Research, Society and Development, v. 9, n. 7, e523974413, 2020
(CC BY 4.0) | ISSN 2525-3409 | DOI: http://dx.doi.org/10.33448/rsd-v9i7.4413

Cardoso, CKM, Santana, RSG, Silva, VL, Meirelles, ACLE, Mattedi, S, Moreira, ITA & Lobato, AKCL (2020). Kinect and equilibrium study of petroleum adsorption using pre-treated coconut fibers. ***Research, Society and Development***, 9(7): 1-31**,** e523974413.

Kinetic and equilibrium study of petroleum adsorption using pre-treated coconut fibers

Estudo cinético e de equilíbrio de adsorção de petróleo utilizando fibras de coco pré-tratadas

Estudio cinético y de equilibrio de la adsorción de petroleo con fibras de coco pretratadas

Recebido: 11/05/2020 | Revisado: 12/05/2020 | Aceito: 15/05/2020 | Publicado: 25/05/2020

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Abstract

The recent oil spill off the Brazilian coast serves as an alert for research to be carried out that includes biotechnological processes and products for cleaning marine environments. Therefore, this work aims to compare the use of residual coconut fibers (*Cocos nucifera L.*) *in natura*, pretreated with Protic Ionic Liquid (PIL) [2-HEA] [Ac] (innovative treatment) and by mercerization/acetylation (traditional treatment) as a biosorbent of petroleum spilled in the marine environment in a hydrodynamic simulation on a laboratory scale. The study of the kinetics and adsorption equilibrium were performed to determine the limiting mechanism of adsorption, as well as the maximum petroleum adsorption capacity for the coconut fibers studied. Characterizations of the fibers were carried out using SEM and FITR, and the kinetics and sorption equilibrium tests with petroleum from the Campos Basin and saline water. It was possible to observe that a minimum time of 5 min of contact between the adsorbent and adsorbent is necessary for biosorption to occur. The fibers treated with PIL (4.63 g/g) had greater sorption capacity, the fiber *in natura* (3.62 g/g) less capacity and the fiber with mercerization/acetylation treatment (4.26 g/g) has sorption with intermediate values. The kinetic model that best fitted the experimental data was pseudo-second order, indicating chemosorption as the limiting step of adsorption. The sorption equilibrium model chosen was Sips, determining adsorption in multilayer (Freundlich) with low concentrations of petroleum and in monolayer (Langmuir) with high concentrations. Based on these results, it can be said that the coconut fibers (*Cocos nucifera L.*) treated have a greater capacity to adsorb petroleum than the fibers *in natura*, and the fibers treated with PIL [2-HEA][Ac] have greater sorption capacity, among those evaluated, to be used in oil spills.

Keywords: Coconut fiber; Protic ionic liquid; Petroleum; Adsorption.

Resumo

O derrame de petróleo ocorrido recentemente no litoral brasileiro serve como um alerta para que sejam desenvolvidas pesquisas que contemplem processos e produtos biotecnológicos para limpeza de ambientes marinhos. Diante disso, esse trabalho tem o objetivo de comparar a utilização de fibras de coco residuais (*Cocos nucifera L.*) *in natura*, pré-tratadas com Líquido Iônico Prótico (LIP) [2-

HEA][Ac] (tratamento inovador) e por mercerização/acetilação (tratamento tradicional) como biossorvente de petróleo derramado no ambiente marinho em uma simulação hidrodinâmica em escala laboratorial. O estudo da cinética e do equilíbrio da adsorção foram realizados para determinar o mecanismo limitante da adsorção, bem como a capacidade máxima de adsorção de petróleo para as fibras de coco estudadas. Foram realizadas caracterizações das fibras usando MEV e FITR, e os testes de cinética e equilíbrio de sorção com petróleo da Bacia de Campos e água salina. Foi possível observar que é necessário tempo mínimo de 5 min de contato entre o adsorvato e adsorvente para ocorrer a biossorção. As fibras tratadas com LIP (4,63 g/g) obteve maior capacidade de sorção, a fibra *in natura* (3,62 g/g) menor capacidade e a fibra com tratamento de mercerização/acetilação (4,26 g/g) tem sorção com valores intermediários. O modelo cinético que melhor se ajustou aos dados experimentais foi pseudo-segunda ordem, indicando quimiossorção a etapa limitante da adsorção. O modelo de equilíbrio de sorção escolhido foi Sips, determinando adsorção em multicamada (Freundlich) com baixas concentrações de petróleo e em monocamada (Langmuir) com altas concentrações. Com base nesses resultados, pode-se afirmar que as fibras de coco (*Cocos nucifera L.*) tratadas possuem maior capacidade de adsorver petróleo do que as fibras *in natura*, e as fibras tratadas com LIP [2-HEA][Ac] possuem maior capacidade de sorção, dentre as avaliadas, para ser utilizadas em derrames de petróleo.

Palavras-chave: Fibra de coco; Líquido iônico prótico; Petróleo; Adsorção.

Resumen

El derrame de petróleo ocurrido recientemente en la costa brasileña sirve como alerta para el desarrollo de investigaciones que contemplan procesos y productos biotecnológicos para la limpieza de ambientes marinos. Por lo tanto, este trabajo tiene como objetivo comparar el uso de fibras de coco residuales (Cocos nucifera L.) en la naturaleza, pretratadas con Líquido Iónico Prótico (LIP) [2-HEA][Ac] (tratamiento innovador) y por mercerización/acetilación (tratamiento tradicional) como biosorbente de petróleo derramado en el medio marino en una simulación hidrodinámica a escala de laboratorio. El estudio de la cinética y el equilibrio de adsorción se realizaron para determinar el mecanismo limitante de adsorción, así como la capacidad máxima de adsorción de petróleo para las fibras de coco estudiadas.. Las caracterizaciones de las fibras se llevaron a cabo utilizando SEM y FITR, y las pruebas de cinética y equilibrio de sorción con aceite de la Cuenca de Campos y agua salina. Fue posible observar que es necesario un tiempo mínimo de 5 minutos de contacto entre el adsorbente y el adsorbente para que ocurra la biosorción. Las fibras tratadas con LIP (4.63 g/g) tenían mayor capacidad de sorción, la fibra *in natura* (3.62 g/g) menos capacidad y la fibra con tratamiento de mercerización/acetilación (4.26 g/g) tiene sorción con valores intermedios. El modelo cinético que mejor se ajustó a los datos experimentales fue el pseudo-segundo orden, lo que indica que la quimiosorción es el paso limitante de la adsorción. El modelo de equilibrio de sorción elegido fue

Sips, determinando la adsorción en multicapa (Freundlich) con bajas concentraciones de aceite y en monocapa (Langmuir) con altas concentraciones. Con base en estos resultados, se puede decir que las fibras de coco (Cocos nucifera L.) tratadas tienen una mayor capacidad de adsorber aceite que las fibras en la naturaleza, y las fibras tratadas con LIP [2-HEA][Ac] tienen mayor capacidad capacidad de sorción, entre las evaluadas, para ser utilizada en derrames de petróleo.

Palabras clave: Fibra de coco; Líquido iónico prótico; Petróleo; Adsorción.

1. Introduction

Despite the variety of renewable energy sources today, as sources of fossil origin are still the main sources in the world (EPE, 2018). The growth of petroleum production that favors the stability of the economy through the positive impacts on the social, scientific and technological sector is the same that presents the risks in the environment and, consequently, in human health, since petroleum uses highly toxic components (Barboza & Freitas, 2019; Beyer, Trannum, Bakke, Hodson & Collier, 2016; Lemos, Souza, Aleixo, Lima & Cotta, 2020; Moreira et al., 2013; Ramirez, Arevalo, Sotomayor & Bailon-Moscoso, 2017).

