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Kinectics of Oil Adsorption by Banana Fibers as Remediation of Oil Spills

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ABSTRACT

Oil is still the main source of today's power generation, however during its production, exploration, transportation, distribution and storage spills may occur, causing serious damage to the environment and the local economy. To minimize the effects of spills various separation processes are used, among them, the adsorption. Among the sorbent materials, natural fibers are noteworthy because they were obtained from renewable sources, present high sorption capacity and low cost. The adsorbent material used in this work is the fiber obtained from the pseudostem of banana of variety silver (*Musa paradisiaca L*). After the banana plant produce fruits and generate a new plant (another banana that will produce fruit) it is cut and left on the plantation. The pseudostem can be used to withdraw the fibers. In this work, the obtained banana pseudostem fibers were characterized by thermal analysis, optical microscopy, scanning electronic microscopy and chemical composition. The fibers were used as an adsorbent of two oils of different viscosities to construct the adsorption kinetics curves at 40°C in a pre-defined time intervals until equilibration time. For both studied oils, the equilibrium was obtained quickly (maximum of 50 min for the less viscous oil). The sorption capacity and kinetics of adsorption are dependent of the oil characteristics. Obtained results show that the fibers have the highest sorption capacity for less viscous oil however it has a slower kinetics and takes a longer time to saturate.

KEY WORDS*:* Oil, spills, adsorption, natural fibers, banana pseudostem fiber.

1. INTRODUCTION

Oil is the main source of energy today also used as raw material for production of various products such as plastics, solvents, pharmaceuticals and many other essential products nowadays. Despite being associated with the economic development of countries, oil is also related to pollution of the marine environment, as during the activities of exploration, transportation, distribution and storage of oil spills actually did occur. Although in recent years statistics show a drop in the number of accidents involving oil spills at sea, they continue to occur.

Oil spills into the sea can cause great damage to marine organisms and the whole environment in general, with a severe bad impact on quality of life of the local coastal community.

According to Milanelli (1994), the severity and extent of the environmental damage resulting from the release of oil into the marine environment depend on several factors that act simultaneously as the spilled amount; the physical, chemical and toxicological properties of the released product; the distance between the source of the leak and the affected areas; the amount and extent of affected areas; the hydrodynamics characteristics of the sea in the region; the degree of sensitivity of affected ecosystems; the socio-economic importance of the affected areas; the procedures adopted for the cleaning of affected environments and the efficiency and speed of containment and remediation procedures.

Currently, there are several techniques and equipment to combat, contain and recover an oil spill at sea. Lopes, (2007) reports that from an environmental point of view, an efficient cleaning process is one that enables the removal of contaminants with minimal additional impacts on the ecosystem achieved and promotes environmental recovery in the shortest possible time. Among the leading techniques for remediation of aquatic oil spills highlights appears for the use of floating containment barriers, the mechanical retrieval by skimmer, the use of dispersing and gelling agents, and the use of sorbents.

In recent years, there were increased the supply of new products with sorbent properties for specific use in oil spills. The sorbent materials are added to the oil, facilitating its subsequent removal from the environment. These materials are developed based on the principles of adsorption. The adsorption can be classified according to the type of bond, physical (physisorption) or chemical adsorption (chemisorption). Most separation processes is based on physisorption. Adsorption is function of the degree of hydrophobicity, porosity, molecular structure of the compounds and changes in volume of the adsorbent material (Ruthven, 1984). The sorbent materials currently used may be classified as polymers, organic mineral or natural fibers. The use of natural fibers in the adsorption processes has attracted the interest of many researchers around the world, especially in Brazil, because of its agricultural vocation.

In this study, the investigation remediation method is based on the use of biomass as a sorbing agent, which concentrates on its surface molecules of the fluid. The chosen biomass was obtained from the fiber of banana (silver variety) pseudostem (*Musa paradisiaca L.*) due to its wide availability in Brazil, especially in Bahia which is one of the largest banana producers in Brazil. (Sebrae, 2008).

2. MATERIALS AND METHODS

Preparation of biomass: The banana pseudostem fibers were obtained by cutting the stem and then brushing with a wire brush. The fibers were washed with water and allowed to dry at room temperature (~27°C). The fibers were cut between 1.0 and 2.0 mm, the particle size appropriate for testing as discussed by Santos, (2007) and Tsai, (2001).

