MODIFICATION OF BIOMATERIALS FOR FUNCTIONAL APPLICATION

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Oil spills are a global concern due to the environmental and economic impact. In this study, natural fibres have been modified using fatty acid to impart acetyl groups and make them hydrophobic, so that they can be used for oil spill cleanup. The plant biomass used here is a renewable resource that can be converted into useful materials. The product soformed was characterized by FT-IR, SEM and its acid value was also evaluated. The extent of modification was measured by weight percent gain and acid value. Studies indicated that a simple squeezing operation was sufficient to remove most of the oil sorbed on the fibres, so that the sorbents could be reused several times for oil spill cleanup. The results suggest that a total or partial substitution of commercial synthetic materials by natural sorbent materials with improved efficiency of oil sorption and biodegradability could be beneficial in the oil spill cleanup operation.

Keywords:oil spill, coir fibre, fatty acid, acid value

INTRODUCTION

In the modern era, unintentional and intentional oil discharges have occurred frequently during shipping, production and refining, resulting in a severe impact on living organisms and environment.[1] The phenomenon of oil spill is a threat to marine life due to the formation of a floating film on water. Its impact has caused human awareness and concern over the environment and marine life. Hitherto, oil skimmers, oil dispersants, oil gelling agents and oil sorbents, including inorganic mineral materials, synthetic organic polymers and organic natural materials,[2] have been used for oil spill cleanup. However, based on currently used methods, most of the spilled oil is wasted and further pollutes water and air. Furthermore, any small fraction that is actually recovered generates a large quantity of solid and liquid waste itself, in the form of tons of soiled boom and other oily waste. It is then treated as industrial waste and buried inspecially designated dumps, some near residential neighbourhoods.[3]

A number of natural sorbents have been studied in oil spill cleanup. Ideally, natural sorbents, such as fruit skin and vegetable fibres, can be used as oil sorbents due to their hydrophobic properties, which contribute to their oil sorption capacity. Thus, it is necessary to develop a relatively efficient method to eliminate the potential oil pollution hazard and recover the spilled oil simultaneously.

The performance properties of composites made from natural and other lignocellulosic materials can be greatly improved by changing the basic chemistry of the cell wall polymers. This research work aims at developing an eco-friendly low cost natural fibre sorbent from coir fibre to remove spilled oil from sea water. Coir fibres are selected here due to their environment-friendly, biodegradable and inexpensive nature. These lignocellulosic fibres are hydrophilic and have a large amount of hydrogen bonds (hydroxyl groups -OH) present between the macromolecules in the plant fibre cell wall.[4] The hydrophilicity can be reduced noticeablyby changing the hydroxyl groups into hydrophobic groups by chemical modification,[5] particularly for the production ofnovel materials for environmentally friendly industrial utilization like for oil sorption.

EXPERIMENTAL

Materials

Coir fibre was obtained from CIRCOT, Mumbai, India, and oleic acid, sulfuric acid and all other chemicals were purchased from S.D. Fine Chemicals, Mumbai, India. Crude oil used for the testing purpose was supplied by HPCL, Mumbai, India.

Preparation of fatty acid-modified coir fibre

One gram of coir fibre was treated with the required amount of fatty acid in the presence of 1-3 drops of concentrated sulfuric acid as catalyst.

The mixture was refluxed in a Dean-Stark apparatus at the required temperature for an optimized period of time. The treated fibre was washed with n-hexane, followed by drying in an oven at 70° C till constant weight, and then was stored in an air tight container until further use.[6] The amount of reacted fatty acid was estimated by weight percent gain (WPG),using the following equation:

$$WPG = \frac{W_2 - W_1}{W_1} \times 100$$

where W_2 andW_1 are the weights of fibre after and before reaction, respectively.

Oil sorption capacity

Oil sorption capacity was determined by using a method reported in the literature.[7]A fixed quantity of crude oil (50 g) was suspended in water in a beaker. The modified coir fibre (1g) was added at room temperature and allowed to absorb oil for 1 h. Themodified fibre sample was then removed and held to drainoff the excess amount of oil. The fibresample was then reweighed to determine the oil absorptivity.[7]

Recovery of sorbed oil and reusability of sorbents

Having determined the oil sorption capacity as per the method described above,[7] the reusability of these sorbents was evaluated following the method described by Choi and Moreau.[8]The oil laden sorbent was weighed and then squeezed between the two rollers at a pressure of 10kgf/cmto remove the oil, and it was reweighed to determine the amount of recovered oil. This cycle was further repeated to determine the amount of oil sorbed during each cycle.

