Abstract
Oil and derivatives leaks are growing concerns worldwide, as they harm the environment, the socio-economic sector, and human beings. Therefore, alternative, and sustainable ways, such as bioadsorption with vegetable fibers, have been studied to clean these oils and derivatives effectively and non-aggressively. In this work, a patent prospection was carried out in the Espacenet® database and the National Institute of Industrial Property - (INPI). The evolution, origin, and applications were analyzed, and the most used fibers in the patents were found. As a result, the first patent was filed in 1999, and the countries that filed the most patents were Japan (45%), Brazil (28%), and China (25%). It is also seen that the most used fibers are cotton and coconut due to their wide availability around the world. Therefore, the development of technologies that use vegetable fibers to clean spilled oil and derivatives has excellent potential since they are environmentally and economically favorable.

Keywords: Patent prospecting; Natural fibers; Oil; Biosorption.

Resumen
Las fugas de petróleo y derivados son una preocupación creciente a nivel mundial, ya que traen consigo daños no solo al medio ambiente, sino también al sector socioeconómico, así como a los seres humanos. Por ello, se han estudiado vías alternativas y sostenibles, como la bioadsorción con fibras vegetales, para que la limpieza de estos aceites y derivados se realice de forma eficaz y no agresiva. En este trabajo se realizó la prospección de patentes en la base de datos Espacenet® y el Instituto Nacional de la Propiedad Industrial - (INPI), donde se analizó la evolución, origen y aplicaciones, así como las fibras más utilizadas en las patentes encontradas. Como resultado, la primera patente se presentó en 1999, y los países que presentaron más patentes fueron Japón con un 45 %, Brasil con un 28 % y China con un 25 %. También se ve que las fibras más utilizadas son el algodón y el coco debido a su amplia disponibilidad.
alrededor del mundo. Por lo tanto, el desarrollo de tecnologías que utilicen fibras para limpiar derrames de petróleo y derivados tiene un gran potencial, ya que son ambiental y económicamente favorables.

**Palabras clave:** Prospección de patentes; Fibras naturales; Petróleo; Biosorción.

1. Introduction

Petroleum is formed by a set of organic components, mostly hydrocarbons. As one of the main sources of energy used, its use is subject to risks of spillage into the environment, whether through transport, storage, production, or even exploitation. Environmental pollution resulting from oil spills in the terrestrial environment, especially in the marine environment, since most of the petroleum is offshore, makes it one of the biggest problems that is currently faced (Cardoso C., Cardoso R. & Moreira, 2017; Neto & Dalla Costa, 2007; Scorsato, 2021). Petroleum contains highly toxic components, such as Polycyclic Aromatic Hydrocarbons (PAHs), which are considered carcinogenic and directly affect the biota in the region where it was spilled, potentially affecting human health. Therefore, a National Contingency Plan (PNC) is needed to facilitate prevention and the oil remediation response with actions coordinated by public and private institutions (ANP, 2021). The choice of technology implemented in the PNC must meet its efficiency according to the type of spill, the characteristics of the spilled oil, and the affected region so that it does not make an undue choice and further harm the affected ecosystem. Preferably, remediation techniques are chosen that make the environment less polluted at a macroscopic level in a short time (Cardoso et al., 2017).

Several cleaning methods are used internationally, such as containment barriers, manual removal, skimmers, chemical dispersants, water blasting, and adsorbents. However, research has been developed to reach technologies with characteristics that extract oil from the environment in a way that does not harm the environment so much (Cardoso et al., 2017).

The search for alternatives to conventional methods that have low cost and high efficiency has boosted, in recent years, research on the use of different biosorbents in adsorption systems (Hammouda et al., 2021). The adsorption method consists of the ability of certain solids to accumulate substances present in fluids, whether liquids or gases, so that a separation of the components of these fluids can occur (Nascimento et al., 2014).

Among the various adsorbent materials currently available, natural adsorbents stand out for being an alternative form of low cost and high efficiency in removing contaminants (Girardello, 2011), such as sisal fiber (Costa, 2018), sugarcane bagasse sugar (Guilarducci et al., 2016) and coconut fiber (Cardoso et al., 2021). The use of these materials is attractive for reasons of economy and high sorption rate and capacity (Hilário, 2019).

