BIOPROCESSING OF LOW-LEVEL RADIOACTIVE AND MIXED HAZARDOUS WASTES

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ABSTRACT

Biologically-based treatment technologies are currently being developed at the Idaho National Engineering Laboratory (INEL) to aid in volume reduction and/or reclassification of low-level radioactive and mixed hazardous wastes prior to processing for disposal. The approaches taken to treat low-level radioactive and mixed wastes will reflect the physical (e.g., liquid, solid, slurry) and chemical (inorganic and/or organic) nature of the waste material being processed. Bioprocessing utilizes the diverse metabolic and biochemical characteristics of microorganisms. For example, complexation or flocculation to concentrate and separate radioisotopes may be used to treat aqueous radioactive waste. The application of bioadsorption and bioflocculation to reduce the volume of low-level radioactive waste are strategies comparable to the use of ion-exchange resins and coagulants that are currently used in waste reduction processes. Mixed hazardous waste would require organic as well as radionuclide treatment processes. Biodegradation of organic wastes or bioemulsification could be used in conjunction with radioisotope bioadsorption methods to treat mixed hazardous radioactive wastes. The degradation of the organic constituents of mixed wastes can be considered an alternative to incineration, while the use of bioemulsification may simply be used as a means to separate inorganic and organics to enable reclassification of wastes.

The proposed technology base for the biological treatment of low-level radioactive and mixed hazardous waste has been established. Biodegradation of a variety of organic compounds that are typically found in mixed hazardous wastes (e.g., toluene, xylene, petroleum-based lubricants and chlorinated solvents) has been demonstrated, degradative pathways determined and the nutritional requirements of the microorganisms are understood. Accumulation, adsorption and concentration of heavy and transition metal species and transuranics by microorganisms is widely recognized. Both the passive and active accumulation processes are understood. Work at the INEL focuses on the application of demonstrated microbial transformations to process development.

I. INTRODUCTION

It is the purpose of this paper to describe the microbial transformations that may be useful for the development of biologically-based technologies in order to treat low-level and mixed radioactive wastes. Biological transformations can accomplish many of the goals of physical or chemical treatments and thus may be used as an alternative to or in support of existing waste treatment processes. The potential use of microbially-based systems will be evaluated not only on what can be accomplished but also the efficiency and cost effectiveness of the process as well as its ability to satisfy local, state and federal regulations.

II. PHYSIOLOGICAL BASIS OF BIOPROCESSING

The diverse metabolic and physiological characteristic of microorganisms in addition to their ability to thrive in a wide range of environments may be exploited for the purposes of waste remediation and volume reduction. While some bacteria are able to modify a wide variety of organics and/or inorganics, others are quite restricted in their abilities. Microorganisms utilize these transformations in order to satisfy the nutritional and energy requirements for growth. Not only do microorganisms vary with respect to the types of chemical transformations they mediate, microorganisms vary with respect to the type of environment in which they are able to inhabit. Some bacteria are restricted to growth in environments typified by neutral pH, moderate temperatures etc., while others are capable of thriving in what appear to be rather extreme environments such as high temperatures and pressures, high salinities and alkalinities.

Microbial transformations applicable to waste treatment are those reactions which microorganisms mediate to: 1) satisfy nutritional requirements; 2) satisfy energy requirements; 3) detoxify their immediate environment; or 4) are the indirect or unexpected result of metabolic processes or the physical or chemical characteristics of the microbial cell. Microorganisms must meet their nutritional and energy requirements for cell growth and maintenance. Nutritional requirements are those elements that are assimilated into cell biomass or serve as co-factors or reaction centers in some enzymes. Carbon, oxygen, hydrogen, nitrogen, sulfur and phosphorous constitute approximately 95% of the dry weight of the cell and for the majority of microorganisms, these constituents are usually utilized in the organic form. Inorganic sources of nitrogen, phosphorous and sulfur can be utilized by most bacteria as well. Carbon dioxide has been shown to be the carbon source for some microorganisms, however those microorganisms which utilize organic carbon can be exploited for the biodegradation of organic compounds found in mixed wastes.

The oxidation and reduction of inorganic ions for the purposes of acquiring energy and reducing power may be useful for the development of waste treatment processes. Changing the oxidation state of an element may change its solubility in aqueous solution. For instance, manganese oxide formation by bacteria will result in the precipitation of this manganese form in water. Anaerobically respiring bacteria may be useful for a variety of purposes. For instance, sulfate reducing bacteria produce sulfide which can result in the formation of insoluble metal sulfides and nitrate reducing bacteria can reduce nitrate to gaseous dinitrogen.

Some microbially mediated transformations which are thought to be detoxification mechanisms may be applicable to radioactive waste treatment. For instance, the formation of organometals such as methyl mercury (Pan-Hou and Imura, 1982; Compeau and Bartha, 1984) would allow the removal of mercury through solvent extraction or volatilization. Similar transformations that may be applicable to the radioisotopes that are typically found in low-level radioactive wastes have not been investigated.