Major accidents involving the oil spill occurred in the world, such as the accident in the Gulf of Mexico in 2010, in Thailand in 2013 and recently in Brazil, in 2019 (IBAMA, 2019; ITOPF, 2019; NOAA, 2019). As a result, remediation techniques are used in the impacted areas to reduce environmental, but also socioeconomic effects (Moreira et al., 2016). The most common offshore techniques are as containment barriers, burning in situ, chemical dispersants and application of sorbent materials. Among these alternatives, the use of sorbents is noteworthy, since they are faster, easier and more efficient to interact with oil (Annunciado, Sydenstricker & Amico, 2005; Bhardwaj & Bhaskarwar, 2018; ITOPF, 2014; Moreira et al., 2011).

Sorbents can be divided into three groups: synthetic materials, such as polypropylene, which are currently the most commercialized, mineral materials such as rocks, silicas, limestones, clays and vermiculites, and natural materials, such as lignocellulosic fibers the exemple as sisal, coconut , banana, sugarcane bagasse and leafy residues (Anuzyte & Vaises, 2018; Cardoso C., Cardoso R. & Moreira, 2017; Ifelebuegu, Nguyen, Ukotije-Ikwuti, & Momoh, 2015; Kaili et al., 2019; Saleen, Riaz & Gordon, 2018; Zubaid, Tamimi & Ahmed, 2016). Although synthesized sorbents are the most used to remove oil in marine environments because they have good affinity for oil and low density, they have high cost and are not biodegradable (Wei, Mather, Fotheringham & Yang, 2003). Within this scenario, some strategies have been studied to make the use of sorbents economically viable, through studies of lignocellulosic fibers.

The use of fibers has as main advantages the low cost, low abrasiveness, atoxicity, low density, in addition to ecological and social aspects, due to the better recyclability and biodegradability (Pessôa et al., 2019). These fibers have in their physical structure a large number of pores and a high resistance to wear, which makes them excellent sorbent (Luis-Zarate, Rodriguez-Hernandez, Alatriste-Mondragon, Chazaro-Ruiz & Rangel-Mendez, 2018). In chemical composition, they contain lignin, with oleophilic characteristics, in addition to cellulose and hemicellulose, with hydrophilic content (Anuzyte & Vaisis, 2018; Wang J., Zheng & Wang A., 2013). As hydrophilicity decreases the oil's sorption power, pre-treatments are used to change its chemical and physical structure and consequently improve the interaction with petroleum (Telli & Valia, 2013).

These treatments can be thermal, mechanical, physicochemical and chemical. As examples the mechanical methods: milling (Silva et al., 2010), physicochemical: steam explosion (Hu, Wang & Li, 2018; Din, Nikogeorgos, Jellesen, Shabadi & Ambat, 2017) and chemicals: acidic solvent, usually acetic anhydride or sulfuric acid (Cheu et al., 2016; Telli & Valia, 2013), alkaline solvent, most often represented by sodium hydroxide (Soares et al., 2016) and organic solvent, recently being represented by ionic liquids (Semerci & Güler, 2018).

Ionic liquids are defined as salts composed only of ionic species that have a melting temperature below 100 °C (Alvarez, Mattedi & Aznar, 2013). There are two types of ionic liquids: Protic Ionic Liquids (PILs) and Aprotic Ionic Liquids (AILs). PILs are electrolytes formed by combining a cation with a weakly coordinated anion with interesting characteristics such as liquids over a wide temperature range, negligible flammability, negligible vapor pressure, low toxicity ("green" solvent), high densities, good thermal stability and chemistry, catalytic ability, high ionic conductivity, as well as simplicity in synthesis in relation to AILs (Peric, Sierra, Marti, Cruanas & Garau, 2014). In addition, toxicity and corrosivity have a great potential of importance when related to the pretreatment of lignocellulosic biomass (Mohtar, Busu, Noor, Shaari & Mat, 2017).

The association of ionic liquid with green chemistry is due to some of its properties, such as negligible volatility, which facilitates its recycling and reuse. This characteristic is an important advantage when compared to volatile organic compounds used in the treatment of lignocellulosic materials. Many studies have correlated the efficiency of the pretreatment with PILs with different effects on the structure and composition of the pre-treated biomass, such as: increase in the pore size and increase in the surface area, in addition to large extraction part of the hemicellulose fraction (Halder et al., 2019; Li, Asikkala, Filpponen & Argyropoulos, 2010). However, these studies use this reagent in the pre-treatment of lignocellulosic material in order to obtain greater efficiency in the process of enzymatic activity and energy production. Therefore, the use of PIL in the pre-treatment of lignocellulosic materials for use as an oil biosorbent is something innovative.

Therefore, this work aims to compare the use of residual coconut fibers (*Cocos nucifera L.*) *in natura*, pretreated with Protic Ionic Liquid (PIL) [2-HEA] [Ac] (innovative treatment) and by mercerization/acetylation (traditional treatment) as a biosorbent of petroleum spilled in the marine environment in a hydrodynamic simulation on a laboratory scale. The study of the kinetics and adsorption equilibrium were performed to determine the limiting mechanism of adsorption, as well as the maximum petroleum adsorption capacity for the coconut fibers studied.

2. Methodology

Physic-chemical characterization of the petroleum sample

The Campos Basin/Brazil petroleum was supplied by PETROBRAS (Petróleo Brasileiro S. A.) and characterized by the determination of the pour point and density according to ASTM D97 and ASTM D4052, respectively. With the value of the density, it was possible to find the ºAPI since they are inverse parameters. These parameters are investigated since they influence the dispersion of the oil in the marine environment and consequently its adsorption in the biosorbent.

Pretreatment of coconut fibers

The coconut fibers were washed with Extran at a concentration of 0.5% v/v and distilled water. Subsequently, the fibers were taken oven for 24 hours at 60ºC for complete drying, until reaching constant mass, and then crushed and sieved until reaching dimensions of 2 to 3 mm in length, in the particle size range between 5 and 10 mesh. For mercerization the crushed coconut fibers were added in NaOH solution (5% w/v) at room temperature (approximately 25ºC). This mixture was stirred through the TECNAL model TE-139 mechanical stirrer for 1 hour. Thereafter, a filtration was performed to obtain only the fibers.

The fibers retained in the filter were washed with distilled water under stirring at room temperature until pH 6 (pH of distilled water) was reached. This procedure ensures the removal of all residual NaOH in the fiber. The samples were then dried in an oven at 100°C until reaching a constant mass (Sá, Miranda & José, 2015; Miranda, Fiuza, Carvalho & José, 2015).

After passing through the mercerization stage, the coconut fibers were immersed in 300 mL of a solution of acetic anhydride and glacial acetic acid (1.5:1.0 by mass) for acetylation. The reaction was catalyzed with 12 drops of sulfuric acid and shaken with the mechanical stirrer with temperature controller (80°C) for 3 hours. The end of the procedure was like mercerization, with filtration, washing with distilled water until reaching pH 6 and oven drying at 100ºC until constant mass (Calado, Barreto & D'Almeida, 2003; Miranda et al., 2015).

