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Review Article

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The effectiveness of cyclic ether biodegradation in groundwater and in soil

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Abstract 1,4-Dioxane was released into the air, water, and soil at production sites and was classified as a probable pollutant carcinogen. Its throwing limit could be controlled by low cost bioremediation substitutes to photocatalytic oxidation, volatilization and sorption. 1,4 dioxane cometabolic biodegradation process depends on using primary substrates as methane. Degradation of 1,4-dioxane and accompanied metabolites were demonstrated by GC-MS analysis.

Keywords metabolic and cometabolic, bioremediation, *Pseudonocardia dioxanivorans* CB119, Redox potential conditions, anaerobic biodegradation, tert-butyl alcohol (TBA).

Introduction

1,4-Dioxane was introduced into production of certain surfactants, including polysorbates, sorbitol, and sorbitan. Also, it is used as a solvent stabilizer that present at many sites contaminated along with chlorinated solvents and other degrasing compounds [1-2]. Therefore, 1,4-dioxane is usually associated with 1,1,1-(TCA) trichloroethane but the improper disposal of industrial waste and accidental solvent spills have resulted in the contamination of groundwater [3-5]. 1,4-dioxane with its heterocyclic structure and two ethers linkages make it resistant to abiotic and biologically mediated degradation.

Although dioxane is miscible with water, it is poorly delayed in aquifers due to its low dimensionless Henry's law constant and low octanol-water partitioning coefficient.1,4-dioxane percolates between soil particles because it is very mobile and persistent to groundwater till it reaches industrial wastewater, domestic sewage and round landfill sites then it leached and threaten drinking water supplies [6-8]. Lower level of dioxane detection is needed to protect human health.

Several biopiles, or other physicochemical treatment methods are economically cost or inefficient for removing 1,4-dioxane from groundwater. e.g., carbon adsorption and air stripping, chemical oxidation with a combination of ozone and hydrogen peroxide, strong oxidants, the use of high energy input, sonication, or UV light [9,10]. Biodegradation represents an important alternative as lower energy demand when used as the sole source of carbon and energy [11]. Despite the known toxicity and persistence of 1,4-dioxane, the success of bioremediation process depends on biomass movement, its deterioration, aquifer permeability, groundwater distribution, and appropriate inhibition. Solvents which inhibit biodegradation of 1,4-dioxane are in the following order: 1,1-dichloroethene > cis-1,2-diochloroethene > trichloroethene > 1,1,1-trichloroethane [12]. On the other hand, bioaugmentation of hybrid trees roots with 1,4-dioxane-degrading micro-organism Amycolata CB1190 were used to remove 1,4-dioxane from shallow subsurface environments, however, most of the dioxane transpired from leaf surfaces into the air instead of undergoing biodegradation [6,13].

The kinetic parameters for 1,4-dioxane metabolism and cometabolism

The most importantkinetic parameters were the initial concentration of 1,4-dioxane, biomass, oxygen, and propane injection rates. The comparison between metabolic and cometabolic, i.e. non-growth linked microbial bioremediation performance depends upon the time to reach an average 1,4-dioxane concentration of 1 µg/ L in biodegradation after 10 years.

1,4-Dioxane is a difficult compound to decompose especially in natural habitats where temperatures are suboptimal for biodegradation and low concentrations. For in situ bioremediation of 1,4- dioxane, the occurrence of metabolic and cometabolic processes was indicated by propane-oxidizing bacteria. When the initial concentration of 1,4-dioxane is less than 7.5 mg/ L gas sparging with air and propane coupled to bioaugmentation with a propanotrophic culture will achieve a faster rate of remediation than air sparging and bioaugmentation with a culture that metabolically biodegrades 1,4-dioxane [14]. Simulation of metabolic and cometabolic biodegradation of 1,4-dioxane at low dissolved oxygen levels showed also that the initial biomass concentration is another important parameter in situ remediations [15]. Pure and mixed bacterial cultures support mineralization of 1,4-dioxane under aerobic conditions, whether by its use as a carbon and energy source or via cometabolism following growth on a primary potential cosubstrates. There was some investigation to apply fungi to degrade 1,4-dioxane, either by itself oral so in cometabolism with structural analogs or supplemented nutrients [6].

Some consortium degrades 1,4-dioxane but can't grow on it. The dioxane ring is hydroxylated prior to cleavage i.e. mineralization to CO_2 has been also demonstrated with mixed microbial populations [16]. Several 1,4-dioxane biotransformation were reported by *My*cobact*erium vaccae* [17], *Methylosinus trichosporium* OB3b, Pseudomonas*mendocina* KR1, *Ralstoniapickettii* PKO1, *Burkholderiacepacia* G4, *Rhodococcus* RR1 strain [18], *Pseudonocardia dioxanivorans* CB1190, *Pseudonocardia benzenivorans* B5, *Pseudonocardia antarctica* [19] and *Rhodanobacter* AYS5 [20].