The wide availability of these fibers and the interest in replacing polymeric materials with materials from a renewable source has driven the development of several types of research using plant fibers as sorbents (Hammouda et al., 2021). Therefore, this article aims to carry out a patent prospection to analyze the technologies registered over the years in sorption in water contaminated with oil using biosorbents and identify possible demands and technological innovations. An analysis will be made of the evolution of technologies (based on the number of patents published per year), the origin of the technology (based on the identification of the countries that deposited the most), the main applications of the documents (based on the patent classification codes), and the types of natural fibers most used in patents.

2. Methodology

Technological prospecting was carried out in June 2021 through the open-access international patent database Espacenet® and the open-access Brazilian patent database, National Institute of Industrial Property (INPI).

An advanced search was performed with keywords present both in the title and in the abstract of the patents. In both databases, the same keywords (natural fiber, oil) were used, together with the Boolean operator AND, to find records
containing both terms. To further specify the research on the topic, a code from the International Patent Classification (C02F1/28 - Cleaning wastewater, sewage, and sludge using sorption) was also used (WIPO, 2021).

With the results obtained, the data were placed in the Microsoft Excel software for graphical analysis of the evolution and origin of the technology of the main depositors and main applications of these documents and the identification of the main types of fibers used worldwide (Cantú & Zapata, 2006; Nunes et al., 2018).

The bibliographic survey was carried out in the Scopus database in which data collection was based on inclusion and exclusion criteria, based on the proposed theme (Ludke & Andre, 2013; Severino, 2018).

3. Theoretical Reference

Any accidental or deliberate release of liquid hydrocarbons into the environment is termed an oil spill (Bhardwaj & Bhaskarwar, 2018). Oil spill risks for marine and freshwater habitats have increased along with crude oil production and transport (Abdelwahab et al., 2017). Several cleaning methods are used to reduce or minimize the environmental damage caused by oil spills.

Cleaning methods that perform primary cleaning aim to remove free oil and heavy contamination as quickly as possible to avoid remobilization and pollution from other areas. For those performing secondary cleaning, it may be necessary to remove additional oil and impregnated materials and, if necessary, residue and stains (Cardoso et al., 2017).

The use of sorbents is among the first primary cleaning techniques in history to remediate contaminated coastal areas from oil accidents (Annunciado et al., 2005). Adsorbent products can be divided into two basic categories: synthetic and natural (Lopes, Milanelli & Poffo, 2007). In the last ten years, the offer of new products with adsorbent properties for specific use in hydrocarbon leaks has grown. Adsorption is the principle of action of these materials, and they are highly efficient for cleaning or removing oil on land or water. This method consists of the ability of certain solids to accumulate substances present in fluids, whether liquids or gases, so that a separation of the components of these fluids can occur. Adsorption has become one of the most popular methods for this purpose, gaining importance as a separation and purification process in recent decades, being able to adsorb up to 25 times its weight in oil and its derivatives (Ferrão, 2005). The use of natural plant materials for adsorption is called biosorption (Nascimento et al., 2014).

Biosorbents are formed mainly from vegetable raw materials, including kapok, sisal, coconut, sawdust fibers, sugarcane bagasse, and leafy residues (Cardoso et al., 2017). Among the various adsorbent materials available today, natural adsorbents stand out as an alternative form of low cost and high efficiency in removing contaminants (Girardello, 2011).

In the literature, many published works present test results that use different types of plant materials, especially lignocellulosic fibers, for the adsorption of oils and derivatives. Paulauskiene and Jucike (2015) studied crude oil and diesel oil adsorption using wool, moss, straw, and peat. Among the biosorbents studied, the one with the highest oil sorption capacity was wool (9.411 g/g), and diesel was peat (6.334 g/g). These results confirm the importance of the spilled oil characteristic for the choice of technology.