Chemical characterization

FT IR

The IR spectra of original and modified coir fibre samples were recorded using an FTIR spectrophotometer (Shimadzu 8400s, Japan), using the ATR sampling technique by recording 45 scans in % T mode in the range of 4000 to 600 cm^{-1}.

Scanning electron microscopy (SEM)

The analysis of the morphology of dried and modified samples was carried out using a scanning electron microscope (JEOL, Japan). The samples were sputter coated with gold layers before images were recorded on the scanning electron microscope.

Acid value

The acid value is the number of milligrams of sodium hydroxide necessary to neutralize the free acid in 1g of sample. A suitable quantity of the sample was taken into a 250 mL flask, followed by the addition of neutralized alcohol, and the temperature was raised to boil. It was allowed to stand at this temperature for at least 30 min and then was titrated against 0.1N sodium hydroxide solution using phenolphthalein as indicator. It was necessary to shake the contents of the flask continuously and vigorously during the titration.[9]

$$Acid\,Value = \frac{N \times 4.0}{W}$$

where N= number of mL of 0.1 N alkali required; W= weight of fibre taken in grams.

RESULTS AND DISCUSSION

The results listed in Table 1 show the effect of various parameters of fatty acid modification on the WPG and on the oil absorbency of the final product.

The results indicate that with an increase in time,the WPG of the fibre increased up to a certain limit, and then after 3 h the WPG value remained more or less constant. This could be due to the saturation of the active sites available for reaction with fatty acid in the coir fibre. Also, the oil sorption capacity (11.62 g/g) was the highest for 3 h reaction time.

It was observed that with an increase in temperature up to 65 °C, the extent of modification increased; however, further increase in temperature up to 75 °C caused no significant increase in WPG. This could be due to the opening of the fibre matrix at higher temperature, which favors the penetration of the reactant molecules inside the matrix in the initial phase.

With the increase in the concentration of oleic acid from 50 to 100%, the WPG increased to a maximum; further increase in concentration beyond 100% did not give any increase in WPG and oil absorbency. The acid value of the optimized sample was also calculated to confirm the modification of the coir fibre with oleic acid and it was found to be 16.89.

The results in Table 2 indicate that the fatty acid modified coir fibre showed higher oil uptake in the first cycle and then its sorption capacity decreased significantly in the subsequent cycles.

This may be due the collapsing of lumen of the fibre during the mechanical squeezing.[10] Thus, the capacity of oil sorption decreased from 11.62g/g to 5.10g/g in the third cycle of use.

Table 1
Effect of different parameters of fatty acid modified coir fibre on oil absorption

Sr. No.	Time (h)	Temperature (°C)	Conc. of oleic acid (owf)*%	**WPG (%)	Oil absorption (g oil/g fibre)
Effect of time					
A	1	65	100	4.67	6.94
B	3	65	100	8.90	11.62
C	5	65	100	9.01	11.60
Effect of temperature					
A	3	55	100	6.28	7.45
B	3	65	100	8.90	11.62
C	3	75	100	8.68	10.70
Effect of conc. of oleic acid					
A	3	65	50	2.7	3.78
B	3	65	100	8.90	11.62
C	3	65	150	9.12	10.40

*OWF: on weight of fibres; ** WPG: weight percent gain

Table 2
Reusability of esterified coir fibre

	Oil sorbed, g oil/g fibre(%)	Residual oil in fibre, g oil/g fibre (%)
First cycle	11.62 (100%)*	3.84 (100%)*
Second cycle	7.21(62.04%)*	2.17 (56.51%)*
Third cycle	5.10 (43.88%)*	1.93 (50.26%)*

*Percentage values as compared to first cycle

FT-IR analysis

The IR spectra of the modified samples presented in Fig. 1 show clear evidence of the esterification reaction. A new ester peak at 1745 cm^{-1} is observed and the intensity of CH_2 peaks increases after modification. The IR analysis confirms the enhancement of the hydrophobic character of the modified fibres, as reflected by the decreased intensity of the band around 1500 cm^{-1}.

