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MM Apetroaei[1], MR Apetroaei[2]

[1] Student, University of Medicine and Pharmacy "Carol Davila" Bucharest, Faculty of Pharmacy, Romania
[2] PhD. Eng., "Mircea cel Bătrân" Naval Academy, Constanta, Department of Naval and Port Engineering and Management, Romania.
Corresponding MR Apetroaei:manuela.apetroaei@anmb.ro

Abstract. Oil pollution is now the type of pollution that has the greatest impact on marine ecosystems. Spilled oil spreads over wide expanses of water due to its chemical nature, damaging both water quality and marine life. Because of their solubility and bioaccumulation in water, hydrocarbons in crude oil, particularly those of the volatile organic compounds, cycloalkanes, and aromatic hydrocarbon types, cause toxicity in the marine environment. All of these cause water acidification, reduce algal and phytoplankton photosynthesis, and have mutagenic, carcinogenic, or teratogenic effects on biocenosis. As a result, in order to mitigate these harmful effects on the marine environment, it is being attempted to discover low-cost eco-friendly procedures and materials to replace the traditional chemical decontamination treatments. The purpose of this work is to assess and demonstrate the significance of developing and employing alternative and novel green chemistry research technologies capable of decreasing or eliminating hazardous chemicals utilized in various decontamination operations. Due to the high absorption affinity of PAHs, there is currently a growing interest in the use of plant residues as biosorbents on various types of water (wastewater, bilge water, inadvertently polluted or operational water) and in various environmental situations.
Key words: *eco-friendly materials, natural biosorbents, plants, PAHs*

1. Introduction

Many sectors, such as science, technology, manufacturing processes, and transportation, have advanced rapidly during the last century's industrial development. As a result of these changes, the term pollution is becoming increasingly significant, as toxins in the air, water, and soil have an impact on the entire human population. The expansion of maritime transport of oil and petroleum products in international trade is a factor that can result in a high level of risk in terms of marine pollution occurrences

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds, consisting of only carbon and hydrogen atoms that are mostly colorless, white, or straw-colored solids. From a chemical perspective, these compounds are comprised of two or more aromatic rings bonded in linear, cluster, or angular arrangements [1], [2].

Natural and anthropogenic incomplete combustion are the primary sources of PAHs in the environment [3]. Petrogenic PAHs are crude oil that has been formed over millions of years at low temperatures (100–1500C), but they can also be obtained during the transportation, storage, and use of crude oil or petroleum-derived products, as well as the accumulation of trace amounts of oil, petrol, motor oils, and substances associated with maritime transport activities [4]. PAHs are accumulating in

marine aquatic habitats as a result of pyrogenic activities (volcanic eruptions, incomplete combustion of motor fuels, forest fires, etc.) as well as those associated with maritime transport operations or accidents.

The two types of pollution seen in the marine environment, operational and accidental, are widely researched in relation to the marine environment's sources of PAH pollution. Operational pollution is caused by spills that occur accidently during the following situations: oil tank loading and unloading operations; bunkering activities; and bilge water evacuation without proper purification throughout the ship's trip. Accidental pollution is caused by navigational errors, the most dangerous of which are: shipwrecks caused by hull ruptures or water holes, fires, and explosions. Accidental pollution is caused by maritime mishaps, the most significant of which include collisions, failures, shipwrecks due to hull ruptures or water holes, fires, and explosions [5].

Due to the chemical composition of oil, it spreads rapidly across enormous bodies of water, impacting both water quality and marine life. The primary physical-chemical features of PAHs are their high melting and boiling temperatures, low vapor pressure, and insolubility in water [6]. PAHs exhibit a wide range of physicochemical properties depending on their molecular weight and chemical structure.

