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Evaluation of ionic liquid treated sisal (*agave sisalana*) fiber as sorbent in biodiesel spill

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Abstract. The global economic development continually demands the use of energy resources, among which various types of oils are widely used. Despite their undeniable economic importance, environmental accidents with these occur frequently. Thus, the search for efficient and low-cost mitigating measures is recurrent. In this context, techniques that use natural adsorbents, such as vegetable fibers, have been studied, since they combine efficiency, selectivity, low cost and sustainability. Studies have been carried out using various types of fibers, natural or chemically treated. The interest in treating the fiber lies in the fact that, changing the chemical structure of the fiber, its oil sorption capacity is increased. Due to the offered advantages, an alternative and promising type of surface treatment using ionic liquids was performed, to the detriment of traditional treatments. Thus, the technical feasibility of the use of sisal fiber treated with ionic liquid for adsorption of biodiesel was studied.

1. Introduction

The use of different types of oils as energy sources began many years ago and these are extremely important for world economic development. Despite the predominant use of fossil fuels and their derivatives, the search and encouragement for the use of cleaner energy sources, such as biodiesel, is increasing. The unstoppable demand for any type of fuel, however, leads increasing problems due to its production, transportation and use. It is undeniable that the burning of biodiesel produces the least amount of pollution, when comparing to petroleum subproducts. However, spills of this biofuel in the marine and / or terrestrial environment are as dangerous as those of other oils, not only causing great damage to the local fauna and flora, but also having a negative impact on the regional economy, leisure and tourism. Therefore, technologies that can reverse this situation in a Sustainable and low cost way[1-4] are extremely necessary, which demonstrates the importance of studies in this field.

Numerous measures to reverse this type of accident are currently known. Mechanical, physical, chemical and biological processes are already employed by oil production and refineries, which aim to recover, remove or degrade the spilled oil. Among these processes, the most used ones are natural dispersion, containment and cloning, on-site burning, adsorption and use of detergents and dispersants. The use of adsorbent materials in this context, allows the oil to be removed in an efficient and selective manner, allied to a low cost of operation, and even sustainable, depending on the material used in the recovery.[5]

The adsorption phenomenon can be defined as a process in which a substance called adsorbate (solid, liquid or gaseous) binds, physically or chemically, to the surface of another solid substance known as adsorbent. Adsorption has been under increasing interest of researchers, since this technique has been shown to be quite efficient in the treatment of organic and heavy metal effluents[6,7]. The adsorbent materials used can be of synthetic or natural origin and are classified as organic minerals, organic synthetic and natural sorbents, depending on the type of material used[8,9]. However, it is the use of natural materials that have been the focus of countless researches lately, because besides presenting high adsorption capacity, they are biodegradable, obtained through renewable sources, of low cost and widely available in the market. The fibers, which are of vegetable origin, are sustainable sorbent materials, which can be justified due to their biodegradability and the possibility of reuse. Moreover, these materials are highly efficient in oil adsorption, due to their great porosity and hydrophobic nature3. Brazilian areas for agricultural activity are quite extensive and the large production of these consumer goods provides the country with a wide possibility of using natural fibers as adsorbents. In this context, sisal (agave sisalana) fiber, for example, can be widely used in the sorption of oil spilled in the environment, due to its high production in Brazil and the enormous amount of waste generated. Some researchers have developed studies on the use of natural fibers as oil adsorbents and have proved the technical efficiency of using these materials to remedy the problem in question. The vegetable fibers are composed of three main components, being them cellulose, hemicellulose and lignin. The first two, due to the large amount of hydroxyl molecules (-OH) in its structure, have a hydrophilic character. The lignin is responsible for the degree of hydrophobicity of the fiber. Thus, in order to improve the sorption capacity of vegetable fibers by oils, surface treatments are used to modify the chemical structure of these adsorbent materials, making them more hydrophobic[10-13]. In the treatment of vegetable fibers for oil sorption, the traditional techniques are acetylation and mercerization. Despite their efficiency, the chemical agents used in the process present disadvantages such as toxicity, aggressiveness on the fibers and high cost. In this scenario, the ionic liquids appear as a new option of chemical treatment of fibers, due to low volatility, thermal stability, besides the possibility of adjustment of properties, such as polarity and miscibility. Researches have shown the efficiency of the ionic liquids in the dissolution and modification of the cellulose [14-17], however few works were performed with pre-treatment for natural adsorbents.

2. Methodology

2.1 Materials
The ionic liquid (IL) 2-hydroxy ethylammonium acetate ([2HEA] [Ac]) was synthesized for this work, and its structure was confirmed by NMR 1H, and FTIR, which was synthesized for this work. The biodiesel used was provided by Process Separation Laboratory (UFBA) [18]. It was synthesized from soybean oil by a methanolic synthesis route18. Sisal (agave sisalana) fibers were supplied as sisal ropes by APAEB a cooperative of small rural producers from Valente, Bahia, Brazil.