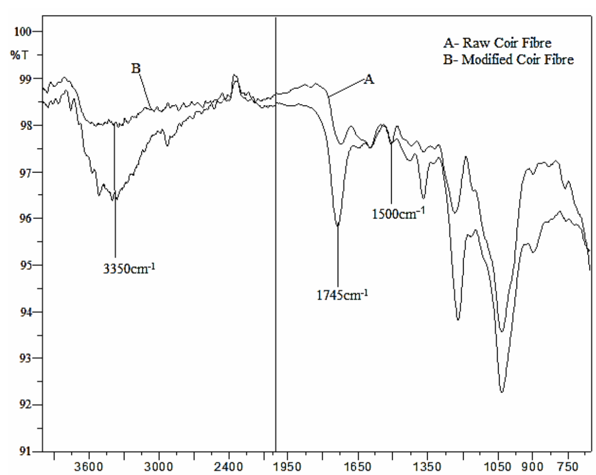

Figure 1: FT-IR spectra of raw and modified coir fibres

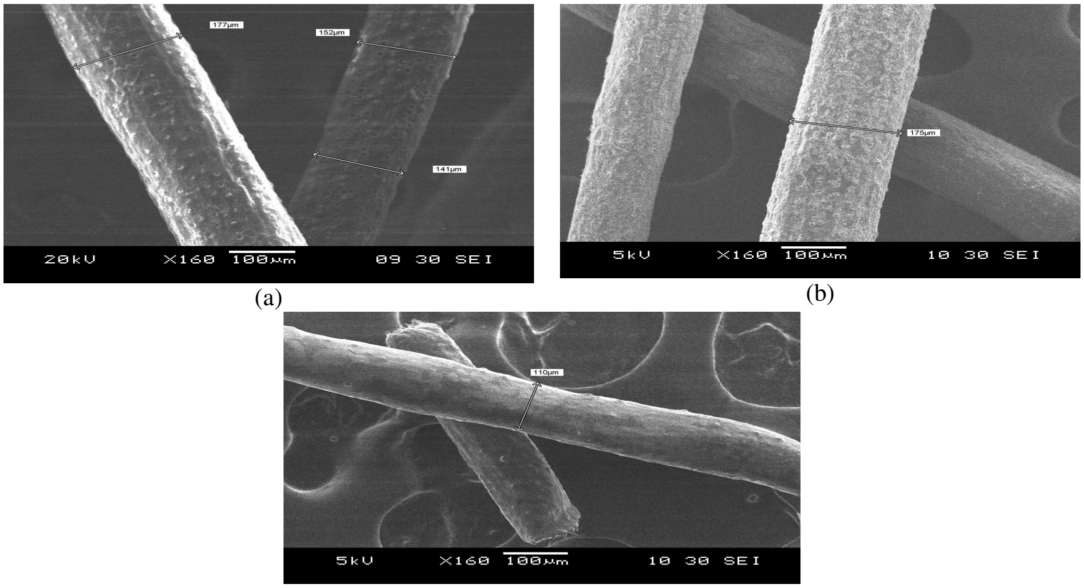

Figure 2: Scanning electron micrographs of raw (a), modified (b) and modified coir fibre with absorbed oil (c)

SEM analysis

The SEM micrograph of the modified coir fibre (Fig. 2b) clearly shows surface deposition, which is absent in the case of the raw fibre (Fig. 2a). This confirms the presence of reacted fatty acid on the fibre surface. Fig. 2c shows a layer of oil sorbed onto the fibre surface, which appears to be smooth.

CONCLUSION

The modification of coir fibre by acetylation with fatty acid imparted hydrophobic properties to the fibre. This modified coir had very little affinity for water and strong affinity for oil. Hence, the modified coir would be suitable for application as an oil sorbent material. Also, coir being natural and biodegradable fibre, its disposal after use would be easy, and thus, it will not cause any environmental pollution.

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