Transformation which happen as an indirect result of metabolic processes or the presence of microorganisms can be exploited for bioprocessing of radioactive wastes. Excreted metabolic acids can act as chelators and mobilize metals in a solid matrix. Likewise, microbially induced changes in pH and Eh can influence the solubility of heavy metals and radioisotopes. Reductive dehalogenation of chlorinated solvents by biogenically produced sulfide is the indirect result of microbial respiration by sulfate reducing bacteria. Adsorption of heavy metals and radioisotopes by microorganisms is often due to the presence of ionically charged polymers such as polysaccharides on cell surfaces.

III. LOW-LEVEL RADIOACTIVE WASTE BIOPROCESSING

Bioconcentration

Bioconcentration can be used as an alternative to ion-exchange resins, coagulants or evaporation for volume reduction of low-level radioactive wastes. Bioconcentration of radioisotopes and heavy metals can be accomplished by passive processes such as adsorption and flocculation or active processes such as intracellular transport and accumulation. Adsorption and flocculation which are cell surface associated phenomena are usually due to non-specific binding of ionic species to extracellular polymers such as polysaccharides or proteins. The advantages of using bioflocculation and bioadsorption are the fact that live biomass is not required and biomass can be regenerated and reused for multiple treatment cycles. Active transport and intracellular accumulation is an energy requiring process of live biomass. However, transport mechanisms are usually enzyme mediated and for that reason can be rather specific processes.

The use of flocculating microorganisms such as Zoogloea sp. would facilitate the separation of radioisotopes and metals from the bulk stream through the spontaneous settling of the metal-biomass complexes from the processed waste stream. Some flocculating microorganisms can grow in an aggregated state, while others will aggregate in response to changes in their environment, such as the addition of metals. But in either case, the results of waste treatment would be similar to the use of coagulants.

Accumulation, adsorption and concentration of heavy and transition metal species and transuranides by microorganisms is widely recognized. Americium-241 was biosorbed by bacteria and green algae (Geesey and Paine, 1977). Uranium is accumulated by bacteria (Nakajima and Sakaguchi, 1986), yeast (Nakajima and Sakaguchi, 1986; Strandberg et al., 1981), fungi (Galun et al., 1984; Tsezoz and Volesky, 1981) and biologically derived emulsifiers (Zosim et al., 1983). On a dry weight basis, microbial biomass adsorbs twice as much uranium as ion exchange resins or charcoal which are the conventional adsorbents for radioactive waste processing (Schumate and Strandberg, 1985). Neptunium-237 is accumulated by yeast, bacteria, fungi and algae (Strandberg and Arnold, 1988). Following solubilization of uranium from rocks by metabolic acids, the uptake and immobilization of uranium into fungal biomass has been observed (Berthelin and Munier-Lamy 1983).

The formation of insoluble metal sulfides or hydroxides by direct or indirect microbial transformations and the degradation of organochelators may also be an approach to the concentration of the inorganic constituents of low-level and mixed radioactive wastes. Insoluble metal sulfides can be formed with biogenically derived sulfides. However, some of the constituents of radioactive wastes such as uranium do not form stable sulfide complexes. The formation of insoluble metals hydroxides as well as changes in the valence state (oxidation or reduction) can occur through microbial activity. The solubility of inorganic constituents of radioactive waste may also be influenced by changes in pH and Eh brought about by microbial activity (Wildung and Garland, 1980).

Decontamination - solubilization

Biotransformations may be an approach to the decontamination of metallic surfaces or the removal of radioisotopes from salt cakes or sludges. Some bioleaching processes would be similar to the use of mineral acids and abrasion for the decontamination of hardware. Leaching activities may be accomplished directly through enzymatic action, or indirectly by a variety of mechanisms. Changes in valence state by enzymatic oxidation or reduction can affect solubility of the metal ion. Solubilization of metals may be achieved by changes in the pH and/or Eh of the system that result from microbial metabolic activity. Leaching or solubilization can also result from the production of chelators or a reagent as well as the removal or transformation of the immobilizing agent.

Solubilization of uranium from rocks by bacteria and fungi is accomplished by the production of small molecular weight carboxylic and phenolic acids produced by metabolic activities (Berthelin and Munier-Lamy 1983). Soil fungal isolates produce metabolites which form complexes with plutonium (Wildung et al., 1979). The bacterium _Thiobacillus_ _ferrooxidans_ solubilizes uranium by the production of ferric ions which reacts with uraninite to form uranyl ions. The activity of sulfate reducing bacteria in (Ba,Ra)SO_4 sludges derived from uranium mining operations can result in the reduction the sulfate to sulfide with the simultaneous loss of barium and radium (Fedorak et al., 1986). Similarly, the use of denitrifying nitrate reducing bacteria may be an approach to the removal of radioisotopes from nitrate containing salt cakes. The alkylation of heavy metals such as mercury, tin and selenium into volatile organometal (Compeau and Bartha, 1984; Francis et al., 1974; Pan-Hou and Imura, 1982) species could be useful for the vapor phase extraction of these metals from a porous matrix such as soils, sludges and cakes.

