

Natural Fruit Peels – Potential Biosorbents for Combating Oil Pollution

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Abstract

The aim of this study is to investigate the efficiency of different biosorbent materials for oil removal from polluted water. Three natural and chemically treated fibers of Banana, Durian, Jackfruits were utilized to absorb two types of oil namely diesel and petroleum from polluted water. The chemical modification of fruits fibers was carried out using acetic anhydride with absence and presence of N-bromosuccinimide (NBS) as catalyst has been investigated. The degree of acetylation was determined to measure the percentage of the fibers that has been modified in the sample. The chemical modification of the fruits fiber was evaluated by degree of acetylation method using FTIR Spectroscopy. This study also investigates the characterization of the fibers using FTIR spectrophotometer and Scanning Electron Microscopy (SEM). The comparison study between untreated and treated fibers was carried out with catalyst. The acetylated fiber show higher oil absorption capacity compare to untreated fiber due to increasing of hydrophobic properties on the surface of fiber. It was found that the weight percent gain increase up to 14% with using the catalyst compared to 7% without using catalyst. Thus, NBS was chosen as catalyst in this study.

Keywords: Acetylation fruits fiber, Environment, Natural Sorbent, Oil spillage, Oil sorption capacity

Introduction

Oil spill has become global issue since decades ago. It has polluted the environment and marine life as well as affect the economic global. The phenomenon of oil spill will cause toxicity to marine life due to forming of floating film in water. The impact of this issue has created human awareness and concern to protect the environment and marine life. A number of natural sorbents have been studied in oil spill cleanup. Ideally, natural sorbent such as fruits and vegetables fibers can be use as oil sorbents due to its hydrophobic properties that important in oil sorption capacity.

Oil is one of the most important sources of energy and used as raw material for synthetic polymers and chemicals worldwide. It has been a part of the natural environment for millions of years. The oil production is significantly influenced by human demand. Thus, the oil spill can easily occur during transportation and imposes a major problem for the environment. (Karan *et al*, 2010). The phenomenon of oil spill has affected and damages the ecosystem especially to sea and coastal area as well as economic charges. Under favorable conditions, physiochemical properties of oil give toxic and hazardous to the environment and marine life. Thus water contaminate with oil should be clean up by using an appropriate treatment method.

Over the years ago, several cleanup techniques have always been used in combating oil spillage and most of the current cleanup practices are not efficient enough. (Majed *et. al*., 2012). Therefore, the new treatment techniques and material should be utilized to find a proper solution for this issue. The oil sorption and retention behavior of sorbents are influenced by the material and structure of the sorbents and oil physical characteristics. The use of sorbents made from organic material does not cause additional problems in the disposal of the spilled oil. (Pasila, 2000). Previous studies had proved that natural sorbents such as cotton and kapok fiber has high efficiency in oil absorption and at the same time, most eco-friendly and cost effective.

According to Sun *et. al*., (2002, 2004) the acetylated agro fibers in oil spill cleanup has higher efficiency than synthetic sorbent. Physical adsorption occur when the contacting molecule of adsorbate and adsorbent are held together by Van der Waals force. Van der Waals force is an attractive force between molecules because the suffusion electrons are not balanced. Many researchers have demonstrated the natural fibers have great potential to cleanup oil spill comparing to synthetic materials such as commercial polypropylene fibers.

The synthetic polymers such as polypropylene can be represent as ideal materials for marine oil-spill recovery due to their low density, low water uptake and excellent physical and chemical resistance. However, according to Annunciado *et al.*, (2005) these sorbents are not renewable and biodegradable. Meanwhile, vegetable fibers are environmentally friendly materials, with densities close to that of synthetic polymers or even lower, and may show high oil sorption capacity at a usually low cost (Wei *et al.*, 2003).

The using of N-bromosuccinimide (NBS) as catalyst in this studies is to determine the efficiency of oil absorbant. Karimi *et. al.* (2001) has reported that NBS is an inexpensive and commercially available reagent, and is a novel and highly effective catalyst for acetylation under nearly neutral reaction conditions.