A sample of the coconut fiber was added to the protic ionic liquid synthesized. The PIL used in this work was 2-hydroxy-2-ethyl acetate [2-HEA] [Ac], using the acid-base neutralization method (Alvarez, Mattedi, Martin-Pastor, Aznar & Iglesias, 2011). To react, the mixture was subjected to a stirring of approximately 206 rpm on mechanical stirrer IKA brand, model RW20, with temperature control of 80ºC ± 10ºC for 2 hours. After the determined time the mixture was filtered, and the fiber retained in the filtrate passed through the washing process with distilled water until reaching pH 6 and does not trace of [2-HEA] [Ac] in the fiber (Rocha, Costa & Aznar, 2016).

After the pretreatment procedures, the fibers were weighed (0.5 g) and conditioned in mini-containment barriers to reduce mass losses throughout the gravimetric experiments of the sorption tests. For containment were used polypropylene fabric the dimensions of 8x2x2cm.

Characterization of coconut fibers

The morphology of the fibers (*in natura*, pretreated by mercerization followed by acetylation and with ionic liquid) was evaluated. A wire of each sample (approximately 3 mm in length) was directed to the Joel Model JSM-6610 LV Scanning Electron Microscope (SEM).

The chemically treated and untreated coconut fibers were directed to infrared spectroscopy (FTIR), to confirm the pre-treatment. This confirmation is made through the identification of the functional groups present, verifying if there was chemical alteration in the fibers. This procedure was conducted on the Shimatzu brand Prestige-21 IR equipment with a spectral scanning range of 4000 to 400 cm^{-1} in the form of spectroscopic purity potassium bromide (KBr) tablets.

Kinetics test

The kinetic tests were performed with the objective of indicating the average time in which the oil saturation is completely reached in the biosorbent, to assist in its use in situ. In addition, obtaining kinetic curves that allow the modeling of experimental data to determine the adsorption speed factors and thus assist in the evaluation of mechanisms or limiting stages of adsorption.

To perform the kinetic adsorption tests in finite bath, a thermostatic reciprocating shake Dubnoff model Q226M1 was used, with approximately 126 cycles/minute and a temperature of 25ºC (average temperature of the marine environment). Initially, saline water was prepared using sea salt and ultra-pure water under stirring until the salinity reached 3.5% (35 parts per thousand).

The experiment was conducted in beakers with 95 mL of saline water and 5 mL of petroleum from the Campos Basin. The mixture was introduced into the bath and the mini barriers with the adsorbent material were added over the petroleum slick. Each experiment lasted 120 minutes during which samples were taken in triplicate at the time intervals of 5, 20, 40, 60, 90 and 120 min for the evaluation of sorption kinetics.

After withdrawal at the pre-set time intervals, the samples were weighed and frozen. Then, they were dried cold in the lyophilizer to remove all moisture present after sorption. This procedure was performed, since the coconut fibers can adsorb water, which could hinder the gravimetric analysis of the quantification of the adsorbed mass of the petroleum by the fibers. Soon after the dehydration, the samples were weighed.

The sorption capacity of the fibers was determined by Equation 1, following the ASTM F726-99 standard method for testing oil spill sorbent, where S is the adsorption capacity (g of sorbate/g sorbent), S_0 (g) is the initial mass of the fiber and S_f (g) is the final mass of the fiber after adsorption. The sorption and kinetic tests were performed by the *in natura* and pretreated fibers.

$$S = \frac{S_f - S_o}{S_o} \qquad (1)$$

The results of the kinetic test were confirmed by applying the Tukey test at the level of 5% probability. With the results of the kinetic test, modeling was performed to determine which model best fits the experimental data. Table 1 shows the models that were used to adjust the experimental data obtained in the tests: pseudo-first order and pseudo-second order. The symbols of the models can be described as follows: q_e e q_t (g/g) are the adsorption capacities of the equilibrium solute and at a time t, respectively, k_1 the velocity constant of the pseudo-first order adsorption reaction in min^{-1} and k_2 the kinetic constant of pseudo-second order adsorption in $g.g^{-1}min^{-1}$.

Table 1 – Kinetic models used for modeling.

Kinetic models	Equation
Pseudo-first order	$\log(q_e - q_t) = log\, q_e - \frac{k_1}{2,303}t$
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e}t$

Source: Authors, 2020.

Sorption equilibrium test

The sorption equilibrium test is performed to indicate the maximum amount of petroleum that the fibers can adsorb. The experimental part was according to the procedure in item previous, with selection of the time that obtained the best sorption result in the kinetics test experiment. The mass of the adsorbents, the temperature, the salinity of the water and the contact time between the adsorbent and adsorbent remained constant. The concentration of petroleum was varied for the construction of isotherms, with increasing volumes of crude oil in the range of 0 to 10 mL (with a variation of 2 mL) and varying amounts of distilled water until the volume of the oil / water mixture reaches 100 mL.

As well as the kinetic results, the data found in the isotherms also passed the Tukey test at the 5% probability level. After the construction of the sorption isotherms, the sorption equilibrium models were applied to adjust to the experimental data: Langmuir, Freundlich and Sips (Table 2). The symbols of the models can be described as follows: q is the adsorbed quantity (g/g), q_{max} is the maximum adsorption capacity of adsorbate in the solid phase (g/g), C_e is the equilibrium concentration (g/g) , K_L is the adsorbent interaction constant (L/mg), 1/n is the constant related to the heterogeneity of the surface, K_F is the Freundlich adsorption capacity constant, q_{ms} is the maximum adsorption capacity of the Sips model, b is the Sips isotherm constant, n is the exponent of the Sips model and C is equilibrium concentration in the solution (mg/L). These models were chosen because they are the most used in the literature.

Table 2 – Sorption equilibrium isotherm models used for modeling.

Isotherm models	**Equation**
Langmuir	$q = \frac{q_{max} K_L C_e}{1 + K_L C_e}$
Freundlich	$q = K_F C_e^{\frac{1}{n}}$
Sips	$q = \frac{q_{ms} (bC)^{1/n}}{1 + (bC)^{1/n}}$

Source: Authors, 2020.

3. Results and Discussion

Physic-chemical characterization of the petroleum sample

The results of the analyzes for density determination, API and flowability of the Campos Basin/Brazil petroleum are shown in Table 3. From these results, the sample used is included in the group of heavy oils (10 <ºAPI< 25) (Mothér & Júnior, 2007).

Table 3 – Densities and fluidity for Campos Basin petroleum.

