Co-Metabolic Degradation of 1,4-Dioxane

Abstract

1,4-Dioxane is a synthetic chemical used as a stabilizer of chlorinated solvents and as a solvent in several commercial and industrial processes. It is identified as an emerging water contaminant and classified as a likely carcinogenic to humans. Removal of 1,4-dioxane from wastewater is challenging due to its high water solubility, low Henry's law constant, and low partition coefficients. Bioremediation is a promising method for treating 1,4-dioxane-contaminated water as it is potentially cost-effective and eco-friendly. Some microorganisms can use 1,4-dioxane as a sole carbon and energy source and the biodegradation of 1,4-dioxane can be enhanced when primary substrates are provided to promote microbial growth.

The main objective of this research was to investigate the co-metabolic biodegradation of 1,4-dioxane. The first objective focused on kinetic parameters for ethane biodegradation and co-oxidations of ethane and 1,4-dioxane. Based on experiments combined with mathematical modeling, it was found that ethane promoted 1,4-dioxane biodegradation when the initial mass ratio of ethane:1,4-dioxane was <9:1 mg-COD/mg-COD, while it inhibited 1,4-dioxane degradation when the ratio was >9:1. A model-independent parameter estimator was used for kinetic-parameter estimation, and all parameter values for 1,4-dioxane were consistent with literature-reported ranges. The results support that bacteria that co-oxidize ethane- and 1,4-dioxane had a competitive advantage over bacteria that can use only one of the two substrates. The minimum 1,4-dioxane concentration required to sustain steady-state biomass with 1,4-dioxane as the sole primary substrate was 1.3 mg-COD/L. As 1,4-dioxane concentrations at most groundwater sites are less than 0.18 mg-COD/L, providing ethane as a primary substrate is vital to enhance biomass growth and 1,4-dioxane bioremediation.

The second objective investigated the biodegradation of 1,4-dioxane using ethane as a primary substrate in an O_2-based membrane biofilm reactor (O_2-MBfR). Based on more than 800 days of continuous operation of two O_2-MBfRs with different influent ethane concentrations over the various stages, it was found that an ethane:1,4-dioxane mole ratio of around 300:1 was required to remove 1,4-dioxane from 100 µg/L to ~10 µg/L and from 10 µg/L to 2 µg/L. Results from the microbial community analysis showed that *Rhodococcus* and *Mycobacterium* were the two dominant genera in both MBfRs.

The third objective of this research investigated the biodegradation of ethane and 1,4-dioxane in the O_2-MBfR by developing a mathematical model. A higher ethane supply resulted in biofilm growth with the biofilm's active biomass dominated by ethane- and 1,4-dioxane-co-oxidizing bacteria. At >200:1 ethane to 1,4-dioxane mole ratio and <1.9 mg m^{-2} d^{-1} 1,4-dioxane loadings, the 1,4-dioxane removal was >70%. On the other hand, high ethane (>300:1 ethane to 1,4-dioxane mole ratio) at high 1,4-dioxane loadings (>4 mg m^{-2} d^{-1}) inhibited 1,4-dioxane biodegradation to <30%. The findings underscore that at low 1,4-dioxane loadings, ethane is an essential primary substrate to maintain sufficient biofilm growth for 1,4-dioxane degradation.

In the fourth objective, 1,4-dioxane-metabolizing mixed cultures were enriched by periodically spiking 1,4-dioxane at low concentrations (<1 mg/L). Five 1,4-dioxane-metabolizing pure cultures LCD6B, LCD6D, WC10G, WCD6H, and WD4H were isolated and characterized. The partial 16S rRNA gene sequencing showed that the five strains were related to *Dokdonella* sp. (98.3%), *Acinetobacter* sp. (99.0%), *Afipia* sp. (99.2%), *Nitrobacter* sp. (97.9%), and *Pseudonocardia* sp. (99.4%), respectively. Compared to the literature, these strains have lower half-maximum-rate concentrations (1.8 to 8.2 mg-dioxane L^{-1}), lower maximum specific 1,4-dioxane utilization rates (0.24 to 0.47 mg-dioxane mg-protein^{-1} d^{-1}), higher biomass yields (0.29 to 0.38 mg-protein mg-dioxane^{-1}), and lower decay coefficients (0.01 to 0.02 d^{-1}). These are characteristics of microorganisms living in oligotrophic environments.

Although the adsorption kinetics and isotherms of several water pollutants have been widely studied, little is known about the adsorption kinetics of 1,4-dioxane. In the fifth objective, the kinetics of 1,4-dioxane adsorption by AmberSorb and Granular Activated Carbon (GAC) were investigated. A homogeneous surface diffusion model was developed to describe the adsorption of 1,4-dioxane in continuous flow and batch systems. The external mass-transfer and internal diffusion coefficients of 1,4-dioxane for AmberSorb (1.79×10^{-3} cm/min and 3.52×10^{-4} cm^2/min) were determined about five- and thirty-fold larger than that of their corresponding parameters for GAC. For both adsorbents, the adsorption was limited by the mass-transfer across the fluid film that covers the adsorbent and the adsorbent-adsorbate interaction at the adsorbent surface but not limited by the diffusion within the adsorbent. While the mass-transfer across the external fluid film affected the maximum 1,4-dioxane removal percentage and the adsorption rate, the isotherm parameters mainly controlled the adsorption capacity and adsorbent service life.