Cao et al. (2017) compared the sorption performance of vegetable oil with kapok, cattail, and cotton fibers. The kapok fiber showed the highest sorption capacity, among the comparison, with a retention of 25.79 g/g. Then, the cotton fiber obtained adsorbing capacity of 14.98 g/g. Finally, the cattail fiber showed the lowest result, adsorbing 11.91 g/g. These results are explained by the chemical and morphological characteristics of the fibers. The authors showed hydrophobic and oleophilic characteristics in kapok fibers, which helps oil droplets not be adsorbed on the fiber surface, but inside the fiber lumen, thus contributing to high sorption and oil retention. On the other hand, the cotton fiber had the lowest presence of pores among the fibers, which affected the sorption capacity of this biosorbent.

The endocarp (husk) and mesocarp (fiber) of green coconut were evaluated for adsorption of dissolved hydrocarbons...
(naphthalene, toluene, and benzene) in the work of Luis-Zarate et al. (2018). Coconut fiber showed the highest adsorption capacities (222 mg / g for benzene, 96 mg / g for toluene, and 5.85 mg / g for naphthalene), which was attributed to its morphological characteristics and its high concentration of groups phenolics that are associated with the structure of lignin. The authors also showed in this work that the heating power of the adsorbent material after use (5064.43 ± 11.6 cal/g) is higher than that of woody biomass (3400-4000 cal/g), concluding that this material has added value for being a promising biofuel.

Ciufu et al. (2019) studied natural Romanian wool as a sorbent in oil spills. They simulated adverse conditions for the tests by varying the fiber density according to two types of supports (cylindrical and flat) for adsorption. As a result, the authors noticed that for both supports, the fiber density was inversely proportional to the sorption (fiber in the cylindrical support with higher density, sorption = 6.381 g/g; fiber in the cylindrical support with lower density, sorption = 7.092 g/g; fiber in the flat support with higher density, sorption = 10.88 g/g; fiber in the flat support with lower density, sorption = 11.76 g/g) for the two types of supports used. The authors state that half of the sorbent on the cylindrical support was immersed in water; however, the sorbent on the flat support remained floating in the water in contact with the oil. This behavior explains the difference in the sorption results. The sorbent that contains more contact with the oil will consequently have more significant interaction and sorption, as in the case of sorbents on the cylindrical support. Hence, evaluating the density of the sorbent being used to clean oil in impacted areas is essential.

The treatment in natural fibers is also frequently mentioned in works published in the literature. This procedure changes the raw material's chemical, physical, and morphological structure, favoring oil sorption (Cardoso C. et al., 2021). Peng et al. (2021) performed chemical treatment in the pith of corn stalks using malic acid to be used as an oil biosorbent. The sorption of 37.2 g/g, 44.1 g/g, 33.8 g/g, and 29.3 g/g was observed for the treated biosorbent for lubricating oil, soybean oil, diesel oil, and isopropyl alcohol, respectively. These data correspond to more than 100% of what was found due to sorption by the fiber without any treatment (Peng, Cheng, Li & Guo, 2021), demonstrating the effectiveness of the treatment in the studied fiber.

In all these works presented, it is essential to highlight the use of fibers found abundantly in the studied region, contributing to the technology's cost. A large number of studies with biosorbents obtaining satisfactory results for oil cleaning favors the expansion of the application of this technology.

### 4. Results and Discussion

The number of technologies obtained in the international (Espacenet®) and national (INPI – National Institute of Intellectual Property) patent database, as the keywords and codes were specified in the research, are shown in Table 1.

<table>
<thead>
<tr>
<th>Key words</th>
<th>Espacenet®</th>
<th>Results</th>
</tr>
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<tbody>
<tr>
<td>Natural fiber</td>
<td>Oil</td>
<td>C02F1/28</td>
</tr>
<tr>
<td>X</td>
<td>X</td>
<td>1.608.396</td>
</tr>
<tr>
<td>X</td>
<td>X</td>
<td>56.230</td>
</tr>
<tr>
<td>X</td>
<td>X</td>
<td>29</td>
</tr>
</tbody>
</table>

