Assessment of a raffia fiber-based biosorbent in hydrocarbon sorption

Avaliação de um biossorvente à base de fibra de ráfia na sorção de hidrocarbonetos

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Abstract

Oil spills and discharges of petroleum products have severely polluted aquatic ecosystems, oceans, rivers, groundwater and even soil. In August 2019, more than 2,000 km of the northeast and southeast coast of Brazil were struck by a major oil spill in the country’s largest ever environmental disaster. Spill remediation is a significant environmental challenge and the economic and socioenvironmental impacts of these events are diverse. Oil spills in oceans and rivers severely affect the fishing and tourism industries of the areas in question, with damage including severe short and long-term effects on plants and animals, such as respiratory and digestive disorders, reduced growth and reproductive capacity as well as weakened immunity due to the bioaccumulation of toxic contaminants. There are several proposed strategies for removing crude oil and petroleum products from surface water. Contaminated areas can be remediated in-situ or ex-situ, with the former considered the best option in terms of cost and efficiency. In this respect, absorbent materials obtained from biomass have received widespread attention due to their ease of use, buoyancy and low cost. Raffia is a natural fiber abundant in eastern Africa with excellent physical properties, such as low specific weight, good liquid sorption and low conductivity. As such, the present study investigated the application of raffia fiber with different particle sizes (< 300 µm, 300 - 850 µm, 850 - 1000 µm, 1000 - 1400 µm and 1400 - 2000 µm) and fiber/hydrocarbon ratios (1, 2, 3 and 4% w/v) as an absorbent for hydrocarbons, using n-heptane as a model molecule. Microscopic analysis of micronized raffia fiber indicated the presence of honeycomb-shaped cells with well-defined borders and an irregular geometry. These honeycomb structures are preserved, especially in large particle size ranges. Among the granulometries assessed, the highest sorption capacities were obtained for 1000 to 1400 µm raffia fibers, suggesting that honeycomb-shaped structures favor hydrocarbon sorption. Additionally, the fact that smaller particles do not require micronization is economically beneficial and...
facilitates application of the absorbent material to remediate hydrocarbon-contaminated areas. The results obtained under the conditions studied indicate that sorption capacity increases as the absorbent content rises. Comparison of fiber contents of 1% and 3% w/v for 1000 - 1400 µm particles showed an increase of approximately 43% in sorption capacity when content rose to 3% w/v. The results of the present study demonstrate the potential of natural raffia fiber as an alternative absorbent for hydrocarbons.

