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THERMODYNAMIC ASSESSMENT OF ANAEROBIC DEGRADATION OF XENOBIOTIC COMPOUNDS

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Persistence of complex organic compounds, from human origin (xenobiotics) through conventional wastewater treatment is a recognized problem for further utilization of primary and activated sludge as fertilizer (Lagenkamp and Part, 2001, http://europa.eu.int/comm/environment/waste/sludge/organics_in_sludge.pdf). Common xenobiotic compounds include polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalic acid esters, alkyl phenyl ethoxylates, and linear alkylbenzene sulfonates (LAS). All of these compounds have a high adsorbance capability (as measured by K_{OW}), and therefore adsorb onto solids in the wastewater. The compounds therefore pass through with the sludge to the sludge stabilization system before final thickening and disposal. The most common used stabilization method is anaerobic digestion, and the capability of anaerobic digestion to deal with these compounds is therefore of critical importance for eventual reuse of sludge. There has been a considerable applied research done to evaluate whether these compounds degrade anaerobically. Unfortunately, aboitic controls are lacking or not fully exploited, and it is therefore very difficult to demonstrate biotic removal. PCBs have been demonstrated to degrade reductively, and there is other evidence that some of the other compounds are removed. However, most results have been ambiguous.

A simple method of evaluating whether a compound is degradable is to assess thermodynamics of the reaction, under typical anaerobic digester conditions. If there is a positive, or zero free energy change in a reaction, the reaction cannot occur, *and* provide net benefit to the microbes mediating conversion. This has been done extensively to investigate observed, marginal reactions in anaerobic digestion (e.g., Schink, 1997, *Micro. Mol. Biol. Rev* **61**(2):262-280). However, it has not been applied to complex molecules, as the free energy of formation for the substrate molecules is not available. There are now excellent methods for estimating free enthalpies of formation, as well as other physical properties, using group contribution methods (Mavrovouniotis, 1990, *Biotech. Bioeng* **36**:1070-1082). The molecule is broken into a number of groups, which contribute to the overall free energies. Contributions of each group are calculated using regression on known compounds. In this work, we have evaluated thermodynamics for conversion of a wide range of xenobiotics, under standard conditions, as well as conditions generally found in anaerobic digesters. Mineralization to acetate, bicarbonate, and hydrogen was used as the criteria for overall degradability. It is also possible to hypothesize theoretical intermediates, and evaluate which intermediate is most likely to occur, using the same technique. Temperature also has an influence, and this can be assessed by the van't Hoff equation, assuming variable enthalpy of reaction.

Our results indicate that most xenobiotic compounds are theoretically degradable, and can be classed as follows: (1) theoretically degradable by reduction; degraders of the compound will compete for electrons with other oxidative reactions (e.g., PCBs); (2) theoretically degradable by fermentation; the compound can be theoretically degraded without a major electron acceptor or

donor (e.g., phthalic acid esters), and (3) degradable by oxidation only under low redox conditions; the compound will generally donate electrons to hydrogen ions, to produce hydrogen gas, and a syntrophic partner (e.g., hydrogenotrophic methanogen) is needed to remove the hydrogen produced (PAHs, LAS, alkyl phenyl ethoxylates). Some compounds, have immediate, and obvious intermediates. These include the hydrolysis products of phthalic acid esters, though different esters have lower free energies of hydrolysis, and therefore will be preferentially degraded. Other compounds (e.g., LAS) do not have favorable intermediates, and although the overall energy of reaction is good, may not be practically degradable.

The molecular modeling approach brings insight to degradation of complex organic molecules, and the results observed have mainly reflected experimental results in engineered, and pure systems done in our lab, and by others. It is a relatively simple method, and we suggest that it be applied as one of the first steps in investigation of conversion the new, prioritized xenobiotics, especially when assessing specific intermediates.