

Photooxidation vs Biodegradation: A Short Review on Fate of Heavy Hydrocarbons after Oil Spill in Sea Water

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ABSTRACT

In August 2019, the Brazilian coast, especially the north-eastern coast, was contaminated by a dense mass of extra-heavy oil, causing environmental and social disturbances of different orders, with deleterious effects that will have impacts for many decades to come. After exposure in the marine environment by recalcitrant hydrocarbons, the fate of these compounds will depend on certain abiotic factors that may increase the bioavailability of these molecules, favoring the biological transformations of the removal of the contaminant, carried out by competent hydrocarbonoclastic microbes. This work presents a brief history of the greatest accidents at sea involving crude oil spills. Further, we defend a fundamental convergence of photo-oxidation and the metabolism of *Pseudomonas aeruginosa*, as natural mechanisms for removing heavy oil.

Keywords – Abiotic loss, Biodegradation, Crude oil spill, *Pseudomonas aeruginosa*

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I. INTRODUCTION

Petroleum remains a main natural energy resource. It is expected that in twenty years, heavy oil will still represent 8% of the total supply of liquid hydrocarbons [1]. Environmental pollution is one of the greatest concerns in modern society [2], demanding criteria for and planning strategies along the entire oil production chain. Actions are imperative to prevent oil spill or mitigate the impact when accidents may occur [3].

Because of their visual and journalistic appeal as well as ecological impact, shipping accidents are widely reported [4]. In addition, sea currents contribute to the spread of oil over large areas, potentially reaching beaches [5], mangroves [6], sandbars and the ocean floor [7]. As a consequence, the food chain is drastically disrupted and the natural recovery process may last for decades [8].

Microbes and plants are the major organisms involved with hydrocarbon removal in nature [9]. On the other hand, given the complexity and magnitude of an accidental oil spill, the degree of microbial inhibition caused by the oil may compromise hydrocarbonoclastic activity [10]. Thus, the abiotic factors act as ways of transforming a contaminant into molecules with better bioavailability [11].

However, heavy oil requires special attention due to its high viscosity and the presence of recalcitrant compounds, particularly aromatic and polycyclic aromatic compounds [12-13].

This short review aims to present how the interaction between photo-oxidation and biodegradation can contribute to the removal of heavy oil after an accident in the marine environment. It also emphasizes the importance of *Pseudomonas aeruginosa* in this process.

II. HEAVY OIL

Petroleum is a dark and apparently homogeneous substance of natural origin composed of a predominantly mixture of hydrocarbons and organic derivatives containing sulphur, nitrogen, oxygen and other elements [14]. Three classes of hydrocarbons occur in crude oil: (i) paraffins, straight or branched chain hydrocarbons; (ii) naphthenic, saturated hydrocarbons containing one or more cyclic chains; (iii) aromatic and polycyclic aromatic hydrocarbons (PAHs), the most complex molecules, composed of benzene rings, or paraffins and naphthenics linked or condensed in the aromatic structure [15].

The hydrocarbon content may vary between 70% and 97%, respectively in light oil and heavy oil, contributing to the different properties exhibited by crude oil [16]. In addition, the hydrocarbon content

is used in the chemical classification of oil and its fractions [17].

Heavy oil is characterized by a high °API, among other properties, indicative of a dense oil, with high viscosity, low H/C ratio and high contents of asphaltenes, resins, aromatic compounds, condensates, heterocyclics, polycyclics, heavy metals and sulphur. In addition, heavy oils can contain up to 30% of PAHs in their composition [18].

PAHs are ubiquitous, highly hydrophobic and chemically stable molecules, composed of aromatic and/or pentacyclic rings, condensed and arranged in linear, angular or in groups, formed by the incomplete combustion of organic matter. PAHs represent risk, having mutagenic and carcinogenic properties [19]. Certain properties of PAHs, such as recalcitrance [20], high adsorption coefficient [21], low water solubility [22] and inhibition of microbial activity [23], ensure efficient sorption of sediments and organic matter.