Basin	**Density [g/mL]**	**Density API [ºAPI]**	**Fluidity [ºCelsius]**
Campos	0.9225	21.7	-39

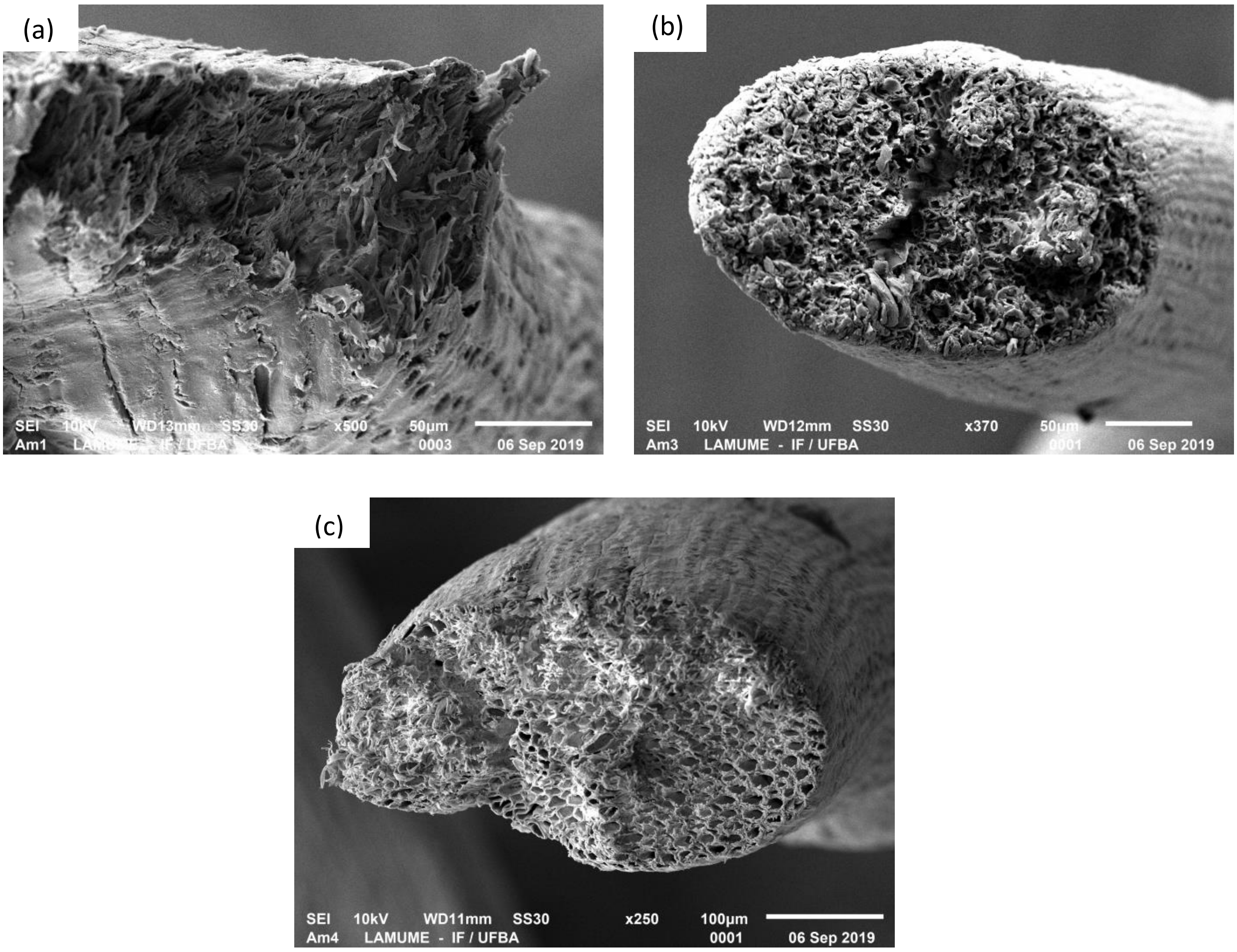
Source: Authors, 2020.

This knowledge is important because, in addition to the environmental conditions (wind and direction of the currents), the physicochemical properties also help in the determination of the remediation behavior when this contaminant is spilled in the marine environment avoiding possible damage not only to the marine community but also to the combat team responsible for the removal of this compound, tailoring a better cleaning procedure for each spill in question. The smaller the API and pour point, the faster the petroleum spreads and the higher the sorption capacity of the fiber (García-Garrido, Ramos, Mancho, Coca & Wiggins, 2016; ITOPF, 2019; Moreira et al., 2014). Therefore, it is feasible to use sorbents in petroleum spills with characteristics like the oil studied in this research.

Morphological characterization of coconut fibers

Through the SEM analysis, it was possible to observe a great irregularity in the end of the fibers natural, as well as pores, which increase the surface area and, consequently, the sorption (Figure 1a). After the treatments, it was possible to identify changes in its morphological structure, where the fiber treated with mercerization/acetylation increased the rough area at the end of the fiber from the cross section, in comparison with the fiber natural (Figure 1b). The fiber treated with PIL, on the other hand, showed a greater number of pores compared to the fiber *in natura* and treated with mercerization/acetylation (Figure 1c), resulting from the unblocking of these pores from the treatment with this organic solvent. In this way, chemically treated fibers have more spaces available for sorption from the pores and surface area free, compared to fibers *in natura*.

Figure 1 – SEM coconut fiber (a) *in natura* (b) treated with mercerization/acetylation (c) treated with PIL.



Source: Authors, 2020.

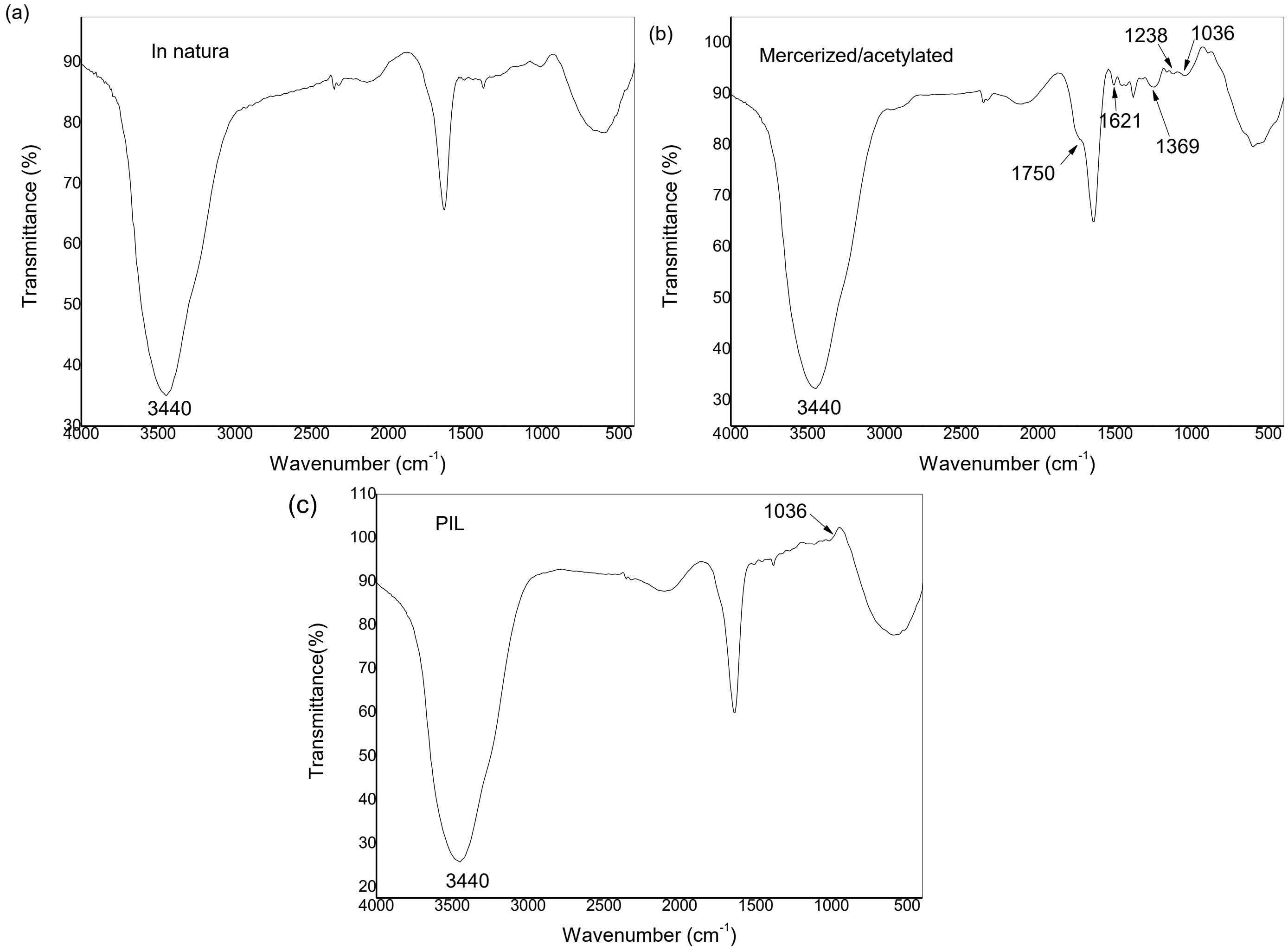
Previous studies have also observed through the SEM images enlarged pores of the lignocellulosic fibers treated with ILs. The increase in pores in maize straw after treatment with n-butylammonium, sec-butylammonium ion, n-butylammonium lactate and sec-butylammonium lactate were confirmed by Morndim-Giannetti et al. (2017) after SEM analysis. Achinivu, Howard, Li, Gracz e Henderson (2013) also observed through SEM enlargement of pores in the corn straws treated with PILs (pyridinium acetate, 1-methylimidazolium acetate and pyrrolidinium acetate). PIL-treated cotton stalks ($HBIMHSO_4$, $HMIMHSO_4$, $TEAHSO_4$ and $TEAMeSO_3$) showed changes in the structure surface, such as pore and split layer formation, increasing the surface area of biomass (Semerci & Güler, 2018).