**Keywords:** Raffia fiber; Sorption; Hydrocarbons; Biosorbent.

**Resumo**

O derramamento de óleo e derivados de petróleo leva a graves efeitos de poluição em sistemas aquáticos, oceanos, rios e águas subterrâneas e, até mesmo, no solo. Recentemente, em agosto de 2019, mais de 2 mil quilômetros do litoral do Nordeste e Sudeste brasileiro foram atingidos por um grande derramamento de petróleo, caracterizando o maior desastre ambiental já ocorrido no Brasil. Um grande desafio ambiental é a remediação de incidentes envolvendo derramamento de óleo e derivados de petróleo. Os impactos econômicos e socioambientais desses incidentes são os mais diversos. Considerando os desastres de derramamento em áreas marítimas e fluviais, os danos podem gerar sérios problemas na indústria pesqueira ou até mesmo em atividades turísticas da região. Entre estes danos, efeitos gravíssimos em plantas e animais a curto e longo prazo, como problemas nos sistemas respiratório e digestivo, na capacidade de crescimento e reprodução e na imunidade devido aos processos de bioacumulação de contaminantes tóxicos. Atualmente, muitas abordagens são propostas para remoção de contaminantes de óleos e derivados de petróleo de superfícies aquosas. A remediação de áreas contaminadas pode ocorrer in-situ ou ex-situ, sendo que as tecnologias in-situ são sempre consideradas as melhores opções devido ao custo e eficiência. Com relação a isso, materiais absorventes provenientes de biomassa têm atraído muita atenção pela sua facilidade de utilização, pois normalmente possuem boa flutuabilidade e baixo custo. A ráfia é uma espécie de fibra natural encontrada em abundância na região ocidental da África e que possui propriedades físicas interessantes, como a baixa massa específica, boa sorção a líquidos e baixa condutividade. Dentro deste contexto, o presente trabalho estudou a aplicação da fibra natural de ráfia em diferentes faixas granulométricas (< 300 µm, 300 - 850 µm, 850 - 1000 µm, 1000 - 1400 µm e 1400 - 2000 µm) e em diferentes razões fibra/hidrocarboneto (1, 2, 3 e 4% m/v) como material absorvente para hidrocarbonetos, utilizando o n-heptano como molécula modelo. A análise microscópica da fibra de ráfia micronizada indica a presença de células formadas com fronteiras bem definidas e fechadas, mas com geometria irregular, cuja forma lembra uma colmeia de abelha. Essas estruturas de colmeia foram preservadas, principalmente nas maiores faixas granulométricas. Dentre as diferentes granulometrias avaliadas, as maiores capacidades de sorção foram obtidas com partículas de ráfia na faixa de 1000 - 1400 µm, sugerindo que a presença de estruturas na forma de colmeia favorece a sorção de hidrocarboneto. Além disso, o fato de não haver necessidade de micronizar a fibra em partículas muito finas, gera vantagens do ponto de vista econômico e de aplicação do material absorvente na remediação de áreas contaminadas por hidrocarbonetos. Os resultados obtidos nas condições estudadas indicam que a capacidade de sorção cresce à medida que a quantidade de absorvente aumenta. Comparando-se os teores de 1% e 3% m/v de ráfia, na faixa de 1000 - 1400 µm verificou-se um aumento de aproximadamente 43% na capacidade de sorção, quando o teor de fibra aumentou para 3% m/v. Os resultados do presente trabalho evidenciam a potencialidade da fibra natural de ráfia como material absorvente alternativo para hidrocarbonetos.

**Palavras-Chave:** Fibra de ráfia; Sorção; Hidrocarbonetos; Biossorvente.

**1 Introduction**
Spill remediation is a significant environmental challenge (NOAA, 2017). Spills can be intentional or accidental and severely pollute aquatic systems and the soil (LAZIM et al., 2019). For example, oil spilled into an aquatic system is spread across the surface by wind and currents, damaging the local ecosystem (REDDY et al., 2002).

The economic and socioenvironmental impacts of these events are diverse. Oil spills in oceans and rivers severely affect the fishing and tourism industries of the areas in question, in addition to modifying the environment, affecting fauna and flora. Spills have different impacts depending on the environmental conditions, type and volume of oil, vulnerability of the ecosystems affected and the efficiency of cleanup measures. Unfortunately, human negligence combined with ineffective prevention measures mean these disasters continue to occur.

Oil is the main component of the global energy matrix, resulting in increased production, commercialization, transport and distribution (FARIAS, 2008). As such, there are a number of records of both onshore and offshore oil spills worldwide. The causes of oil spills are generally associated with routine operations such as loading/unloading and transport, accidents involving tankers and barges, structural failures and explosions or fires at storage facilities or drilling rigs.

During the 1991 Gulf War, 11 million barrels of crude oil were intentionally released into the Persian Gulf, resulting in the world’s largest oil spill. The first accident-related oil spill was in 1967, when the supertanker Torrey Canyon ran aground on a reef off the coast of Cornwall, England, releasing 860,000 barrels (123,000 metric tons) of oil over a period of 12 days. In Brazil, the first recorded oil spill with environmental damage was in 1974, when the oil tanker Takimyia Maru spilled 37,790 barrels (6,000 metric tons) of oil into the São Sebastião Channel on the northern coast of São Paulo state (GREIF, 2017). In August 2019, more than 2,000 km of the northeast and southeast coast of Brazil were struck by a major oil spill in the country’s largest ever environmental disaster. Research on the negative impact of oil spills on marine life in affected areas is still scarce. However, oil is known to have severe short and long-term effects on plants and animals, such as respiratory and digestive
disorders, reduced growth and reproductive capacity as well as weakened immunity due to the bioaccumulation of toxic contaminants.