2.2 Fiber treatment
The treatment of the sisal fibers was done in a thermostatic bath for 2 hours at 353.15K, with the immersion of a certain amount of fiber [14] in rope form in the solution of ionic liquid and distilled water (0.75 g IL/g solution). After the treatment time, the fibers were washed with distilled water until wash water had a neutral pH. Finally, the treated fibers were placed in a greenhouse at 333.15K for 24 hours. The surface morphology was studied through SEM images before and after treatment.

2.3 Kinetics and adsorption equilibrium
To evaluate biodiesel sorption by the treated fiber, 0.5g of the fiber in a solution of biodiesel/water was placed in a thermostatic finite bath at 303.15K for 1 hour .The mass of the fiber was weighed before and after the sorption process, which was calculated by the following mathematical expression:

$$S = \frac{(m_f - m_i)}{m_i} \quad (1)$$

For adsorption kinetics, the fiber was kept in contact with the oil at different times (5 to 90min), while in equilibrium experiments the amount of oil in the solution (1 to 10ml) was varied. These tests were done with the treated and untreated fibers and the sorption was calculated in all cases through

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Equation 1. These tests have the objective of evaluating the mechanism of the adsorption process that occurs between the fiber and oil, besides measuring the maximum amount of oil that can be adsorbed.

3. Results and discussion

3.1 Surface modification

SEM images of the treated and untreated fibers are shown in Figures 1-2. It could be observed that the treatment was effective and removed wax and impurities from fiber surface thus altering the surface area and exposing the internal fibrillar structure enhancing oil sorption by the fiber.

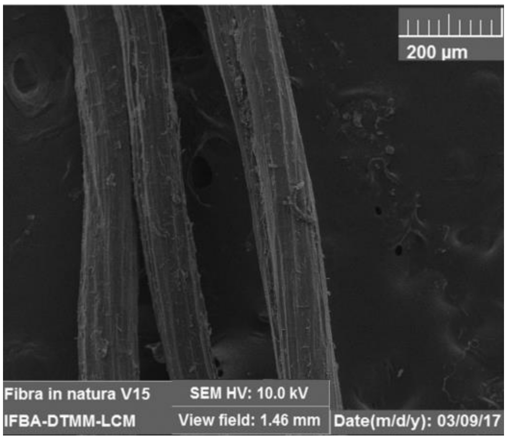

Figure 1. SEM micrograph of untreated sisal fiber.

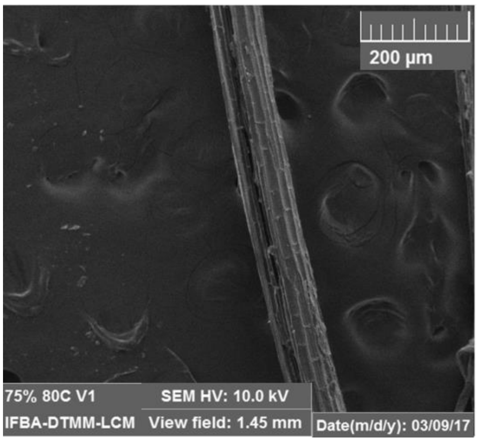

Figure 2. SEM micrograph of treated sisal fiber.

3.2 Sorption kinetics

The adsorption kinetics tests, using biodiesel, were performed for treated and untreated sisal fibers. Based on Figure 3, it can be inferred that the use of vegetable fibers to adsorb oils lighter and less viscous than petroleum, in this case biodiesel, is also efficient. In addition, an increase in the sorption of this oil was obtained by using the treated fiber, demonstrating the effectiveness of the treatment with the ionic liquid.

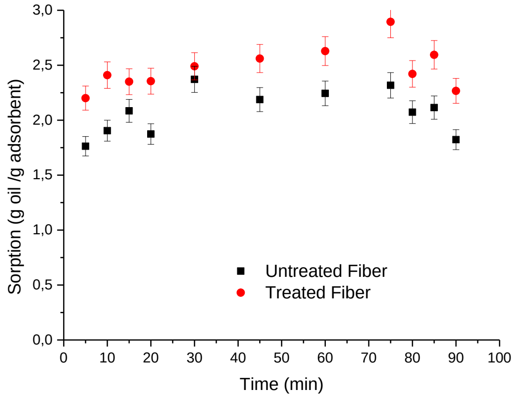

Figure 3. Sorption Kinetics – Biodiesel.

The modeling of the experimental kinetic data was done through three models: pseudo-first order, pseudo-second order and intraparticular diffusion[19-22]. These models were chosen because they are the most used in the literature and have good correlations in general. The three models were applied to the experimental data, and the best fit occurred with the pseudo-second order model. The correlation factors presented a very good value, besides small errors for the calculated parameters, as can be observed in figures 4 and 5.

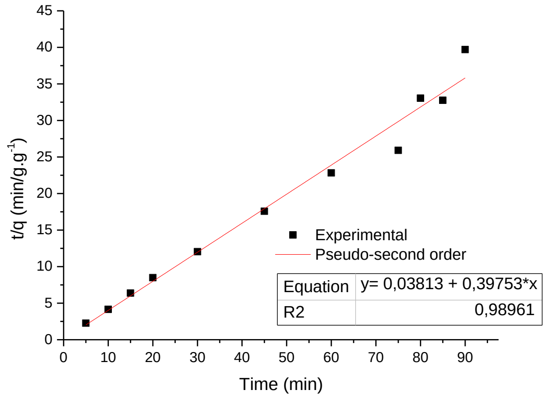

Figure 4. Kinetic model– treated fiber/ biodiesel.