FTIR characterization of coconut fiber

Figure 2 presents the spectra of the *in natura* coconut fibers, mercerized/acetylated and treated with [2-HEA] [Ac], where the chemical modification performed after the treatments.

The comparison between the spectra in the infrared region of *in natura* fiber (Figure 2a) and treated with mercerization and acetylation (Figure 2b) shows the appearance of the 1750 cm^{-1} band (C = O), which represents the acetate carboxyl bound to hydroxyl group of cellulose after treatment. The presence of carboxylate (1621 cm^{-1}), acetic acid or methyl acetate (1369 cm^{-1}) and stretching of the C-O group (1238 cm^{-1}) were also verified, which also show the acetylation performed.

Figure 2 – FTIR spectra of coconut fiber *in natura* (a), mercerized/acetylated (b) and treated with PIL [2-HEA] [Ac] (c).



Source: Authors, 2020.

The comparison between the natural fiber spectra and the fiber treated with PIL [2-HEA] [Ac] (Figure 2c) does not demonstrate many differences. The main one is the reduction of the intensity of the band at the wavelength 1036 cm^{-1}, which corresponds to a change in the hydroxyls (OH) binding plane, indicating a change in the chemical properties of the coconut fiber after the reaction carried out by the treatment.

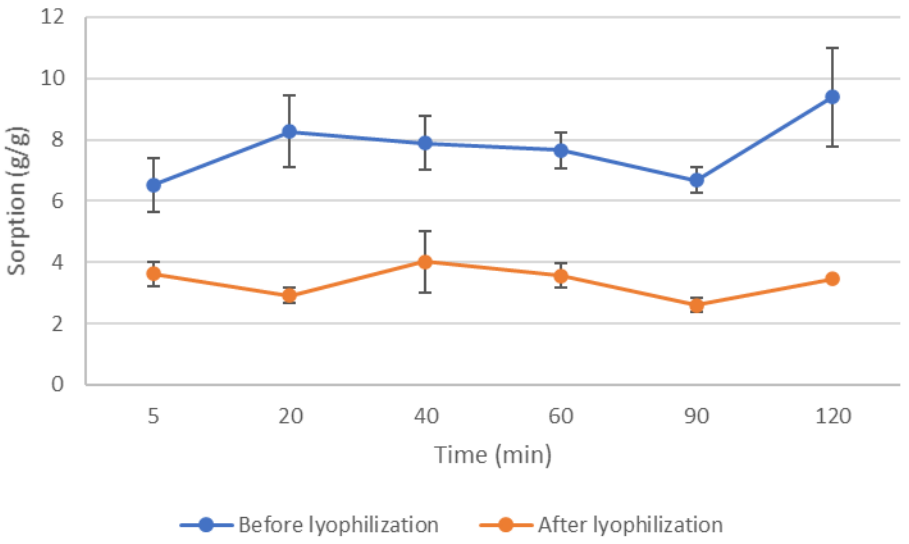
All samples showed an intense band in the 3440 cm^{-1} region typical of the O-H stretch, this functional group being characteristic of the structure of lignin, cellulose and hemicellulose. There was an increase in absorption in this band in the fiber treated with PIL, implying the removal of wax on the fiber surface (Wang et al., 2013). The presence of this band may indicate that the reactions of the treatments carried out did not reach the totality of the fiber, requiring a greater degree of acetylation and treatment with PIL, increasing the adsorption capacity of the coconut fibers.

Kinetic study

The kinetic curves resulting from this test are expressed before and after dehydrating the fiber in the lyophilizer. This comparative analysis is of fundamental importance, since the fiber has the capacity to adsorb water, interfering in the gravimetric analysis of petroleum sorption.

In the test for *in natura* coconut fiber (Figure 3) without dehydrating, there was a marked sorption up to 5 minutes and then that sorption remains practically constant. Analyzing the data using the Tukey test at 95% confidence (Table 4), after 20 min the fiber sorption does not differ until 90 min. In 120 min there was an increase in sorption, which can be explained by the simulated marine hydrodynamics, which makes the fibers have the ability to adsorb and desorb petroleum over time. After the dehydration of the fiber, it was possible to observe the interference of the highest percentage of hydrophilic structures present in the coconut fiber, which caused a large amount of the material adsorbed to be water, changing the average sorption of 6.80 g/g without dehydrating to 3.62 g/g after dehydration, within 5 minutes. In addition, the kinetic behavior of sorption over time remained practically unchanged, with sorption variation occurring only in the 40 min (increased sorption) and 90 min (desorption) times, according to the Tukey test.

Figure 3 – Fiber sorption kinetics *in natura* before lyophilization and after lyophilization.



Source: Authors, 2020.

Table 4 – Average sorption before and after lyophilization of *in natura* fibers and application of the Tukey test.