Due to their high volatility and solubility, PAHs constituted of two or three aromatic rings (with a low molar mass) degrade much more rapidly than PAHs composed of more than four aromatic rings (with a high molar mass). Furthermore, it is well established that PAHs with a high molar mass are highly attached to soil sediments, rendering them resistant to microbial breakdown. The vapor pressure of PAH falls as the molar mass increases, while the solubility in water reduces as the molar mass increases.

Additionally, resistance to oxidation and reduction reactions increases as molar mass increases. PAHs are extremely lipophilic, and their water solubility diminishes with the number of aromatic rings in their structure, resulting in their high mobility in the environment, buildup, or evaporation [7]. PAHs have been shown in numerous studies to volatilize, photolyze, biodegrade, or bind to suspended particles or sediments in surface water. The presence of PAHs in the aquatic environment can be measured using bioindicators similar to fish, which accumulate them in adipose tissue [8] when eaten via food [9] or sorption through the skin and gills [10]. The presence of these xenobiotics in these habitats results in their bioaccumulation and implicit bioamplification throughout the aquatic food chain, resulting in aquatic toxicity.

The United States Environmental Protection Agency (USEPA) has designated approximately 16 polycyclic aromatic hydrocarbons (PAHs) as priority pollutants in the environment. Due to the high bioaccumulation, mutagenesis potential, and carcinogenic qualities of PAHs, it is critical to develop innovative methods for their removal that are as ecologically friendly as feasible, inexpensive, and have no adverse effect on the environment. Conventional chemical treatments such as chlorination, oxidation, ultrasonic irradiation, coagulation, flocculation, sedimentation, and filtration have been shown to be ineffective at removing PAHs from the environment due to their low solubility and the potential for secondary pollution at an added cost [11-14].

Nowadays, an increasing emphasis is being placed on environmentally benign and cost-effective biological approaches that utilize microbes, plants, and derivative products to remove or degrade, or reduce PAHs in the environment [15, 16].

The purpose of this paper is to analyze and demonstrate the importance of developing and implementing alternative and innovative green chemistry research technologies capable of reducing or eliminating hazardous chemicals such as polycyclic aromatic hydrocarbons used in various decontamination operations.

2. Biosorptions and biosorbents

Various types of oil spill cleanup are currently being used, including in situ burning, dispersants (chemical treatments), marine bacteria, and sorbent materials (biological treatments) (Fig. 1).

Sorption is a cost-effective method for eliminating PAHs from the environment at low concentrations [17]. The use of microorganisms, plants, and related products for the removal or degradation of PAHs present in an aquatic environment was validated as a cost-effective and environmentally beneficial method of treating these environmental contaminants.

Phytoremediation is a rapidly developing biotechnology that utilizes plants, associated microorganisms, and agricultural techniques to regenerate an environment that has been contaminated by inorganic and organic pollutants, which it removes from the environment and does not transfer to other locations, as other traditional methods do.
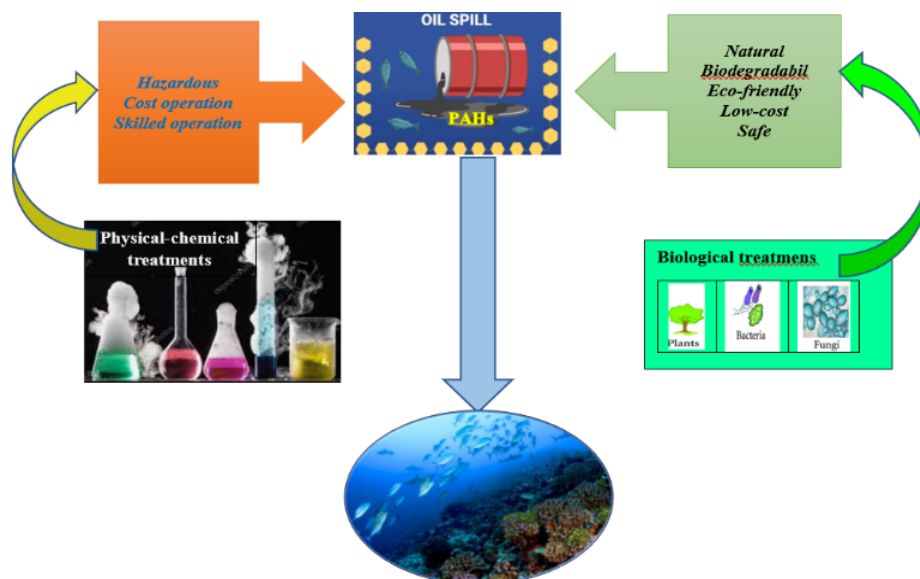