Contaminated areas can be remediated in-situ or ex-situ, with the former considered the best option in terms of cost and efficiency. In this respect, physical, biological and chemical processes have been proposed to remove and/or break down organic contaminants. Selecting the appropriate process depends on a number of factors and the ideal solution from an environmental and economic perspective may be a combination of methods.

With respect to physical and chemical processes, the use of chemical dispersants is a technically viable alternative to remove oil and petroleum products from the water surface. Although dispersants are chemically stable, they are not biodegradable. Sorbents and advanced materials such as aerogels, membranes and nanoparticles can also be used to separate oil-water mixtures. However, there is a growing demand for low-cost, easily accessible eco-friendly materials, which has prompted a widespread increase in studies on natural materials (DOSHI et al., 2017; OLGA et al., 2019).

Natural fibers are an attractive and promising alternative for developing materials with a high sorption capacity for organic contaminants. They can be obtained from biomass and plant residue, and their biodegradability, abundance, low cost and ease of use favor their large-scale application. Cotton (SUNI et al., 2004) and coconut fibers, peat (OLIVEIRA et al., 2011), silk, sisal and sawdust (ANNUNCIADO et al., 2005) are examples of natural materials investigated as sorbents for the oil industry, with sorption capacities varying in accordance with their physical, chemical and structural characteristics.

Natural fibers are elongated materials that occur as continuous filaments or discrete pieces. They serve as raw material in manufacturing and can be spun into thread or ropes or used to produce paper, felt and other products (FRANÇA, 2012). The use of natural fiber as raw material is motivated by the different properties of each family or type. Plant fibers are basically composed of cellulose, hemicellulose, lignin and smaller amounts of other components, such as pectin, waxes and water-soluble substances (FRANCO, 2010).
Raffia is a natural fiber abundant in the intertropical convergence zone, particularly in Africa, and consists of several families, including *Raphia ruffia* (native to Madagascar) and *Raphia vinifera* (found primarily in East Africa from Angola to the Senegambia), also found in Malawi and the Amazon coastal zone. Raffia palms propagate rapidly and on a large scale, and in some areas of the African continent they are considered undesirable for agriculture and burned, especially for rice crops (FOADIENG *et al*., 2014). The plants can grow up to ten meters tall and thirty centimeters in diameter. In most cases they sprout together, with up to four trunks on a same root. The upper portion of the trunk features straight rigid branches that contain the leaves and from which bamboo is extracted (MANN AND WENDL, 2002).

According to recent studies by our research group, raffia fiber is a self-extinguishing material with interesting physical and thermoacoustic properties, such as low specific weight, good liquid sorption and low conductivity (MVEH, 2015). In this respect, and considering the liquid sorption and inflammability of raffia fiber, the present study aimed to assess its application as a hydrocarbon absorbent, using n-heptane as a model molecule. The effect of particle size (< 300 µm, 300 - 850 µm, 850 - 1000 µm, 1000 - 1400 µm and 1400 - 2000 µm) and the fiber/hydrocarbon ratio (1, 2, 3 and 4% w/v) on sorption capacity were also evaluated.

## 2 Material and Methods

### 2.1 Extraction and preparation of raffia fiber

The raffia fibers used here were extracted from *Raphia hookeri* palms (family *Hookeri*) grown in the village of Akounou, 25 km from Yaoundé, the capital of the Republic of Cameroon in Central Africa. The portion extracted from the raffia branch for sorption tests was a 50 cm long perfectly circular section (L) and all the plants were approximately three years old. Figure 1 shows an image of a *Raphia hookeri* palm and a representative figure of the bark and raffia fiber. The stems of the fresh plants were cut, the fibers separated from the outer sheath and dried in the sun for about one month at the cultivation site, under the following environmental conditions: $T = 18 - 32 \, ^\circ\text{C}$ and relative humidity between 70 and
80%. Studies have shown that the chemical composition of raffia fiber varies with the age of the plant and is similar to that of wood, except for carbon content (24 - 33% for raffia and 49 - 50% for wood) (FOADIENG et al., 2014; MVEH, 2015).

