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## Review

### Biosurfactant-enhanced hydrocarbon bioremediation: An overview



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#### ABSTRACT

The water and soil contamination by aromatic hydrocarbons has been increasing over the years, due to its use in several industrial segments. Hydrocarbons are described as extremely pollutant, toxic, with carcinogenic and mutagenic potential for humans. The concern with these compounds increases due to the difficulties in removing them from the environment. The remediation methods for contaminated environments are based on chemical, physical or biological activity. With the advance of sustainable technologies, the search for natural methods for the removal and/or degradation of soil and water contaminants has increased. Biosurfactants are surfactants produced mainly by microorganisms that promote the cracking of hydrocarbons molecules by micelle formation, increasing their mobility, bioavailability and exposure to bacteria, thus favoring hydrocarbon biodegradation. There is a great diversity of microorganisms that are capable of biodegrading pollutants such as oil and producing biosurfactants, but they are not well known. This study aims to address the issues related to a series of parameters involved in the production and in the mobilization and action mechanism of biosurfactant monomers in sites containing hydrocarbons.

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### 1. Hydrocarbon contamination

Concerns related to the potential for soil and water contamination by oil and its byproducts are increasing, as they are one of the main contaminants in the environment. The contamination sources are diverse: accidents in fuel transportation by ships and trucks; leakages from underground storage tanks, which are subject to corrosion, as in gas stations; oil extraction and processing operations; and inadequate release of oily waste generated by industries that use oil byproducts in the production of plastics,

solvents, pharmaceuticals and cosmetics (EPA – Environmental Protection Agency of United States, 2008; Lin et al., 2010).

Although petrochemical plants and oil refineries are beneficial to society, they produce a great quantity of solid oily waste (about 10,000 m<sup>3</sup> per day) classified as hazardous waste, which cannot be reused or recycled, as they are flammable, corrosive, toxic or pathogenic (Gafarov et al., 2006).

In refineries, oil is converted into autogas and diesel fuel. The gasoline consists of relatively volatile hydrophobic hydrocarbons such as alkanes, cycloalkanes, BTEX (benzene, toluene, ethylbenzene, and xylene), phenol and polycyclic aromatic hydrocarbons. Many of these compounds are described as highly pollutant, as they present a carcinogenic and mutagenic potential for humans,

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in addition to being toxic (Janbandhu and Fulekar, 2011). BTEX hydrocarbons have become a major concern in water pollution due to their toxicity and easy movement in the environment (Mazzeo et al., 2011).

According to the Environmental Sanitation Technology Company (CETESB, 1996) – the environmental control agency of the State of São Paulo, Brazil – leakages in gas stations accounted for 78% of the cases of contaminated areas in the State of São Paulo in 2011, which corresponds to 3217 areas.

About 90% of the gasoline hydrocarbons spilled into the environment, found in drinking water sources, are composed of BTEX, which raises concerns on environmental health because of their toxic, mutagenic and carcinogenic properties (Janbandhu and Fulekar, 2011).

When there are leakages in fuel tanks, hydrocarbons are dispersed and penetrate the soil. According to Bachu (2008), the migration of these compounds is regulated by the formation of four distinct phases, known as: Residual liquid phase – liquid waste are relatively immobile, adsorbed or retained in soil solids; Free liquid phase – without the presence of waste, they easily migrate through the soil and may reach groundwater; Dissolved phase – in this phase, the hydrocarbons form a layer on solid surface or soil water, and form a contamination plume when they reach groundwater; and Vapor phase – they join the soil vapor and may condense and adsorb on solid surface or dissolve in soil water.

The high soil–water mobility of these hydrocarbons is related to their low octanol–water partition coefficient, which ensures a slow absorption by the soil and allows its transportation by water, quickly moving through the soil, thus favoring water table contamination (Farhadian et al., 2008).

### 1.1. Risks posed by hydrocarbons

Soil and groundwater contamination by hydrocarbons present in fuels has become a focus of great concern both in industrialized and developing countries, due to its broad environmental distribution, which can reach soil, groundwater and air (Lebrero et al., 2012). BTEX hydrocarbons, present in the composition of gasoline and diesel fuel, are the first to reach the water table, as their constituents are highly soluble in water (Mariano et al., 2007). Consequently, these highly toxic compounds (except ethylbenzene) are the main causes of death by toxicity (Janbandhu and Fulekar, 2011).

Fellenberg (1980) reported that, when in contact with water, oil and its byproducts spread and form a thin layer on the surface that prevents gas exchange between air and water and blocks sunlight to phytoplankton, breaking the food chain. Confirming this theory, Asimiea and Sam-Wobo (2011) observed the impact of hydrocarbon waste on phytoplankton communities, which suffered structural changes due to the presence of these compounds.

