

Mini Review

Advances in the Effects of Added Chemicals or Biosurfactants on Bioremediation

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Introduction

Biosurfactants are amphiphilic molecules that have both hydrophilic and hydrophobic moieties which partition preferentially at the interfaces such as liquid/liquid, gas/liquid or solid/liquid interfaces. Such characteristics enable emulsifying, foaming, detergency and dispersing properties. Their low toxicity and environmental friendly nature and the wide range of potential industrial applications in bioremediation, health care, oil and food processing industries makes them a highly sought after group of chemical compounds. Interest in them has also been encouraged because of the potential advantages they offer in many fields spanning environmental, food, biomedical, petrochemical and other industrial applications. In this paper, we review the current knowledge and latest advances in the effects of added chemical- or biosurfactants on bioremediation.

Effects of Added Chemical or Biosurfactants on Bioremediation

Bioremediation typically involves the augmentation of soil or other media, contaminated with pollutants, nutrients and sometimes microorganisms, to improve contaminant biodegradation processes. The biodegradation rate of a contaminant in soil depends on its bioavailability to the metabolizing organisms which is influenced by factors such as desorption, diffusion and dissolution. Many of the most persistent contaminants exhibit low water solubility and hence, contaminants bioavailability can often be improved by the addition of emulsifiers. By reducing surface and interfacial tension between liquids, solids and gases, allowing them to disperse readily as emulsions, chemical or biological surfactants may have variable effects on contaminant biodegradation [1]. Bacteria that overproduce biosurfactants may have an important role in the biodegradation process. Although substrate-surfactant interactions such as emulsification, pseudo solubilisation and hydrocarbon partitioning between phases are expected to increase microbial accessibility to the contaminant, both improvements and reductions in bioremediation performance have been observed [1]. The use of surfactants enhances bioremediation processes relate to overcome bioavailability problems,

due to contaminant aqueous insolubility and or contaminant inaccessibility due to soil adsorption. Researchers for the most part have investigated effects of surfactants on bioremediation from an efficacy rather than a mechanistic standpoint such that the precise action of the surfactant has seldom been established [1]. It is acknowledged that precise mechanisms are not easily elucidated in bioremediation systems because multiple variables are typically in play.

Micellization

With hydrophobic molecular species such as PAHs or PCBs as predominant contaminants, surfactant degradation promotion is rarely achieved. At a surfactant concentration significantly below the cmc value no enhancement or inhibitory effect on biodegradation is observed whereas at or above the cmc value biodegradation is inhibited, suggesting that the substrate, contained within the micelles, is not bioavailable. Witconol SN70 (a nonionic alcohol ethoxylate), at a concentration below its cmc, did not affect the mineralisation rates of hexadecane or phenanthrene [2], whereas above the cmc, it inhibited mineralisation of both hydrocarbons. Surfactant concentrations, greater than or equal to the cmc for all 4 surfactants tested, inhibited phenanthrene mineralization by *Pseudomonas aeruginosa* in soil-water cultures and lower surfactant concentrations had no effect [3]. Biodegradation of 4 PCB congeners 2,4,2',4'-Chlorobiphenyl (CBP), 2,3,5,2'-CBP and 2,4,5,2',4',5'-CBP in aqueous media by *Pseudomonas LB-400* was inhibited by Igepal CO-630, a non-ionic surfactant, at concentrations above its cmc [4,5]. The inhibitory effects were eliminated by diluting the surfactant/PCB solution to a concentration close to the surfactant cmc. In contrast, at concentrations above the cmc, the presence of an anionic surfactant promoted PCB transformation, compared to a control with no surfactant [4]. The surfactant effects on PCB biodegradation have been studied by other research groups too [6-8]. In some cases an increase in degradation rate was observed, whereas in other cases a decrease in these rates was noted after the addition of surfactants. There appear to be other cases where micellization does not affect degradation. Many authors [9] quantified the bioavailability of micelle-solubilized naphthalene to a naphthalene-degrading mixed microbial population isolated from contaminated waste and soils using two nonionic surfactants, an alkylethoxylate, Brij 30 and the alkylphenol ethoxylate, Triton X-100. Surfactant concentrations above the cmc were not toxic to the naphthalene-degrading bacteria and the presence of surfactant micelles did not inhibit naphthalene mineralization. Naphthalene, solubilized by the micelles in liquid media, was bioavailable and degraded by the mixed bacterial culture. Rhamnolipids added above Critical Micellar Concentration (cmc) enhanced the apparent aqueous solubility of hexadecane, the biodegradation of hexadecane, octadecane, n-paraffins, creosotes and other hydrocarbon mixtures in soil, and promoted the bioremediation of petroleum sludges [10-13]. Above the cmc, the micelles formation occurs, and hydrocarbons can