Figure 1 – *Raphia hookeri* palm and representative figure of the bark and raffia fiber

![Image of Raphia hookeri palm and representative figure of the bark and raffia fiber](source: The authors (2020)).

### 2.2 Raffia fiber granulometry and morphology

The raffia fibers were cut horizontally into small slices, ground in a household blender and sieved in a vibrating sieve system, which separated the micronized material into five different particles sizes, in accordance with technical standard ABNT NBR 7211. Starting from the largest granulometry (1400 - 2000 µm), the mesh size of the sieves was reduced to obtained medium (1000 - 1400 µm, 850 - 1000 µm and 300 - 850 µm) and fine particles (< 300 µm). The average particle sizes obtained after sieving are described in Table 1 and particle appearance is shown in Figure 2.
Table 1 – Raffia fiber particle sizes in sorption tests with n-heptane

| Sieve | Mesh | Sieve grid (mm) | Average size of retained particles (mm) |
|-------|------|----------------|----------------------------------------|
| 1     | 9    | 2.000          | -                                      |
| 2     | 12   | 1.400          | 1.700                                  |
| 3     | 16   | 1.000          | 1.200                                  |
| 4     | 20   | 0.850          | 0.925                                  |
| 5     | 28   | 0.300          | 0.575                                  |
| Sifter bottom | -    | -              | < 0.300                                |

Figure 2 – Raffia fiber particles in the different size ranges

Source: The authors (2020).

The particles obtained in the different size ranges were characterized by scanning electron microscopy (SEM) to assess fiber morphology. The micrographs were obtained using a FEI Inspect F50 scanning electron microscope at 10 kV, in secondary electron (SE) mode, available at the Central Laboratory of Microscopy and Microanalysis (LabCEMM) of the Pontifical Catholic University of Rio Grande do Sul (PUCRS). The samples were placed on stubs and coated with a fine layer of gold. The images of the particles in the different size ranges were obtained at 100 x and 500 x magnification.
2.3 Sorption tests

The sorption tests were performed in triplicate, using \( n \)-heptane \((C_7H_{16})\) as a hydrocarbon model molecule. Tests were conducted at ambient temperature under static conditions, with 1 h of contact between the absorbent and hydrocarbon. Next, the raffia samples were filtered and allowed to rest for 15 min. The amount of hydrocarbon absorbed into the particles was determined by gravimetric analysis. The sorption potential of raffia was assessed for the different particle size ranges (< 300 µm, 300 - 850 µm, 850 - 1000 µm, 1000 - 1400 µm and 1400 - 2000 µm) and fiber/hydrocarbon ratios. The latter was evaluated by establishing a raffia weight/\( n \)-heptane volume ratio of 1% (0.1 g of raffia), 2% (0.2 g of raffia), 3% (0.3 g of raffia) and 4% (0.4 g of raffia) for a fixed volume of 10 mL of \( n \)-heptane.

3 Results and Discussion

The properties of a good absorbent go beyond a large surface area and pore volume. It is important to other aspects that influence the sorption process, such as the presence of functional groups in the chemical structure of the material and its morphology, among others. In this respect, the morphology of the micronized raffia fiber particles with different granulometries was assessed by SEM (Figure 3).
The five particle size ranges obtained and evaluated were: < 300 µm, 300 - 850 µm, 850 - 1000 µm, 1000 - 1400 µm and 1400 - 2000 µm. Particles < 300 µm are arranged in clustered sheets with destruction of the internal cell structure of the fiber, whereas the
internal structure of 850 - 1000 µm fibers (or medium ranges) was partially, and in some cases, fully preserved. The micrographs of 1000 - 1400 µm and 1400 - 2000 µm particles show better cell arrangement with well-defined borders, where individual fiber bundles are interspersed with partially open cells or those whose membranes have been damaged by micronization. This arrangement is responsible for the lightness (low specific weight) and, in part, the sorption capacity of the material.