Most research done in the area of chemical modification involves the reaction the hydroxyl group. Acetylation process is important technique to chemically modify the cell wall polymers, as well as modify the physical properties of the ligocellulosic composite. Ideally, the most abundant reactive chemical sites in natural fibers are the hydroxyl groups on cellulose, hemicelluloses and lignin. (Sun et al., 2002)

The criteria for good polymer are its capacity to absorb a large amount of oil. Previous researcher proved that acetyl groups are more hydrophobic than hydroxyl groups, therefore replacing some of the hydroxyl groups with acetyl groups reduces the hydrophilic properties of the cell wall polymers. Thus, it will increase the oil absorptivity of fibers. Natural sorbent such as tropical fruits were used as sample in this study. The chosen of the type of fruits are based on the cellulose content in a fruits fiber. Ideally, the higher content of cellulose in fruits fiber can absorb the higher volume of oil. This study has investigated the efficiency of the cellulosic fiber that was modified and unmodified.

Materials and Reagent

Different fruits fiber materials were used as sorbent namely, bananas (*Musa acuminata*), durians (*durio zibethinus*), and jackfruits (*Artocarpus heterophyllus*). All the fibrous materials were obtained from the market. The fibers were cut into required (1-3 cm) length and dried in oven at 60 ^{0}C for 24 hours. The fibers were separately grounded using 0.5cm knife mills. Acetic anhydride and NBS were purchased from Sigma Chemical Company. Types of oil used in this study were diesel and petroleum.

Methodology

Acetylation

A fixed quantity of fruits fiber (10g) was placed in a 500-mL flat bottom flask. Then 200 mL of acetic anhydride and 2% of N-Bromosuccinide (NBS) were added respectively. The flask with the fiber was dipped into an oil bath set at the required temperature (120 ^{0}C) with a reflux condenser fitted. After the reaction time was completed, the flask was removed from the oil bath and the excess acetic anhydride and by-product acetic acid were filtered off. The acetylated fiber was then washed with ethanol and acetone to remove unreacted anhydride and acetic acid by-product. The acetylated fiber was oven dried at 60 ^{0}C for 16 hour. The oven-dry materials were weighed to determine the weight gains on the basis of initial oven-dry weight. The weight percent gain (WPG) due to acetylation was calculated using formula:

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

W_1 and W_2 are the weights of fruits fiber and acetylated fruits fiber respectively.

Water Sorption Capacity (g g^{-1})

Method of water sorption capacity was adapted by Chung et al, (2011). The water sorption capacity was measured in triplicate with time. Each sorbent material (1g) was applied to the water surface in a 100 ml beaker and allowed to absorb water for specific soaking time (1 hour). Next, the wet sorbent was drained on the filter paper for 10 min under vacuum filtration. The water sorption capacity of the sorbent was calculated as follows:

$$\text{Water Sorption Capacity (g g}^{-1}\text{)} = \frac{\text{amount of wet sorbent (g)} - \text{amount of dry sorbent (g)}}{\text{amount of dry sorbent (g)}}$$

Oil absorptivity

A fixed quantity of machine oil (5ml), petroleum and diesel was suspended in water in measuring cylinder. The fruits fibers (0.5 g) was added at room temperature and allowed to absorb oil for 24 hours. The observation of oil absorbtivity can be seen by decreasing the amount of machine oil after 24 hours.

Degree of substitution

Degree of substitution was determined by using methods reported by Teli *et. al.*, (2012). The percent of acetylation (acetyl %) was determined by using titration method. Acetylated banana fiber (1g) was placed in a 250ml flask, and to this 50ml of 75% ethanol in distilled water was added. The loosely stopper flask was agitated, warmed to 50 ^{0}C for 30 minute, cooled and 40ml of 0.5M KOH was added to it. The excess of alkali was back titrated with 0.5M HCl with phenolphthalein as an indicator. The solution was allowed to stand for 2 hour and then any additional alkali which may have leached from the sample was titrated (S_R). A blank reading (B_R) using the original unmodified banana sample was taken.

$$\text{Acetyl \%} = \frac{\{(B_R - S_R) \times \text{molarity of HCl} + 0.043\} \times 100}{\text{Sample weight (g)}}$$

B_R and S_R are titration volumes in ml and sample weight is in grams on dry weight basis. Degree of substitution (DS) was calculated as reported in literature (David, Huijun, Duohai, & Harold, 1999)

$$DS = \frac{(162 \times \text{acetyl \%})}{\{4300 - (42 \times \text{acetyl \%})\}}$$

IR Spectra Characterization

The IR spectra of modified and unmodified acetylation fruits fibers were recorded using FTIR spectrophotometer. The sample preparation was using KBr pellet containing 1% finely ground samples. The ranges of spectrums were recorded between 4000 – 400 cm^{-1}.