The resulted CO_2 from the mineralization of dioxane was initially reported for *Pseudonocardia dioxanivorans* CB1190. The intermediates ethylene glycol, glycolic acid, and oxalic acid were detected for the fungal isolate *Cordyceps sinensis*. A degradation pathway was followed by incorporation of the acids into the tricarboxylic acid cycle. *C. sinensis* was isolated from soil and able to utilize 1,4-dioxane and other kinds of cyclic ethers as the sole carbon source and was identified as *C. sinensis* from its 18S rRNA gene sequence. *C. sinensis* is an insect's inhibitor fungus identified as mushrooms on host larvae of Hepialusarmoricanus from mountainous regions in China. Usually, it makes a fruiting body, and it has been consumed as herbal medicine in Asia for its antioxidant activity for prevention and treatment of various diseases but it has not yet been used in bioremediation [21].

16S rRNA and meta-transcriptomic methods were applied to analyze the dioxane biodegradation mechanism by activated sludge. Ammonia-oxidizing and denitrifying bacteria with methane monooxygenases (MOS) and ammonia MOs played an important role during the degradation of dioxane. 16S rRNA sequences and primers should be designed to identify specific bacteria and MOS during dioxane degradation [22-23].

Biodegradation could be achieved by growth on other carbon sources that support faster growth rate as a primary substrate, including propane, methane, toluene, and tetrahydrofuran (THF). When THF concentrations increased, the dioxane removal ratio increased. Little is known the kinetic parameters for propane-oxidizing bacteria that degrade 1,4-dioxane.Hwever,the simulation results indicated that propanotrophic cometabolism achieves remediation at a faster rate with low initial 1,4-dioxane concentration, because lower concentrations do not support enough growth of microorganism to equalize the effect of cell decay. A continuous supply of propane to support cometabolism cancel that effect [24-25]. Batch simulations showed that co-metabolism is more advantageous than metabolism when the initial concentration of 1,4-dioxane is low 1 mg L/1 and that both processes are heavily impacted by dissolved oxygen.

***In situ* bioremediation of a 1,4-dioxane**

Aerobic bioremediation occurs with oxygen delivery, which is the electron acceptor. Oxygen can be added directly to the subsurface, or as chemical oxidants that release oxygen when dissolve or decompose. Aerobic biodegradation of 1,4-dioxane were carried out under metabolic and co-metabolic conditions to compare the bacterial performances

in situ conditions [26]. Biosparging and bioaugmentation were tried by simulating a subsurface transport model to find out the effect of biodegradation reactions on dioxane plume. Similarly, Gas-sparging using propane and methane as growth substrates were carried out to assess the possibility of in situ aerobic cometabolism of trichloroethene (TCE) and cis-1,2-dichloroethene (cis-DCE) [27]. Gas-sparging using oxygen had stimulated organisms' capacity to transform TCE and cis-DCE. The monooxygenases performance in dioxane degradation describes the kinetics of metabolic and cometabolic dioxane degradation [28-29].

Pure cultures and industrial activated sludge samples propose the presence of genes associated with dioxane monooxygenase, propane monooxygenase, alcohol dehydrogenase, and aldehyde dehydrogenase which are promising indicators of 1,4-dioxane biotransformation; however, genes were inadequate to predict actual biodegradation.

Co-metabolism and bioaugmentation

Although *actinomycetes* were able to utilize the dioxane as a sole carbon source [11, 30], there isn't a proposed degradation pathway. Studies on the degradation of 1,4-dioxane have been done with microorganisms that cometabolized THF and/or supplemented nutrients.

Bioremediation by metabolizing 1,4-dioxane has several advantages, including a reduced clogging the aquifer, lower oxygen demand, and without a primary substrate. But, when the concentration of 1,4-dioxane is below 1,000 µg/ L as below concentrations that could provide a carbon or energy benefit to the bio degrader, then cometabolism could be an alternative for in situ remediations. Most contaminated aquifers have reducing conditions in which anaerobic biodegradation would be more advantageous due to the challenges of delivering oxygen to a deep aquifer. Redox potential conditions (electro-redox contribution) that are common in aquifers (e.g., iron reducing, sulfate reducing, and methanogenic bacteria) and electrical conductivity of groundwater are important for bioremediation under in situ conditions. Considering, the effect of co-contaminants and the application of bio stimulation additives (e.g., lactate; molasses, vegetable oils) [6].