In order to assess the hydrocarbon sorption capacity of raffia fibers with different particle sizes, an initial study was conducted using \( n \)-heptane as a model molecule. With respect to the fiber/hydrocarbon ratio, contents of 1 to 4% m/v were chosen. Higher fiber contents were not tested due to the fiber/hydrocarbon volumetric proportion. In other words, the low specific weight of raffia fibers means their volume is far greater than the predetermined 10 mL of \( n \)-heptane, preventing contact between the absorbent and hydrocarbon. As such, the \( n \)-heptane sorption tests were conducted using raffia fibers with five different granulometries and fiber contents of 1, 2, 3 and 4% m/v as a biosorbent. The results (Figure 4) demonstrated a rise in sorption capacity as fiber content increased and, from 300 µm onwards, the highest \( n \)-heptane sorption values were obtained with 3 and 4% m/v of raffia fiber (> 0.5 g \( n \)-heptane/g fiber). Additionally, higher sorption values were recorded for particle sizes of 1000 - 1400 µm and 1400 - 2000 µm, with > 1.4 g \( n \)-heptane/g fiber (> 14 mmol/g) and > 0.9 g \( n \)-heptane/g fiber (> 9 mmol/g), respectively.

Considering that raffia fiber is hydrophilic due to its chemical composition (≥ 80% cellulose) (MVEH, 2015), it showed excellent \( n \)-heptane sorption capacity when compared to other lignocellulosic materials. Olga et al. (2015) assessed the sorption capacity of different lignocellulosic materials (e.g. sawdust) for aliphatic hydrocarbons (HC) such as \( n \)-octane and \( n \)-pentane, obtaining values of 1 - 3 g HC/g sawdust. Sorption values > 9 mmol \( n \)-heptane/g fiber (1400 - 2000 µm particles) and > 14 mmol \( n \)-heptane/g fiber (1000 - 1400 µm particles) are comparable to those obtained for activated carbon with different structures (13 - 14 mmol \( n \)-heptane/g carbon) in \( n \)-heptane sorption (CARVAJAL-BERNAL et al., 2019).
Natural absorbents (biosorbents) are low-cost, have limited hydrocarbon and oil sorption capacity, and good buoyancy. The final application of these materials and their recovery for reuse are important aspects when selecting them as absorbents. On the other hand, activated carbon, the most widely used absorbent, is relatively costly to obtain with a large surface area and to reactivate (CARVAJAL-BERNAL et al., 2019). This has prompted the use of environmentally friendly and less costly alternatives, such as lignocellulosic materials. The properties of biosorbents are significantly influenced by structural characteristics such as polarity and aromaticity. Biosorbents derived from biomass and/or agroindustrial residues, such as the raffia fiber used here, contain a certain amount of lignin. Lignin is the main aromatic component of these materials and its sorption potential for hydrophobic components is significantly limited by the presence of polysaccharides (polar component). Xi and Chen (2014) found that hydrocarbon sorption capacity increased with greater exposure of the lignin domains. As such, in the case of raffia fiber particles, the lignin present may be more accessible for interaction with the hydrocarbon studied. On the other hand,
the cell structure of the fiber is likely one of the main factors responsible for its good sorption capacity.

4 Conclusion

Morphological analysis of the raffia fiber indicated the presence of honeycomb-shaped cells with well-defined borders and irregular geometry. Raffia fiber showed potential for \( n \)-heptane sorption, with the best sorption capacity (1.48 g \( n \)-heptane/g raffia fiber, 1 hour of contact) observed for 1000 - 1400 µm particles at a fiber content of 3% m/v. In addition, there was a gradual rise in \( n \)-heptane sorption capacity as fiber content increased, particularly for larger particle sizes. The fact that smaller particles do not require micronization is economically beneficial and facilitates application of the absorbent material to remediate hydrocarbon-contaminated areas.

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