Scanning electron microscopy (SEM)

Analysis of the morphology of unmodified and modified fiber was carried out from Faculty of Applied Science, Material Technology Laboratory using scanning electron microscope with magnification of 2000x and 10 000x.

Data analysis and results

Effect of catalyst on Weight Percent Gain (WPG)

Table 1: Effect of catalyst on WPG

Sample fiber	Catalyst (%)	Solid to liquid ratio	Reaction time	WPG
Banana	-	1:20	8	8.0
	2%	1:20	1	9.4
Durian	-	1:20	8	8.1
	2%	1:20	1	8.8
Jackfruit	-	1:20	8	7.3
	2%	1:20	1	8.7

Water sorption capacity

Table 2: Water sorption capacity (g g^{-1})

Sample		Water sorption capacity (g g^{-1})
Banana	Unmodified	2.146
	Without catalyst	1.294
	With catalyst	0.369
Durian	Unmodified	3.334
	Without catalyst	2.935
	With catalyst	2.183
Jackfruit	Unmodified	4.616
	Without catalyst	2.797
	With catalyst	2.425

Oil absorptivity

Table 3: Oil absorptivity of modified and unmodified fibers

Sample		Oil absorptivity	
		Diesel	Petroleum
Banana	Unmodified	0	0
	Without catalyst	0.8	1.0
	With catalyst	1.6	1.4
Durian	Unmodified	0	0
	Without catalyst	0.6	1.4
	With catalyst	1.2	1.6
Jackfruit	Unmodified	0	0.6
	Without catalyst	0.4	1.2
	With catalyst	1.4	1.6

Degree of substitution

Table 4: Degree of acetylation of modified fiber

Sample		Percent acetyl	Degree of substitution
Banana	Without catalyst	34.3	1.94
	With catalyst	49.3	3.58
Durian	Without catalyst	29.3	1.55
	With catalyst	34.3	1.94
Jackfruit	Without catalyst	24.3	1.20
	With catalyst	34.3	1.94

IR spectra analysis

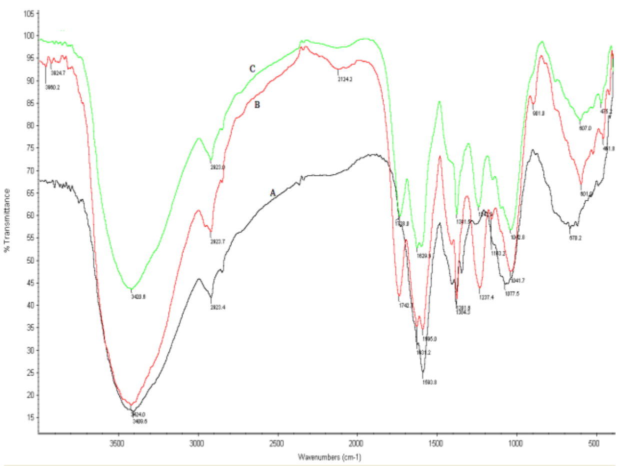

Figure 1: Spectrum of banana fiber: (A) unmodified , (B) modified without catalyst, and (C) modified with present of catalyst.

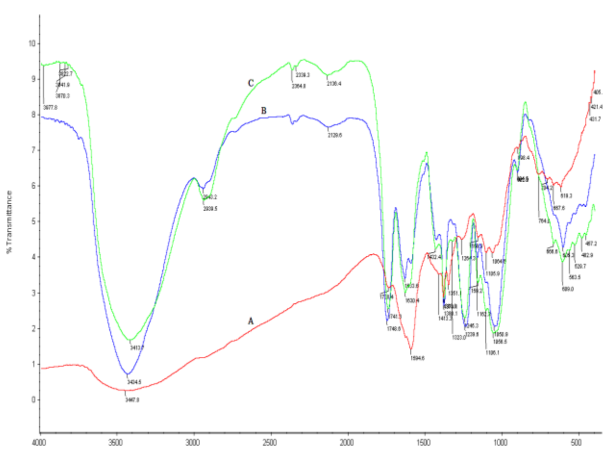

Figure 2: Spectrum of durian fiber: (A) unmodified, (B) modified without catalyst, and (C) modified with present of catalyst