| Source: Own authorship (2022). |
The technologies involving natural fibers found in Espacenet® were 23,285 and 1,145 in INPI, demonstrating an increasingly recurrent concern of using cheaper raw materials and available in the form of natural waste through the large number found. When dealing only with the oil category, the number of results was the highest since a large part of the economy revolves around this good, thus requiring more and more technologies. It is to be expected that the number of patents found on the Espacenet® platform is higher than that found by the INPI (Figure 1) since these are technologies registered in several countries. However, it was possible to observe that the Brazilian database found a significant number of technologies involving oil cleaning using natural fibers, corresponding to 37.9%. This result can be explained by Brazil's extensive agricultural and natural fiber production, such as bamboo, coconut, piassava, silk, sisal, and others (CSFN, 2019). Therefore, after verifying the patents found on both platforms, 40 patents were selected for qualitative and quantitative analysis and discussion.

**Figure 1 – List of number of patents published on Espacenet® and INPI.**

![Figure 1](image)

Source: Own authorship (2022).

Based on the records of the platforms used in the searches, the first patent was deposited in 1977 (Figure 2). Before that, there were already many oil spills; however, it was only in 1967 that the environmental impacts received notoriety after the oil tanker Torrey Canyon, with a carrying capacity of more than 100,000 tons of oil, ran aground in England, causing an environmental disaster (Professional Mariner, 2007). The Deepwater Horizon spill in 2010 is considered the largest oil spill in the oil industry history. It took place in the Gulf of Mexico, became internationally known. With its challenges in remediation, many works aimed at cleaning this oil were developed, which in the future resulted in technologies (ITOPF, 2018). In 2019, a major environmental disaster in Brazil stood out for being considered one of the largest oil spills concerning the extent of impacted areas worldwide (Oliveira et al., 2020). With this historic disaster, the Brazilian population realized the importance and need to have efficient and safe technologies to clean this contaminant and reduce environmental and socioeconomic impacts.
Figure 2 – Number of patents published per year.

When analyzing the evolution of patent filing (Figure 2), an increase in the number of patents in 1978, 1982, 2008, and 2017 can be noted. This increase in patents may be the result of investigations and experiences in major accidents involving spills of oil that occurred around the world, both in the years that were anticipated and in the same years of this increase in the number of registered technologies. For example, in 1978, when the ship Amocco Cadiz broke in two and had 300 thousand liters of oil spilled off the coast of Brittany, France (Silva, 2001), and the Agia Zoni II, which in September 2017 sank in the Saronic Gulf, Greece, releasing approximately 500 tons of heavy fuel oil, contaminating the coasts of Salamis and Athens (Thomas et al., 2020).

Figure 3 shows the origin of the analyzed patents. Among the countries where patents were published, Japan leads, representing 45% of patents, followed by Brazil with 27.5%, China with 25%, and the United States with only 2.5%. China and Japan have many patents as they are prominent developers of technology-related intellectual property (Rodrigues & Braghini Junior, 2019). Brazil is the largest producer and exporter of sugar in the world (Andrade & Martins, 2021), as well as one of the largest producers of coconut with Indonesia (Santos et al., 2019), in addition to other agricultural products that the processes generate tailings. Industrial plants can be reused as petroleum biosorbent (Cardoso et al., 2020; Guilarduci et al., 2016). These are justifications that lead to a significant amount of patent publications in the area in these countries.
Figure 3 - Patent depositary countries.

Source: Own authorship (2022).

The International Patent Classification is an excellent tool to identify the technical content of patent documents through their codes. The evaluated codes are shown in Table 2.

Table 2 – CIP codes and their evaluated descriptions.