PAHs are the most prevalent contaminants among all organic molecules [24] and despite their recalcitrance, they are susceptible to transformations through various abiotic routes, which include photo-oxidation, auto-oxidation, photolysis and volatilization [25]. Biological removal, however is the main mechanism for transforming these hydrocarbons, requiring abundant and competent hydrocarbonoclastic microbiota [26].

III. ICONIC ACCIDENTS INVOLVING CRUDE OIL AT SEA

Contamination caused by oil and its derivatives may occur in different degrees along all of the production chain of petroleum exploration [27], involving accidental spills and contributing to a significant contamination of soil [28] and water [29]. The release of oil from natural sources is approximately 0.5 million tons annually, but the greatest source of oil pollution originates from human activity [30].

Several accidents involving oil spills occur annually. In the past 50 years, millions of tons of oil have been released in almost 2000 reported accidents and incidents. Most of the sources of the spill were ships and only a small portion of these accidents reported damage to wildlife [31]. In most of oil spills, however, legal action against those responsible were not effective, indicating that the regulatory acts concerning the transportation of oil and petroderivatives are still insufficient [32].

Some of these accidents were of significant proportions or suffered intense media attention, making them iconic, as follows: The first oil spill accident with international repercussions occurred

on March 18, 1967, involving the SS Torrey Canyon in the English Channel. The ship ran aground on the Seven Rocks reef due to a navigation error and caused the leakage of 120,000 ton of crude oil. The environmental impact was inevitable and both the northern coast of France and the coast of Cornwall were strongly affected. The death of seabirds reached hundreds of thousands. The case was exhaustively covered by the press at the time [33]. As a consequence, several international agreements were signed and in 1969 the International Oil Pollution Compensation Funds (IOPC) was created [34].

On March 24, 1989, the Exxon-Valdez spilled more than 35,000 tons of oil and caused the most emblematic environmental accident involving a historic oil spill. The accident occurred in Prince William Sound, Gulf of Alaska. Approximately 40% of the spilled oil reached 783 km of coastline, covering 26,000 km² of the water surface and the consequences of that disaster persist to this day [35-36]. Although the accident occurred in a region with mostly cold temperatures, monitoring over the decades, of the area affected by the oil, has become a landmark for the evolution of studies in bioremediation, contributing significantly to the knowledge and applications currently used [37-38]. In 2012, the ship involved in the accident was purchased by an Indian company and after several controversial lawsuits was finally turned into scrap metal a few years later [39].

The next accident occurred during a military conflict in 1991, with live coverage on television, during the Gulf War (1990-1991). The oil spill is believed to be the largest in history, in times of war or peace [40]. More than 800 oil wells were bombed and it is estimated that between 1 and 1.7 million ton of crude oil were leaked into the Persian Gulf, causing severe damage to the marine and terrestrial ecosystems, especially along the Kuwaiti and Iraqi coasts [41].

On November 13, 2002, the oil tanker Prestige sank off the coast of Galicia, Spain after a storm and more than 20 million gallons of oil were spilled, affecting more than 1000 Spanish and French beaches, also compromising the bird population [42]. The case was treated as a criminal by Spanish authorities and currently the region is still being monitored [43].

On April 20, 2010, a huge explosion destroyed the Deepwater Horizon oil rig in the Gulf of Mexico and for 83 days a volume of about 4 million barrels of crude oil spilled directly into the water, impacting aquatic and terrestrial life. To minimize the hazards, different strategies were applied, and millions of gallons of dispersing agents

were used. In the following years, many efforts have been made to recover the affected area, including photoremediation [44-45].

The biggest environmental tragedy related to oil spills in Brazil started on August 30, 2019. The first dense patches of crude oil appeared on the north-eastern coast and, by November had reached 643 areas in 116 municipalities in the region [46]. There was no immediate intervention on the part of the Brazilian government; despair of the people affected motivated and impelled the first actions. These actions were carried out in an incorrect and dramatic way, whose consequences will only come to light in the medium to long term [47]. The accident had a direct impact on more than 870,000 people, dependent on artisanal fishing and tourism, among other activities. The origin and responsibility for the oil spill are still unknown, but its nature was characteristic of an extra-heavy oil [48]. In the beginning of January and up to May 2020, small new spots resurfaced on the beaches of the Northeast and Southeast regions of Brazil.