Fiber Characterization: Thermogravimetric analysis (TGA) was performed on Seiko TGA-50H equipment under a nitrogen atmosphere, flow 50 mL per minute and a heating rate of 10°C per minute in a range between 20 and 800°C.

The fiber image with 10-fold increase on the natural size was obtained through an Optical Microscope ZEISS model AX10Lab.A1 coupled with a Digilab camera.

The scanning electronic microscopy was performed on a Jeol equipament JSM-6610LV model. The sample was metallized with gold in a Denton Vacuum Desk V.

The chemical composition of the fiber was performed according to the method described by Van Soest and Wine (1967). This method allows the separation of fiber in cell content and cell wall. It determines the soluble fractions in neutral and acid detergent.

Characterization of Oil: Two oils were used, the oil 1 was produced in Reconcavo region, Bahia and supplied by the Field-School Project evolving the National Petroleum and Gas Agency (ANP) and Federal University of Bahia (UFBA) and the oil 2 was produced by Petrobras in Sergipe/Brazil.

Oil 1 was characterized in a previous work (Barreto, 2011) and Oil 2 had its density determined in a Anton Paar densimeter DSA5000, with uncertainity of 0.00001g/cm^3 and the viscosity was obtained using a Anton Paar viscometer SVM3000, with uncertainity of 2%, both in the temperature range of 25 to 70°C with 5°C intervals.

Kinetics of adsorption: In this adsorption study, the adsorbent is the banana fiber and the oil is the adsorbate. To evaluate the kinetics of sorption of the fiber, the experiments were performed using 5 mL of oil, 95 mL of water and 0.5 mg of fiber (measured in a precision gravimetric balance Shimadzu AX200 with precision of ±0.0001 g). The mixture water, oil and fiber was placed in a bath Dubnoff Q226M1, from Quimis/Brazil, temperature 40°C (±2.0°C), and agitation of 180 rpm. After fixed time for each sample, the mixture was vacuum filtered with the aid of a quantitative filter paper (pore diameter of 8μm) and the product obtained, consisting of the fiber and the material adsorbed was weighed.

The values obtained were used to calculate the mass balance, in which the sorption was expressed as the amount of oil sorbed per mass of dry fiber according to Equation 1.

$$S = \frac{(m_t - m_o)}{m_o} \qquad (1)$$

Where S is the fiber adsorption capacity (expressed in $g_{adsorbate}/g_{adsorbent}$), m_t is the total mass of the sample after sorption in g and m_o is the dry fiber weight in g. The values obtained were used to construct the adsorption kinetic curves.

3. RESULTS AND DISCUSSION

Fiber characterization: The result of thermo gravimetric analysis (Fig.1) shows that the material starts losing water at ~ 22°C. and that the fibers begin to decompose above 236°C. In Fig.2, it is shown the surface of the fiber observed with 10 times magnification through an optical microscope.

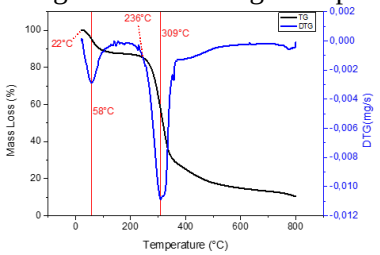

Figure.1. Thermo gravimetric analysis.

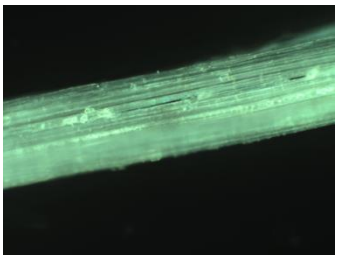

Figure.2. Optical microscopy of banana fiber (x10)

The scanning electronic microscopy of a cross section of the fiber is showed in Fig.3. It could be observed elliptical channels in the axial direction. The opening of the pores at the end of the cross section of the fiber, was found to have 25 μm on the *x* axis (Fig.3a) and 14 μm on the *y* axis (Fig.3b). The sorption capacity of this fiber can be attributed, among other factors, the existence of these pores.