<table>
<thead>
<tr>
<th>CIP code</th>
<th>Description</th>
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<tbody>
<tr>
<td>C02F1/40</td>
<td>Devices for separating or removing greasy, oily substances or similar floating material</td>
</tr>
<tr>
<td>B01J20/24</td>
<td>Naturally occurring macromolecular compounds and humic acids or their derivatives</td>
</tr>
<tr>
<td>B01J20/28</td>
<td>Solid sorbent compositions or filter aid compositions; Processes for their preparation, regeneration or reactivation characterized by their form or physical properties</td>
</tr>
<tr>
<td>C09K3/32</td>
<td>Materials to absorb liquids and remove oil, gasoline and grease pollution</td>
</tr>
<tr>
<td>B01D17/022</td>
<td>Separation of immiscible liquids by absorption or absorption</td>
</tr>
<tr>
<td>B01J20/30</td>
<td>Processes to prepare, regenerate or reactivate</td>
</tr>
<tr>
<td>B01D15/00</td>
<td>Separation processes involving the treatment of liquids with solid sorbents</td>
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Figure 4 shows the number of patents for the technical areas of this set of identified patent documents. Code C02F1/40, which concerns devices for separating or removing fatty, oily, or similar floating material (cleaning or keeping the water surface free of oil or similar material), presented the highest number of patents (13 units). The code B01J20/24 was followed by 10 patents and is specific for naturally occurring macromolecular compounds and humic acids or their derivatives. The code B01J20/28 is the third that stood out the most. It is used for solid sorbent compositions or filter aid compositions; Processes for their preparation, regeneration, or reactivation characterized by their form or physical properties and filed 7 patents.
In addition, the natural fibers that appear among the patents found were also evaluated (Figure 5). Several fibers were found, such as straw fiber, cellulose fiber, and hair fiber. Among the patents selected for study, the most used fibers are cotton fibers. This fiber is one of the most used in the world, with Brazil being the fourth largest producer of cotton, behind India, China, and the United States (Carmona et al., 2014; Coêlho, 2019). The second most used fiber among the patents is coconut, considered one of the ten most useful trees on earth (Alburquerque et al., 2020). Next comes the kapok and hemp fiber.

The wide variety of fibers available in the world facilitates the application of sorption in a more economically viable way. However, it is evident in this analysis a constancy concerning the fibers that are used in the technologies. Sisal fiber is relatively abundant in Brazil, has a very high sorption capacity and efficient characteristics to be used as an oil adsorbent (Cardoso et al., 2021). However, none of the deposited technology found in this study uses this fiber. As with sisal fiber, other
plant residual fibers could also be reused in technologies, covering the possibilities of adsorbent materials, and making the patent increasingly sustainable.

Cotton fiber was the most used vegetable raw material in the patents field. However, this vegetable fiber has many other applications, such as, mainly, fabric making. This material is not found in a residual form like other materials mentioned. This feature reduces the sustainability that could be promoted from waste fibers. In addition to being sustainable, the technology that uses waste as a raw material is also favored in terms of economics.

It is essential to evaluate the physical, morphological, chemical, and physical-chemical characteristics of these biofibers, as this directly interferes with the efficiency of their use in cleaning up spilled oil in marine environments. The three fibers that stood out the most have characteristics that favor their adsorptive power, except for the chemical characteristic. As they are lignocellulosic materials, these fibers have cellulose and hemicellulose in their chemical composition, which is considered hydrophilic and thus reduces the interaction with the oil desired to be removed from the marine environment (Sun et al., 2021). Despite this knowledge, the technologies found did not present any solutions to these challenges, which could be fiber treatments (Cardoso et al., 2021), leaving a gap for technologies in this area.

5. Conclusion

The analysis of existing patents in plant sorbents for the adsorption of oil and derivatives revealed a significant number of patents filed. There was an increase in the deposition in specific years, which can be linked to events that occurred in the world involving oil spills in that year or previous years, with Japan and Brazil as the countries that most stood out in the origins of these technologies (representing 45% and 28% of patents, respectively). It is also seen that the most used fibers are cotton and coconut due to their wide availability around the world. However, a gap was identified in the use of treatments in plant fibers to improve their characteristics and, consequently, evolve the adsorption and removal capacity of the contaminant in the aquatic environment. Therefore, for the development of future technologies, it is important to explore not only the action of treatment but the use of other fibers that are available in Brazil and the world in the form of solid waste to leverage sustainability and a circular economy. Furthermore, as it is the most used energy source today, oil exploration will continue to involve risks of accidents, and this presents an ideal scenario for investment in this technology.

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References