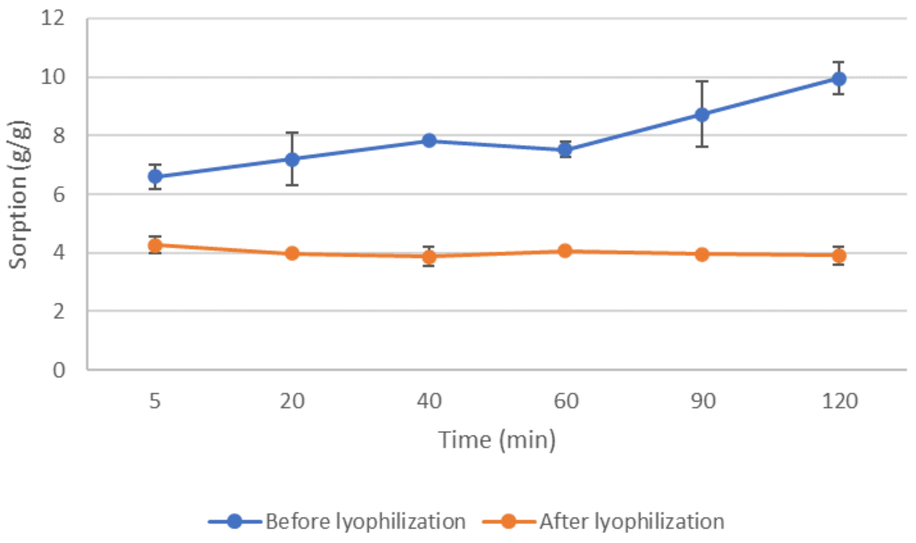
Time	Sorption (before lyophilization)	Sorption (after lyophilization)
5	6.53±0.88^{b}	3.62±0.40^{b,a}
20	8.27±1.17^{b,a}	2.91±0.24^{b,a}
40	7.89±0.89^{b,a}	4.02±1.01^{a}
60	7.66±0.59^{b,a}	3.55±0.39^{b,a}
90	6.68±0.41^{b,a}	2.60±0.23^{b}
120	9.39±1.60^{a}	3.44±0.07^{b,a}

Means followed by the same letters, in the same column, do not differ by the Tukey Test at 95% confidence.

Source: Authors, 2020.

The coconut fibers treated by mercerization and acetylation (Figure 4), before dehydration, showed a marked sorption in the first 5 minutes and then there was a small increase in the sorption that remained in balance until 60 min, according to Tukey test (Table 5). In the next two times (90 and 120 min) there was a slight increase in sorption. After lyophilization, the treated fibers had a kinetic behavior similar to those *in natura*, with no change in sorption over time, according to the Tukey test. In addition, there was a reduction in the average sorption value after dehydration (from 6.79 g/g before lyophilization to 4.26 g/g in 5 min).

Figure 4 – Fiber sorption kinetics mercerized/acetylated before lyophilization and after lyophilization.



Source: Authors, 2020.

Table 5 – Average sorption before and after lyophilization of mercerized/acetylated fibers and application of the Tukey test.

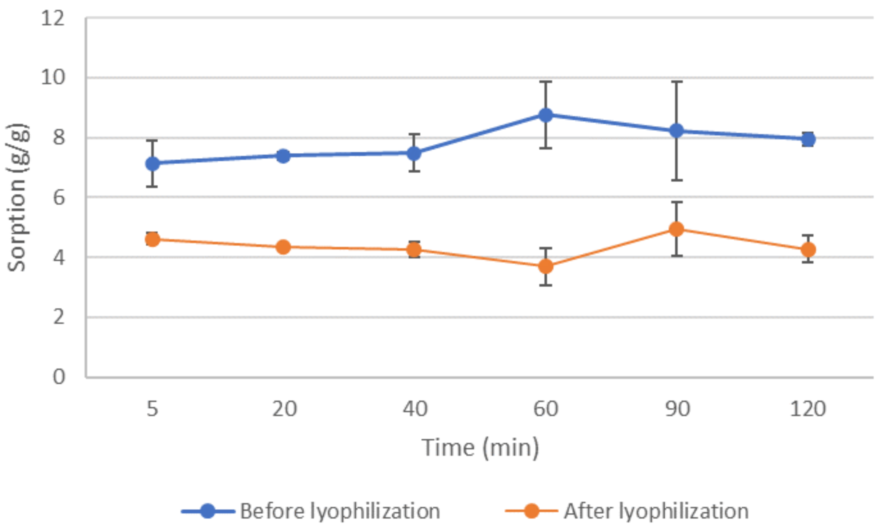
Time	Sorption (before lyophilization)	Sorption (after lyophilization)
5	6.60±0.40^{c}	4.26±0.28^{a}
20	7.20±0.89^{c,b}	3.99±0.04^{a}
40	7.83±0.02^{c,b}	3.87±0.32^{a}
60	7.53±0.20^{c,b}	4.07±0.10^{a}
90	8.74±1.10^{b,a}	3.95±0.09^{a}
120	9.95±0.55^{a}	3.91±0.31^{a}

Means followed by the same letters, in the same column, do not differ by the Tukey Test at 95% confidence.

Source: Authors, 2020.

The fiber treated with PIL [2-HEA] [Ac] had similar kinetic behavior before and after lyophilization (Figure 5), where the sorption did not change over time after 5 minutes, as can be seen from the results of Tukey test (Table 6). With cold dehydration, coconut fiber reduced its sorption result from 7.06 g/g to 4.62 g/g in 5 min. Comparing only the fibers after dehydration, it is possible to observe the similarity in relation to the sorption kinetics in all fibers (*in natura* and treated).

Figure 5 – Fiber sorption kinetics PIL before lyophilization and after lyophilization.



Source: Authors, 2020.

Table 6 – Average sorption before and after lyophilization of PIL fibers and application of the Tukey test.

Time	**Sorption (before lyophilization)**	**Sorption (after lyophilization)**
5	7.13±0.78^{a}	4.63±0.20^{a}
20	7.39±0.14^{a}	4.34±0.08^{a}
40	7.47±0.62^{a}	4.24±0.26^{a}
60	8.77±1.11^{a}	3.70±0.63^{a}
90	8.22±1.64^{a}	4.95±0.88^{a}
120	7.95±0.21^{a}	4.28±0.43^{a}

Means followed by the same letters, in the same column, do not differ by the Tukey Test at 95% confidence.

Source: Authors, 2020.

From these results, it can be concluded that the lyophilized fibers after the treatments obtained the same equilibrium behavior in the sorption after 5 min of contact. The *in natura* fiber after lyophilization was the only one that did not show the equilibrium behavior, which can be justified by the greater amount of hydrophilic structures that interfere in the adsorption process since the spaces are occupied not only by oil, but also by water. Even so, the *in natura* fiber achieved the most significant sorption result in the first 5 minutes, as well as the other fibers studied. Therefore, 5 min of contact between the adsorbent and the adsorbent has better efficiency in adsorption, since this time was the one that obtained the most representative sorption in relation to the other studied times. These results are satisfactory since a minimum contact time between the adsorbent material and the petroleum (only 5 minutes) is required to remove this contaminant in a marine environment. Thus, it reduces the time that petroleum is in the ocean and spreads to more sensitive areas. In addition, coconut fiber sorption technology brings less risk to other types of contamination, such as possible losses of the biosorbent in the ocean, due to the short time in the marine environment suffering interference from marine hydrodynamics, as well as less contact time of technology operator with toxic oil.

Research published in the literature indicates that the adsorption of oil by biomass increases significantly in the first 5 minutes, then there is an insignificant increase until equilibrium (Abdelwahab, Nars & Thabet, 2017; Annunciado et al., 2005; Din et al., 2017; Luis-Zarate et al., 2018; Nwadiogbu, Ajiwe & Okoye, 2016). This can be explained by the initial amount of pores and available surface in the fibers, which are occupied over time (through the interaction of oil and water with the available functional groups), reducing the availability and consequently the sorption capacity.

Performing an analysis of the influence of the treatment in the time of 5 minutes (the time considered with the best applicability), it can be seen that the fibers treated with the organic solvent PIL (average sorption 4.63g/g) have a sorption capacity higher than the other fibers studied. *In natura* fiber (average sorption of 3.62 g/g) has less sorption capacity and fiber with mercerization/acetylation treatment (average sorption of 4.26 g/g) has sorption with intermediate values (similar to that of natural fiber and treated with PIL), according to the Tukey test (Table 7).