partition into the hydrophobic micellar core, increasing their apparent aqueous solubility. Chlorinated hydrocarbons biodegradation can be enhanced by the addition of glycolipids to the medium as has been reported even for polychlorinated biphenyls [14]. Pesticide biodegradation was also reported to be promoted by surfactin [15].

Contaminant desorption from soil

Very hydrophobic contaminants tend to bind very tightly to soil particles in a manner which renders them inaccessible to the microbe degradation. Chemical and biosurfactants can be effective in facilitating of the contaminant desorption from soil as a possible integral part of a bioremediation process or in an aqueous soil washing process, where a biological or non-biological process is subsequently applied to remove the contaminants from the recovered aqueous washings. Traditionally, chemical surfactants are used in soil washing. Surfactants can be used in mixture or with additives such as an alcohol and/or salts such as sodium chloride [16]. They have also been found useful in displacing Dense Non-Aqueous Phase Liquids (DNAPL) by reducing interfacial tension between DNAPL and the groundwater [17]. Typical surfactant concentrations for contaminant soil washing are 1–2%, whereas the same contaminants may be solubilized in an aqueous solution at a surfactant concentration of 0.1–0.2%. Nonionic surfactants can remove over 80% of total hydrocarbons from the contaminated soil. They washed more of the PCBs from contaminated soil (up to 89%) as compared to anionic surfactants, but the latter proved to be more effective in the subsequent biodegradation tests of the PCBs in the washings, mediated by *Pseudomonas* sp. LB-400 [18]. PCBs have lower affinity for the interior of anionic rather than non-ionic micelles with a similar non-polar chain length [19], and this may have promoted the release of the PCBs from the micelles, bringing them in contact with the degrading bacteria. Biosurfactants have also been found useful for remediating oil spills, dispersing oil slicks into fine droplets and converting mousse oil into oil-in-water emulsion [20,21]. Authors [22], examined the use of biosurfactants in cleaning oil from coastal sand. Rhamnolipid biosurfactants have also been evaluated in soil washing applications. Rhamnolipids were effective in removing PAHs [23,24] and pentachlorophenol [25] from soil. Removal efficiency varies with contact time and biosurfactant concentration, but is typically about 60–80% as has been reported by different researchers [26,27]. Biosurfactants appeared to be more effective in increasing the apparent solubility of PAHs by up to five times as compared to the chemical surfactants [28,29]. Sophorolipids released bitumen from tar sands [30] and surfactin was used to wash oil from a sand column [31]. Biosurfactants can enhance the removal of n-alkanes and Polycyclic Aromatic Hydrocarbons (PAHs) from contaminated soils. Improved biodegradation of various PAHs in contaminated soil by the addition of rhamnolipids has been reported by different research groups [32–35]. Rhamnolipids removed heavy metals such as Ni and Cd from soils due to their anionic nature, with efficiencies of 80–100% in the lab and 20–80% in the field samples as has been reported [36,37]. Surfactin glutamate residues can bind metals such as Mg, Mn, Ca, Ba, Li and rubidium [38]. Soil washing with 0.25% surfactin removed 70% of Cu and 22% of Zn [39]. Foaming surfactant technology is a relatively new approach in surfactant-assisted soil remediation. Polymers or foams can also be added to control the mobility of the contaminants. Metal-biosurfactant complexes can be removed by addition of air to cause foaming. By

use of a technique called micellar-enhanced ultra-filtration, 85–100% removal of cadmium, copper and zinc by surfactin from contaminated water was achieved. The role of assisted natural remediation using surfactants in metal-contaminated environments and subsurface has also been explored.

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