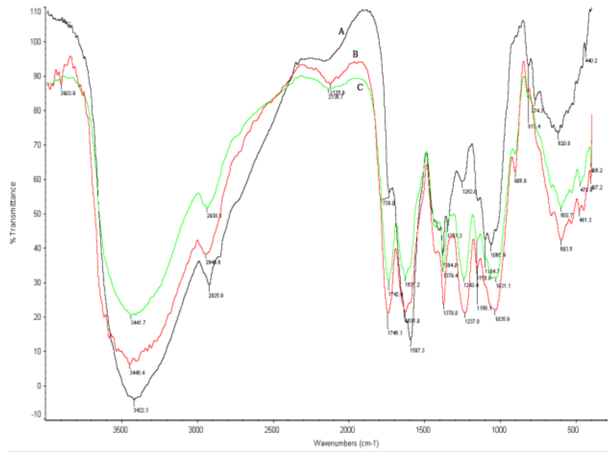

Figure 3: Spectrum of jackfruit fiber: (A) unmodified, (B) modified without catalyst, and (C) modified with present of catalyst.

Scanning electron microscope

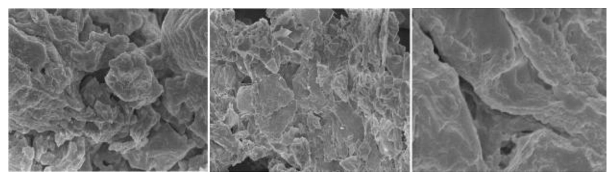

Figure 4: Bananas fiber under 10 000x magnification, unmodified fiber (left), modified without using catalyst (center), and modified using catalyst (right)

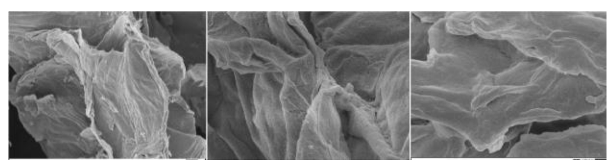

Figure 5: Durian fiber under 10 000x magnification, unmodified fiber (left), modified without using catalyst (center), and modified using catalyst (right)

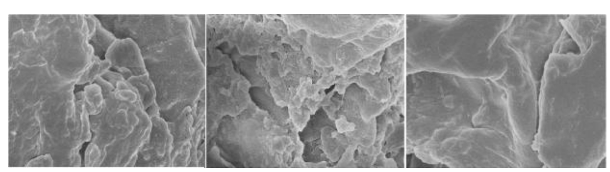

Figure 6: Jackfruit fiber under 10 000x magnification, unmodified fiber (left), modified without using catalyst (center), and modified using catalyst (right)

Discussions

Effect of catalyst on Weight Percent Gain (WPG)

In this study, sample fibers were partially acetylated by a simplified procedure, proposed by Sun *et al.*, (2004) with constant temperature, 120 ^{0}C. The reaction catalyst plays a significant role on the effect of acetylation. Table 1 gives weight percent gain of acetylated sample fibers obtained with or without NBS as catalyst.

As expected, the WPG increased with addition of the catalyst. According to Karimi et al. (2001), NBS catalyst act as source for Br^+ which could activates the carbonyl groups of acetic anhydride to produce the highly reactive acylating agent. This acylating agent further will reacts with hydroxyl group to form the hydrophobic characteristic. Therefore, the WPG will increase with addition of the catalyst.

Results show banana fibers with catalyst consists highest amount of weight percent gain (WPG). During the acetylation process, the fiber swells as the reaction proceeds, requiring disruption of the hydrogen bonding network. The modification process that used acetic anhydride has substitutes the hydroxyl group of cell wall with acetyl group to become more hydrophobic.

Water sorption capacity

Unmodified fruits fiber can hold significantly amounts of water due to hydrogen bonding between hydroxyl groups and water molecules. Ideally, modified fiber either with using catalyst or without using catalyst can absorb less water than unmodified fiber due to an enhanced hydrophobicity. The result of water sorption capacity can be seen in Table 2. It shows that, the modified fiber with catalyst have less water sorption capacity than modified fiber without catalyst. However, when comparing to the type of fiber, bananas fiber has less water sorption capacity following durians and jackfruits fibers respectively. This shows that bananas fiber has highest hydrophobicity in terms of WPGs as well as holds the minimum moisture required for hydrocarbon biodegradation.