Fig. 1 Physicochemical compared to biological treatments procedures for PAHs removal [adapted from 16]

The efficiency of removing pollutants from the aquatic environment is conditioned by the physical-chemical characteristics (temperature, pH, salinity), aquatic species, planting patterns, and the nature and chemical structure of pollutants [18].

2.1. Side effects of using bioabsorbents based plants

When using plants as bioabsorbable materials in an aquatic environment, it is necessary to consider how the nutrient levels in the water must be impacted.

Nitrogen and phosphorus-containing nutrients are called "pollutants" when they reach dangerous levels in aqueous environments and promote the growth of toxin-producing cyanobacteria and algal biomass, resulting in a shortage of oxygen and eutrophication [18].

Nutrients are critical for plant development and reproduction, as they are absorbed by plants via their root systems. However, the presence of these nutrients in the aquatic environment must be closely controlled, since an excess of them results in eutrophication, a potentially dangerous process for aquatic ecosystems. Additionally, phytoremediation technology can be used to lessen the level of eutrophication in water by planting macrophytes in the aquatic environment [19].

Phytoremediation is one of the most successful and viable procedures for removing organic pollutants from the environment, such as PAHs. Numerous studies have been conducted on the phytoremediation of oil-contaminated soils using various plants [20], particularly those belonging to the genera *Poaceae* and *Fabaceae*. Additionally, the Medicago genus (*Fabaceae* family) is one of the most frequently employed species in phytoremediation research [21].

Due to the high absorption capacity of plant residues, which can be enhanced depending on the chemical composition of the plant [22; 23], the development of plant residues as biosorbents is a

novel, ecological technique. Plant residues are one of the most numerous, economical, and renewable sources of biosorbents. These are obtained from agriculture and constitute a sizable portion of bio-solid waste [24]. Numerous absorbents, including inorganic salts, synthetic polymers, biopolymers (chitin), and plant residues, are utilized to remove PAHs from the marine environment with low influence on the ecosystem [25, 26, 27]. Plants are natural, biodegradable, eco-friendly, have a density comparable to manmade polymers, and are less expensive [28].

Boving and Zhang (2004) demonstrated that aspen wood was an effective sorbent for PAH removal in their study [29]. Another study demonstrated phenanthrene's (a polycyclic aromatic hydrocarbon constituted of three fused aromatic rings) excellent biosorption affinity for raw and brewed tea leaves [30]. There is considerable interest at the moment in the research of PAH uptake by modified plant residues.

The structural qualities of biosorbents, such as polarity and aromaticity, have a substantial impact on their sorption properties. Li et al. (2010) demonstrated in their study that lignin is the primary aromatic component of natural plant residues, and that lignin's higher sorption capacity is severely limited by the presence of carbohydrates (polysaccharides) in the chemical structure of the used plant, which acts as a polar group [23]. Numerous investigations have been conducted on plant fibers as oil biosorbents. Among these, kapok fibers [31], banana peels [32], coconut [33], sisal, sawdust, and leaf wastes [34], and sugarcane bagasse [35] have shown promising results in eliminating PAHs. To increase the biosorption capacity of plant residues, it is important to acid hydrolyze carbohydrates (polysaccharides) from their chemical structure. To gain a better understanding of the pollutant removal process from the environment, comparative analytical studies of raw and modified plant samples are required, based on absorption kinetics and structural properties [23].

