

ANAEROBIC BIODEGRADATION OF XENOBIOTIC COMPOUNDS

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Key Words: Anaerobic Biodegradation, Reductive Biotransformation, Anoxic Electron Acceptors

Introduction. Anthropogenic compounds containing structural elements uncommon in nature are referred to as xenobiotic compounds (foreign to life). They include compounds containing chloro, nitro or sulfonate groups. Although petroleum hydrocarbons are natural, they occur at unnaturally high concentrations in the biosphere due to man's activity. Initially, it was feared that such compounds would accumulate in the environment. However, over the years, increasing evidence indicates that biodegradation is an important fate of many xenobiotic compounds. Biodegradation mechanisms in anaerobic environments are important due to the low solubility of oxygen in water. The objectives of this talk are to review the new developments concerning the biodegradation of xenobiotic compound in the absence of oxygen.

Table 1. Standard Reduction Potentials of Terminal Electron Acceptors (25°C, pH 7)

Electron Acceptor	Reduction Potentials (V)
O ₂ /H ₂ O	0.82
NO ₃ ²⁻ /N ₂	0.75
CCl ₂ CCl ₂ /CHClCCl ₂	0.56
MnO ₂ /MnCO ₃	0.50
FeOOH/Fe ²⁺	0.05
AQDS/AH ₂ QDS*	-0.18
SO ₄ ²⁻ /S ²⁻	-0.22
HCO ₃ ⁻ /CH ₄	-0.25

*A(H₂)QDS = anthra(hydro)quinone-disulfonate,

Results and Discussion. Elemental oxygen is one of the most energy yielding electron acceptors for the oxidation of organic compounds. In order to initiate biodegradation, aerobic microorganisms utilize elemental oxygen to introduce functionality into recalcitrant compounds (oxygenases). The main challenge to anaerobic microorganisms is to utilize inferior electron acceptors and to activate compounds for degradation without elemental oxygen. Certain anoxic electron acceptors such as nitrate manganese oxide and geothite offer high electron potentials. Consequently, the possibilities for anoxic biodegradation of hydrocarbons with these electron acceptors in the subsurface are great due to the high energy-yielding metabolism. On the other hand, sulfate and bicarbonate have by comparison much lower reduction potentials (Table 1). Nonetheless, evidence is growing that even these electron acceptors are utilized in historically contaminated sites to support biodegradation of petroleum hydrocarbons. Recently, it has been discovered that some xenobiotic pollutants are utilized by microorganisms as the terminal electron acceptor to support the anoxic oxidation of simple substrates (e.g. H₂, acetate, lactate, etc.). An important example is the major groundwater contaminant, tetrachloroethene (CCl₂CCl₂). Humic substances are inert organic compounds that can also behave as terminal electron acceptors to support the anoxic

degradation of simple and xenobiotic substrates, such as toluene. The redox active functional groups are quinones and anthraquinone-disulfonate (AQDS) is utilized as model. AQDS is a more favourable anoxic electron acceptor compared to sulfate reduction and methanogenesis (Table 1). Reduced quinones (hydroquinones) can directly reduce poorly bioavailable metal oxides, thus humic substances play an important role linking microorganisms to dissimilatory metal reduction.

Without oxygen, anaerobic microorganisms utilize bicarbonate and organic acids to activate inert hydrocarbons for degradation. For example, anaerobic degradation of alkylbenzenes and alkanes is initiated with an unusual addition reaction with fumarate, forming a hydrocarbon-succinate adduct (Figure 1).

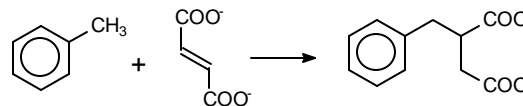


Figure 1. Activation of toluene for anaerobic biodegradation by adduct formation with fumarate.

Xenobiotic compounds with multiple electron-withdrawing groups such as chloro-, nitro- or azo-aromatic compounds are problematic compounds for aerobic degradation. However, such compounds are readily converted by reductive biotransformation reactions in anaerobic environments provided with electron donating substrates. Redox mediators such as quinones or biochemical cofactors (e.g. FAD) have been shown to greatly accelerate the reduction process. In the case of azo dyes, first order rate constants of dye reduction can be increased by one order of magnitude utilizing low concentrations of quinones (Figure 2).

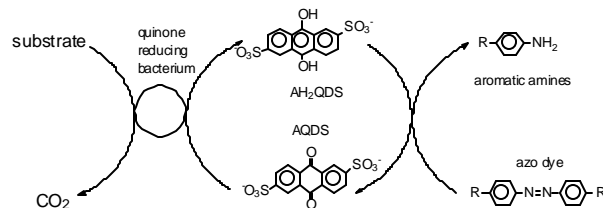


Figure 2. AQDS as redox mediator of azo dye reduction.

The reduced products of anaerobic biotransformations, lower chlorinated hydrocarbons or aromatic amines are more readily mineralized under aerobic conditions. For such compounds, sequenced anaerobic-aerobic degradation is the optimal strategy to mineralize the compounds.