Oil absorptivity

Acetylation of fruits fiber led to a substantial increase in acetyl group (Teli *et. al.,* 2013). The modified fiber was treated using acetylation methods with present and absence of catalyst. The modification of cellulosic fiber has increased the oil sorption capacity based on changing of hydrophilic characteristic to hydrophobic. Thus the fibers absorb less water instead of oil. Table 3 shows the oil absorptivity of fruits fiber. The samples of oil used in this study are diesel and petroleum. Results shows sample of modified banana fibers with catalyst has absorbed higher volume of diesel. Meanwhile, jackfruits and durian fiber that was modified with presence of catalyst absorbed the highest volume of petroleum. These are due to chemical composition of petroleum which has short length of carbon chains 5 to 12 carbon atoms compare to diesel that has longer carbon chains with 12 or more carbon atoms. Besides that, the percentage of cellulose in fruits peels also influence the volume of absorption. Jackfruit and durian fibers that contain 59% (Prakash et.al, 2009) and 60% of cellulose respectively are easier to retain the light oil such as petroleum, while banana fibers that contain 83% of cellulose (Brinda et. al, 2012) in it fiber are easier to retain the diesel.

Degree of substitution

The percentage of acetylation and degree of substitution can be determined by acid titration methods. In this method, the percentage of fibers that undergo acetylation process can be calculated. Table 4 shows the percent acetylation and degree of substitution of modified fibers. It shows the higher amount of weight percent gain (WPG) exhibits the higher of percentage of acetylation and degree of subtitution. This statement proves the fibers have successfully undergo modification as well as proving the action of NBS catalyst.

IR spectra analysis

In order to determine the chemical changes between the modified and unmodified fibers, FTIR spectra analysis was chosen. Theoretically, the reaction occurs during the acetylation process will change the chemical position of fibers. The spectra were recorded on a Nicolet-6700 FTIR spectrophotometer.

Figure 1 represents the spectrum of banana fibers. There are three major changes that are observed in the FTIR spectrum of unmodified fiber (A), modified fiber without catalyst (B), and modified fiber with presence of catalyst (C). Firstly, the change that occurs is reduction in hydroxyl (O-H) absorption band at 3424.0 cm^{-1} to 3409.6 cm^{-1}. Besides that, an increasing in the carbonyl (C=O) stretching absorbance has occurs at 1593.8 cm^{-1} to 1742.7 cm^{-1}. Meanwhile, an increasing of strong band for C-H are assigned at 1381.0 cm^{-1} , 1381.6 cm^{-1} and 1384.3 cm^{-1} , for unmodified fiber, modified fiber without catalyst and with catalyst respectively.

Figure 2 and Figure 3 shows same pattern as Figure 1. Obviously shows the reduction in (O-H) group, an increment in carbon-hydrogen bending (C-H) and increase in the carbonyl (C=O) stretching absorbance for the spectrum unmodified fiber and modified fiber without catalyst and with the presence of catalyst.

Scanning electron microscope

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The SEM is routinely used to generate high-resolution images of shapes of objects (SEI) and to show spatial variations in chemical compositions. Figure 4, Figure 5 and Figure 6 shows the image of the unmodified fiber and modified fibers.

Observation shows that the unmodified fiber has rougher surface than modified fiber. However, modification of fiber with the presence of catalyst produced smoother surface. This indicates that lumen has undergone swelling during acetylation process (Chung, et. al., 2011). In general, the treatment can increase the specific surface area of fiber, which enables the oil to adhere to outer surface and enter easily into the inner surface of lumen of fiber.

Conclusions

This study was done to synthesize and characterize the banana, durian and jackfruit fibers as well as to investigate the oil absorptivity of the sample fibers. The modifications of fiber via acetylation treatment has change the hydrophilic characteristic to become hydrophobic, thus gave the less water absorption while increase the oil absorptivity. Banana fibers have highest diesel absorptivity, while durian and jackfruits fibers absorb petroleum more than banana fibers.

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