, pp. 59-68 Nepolian, B., H. Jung, H. Choi, J. H. Lee, and J. Kang, (2002) " Sonolytic degradation of methyl tert-butyl ether:the role of coupled fenton process and persulphate ion " Wat. Res. Vol. 36, pp. 4699-4708 Piel W. J. and R. X. Thomas, (1990) " Oxygenates for reformulated gasoline " Hydrocarbon Processing, Vol. 69, pp.68-73 Suflita, J. M., and M. R. Mormile (1993) " Anaerobic biodegradation of known and potential gasoline oxygenates in the terrestrial subsurface " Environ. Sci. Technol. Vol. 27, pp. 976—978 Salanitro J. P., L. A. Diaz, M. P. Williams, and H. L. Wisniewski (1994) " Isolation of a bacterial culture that degrades methyl t-butyl ether. " Appl. Environ. Microbiol. Vol. 60, pp. 2593—2596 Steffan, R. J., K. McClay, S. Vainberg, C. W. Condee, and D. Zhang, (1997) " Biodegradation of the gasoline oxygenates methyl tert-butyl ether, ethyl tert-butyl ether, and tert-amyl methyl ether by propane-oxidizing bacteria " Appl. Environ. Microbiol., Nov. pp. 4216-4222 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. Vol. 64, pp. 930-939 Salanitro J., G. Spinnler, P. Maner, H. Wisniewski, and P. Johnson (1999) " Potential for MTBE bioremediation-in situ inoculation of specialized cultures " In: Proceedings of the API/NGWA Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Remediation Conference, 17-20 November, Houston , TX Shojaosadati, S. A., and S. Elyasi, (1999) " Removal of hydrogen sulfide by the compost biofilter with sludge of leather industry " Conservation and Recycling Vol. 27 pp. 139-144 Sun, Y., X. Quan, J. Chen, F. Yang, D. Xue, Y. Liu, and Z. Yang, (2002) " Toluene vapour degradation and microbial community in biofilter at various moisture " Biochemistry Vol. 38, pp. 109-113 Schirmer, M., B. J. Butler, C. D. Church, J. F. Barker, and N. Nadarajah, (2003) " Laboratory evidence of MTBE biodegradation in Borden aquifer material " Journal of Contaminant Hydrology Vol. 60 pp. 229-249 Togna, A. P. and B. R. Folsom, (1992) " Removal of styrene from air using bech-scale biofilter and biotrickling fliter reactors " the 85th Annual Meeting & Exhibition of the AWMA, Kansas city, Missouri Van Lith, C., G. Leson, and R. Michelsen, (1997) " Evaluating design options for biofilter " J. Air and Waste Manage. Assoc., Vol. 47 pp.37-48 Yeom, S. H., and Y. J. Yoo, (1999) " Removal of benzene in a Hybrid bioreactor " Biochemistry Vol. 34, pp.