Table 7 – Sorption average showing the influence of the treatment on the fibers in the time of 5 minutes after lyophilization using the Tukey test.

In natura	**Mercerized/acetylated**	**PIL**
3.62 ± 0.40^{b}	$4.26 \pm 0.28^{a,b}$	4.63 ± 0.20^{a}

Means followed by the same letters, in the same column, do not differ by the Tukey Test at 95% confidence.

Source: Authors, 2020.

The chemical treatments on the fibers allowed the reduction of the proportion of hemicellulose/cellulose contained in the fiber, in addition to reducing the proportion of extract/cellulose, resulting in an increase in surface porosity (confirmed by scanning electron microscopy analysis), which can have led to an increase in the active surface area, thus increasing the adsorption rate.

Abdelwahab et al. (2017) performed acid and alkaline treatment on palm fibers and the sorption efficiency of the biosorbent remained almost constant compared to the untreated fiber. They identified this behavior of the treated fibers as acid and base removed compounds that remain on the outer surface of the fiber, such as lignin and waxes, reducing the functional groups available to interact with the oil.

However, Nwadiogbu et al. (2016) stated that at all sorption times studied, the acetylated maize cob adsorbed more oil than the native maize cob. This result may be due to the reduction in water adsorption capacity of the acetylated maize ear, increasing its potential to adsorb more oil in an aqueous medium (Nwadiogbu et al., 2016). This behavior was similar in mercerized pineapple leaves (Cheu et al., 2016), acetylated *Dacryodes edulis* leaves (Nnaji, Onuegbu, Odokwe, Ezeh & Ngwu, 2016) and acetylated banana fibers (Telli & Valia, 2013).

Studies with natural fibers show satisfactory results in the oil sorption capacity. As an example, the banana stem fiber, with 4.5 g/g adsorbed (El-Din, Amer, Malsh & Hussein, 2018), palm fiber adsorbing 5.31 g/g (Abdelwahab et al., 2017) and corn cob fibers that adsorbed 4.78 g/g (Nwadiogbu et al., 2016).

The pseudo-first order and pseudo-second order models were used to correlate the experimental data. An analysis of the graphs was carried out, as well as of the correlation coefficients (R^2). The model with R^2 close to 1 indicates that the experimental data agrees with the theoretical data and from then on it becomes the most appropriate model. Table 8 shows the kinetic parameters calculated for each of the models studied.

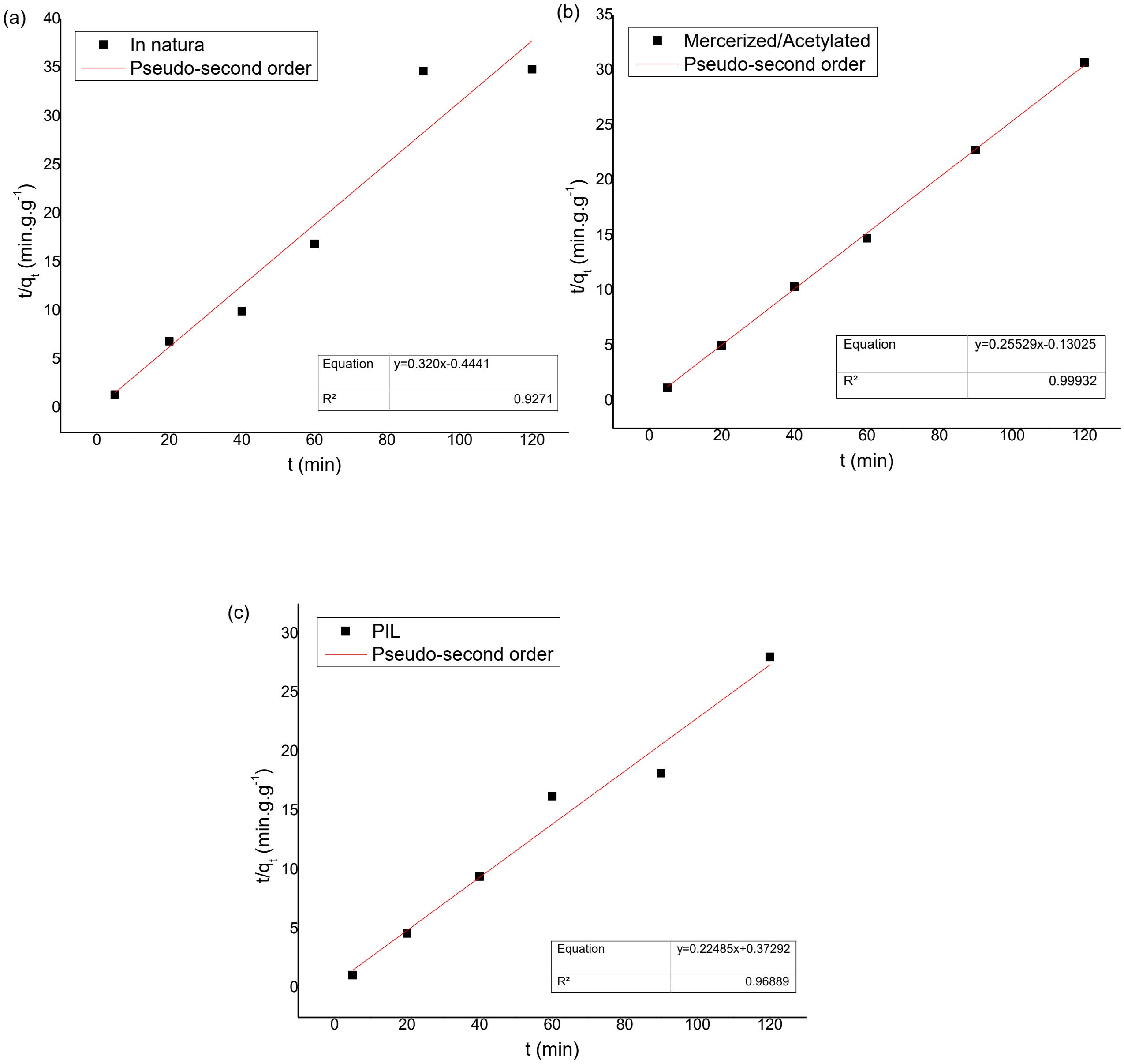
Table 8 – Kinetic model parameters of the fibers *in natura*, mercerized/acetylated and PIL.

Parameters of kinetic models					
		Pseudo-first order		**Pseudo-second order**	
Fibers	q_e (g/g)	K_1(m^{-1})	R^2	K_2 (m^{-1})	R^2
In natura	3.62	0.03480	0.8181	0.2306	0.9270
Mercerized / acetylated	4.26	0.03503	0.8256	0.5004	0.9993
PIL	4.63	0.03389	0.8586	0.1356	0.9680

Source: Authors, 2020.

The values of R^2 were higher for the pseudo-second order model, confirming that it fits better to the experimental data for all the studied coconut fibers. This better adjustment to the pseudo-second order mechanism is also related to the proximity obtained by the experimental q values with the q values calculated by the models (Figure 6), as can see from the graphs of t/qt as a function of t. The points in the graphs represent the data obtained experimentally and the solid lines represent the values generated theoretically from the linearized kinetics.

Figure 6 – Graphs of the correlation of experimental data of fibers *in natura* (a), mercerized/acetylated (b) and treated with PIL (c) with the pseudo-second order model.



Source: Authors, 2020.