3. Techniques for increasing the hydrophobicity of plants
Hydrophobicity is a significant sorbent property that describes the efficiency with which oil is absorbed from the water surface. Additionally, hydrophobicity is defined as the association of nonpolar groups or molecules (lipophilic compounds) in an aqueous medium as a result of the nonpolar molecules' tendency to be rejected by water.

Hydrophobic-oleophilic qualities are determined by the chemical structure and composition of the sorbent, as well as the physical shape, roughness, and porosity of the vegetable fiber. Additionally, these parameters are dependent on the oil's concentration, specific gravity, temperature, and volume [36, 37]. Chemically, biosorbents derived from plants are principally constituted of cellulose, lignin, and hemicellulose (polysaccharides), all of which are composed of carbon, hydrogen, oxygen, and nitrogen.

Lignin (fig. 2 c) is the chemical component of lignocellulosic materials. It is composed of aromatic rings linked together in a long polymer chain primarily by β-O-4 ether bonds and some C-O and C-C bonds, which gives it an oleophilic characteristic [38], in contrast to cellulose (2a) and hemicellulose (2b), which are composed of hydroxyl groups (-OH) that give the fibre hydrophilic properties [39]. Thus, lignin's propensity on the surfaces of lignocellulosic fibers enhances their potential to absorb oil [40].

As a result of the presence of hydroxyl (-OH) groups in the cellulose and hemicellulose structures, it has a hydrophilic nature, preventing it from being used to remove oily (nonpolar) groups from the aqueous environment (fig. 2).
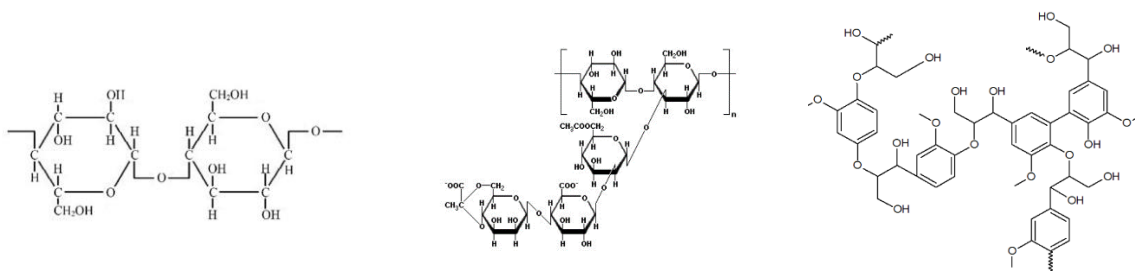
Fig 2 a Cellulose structure   b hemicellulose structure   c lignin structure

The hydrophobicity of plants can be increased by removing the OH groups from the cellulose structures and carbohydrates or by adding particular functional groups to the OH groups using various physical-chemical procedures [31]. Physical treatments such as mechanical pressing or grinding have no effect on the natural sorbent's hydrophobicity. As a result, low-temperature heat treatments, such as drying, have no effect on the absorption capacity of organic natural sorbents in comparison to crude fiber. The packing density of the biosorbent is a critical element in determining its hydrophobicity. The packing density qualities are enhanced when the absorbent materials are mechanically pressed (crushed), and the higher the packing density, the greater the absorber's dynamic oil retention capacity [41].

Chemical treatments such as mercerization, acetylation, benzoylation, coupling agents, and grafting are used to increase the hydrophobic capacity of cellulosic material. Alkali, acetylation, benzoylation, acrylation, and grafting compounds, coupling agents, peroxide, stearic acid, and fatty acid derivate (oleoyl chloride) are all chemicals that are frequently used to treat cellulose material [42].

Alongside physical-chemical treatments to promote hydrophobicity, there are also ecofriendly therapies for cellulosic material surface treatment, such as plasma therapy, hot water treatment, lignin coating, bacteria-based treatments, and surface modification with plant triglycerides [28].

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