281-288 Yoon, I. K., and C. H. Park, (2002) "Effect of gas flow rate, inlet concentration and temperature on biofiltration of volatile organic compounds in a peat-packed biofilter" J. of Biosci. And Bioeng., Vol. 93, pp. 165-169 王嘉禧(2000), 「以生物滴濾塔處理排氣中氨之操作性能研究」, 國立中山環境工程研究所, 碩士論文 方瑋寧(2002), 「MTBE好氧分解之可行性研究」, 國立中山大學環境工程研究所, 碩士論文 白旭峰(2003), 「生物濾床乾燥模式之研究」, 中華大學土木工程學系碩士班, 碩士論文 朱文昌(1996), 「生物濾床法處理含BTEX廢氣之研究」國立中興大學環境工程研究所, 碩士論文 朱振華(1998), 「生物濾床法處裡含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 台中縣環境保護局(2000), 「台中縣推動宣導減少使用含有揮發性有機溶劑消費商品計畫其末報告修正版」江俊亮(2001), 「垃圾掩埋場惡臭與有害氣體」, 國立成功大學環境工程學系, 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 李家偉(2000), 「汽油添加劑MTBE(甲基第三丁基醚)之環境污染特性」, 環保訓練園地雙月刊第49期 李惠娟、李季眉、黃思蕙(2000), 「甲苯與乙酸乙酯在生物濾床中分解機制之探討」, 中華民國環境工程學會第十七屆空氣污染控制技術研討會, 雲林縣 吳國雄(2003), 「食品廢棄物好氧生物降解(堆肥化)」, 國立高雄第一科技大學環境與安全衛生工程系, 碩士論文 林春賓(2000), 「加油站附近空氣中MTBE暴露評估過程中之不定性研究」, 國立雲林科技大學環境與安全工程研究所, 碩士論文 林志芳(2002), 「以理論探討生物濾床法處理VOCs之研究」, 國立中興大學環境工程研究所, 碩士論文 林晉成、黃思蕙、李惠娟、李季眉(2000), 「以純菌(*Pseudomonas putida* & *Rhodococcus* sp.)生物濾床處理含甲苯及乙酸乙酯混合廢氣之研究」, 中華民國環境工程學會第十七屆空氣污染控制技術研討會, 雲林縣 洪國騰(2001), 「沼氣脫硫·實場生物洗滌塔操作性能研究」, 國立中山大學環境工程研究所, 碩士論文 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 徐瑋德(2003), 「生物滴濾床處理甲苯與三氯乙烯」, 國立清華大學化學工程學系, 碩士論文 徐樹剛、徐雲郁、賴子仁(2003), 「廢氣生物濾床處理技術應用」, 環保產業雙月刊第18期 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 許世杰(2003), 「生物濾床法應用於半導體實場操作之研究」, 國立中興大學環境工程研究所, 碩士論文 陳彥全(2000), 「生物濾床應用於厭氧脫硝處理含NO廢氣相關操作因子之研究」, 國立台灣大學環境工程研究所, 碩士論文 陳良誌(2000), 「題目:1.以模場生物滴濾塔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」, 國立中山學環境工程研究所, 碩士論文 黃俊哲(2002), 「應用浸水式生物濾床處理含酚及硫化物廢水之研究」, 國立臺灣大學環境工程學研究所, 碩士論文 陳信源(2003), 「甲基第三丁基醚分解菌之分解能力與重金屬抑制效應研究」, 大葉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」, 國立中山學環境工程研究所, 碩士論文 黃俊傑、賴慶智、王耀銘(1998), 「電子半導體廠之有機廢氣處理 生物濾床處理案例研究」, 化工資訊, pp.14~23 黃君逸(2003), 「生物濾床處理廢棄物儲存場VOCs 廢氣之實場研究」, 國立交通大學產業安全與防災學程碩士班, 碩士論文 黃土軒(1999), 「甲基第三丁基醚(MTBE)在土壤中傳輸之研究」, 國立台灣大學環境工程研究所, 碩士論文 張全勝(1994), MTBE及TAME製程與觸媒發展及反應原料之取得, 觸媒與製成, 第三卷第三期, pp.54~58 張國財、盧重興、林明瑞(2000), 「生物濾床處理實場廢氣的研究有處理PU樹脂實廠廢氣之研究」, 中華民國環境工程學會第十七屆空氣污染控制技術研討會, 雲林縣 張筱瑜(2001), 「以活性污泥洗滌法處理排氣中揮發性有機物質之研究」, 國立中山大學環境工程研究所, 碩士論文 張國財(2003), 「生物濾床法處理光電產業揮發性有機廢氣之研究」, 國立中興大學環境工程研究所, 博士論文 楊佑群(1998), 「應用生物濾床法處理含氮氧化物廢氣之研究」, 國立臺灣大學環境工程學研究所, 碩士論文 廖庭寬(2001), 「生物濾床中乙酸乙酯抑制二甲苯去除現象之研究」, 國立中興大學環境工程研究所, 碩士論文 環保政策月刊第1期-汽油添加劑MTBE禁用環署評估, 2001 魏銀河(2000), 「生物濾床處理五種樹脂工廠混合VOCs廢氣之研究」, 國立中興大學環境工程學系, 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