1,4-Dioxane biodegradation pathway

Accumulation of β-hydroxy ethoxy acetic acid (HEAA) resulted during cometabolic degradation of dioxane *by Pseudonocardia sp.* strain ENV478 initially grown on THF [31]. Strain ENV478 degraded total suspended solids, 1,4-dioxane, 1,3-dioxolane, bis-2-chloroethyl ether (BCEE)), and methyl tert-butyl ether (MTBE). Although the highest rates of 1,4-dioxane degradation occurred after growth on THF, strain ENV478 also degraded 1,4-dioxane after growth on sucrose, lactate, yeast extract, 2-propanol, and propane, indicating that there was some level of constitutive degradative activity. The inability of strain ENV478 and possibly other THF-degrading bacteria to grow on 1,4-dioxane is related to their inability metabolize the 1,4-dioxane degradation product, 2-hydroxy ethoxy acetic acid(2HEAA). It could be noticed that, degradation of 1,4-dioxane resulted in the accumulation of 2HEAA and Para-dioxane (PDX). ENV478 culture was able to degrade the related solvent 1,3-dioxolane, the gasoline additive MTBE, and the plasticizer BCEE [32].

Interestingly, the strain degraded 1,4-dioxane faster after growth on THF than after growth on propane, and it degraded BCEE about three times faster when growth on propane than after growth on THF. Although the products of BCEE and 1,3-dioxolane degradation were not analyzed, MTBE oxidation resulted in accumulation of tert-butyl alcohol that was not degraded further by the strain [33]. HEAA and other detected intermediates of degradation-based pathway for strain CB1190 includes 2-hydroxy-1,4-dioxane, 2-hydroxy ethoxy acetaldehyde, 1,4-dioxane-2-one, 1,3-dihydroxy ethoxy acetic acid, 2-hydroxyethoxy-2-hydroxyacetic acid, glycolaldehyde, glyoxal, and formic acid.

1,4-dioxane anaerobic biodegradation

Anaerobic reductive bioremediation takes place in the absence of oxygen. It depends on the presence of available organic carbon, which is naturally present or added as a stimulant. The organic carbon, also commonly called an

organic substrate or an electron donor source, creates anaerobic conditions by consuming oxygen and other electron acceptors during its biodegradation. Anaerobic metabolism includes fermentation, methanogenesis, reductive dechlorination, sulfate- and iron-reducing activities, and denitrification. Anaerobic conditions are present at most contaminated sites that contains high levels of acetone, isopropanol, and halogenated solvents. Anaerobic microcosms were set up with groundwater and sedimented soil from contaminated sites to prove biodegradation. The microcosms were amended with labeled [14C]-1,4-dioxane [34-35], under iron-reducing conditions and a wastewater treatment plantinoculum. Amendments included Fe (III) oxide, Fe (III)- ethylene-diamine-tetra-acetic acid (Fe (III)-EDTA), anthraquinone di-sulfonate, sulfate and oxygen. Following four years of incubation, biodegradation of many of the halogenated solvents was investigated, as there was an iron reduction, sulfate reduction, and methanogenesis. Researches indicated that high percentages of biodegradation occurred in unaltered anaerobic microcosms prepared with anaerobic sludge and improvement has occurred when the microcosms were amended with humicacids.

Regarding the possibility for anaerobic degradation of (MTBE) and tert-butyl alcohol (TBA) in laboratory, incubations of sediments from a petroleum-contaminated aquifer and in aquatic sediments with addition of humic substances (HS) to assures the anaerobic conditions .HS and other extracellular quinones have a role inactivation of Fe (III)-reducing microorganisms by acting as an electron replacement between Fe (III)-reducing microorganisms and insoluble Fe (III) oxides. Degradation of MTBE in aquifer sediments must carried out in presence of be with Fe (III) as an electron acceptor as it is not degraded in aquifer sediments without Fe (III) and HS [36]. CO_2 and methane were the degradation products of M TBE and TBA in aquatic sediments. Ethyl tert-butyl ether and TBA were biodegraded under sulfate-reducing, denitrifying and methanogenic conditions.

Detection of degradation products

The cyclic ethers including 1,4-dioxane in the culture medium were determined by HPLC. Lower concentrations of 1,4-dioxane were estimated using a micro-frozen extraction method. Gas chromatographic (GC) analysis of aqueous filtered samples could be also applied.

The presence of a 1,4-dioxane IR spectrum distinctive bands occurs in 1126-cm^{-1},also, the whole group of bands present in the frequency ranges 800–950, 1000–1150, and at 1200–1300 cm^{-1} spectral regions [37].

Modified techniques such as Purge and Trap-Gas Chromatography-Mass Spectroscopy or GC–MS–MS was evaluated for the determination of dioxane compounds in aqueous samples result in inefficient purge recovery because Henry's law constant greatly favors dioxane in the aqueous phase concentration over the gaseous phase as dioxane has a high boiling point [20].

Some degradation products of 1,4-dioxane were derivatized with phenyl boronate [38].

Surfactants containing 1,4-dioxane are used in a wide variety of products including foods, cosmetics, and detergents [6], the level of 1,4-dioxane in various cooked food samples assayed by GC-MS spectrometry [20]. Degradation of 1,4-dioxane and concomitant formation of metabolites were demonstrated by GC/MS analysis using deuterium labeled 1,4-dioxane (1,4-dioxane-d8) [39].

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