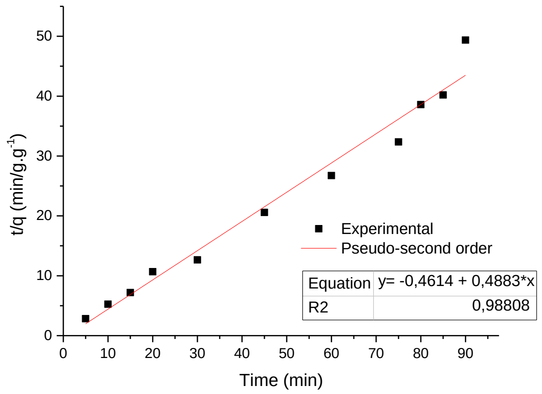

Figure 5. Kinetic model – untreated fiber/ biodiesel.

This result indicates that the adsorption occurred between sisal fiber and biodiesel was a chemical adsorption, and the reaction itself is the limiting stage of the process.

3.3 Equilibrium of sorption

In the equilibrium tests, the amount of biodiesel in a final solution of 100ml was varied. From these results, it is possible to identify the maximum degree of sorption by the fiber, important information when defining the necessary amount of adsorbent to suck the spilled oil. In the figures 6 and 7, the equilibrium data for the treated and untreated fibers were presented, as well as the modeling of these data through four models: Freundlich, Langmuir, Sips and Toth. The first two models were chosen because they are the most traditional, while the last two are adaptations of these first, correcting some of their failures[23,24].

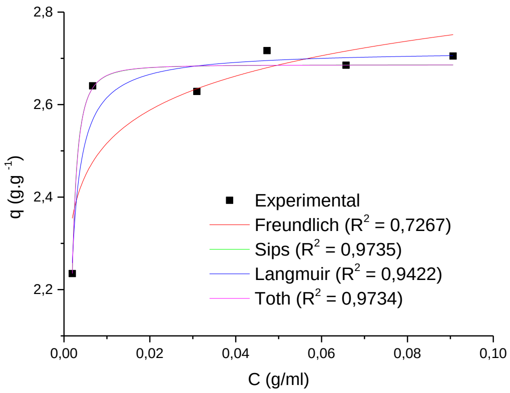

Figure 6. Equilibrium of sorption – treated fiber.

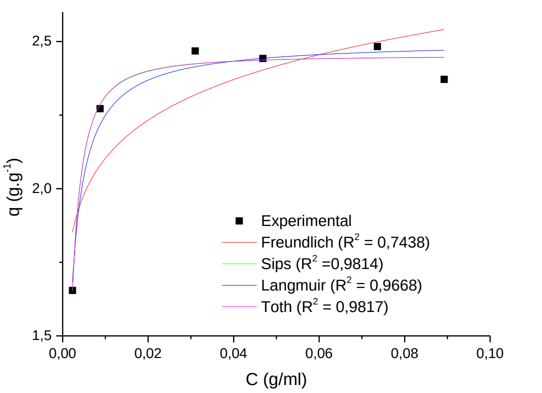

Figure 7. Equilibrium of sorption – untreated fiber.

Among the models used, those of Sips and Toth were the ones that best adjusted the experimental points, whose curves are practically superposed. While the Toth model minimizes the deviations between the experimental and theoretical points present in the Langmuir model, the Sips model is a combination of the Freundlich and Langmuir models. Depending on the adsorbate concentration, the Sips model falls into one model or the other. In the present case, in which there is a high concentration, the Sips model relies on the Langmuir model. Because of this, it is that the Sips and Toth curves are practically overlapping and the Langmuir model also presented a good value for the correlation factor, but lower than for Sips and Toth. These results suggest that the adsorption, in this case, happens in monolayers, besides indicating a heterogenous adsorptive surface, from the energetic point of view.

4. Conclusion

Considering the results obtained, the use of new solvents, such as ionic liquids, less toxic and less aggressive, proved effective in the treatment of these fibers, providing an increase in oil sorption. Because it is a very small area still studied, the use of other ionic liquids, combined with new treatment conditions, could produce even better results. In addition, it can be concluded that the use of vegetable fibers for adsorption of oils, which is already studied mainly for petroleum, is also effective in the case of oils that are lighter and less viscous. This signals that studies with these sorts of adsorbents should continue in order to improve this technique and make it as viable as using synthetic adsorbents. It was also possible to conclude from this work that the adsorption occurred between sisal fiber and biodiesel was of the chemical type, which reduces the possibility of desorption, since the interactions between the components in question are strong. Finally, the fact that adsorption occurs in monolayers is favorable, as it also decreases the level of desorption, and the presence of active sites with different energies allows the effective interaction of the adsorbent with different types of adsorbates.

5. References

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