IV. PHOTOOXIDATION AS THE MAIN ABIOTIC FACTOR IN THE ELIMINATION OF HEAVY OIL

After an oil spill in the sea, the functioning of the aquatic ecosystem is affected by different variables. These variables determine the fate of the natural removal of hydrocarbons through routes governed by biotic and abiotic factors [49]. It has been known for some decades that photo-oxidation plays a major role in the fate of PAHs in the photic zone of the seawater [50]. In addition, biotic and abiotic factors may interact, positively enhancing the rate of hydrocarbon removal [51].

The biotic factors concern the availability of nutrients and the ability of the indigenous microbiota to tolerate and initially uptake the lower carbon chain compounds [52]. This initiates a process involving successions of the dominant microbiota, conditioned to the bioaccess and bioavailability of carbon and energy sources [53-55], as well as on the hydrocarbon type [56]. The abiotic factors are related to the physicochemical transformations of hydrocarbons, as well as temperature, humidity, pH variations and physicochemical properties of contaminants [57].

Hydrocarbons are degraded by different abiotic routes [58]. Light oil and simple, straight or branched chain hydrocarbons tend to be eliminated more quickly, especially by volatilization and chemical reactions in the presence of light [59]. On the other hand, the elimination of heavy oil is more prolonged because it is temporarily limited [60]. This occurs due to the sorption of these molecules to

the different substrates [61], as well as sedimentation in the beds [62], reefs [63] coastal and mangrove areas [64]. Despite this, heavy oil is also susceptible to the abiotic degradation routes, in which light oils are transformed.

The main abiotic routes for hydrocarbon transformation in water are volatilization [65], autooxidation [66], dispersion [67], formation of stable oil/water emulsions [68], dissolution [69] and sorption/sedimentation [70]. Photooxidation, however is the most important transformation route. Photooxidation is the most important weathering processes and contributes to the physicochemical degradation of oil hydrocarbons. Intense solar radiation on the surface of spilled oil allows the formation of high polarity compounds, such as aliphatic and aromatic ketones, aldehydes, carboxylic acids, fatty acids, esters, epoxides, sulfoxides, sulfones, phenols, anhydrides, quinones, aliphatic hydrocarbons and aromatic alcohols [71].

Aromatic hydrocarbons are more susceptible to photooxidation, compared to branched hydrocarbons, which are more resistant compounds. Photooxidation transforms aromatic hydrocarbons through two mechanisms [72]. The first occurs directly on the degradation of aromatic hydrocarbons with high molecular weight, including PAHs because these molecules absorb wavelengths in a range between 300 and 500 nm, comprising ultraviolet radiation and visible light [71].

The process of eliminating these compounds can occur within up to 36 days of exposure to sunlight [73]. In addition, the degradation of high molecular weight hydrocarbons is favored because the singlet oxygen photodegradation pathways are facilitated in aqueous media [74]. Additionally, in seawater, photosensitizing molecules participate in the production of reactive oxygen species that attack some aromatic compounds and PAHs. Thus, the more intense the solar radiation, the higher the rate of hydrocarbon photooxidation [75].

The second mechanism of hydrocarbon photo-oxidation occurs indirectly, via the formation of photochemical metabolites of aromatic compounds and PAHs, especially ketone metabolites. They may act as photosensitizers and participate in the transformation of other hydrocarbons, including high molecular weight n-alkanes resistant to ultraviolet radiation [73].

Photolytic transformations are enhanced in natural waters and this also contributes to an increase in the bioavailability of petroleum hydrocarbons in the environment [76-77]. When there is a limitation in the levels of nutrients, photooxidation is the most important process to

transform organic matter. In parallel, in marine photic zones, the combination of photooxidation, dissolution, and biodegradation allow the depletion of hydrocarbons at rates faster than just biodegradation under aphotic conditions [78]. Given this, microbial growth in the marine environment is minimal when non-irradiated hydrocarbons are used as the sole carbon and energy sources. On the contrary, the concentration of dissolved organic carbon increases linearly during sunlight irradiation, especially the ultraviolet-absorptive hydrocarbons [79].