One liter of oil can deplete the oxygen in one million liters of water and form a thin layer of 1000 m<sup>2</sup> on the soil surface in a few days, blocking the passage of sunlight and water and thus preventing the respiration and photosynthesis of the plants present therein (Yeung et al., 2011). Plants are prevented from performing respiration and photosynthesis due to a sealing the entrance of the stomata and plant roots are inhibited from absorbing soil nutrients (Fellenberg, 1980).

The marine environment has suffered with constant oil spills, making oil one of the most abundant organic contaminants in the sea. The media has been constantly denouncing the leakage of thousands of tons of oil that contaminate seawater (OESP, 2000–2013).

Half of world's oil production (around three billion tones/year) is transported by ships through the oceans, increasing hydrocarbon contamination levels in various marine ecosystems due to possible accidents. However, the major hydrocarbon source in the marine

environment comes from routine operations of ship washing, natural oil leakages on sea bed and especially accidents in oil exploration and transportation (Marques Jr. et al., 2009).

One of the most impacting spills occurred recently, in November 2011, in the Sedco 706 oil platform, operated by Chevron Brasil in Campos Bay (Rio de Janeiro, Brazil). The oil leakage was equivalent to 5943 L and reached about 163 km<sup>2</sup> (ANP, 2011).

The potential threat to human health posed by hydrocarbons is connected to their physical and chemical properties, which allow these compounds to be absorbed by the skin and quickly spread through the organism if ingested or inhaled (Costa et al., 2012).

Exposure to BTEX hydrocarbons for a long period of time at low concentrations presents a series of chronic effects. Among them, benzene is regarded as the most toxic, and may cause depression of pluripotent primitive blood cells, extending through any cell maturation stage; damage to bone marrow, such as necrosis, edema, hemorrhage and fibrosis, which also interfere with blood cell production; leukemia and liver cancer. The estimated value of the minimum lethal dose (LDL) for humans is 194 mg kg<sup>-1</sup> (Melo et al., 2007).

In 2000, Machado described the embryotoxicity of hydrocarbons and reported that women who had been exposed to high benzene levels in their professions had menstrual abnormalities, decrease in ovary size and potential fertility reduction.

Toluene presents moderate systemic toxicity to humans. If ingested, toluene is completely absorbed by the gastrointestinal system and is rapidly distributed to the body, mainly on adipose tissues, metabolized and excreted in the urine. When inhaled, this hydrocarbon compromises the central nervous system and may cause excitement or depression, with euphoria in induction stage, and later disorientation, tremors, fatigue, hallucinations, convulsions and coma. It may cause electrolyte abnormalities, metabolic acidosis, arrhythmias, muscle weakness; and causes mucosa irritation, transitional anomalies on liver enzyme activities and kidney problems. Moreover, embryotoxic and fetotoxic effects have been observed, though there are no clear evidences of teratogenic or carcinogenic activity in humans or laboratory animals (World Health Organization, 2006; Asimiea and Sam-Wobo, 2011).

Ethylbenzene and xylene, which have low systemic toxicity, are usually stored on adipose tissues and are almost completely metabolized and excreted in the urine. Both are central nervous system depressants; the first being a sensorineural irritant, and the latter, a skin and mucosa irritant. Studies carried out with both hydrocarbons have shown negative evidences for teratogenicity, carcinogenicity, metagenesis or genotoxicity (World Health Organization, 2006).

According to the EPA (2012), the specific chemical concentration to reach the risk level of a contaminant is called Risk-based concentration (RBC). According to the agency, in groundwater, benzene RBC is  $2 \times 10^{-4}$  (mg kg<sup>-1</sup>), toluene RBC is  $5.9 \times 10^{-1}$  (mg kg<sup>-1</sup>), ethylbenzene RBC is  $1.5 \times 10^{-3}$  (mg kg<sup>-1</sup>), and xylene RBC is  $1.9 \times 10^{-1}$  (mg kg<sup>-1</sup>). In 2001, the organization determined that the maximum BTEX component level in drinking water is 0.005 mg L<sup>-1</sup> benzene, 1.0 mg L<sup>-1</sup> toluene, 0.7 mg L<sup>-1</sup> ethylbenzene and 10 mg L<sup>-1</sup> xylene.

In 2006, the World Health Organization (WHO) determined that the maximum BTEX compound concentrations allowed in drinking water were: 0.01 mg L<sup>-1</sup> benzene, 0.7 mg L<sup>-1</sup> toluene, 0.3 mg L<sup>-1</sup> ethylbenzene and 0.5 mg L<sup>-1</sup> xylene. In Brazil, the maximum concentration of these hydrocarbons, established by the Brazilian National Environment Council for effluents discharge in water is 1.2 mg L<sup>-1</sup> benzene and toluene, 0.84 mg L<sup>-1</sup> ethylbenzene and 1.6 mg L<sup>-1</sup> xylene (CONAMA, 2011).

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