The major components of natural fibers are cellulose, hemicellulose and lignin. According to Silva (2009), hemicellulose is quite hydrophilic, contains considerable degree of branching of their chains with highly amorphous nature while the cellulose and lignin structures have hydrophobic character, which makes the oil adsorption by the fiber. Analysis of the chemical composition of the fiber determined the composition (expressed in weight fraction in percentage) of lignin, cellulose and hemicellulose present in the constitution of the material revealing that 48.00% of the material composing the fiber has oleophilic features and 40.08% material has hydrophilic characteristics.

Figure.3. Scanning electronic microscopy (with a magnification of 800x),(a) the opening of the pores on the x axis was marked (b)the opening of the pores on the y axis was marked

Table.1. Chemical composition in weight fraction in percentage (%)

FDN	FDA	Lignin	Cellulose	HEM
88.08	48.00	11.63	36.37	40.08

(FDN) and (FDA): FDN = hemicelluloses + FDA (without pectin); FDA (acid detergent) = cellulose and lignin soluble + insoluble in alkali of the pectin; HEM=hemicellulose

Characterization of Oil: The oil characterization data are shown in Table.2. As it has WAT (wax appearance temperature) of 34°C, the experiments were performed in 40°C temperature to ensure that the oil was fluid. Oil 2 has a higher density, lower WAT, viscosity and API degree with respect to oil 1. It is more light sample of oil.

Table.2. Oil physical properties.

Sample	WAT /°C	Viscosity at 40°C /cp	Density at 40°C/gcm^{-3}	°API
Oil1	34*	10.49*	0.8064*	40.07*
Oil2	>25	9.384	0.8473	32.2

Kinetics of adsorption: Adsorption kinetics curves were built with the values obtained in the experiments (Fig.4). The oil sorption capacity of the fibers was monitored from 0 to 60 minutes. As expected, the adsorption capacity of the fibers raises with increasing contact time between the fiber and the water/oil until reaching equilibrium time. The oil characteristics influence the adsorption process so it is not possible to compare the adsorption capacity of different fibers if different oils are used. The adsorption kinetics curves revealed that oil 1, more viscous, the reaches equilibrium after 20 minutes of contact between the fibers and the system, while the oil 2, less viscous, had a slower kinetics of adsorption and reached equilibrium around 60 minutes of contact between the fibers and the system. Moreover, the fiber showed higher sorption capacity oil 2 (7.7$g_{adsorbate}/g_{adsorbent}$) with respect to oil 1 (4.26$g_{adsorbate}/g_{adsorbent}$). Considering the contact between the fibers and the system for 60 minutes, the fiber sorption capacity was 80% higher for oil 1 than for oil 1. It could be explained that the more viscous oil creates a film around the fiber limiting the capacity of adsorption.

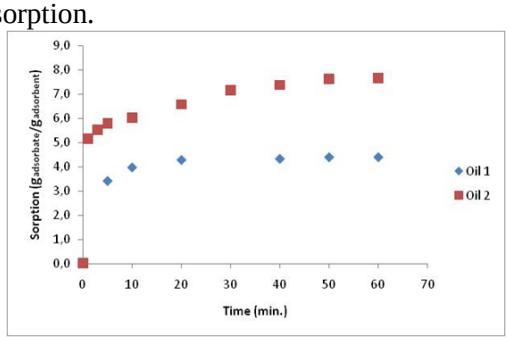

Figure.4. Adsorption kinetics curves obtained by banana fibers for both oil

4. CONCLUSIONS

The characterization of the fibers by optical microscopy confirmed the presence of porosity in the material and allowed to see the elliptical channel characteristics and measure the open in yx axis in a cross sections. The chemical composition analysis revealed slightly higher mass composition of hydrophobic structures, which reflects the selectivity of adsorption, thus favoring the oil adsorption compared with the water adsorption. Thus, it is possible to assume that the fiber actually adsorbs more oil than water, however part of the sorbed mass can be attributed to water.

The adsorption kinetics curves revealed that equilibrium was reached sooner for oil 1, although the banana fiber had a greater sorption capacity of less viscous oil (7,7$g_{adsorbate}/g_{adsorbent}$) relative to the more viscous oil.

The results of this study show the viability of the use banana pseudo stem as sorbent agent option for the remediation of oil spills, representing a promising alternative in the environmental, social and economic aspects. As the oil characteristics affects the sorption capacity direct comparison with other biomass sorption data are not possible as the oil varies a lot from one field to another.

5. ACKNOWLEDGEMENTS

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