V. ASSIMILATION AND DEGRADATION OF HEAVY OIL BY HYDROCARBONOLASTIC BACTERIA

At the beginning of the 20th century, some microbes were discovered to use hydrocarbons as sources of carbon and energy. The term hydrocarbonoclastic was coined to designate these microbes. In the 1940s, studies deepened on the theme after publication of a classic study by Bushnell and Haas [80] when they proved that more complex hydrocarbons can be mineralized.

Hydrocarbonoclastic microbes are widely distributed in the environment due to their diazotrophic nature [81]. The microbial cell alterations caused by hydrocarbon exposure promote drastic changes in the indigenous biota [82], especially because the C:N:P ratio is unbalanced [22]. In contrast, after exposure to crude oil, the population of hydrocarbonoclastic microbes becomes more prevalent [83].

Microbial metabolism is the key role to the recovery of a specific oil-contaminated site [84-85]. Bacteria exhibit different mechanisms to uptake hydrocarbons, among them, the expression of oxidoreductases [86], synthesis of surfactants [87], biofilm formation [88] and production of compatible solutes [89]. In addition, the presence of macro and micronutrients is crucial. Simple molecules with higher bioavailability may enhance the removal of recalcitrant hydrocarbons, acting as cosubstrates [90].

In fresh water, hydrocarbon biodegradation processes are more favored, compared to the marine environment. The salinity of sea water promotes salting out, i.e., a reduction of hydrocarbon solubility and bioavailability caused by increased hydrophobicity of hydrocarbons due to interactions of these molecules with cations [91]. Thus, photooxidation plays a crucial role in the marine environment, as it promotes the formation of assimilable photoproducts that contribute to the

acceleration of the rate of elimination of the contaminant [92].

Several hydrocarbonoclastic microorganisms are capable of removing oil in seawater and on soil and beaches contaminated by hydrocarbons [93-95]. Due to its metabolic versatility, *Pseudomonas aeruginosa* is acknowledged as a representative hydrocarbonoclastic microbe [96]. The bacterium exhibits resistance and tolerance to toxic molecules in environments with different degrees of selective pressure [97]. In addition, *P. aeruginosa* uses more than 90 molecules as carbon and energy sources [98], including paraffins [99], naphthenics [100], (2015), aromatics [101] and PAHs [102]. The hydrocarbon mineralization process is divided into two distinct stages. The first is more accelerated and mediated by the bioavailability of the contaminant. The second stage is slower and controlled by the hydrocarbon sorption/desorption ratio [103]. It may be enhanced when other abiotic factors are interacting [104].

The degradation of different recalcitrant hydrocarbons by *P. aeruginosa* is complex. The bacterium may have preferential choices for the carbon sources [105] especially those with high molecular weight hydrocarbons [106]. Given this, the role of photooxidation and other abiotic factors in the transformation of these molecules is extremely important because this process enhances bioavailability. In parallel, *P. aeruginosa* can assimilate hydrophobic compounds because it is capable of producing rhamnolipids, i.e., molecules with tensoactive properties that enable bioaccessing [107], as well as increase bacterial respiratory activity [108]. Therefore, the reduction in the surface tension of heavy oil becomes proportional to the increase in the kinetic parameters of hydrocarbon degradation [109] and the products of this degradation comprise intermediates of different pseudomonad metabolic routes for the production biomass and attainment of energy [110].

VI. CONCLUSION

The interaction of biotic and abiotic factors is crucial for the fate of hydrocarbons introduced into the marine environment. Photic transformations in particular are responsible for the formation of products with higher bioavailability and thus, able to be assimilated and mineralized by competent microbes, especially *Pseudomonas aeruginosa*, one of the most versatile and ubiquitous hydrocarbonoclastic microorganisms.

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