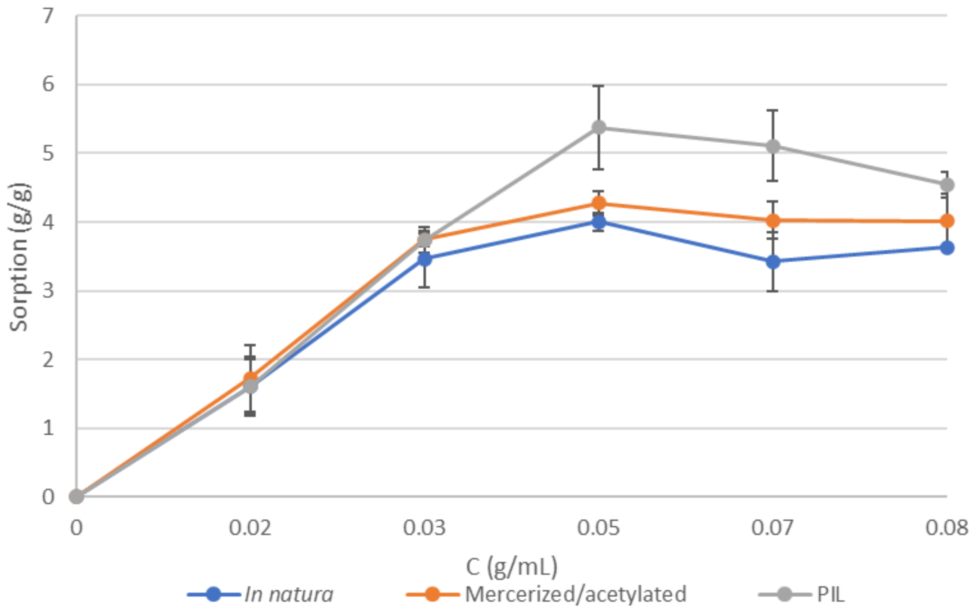
With the pseudo-second order model defined, it is believed that the limiting mechanism of the global petroleum adsorption process by the studied fibers is chemisorption, involving electron transfer with formation of covalent forces between adsorbate and adsorbent. The result of higher sorption of the treated coconut fibers can be explained by the chemical, structural and morphological modification presented in relation to the natural fibers. The larger amount and density of pores resulting from the removal of chemical constituents, such as lignin and hemicellulose, waxes and impurities, made the pores of coconut fibers clear and consequently increased the surface area for interaction with petroleum. The results were according to the SEM images, where the fibers treated with PIL [2-HEA] [Ac] presented larger pores and obtained higher oil sorption capacity, suggesting their use in an oil leak similar to that studied in this research.

Sorption equilibrium test

From the kinetic study, the time of 5 minutes was chosen to proceed with the sorption equilibrium tests. The results obtained with the equilibrium sorption of petroleum with *in natura* coconut fibers, mercerized and acetylated and treated with PIL are presented (Figure 7). According to the graphs, it was observed that coconut fibers *in natura* initiated a significant inalterability in sorption from the spill of approximately 4.0 mL of oil in 96 mL of saline water. As for fibers with chemical treatments, this behavior occurred from approximately 6.0 ml of oil spilled in 94 ml of saline water to 0.5 g of fiber.

Thereafter, the fibers with treatments have the ability to adsorb a greater amount of petroleum compared to the *in natura* fiber, due to the superficial changes that have made the spaces more available to interact with the crude oil.

Figure 7 – Sorption equilibrium curve for fibers.



Source: Authors, 2020.

The experimental results of the adsorption equilibrium were correlated using the Langmuir, Freundlich and Sips models. The parameters of each equilibrium isotherm model and the correlation coefficients are shown in Table 9. The model that best fitted the experimental equilibrium data was the Sips isotherm for all fibers studied. For the *in natura* fiber the R^2 found was 0.9744, for the fiber treated with mercerization/acetylation the value of R^2 0.9925, whereas the fiber treated with PIL found R^2 0.97. These values indicate that when applied low oil concentrations, the adsorption of coconut fiber is reduced to the Freundlich isotherm (multilayer), whereas, at high concentrations, the model predicts an adsorption capacity in monolayers (Langmuir). For this reason, the correlation coefficients of the Langmuir and Freundlich models are statistically acceptable but are not appropriate to describe the process of adsorption of oil by coconut fibers individually.

Table 9 – Parameters of the equilibrium sorption models of *in natura*, mercerized/acetylated and PIL fibers.

Model parameters										
	Freundlich			**Langmuir**			**Sips**			
Fibers	R^2	K_F	n	R^2	K_L	Q_{max}	R^2	Q_{ms}	B	n
In natura	0.856	9.337	2.918	0.899	47.661	4.902	0.974	3.679	2.85E8	4.783
Mercerized/ Acetylated	0.888	10.928	2.757	0.931	44.525	5.531	0.993	4.118	3.63E6	3.692
PIL	0.839	17.573	2.101	0.884	26.829	7.641	0.971	5.810	900.27	2.461

Source: Authors, 2020.

In low concentrations, it is possible to verify a more accentuated adsorption, resulting from the multilayer adsorption behavior, where petroleum and fiber interact with the petroleum itself. As the concentration increases, the adsorption is reduced to equilibrium, since the interaction is monolayer, with fewer functional groups available for the interaction of adsorbent and adsorbent, since the interaction of oil is only with coconut fiber.

4. Conclusion

Based on the results found, it can be said that chemically treated coconut fibers (*Cocos nucifera L.*) are more efficient than *in natura* to be used in the remediation of oil spilled in marine environments. The fiber treated with PIL [2-HEA] [Ac] obtained greater petroleum sorption, followed by the fiber treated by mercerization/acetylation and finally the fiber *in natura*, which are explained from the morphological and FTIR characterizations of the fibers.

Kinetic analysis showed that it takes a short time (only 5 minutes) to remove petroleum from marine environments by biosorbents. The pseudo-second order model better represented the experimental data for the three samples under study, assuming that the limiting step of the adsorption process is chemisorption. As for the experimental results of the adsorption equilibrium, the model that presented the greatest correlation factor was the Sips, indicating the existence of more than one type of adsorption site (monolayers and multilayers).

The use of pretreatment of natural fibers with PIL becomes more attractive than conventional treatments (mercerization and acetylation). This happens, since coconut fiber treated with PIL brings slightly more satisfactory sorption results, has simplicity in the synthesis of solvent [2-HEA] [Ac], are not toxic and is a solvent that can be reused, although it is necessary conduct an economic viability study.

Therefore, the results found in this study reveal that coconut fibers treated with PIL have adequate adsorption capacity to be used as a petroleum adsorbent in aqueous effluents, with the advantage of being obtained from a renewable and residual source, in addition to the use solvent considered green solvent.

In the development of this work, some items were interesting to be approached in more detail. As suggestions for future work, it is recommended, in addition to the economic viability study of coconut fiber treated with PIL, the evaluation of the possibility of reusing the fibers in a new cleaning of marine environments impacted by oil, tests with other types of oils, others surface characterizations of the treated fiber in order to understand the modification and adsorption process and evaluation of the interference of temperature and salinity in oil sorption by the studied biofibers.

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Verônica Lima da Silva – 5%

Ana Carolina Lima Eyng Meirelles – 5%

Silvana Mattedi – 15%

Ícaro Thiago Andrade Moreira – 20%

Ana Katerine de Carvalho Lima Lobato – 20%