Transformations involved with microbially induced corrosion may be applicable to the decontamination of metallic hardware. Decontamination may be achieved by the microbial production of mineral or organic acids and reactants which would leach metallic surfaces. The presence of sulfate reducing bacteria has been associated with the acceleration of ferrous metal corrosion through cathodic depolarization by removing adsorbed hydrogen from cathodic surfaces or through the formation of ferrous sulfide.

IV. Mixed Radioactive Waste Bioprocessing

Treatment strategies that are being developed are dependent on the nature and form of waste that is to be treated. Two approaches to the biological treatment of mixed waste would be the degradation of the organic phase of the waste or the separation of the inorganic from the organic phase which would allow reclassification of the waste. With the appropriate bioreactor design, the microbial degradation of organics would be effective in a range of concentrations. e.g., 100 ppm to 100%. Separation of organics from the inorganics using biologically derived emulsification coupled with bioadsorption or bioflocculation to concentrate the radionuclides, heavy metals etc. is similar to the use of synthetic emulsifiers and coagulants.

The complete conversion organics to carbon dioxide and water is termed mineralization which is comparable to incineration. Typically organics which are mineralized can serve as growth substrates for microorganisms. Co-metabolism is the incomplete conversion of organic compounds and often requires an additional growth substrate. With co-metabolism the organic is often transformed to water soluble intermediates and in the case of toxic chemicals co-metabolism may or may not result in detoxification.

The predominant organic phases in the mixed waste in storage at DOE facilities are: petroleum based lubricating and machining fluids;

chlorinated solvents such as trichloroethylene, tetrachloroethylene, tetrachloromethane and methylene chloride; liquid scintillation cocktails which contain xylene and toluene; and tributyl phosphate containing wastes. All of these organics have been demonstrated to be degraded by microorganisms. However, for a more cost effective bioprocess, growth on these organics would be preferable.

The degradation of petroleum by microorganisms has been well established (Atlas, 1981). Most of the information pertains to the biodegradation of fuel oil spills (Atlas, 1981; Bossert et al., 1984; Wang and Bartha, 1990). However, this information is applicable to the development of a bioprocess for the treatment of petroleum based mixed wastes. The lighter fractions of the oil, which include the aliphatic and aromatics, are typically mineralized first (Fedorak and Westlake, 1981). The heavy chain aliphatics and multiple ring aromatics tend to be degraded later. The degradation of petroleum is predominantly an aerobic process. There are some reports of the anaerobic degradation of petroleum although rates would tend to be slower than the aerobic degradation.

Chlorinated solvents tend to be co-metabolized by both aerobic and anaerobic microorganisms. There are many reports of microorganisms mediating the degradation of chlorinated solvents (Egli et al., 1988; Tsien et al., 1989). Although many cultures mediate transformations of chlorinated solvents to less chlorinated products, some studies have demonstrated further degradation to non-chlorinated products (Freedman and Gossett, 1989; Nelson et al., 1986). Perhaps a consortium of microorganisms may be able to effectively degrade these chlorinated solvents to non-chlorinated products which are eventually mineralized to carbon dioxide and water.

Tributylphosphate is a solvent used for fuel reprocessing at nuclear facilities worldwide. Although the chemical, irradiation and thermal degradation of TBP has been extensively examined, little work has been done regarding the microbial degradation of this solvent. TBP is degraded by river water (Kawai et al., 1986, Saeger et al., 1979), the bacterium, *Pseudomonas diminuta* (Kawai et al., 1986) and municipal sewage sludge (Demirjian et al., 1984).

V. CONCLUSION

Bioprocessing is already being used in the commercial sector for waste treatment in the food, pharmaceutical, chemical and mining industries as well as for environmental remediation. The appropriate microorganisms are available, the mechanisms of the transformations are known and there are successful bioreactors in operation. In addition, there is the necessary knowledge and expertise available to aid in the development of bioprocesses for the treatment of low-level and mixed hazardous radioactive waste. With particular attention to the fate of radioisotopes, the development of appropriate bioprocesses for volume reduction and/or reclassification of wastes should be readily achievable.

A developed bioprocess, as all treatment technologies, will have to be assessed on its reliability, cost effectiveness, the permanency of the treatment, the acceptance by the local community and the ability to satisfy local, state and federal regulations.

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VII. LITERATURE CITED

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