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Acetylation of Corn Silk and Its Application for Oil Sorption

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Abstract: Oil sorbents for cleanup operation should be of high sorption capacity, biodegradable, readily available, and low-cost. This is important for protection of the water environment, especially for oil spillage. Corn silk is a low-cost sorbent. In this study corn silk was treated by acetylation process to improve the sorption capacity. The process involved acetylation by acetic anhydride using N-bromosuccinimide (NBS) as a catalyst. Reaction time of 1, 3, 6, and 9 h, temperature of 90-120 ^oC and percentage of catalyst of 1-3 % were used in the experiment. The results showed that the highest oil sorption was 11.45 % weight percent gain (WPG). This was achieved at 3 % catalyst concentration in acetic anhydride and temperature of 120 ^oC for 6 h. A weight percent gain of 11.45 % was achieved. The effect of contact time on oil sorption capacity for different crude oil (Tapis and Arabian crude oils) was investigated. In general the sorption capacity reduced after the fifth cycle of sorption/desorption. The characteristics of raw and treated corn silk were examined using FT-IR and FE-SEM. The treated corn silk as an organic waste material was found to have higher sorption capacity than that of the commercial synthetic sorbents such as polypropylene. This agriculture waste may be used to replace those of non-biodegradable oil sorbents.

Keywords: Oil spill, Sorption capacity, Corn silk, Weight percent gain, Acetylation

Introduction

In recent years, one of the environmental distresses in the petroleum industry is spilled oil on sea water. Marine pollution by petroleum crude or product may cause serious problems to aquatic life. Therefore oil spill cleanup is one of the important challenges in the environment section. Common methods used to remove oil from water involve booms, skimmers, dispersants, and sorbents, etc. Use of sorbents is getting more attention in recent years due to effectiveness of the method in removing oil from water [1]. Synthetic sorbents such as polypropylene and polyurethane are commercially used for oil recovery. Despite having high oil sorption capacity, high buoyancy, and ease in acquisition, they are non-biodegradable and will persist in the environment for long periods of time. Inorganic materials such as vermiculite, organoclay, perlite, and exfoliated graphite also have been used as oil sorbents. Most of these materials have low oil sorption capacity, low buoyancy, and poor reusability; except exfoliated graphite which is an excellent oil sorbent, but it is fairly expensive [2]. Organic sorbents such as agricultural products are excellent materials for oil sorption. They are inexpensive and available locally. Most of them are waste product of agricultural industry. Kapok, kenaf, corn cob, cotton, peat moss, milkweed floss, barks, and rice straw have been examined as sorbents for oil spill cleanup [3-7].

Corn stover (Zea mays), resulting from the harvest of corn grain, is one of the most plentiful agricultural residues in the world. It was estimated that approximately 82 million tons corn dry stover was available in the United States [8]. It comprises of several constituents including husks, shanks, silks, and cobs. Corn stover typically has about 35 % cellulose, 21 % hemicellulose (xylan), and 17 % lignin [9]. The cobs, leaves, silk, and husks represent the portion with the highest glucose potential. The corn portion is called zein. Zein is hydrophobic in nature [10]. Corn silk is an excellent source of many bioactive compounds such as steroids, alkaloids, volatile oils, and natural antioxidants such as flavonoids and phenolic compounds [11]. Hydrophobicity of protein is due to the presence of an acetyl group in it. Phenolic (C_6H_6O) and flavonoids ($C_{21}H_{20}O_{13}$) components in corn contain hydroxyl group with hydrophilic property.

Many natural sorbents have low hydrophobicity that could lead to low oil sorption capacity. Fortunately, this defect can be changed by chemical modification. Numerous researchers have made significant modifications of natural sorbents to improve their sorption capacity [12-14]. Chemical reagents such as ester and anhydrides are employed to modify the cellulosic materials based on the fact that ester (C=O) and acetyl (C-O) group have higher hydrophobicity than the hydroxyl group (-OH).

These treatments reduce -OH and enhance the ester bond. Hence, replacing some of the hydroxyl groups with acetyl groups increases the hydrophobic and decreases the hydrophilic properties of the plant cell wall. Wheat straw, rice straw, sugarcane bagasse, banana fiber, cotton, and kapok fiber were successfully acetylated by acetic anhydride with or without catalysts [6,13-17]. Several methods were studied

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for acetylation of agricultural by product. Various catalysts have been used to accelerate the rate of reaction of acetic anhydride with the materials. Pyridine, N-methylpyrrolidine (MPI) [6], 4-dimethylamino pyridine (DMAP) [18], and N-bromosuccinimide (NBS) have been used as acylation catalysts in chemical synthesis. Of these, NBS is commercially available and inexpensive catalyst. This chemical is not toxic and is highly effective [14,19].

Corn silk is a kind of natural plant fiber that has good buoyancy, huge hollowness, and low density. It is easily available and biodegradable. Nevertheless, smooth surface of the fiber makes it difficult to impressively retain oil to fiber assembly. It would be more useful for the oil spill cleanup, if the oil sorption capacity of corn silk could be further enhanced by modification. The aim of this study is to investigate oil sorption characteristics of raw and acetylated corn silk. Several parameters such as the contact time and the types of oil were studied in a batch system. The oil sorption capacity and reusability of corn silk were investigated.

Experimental

Materials

Corn silk was collected from a local market (Seri Iskandar, Malaysia). It was first washed with distilled water to remove dust and mechanical impurities and was dried in an oven at 40 °C for half a day. Arabian crude oil and Malaysian crude oil (Tapis) were used as high viscosity and low viscosity crude oils, respectively in this experiment. Acetic anhydride, NBS, and all other chemicals were supplied by Sigma Aldrich, Malaysia.

Preparation of Acetylated Corn Silk Fiber

A fixed quantity of dried corn silk (4 g) was placed in a 500 m*l* two neck round bottom flask containing required acetic anhydride (solid-to-liquid ratio of 1 g/30 m*l*) and NBS (1-3 % by weight of sorbent) as a catalyst for reaction under atmospheric pressure. The flask was provided with a mechanical stirrer, a reflux condenser, and a thermometer. The flask was then placed in an oil bath at 90 and 120±5 °C and was kept for 1, 3, 6, and 9 h. Reaction was terminated after required time then the material was filtered and thoroughly washed with ethanol and acetone to remove the un-reacted acetic anhydride and acetic acid by-product. The acetylated corn silk was then dried in oven at 40 °C for 8 h. The oven-dry corn was weighed to determine the weight percent gains (WPG) on the basis of initial oven-dry weight [14]. Each experiment was conducted three times under the same conditions and the average value was used for WPG. Weight percent gain of the corn silk fiber was calculated using the following formula:

$$WPG = \frac{Weight\ gain}{Original\ weight} \times 100$$

Methods

Characterization of Corn Silk and Experimental Oils

The characteristics of the raw and acetylated corn silk was examined using Fourier transform infrared (FTIR) spectra; 1 % by weight of corn silk was mixed with KBr and compressed into a pellet using a mechanical compressor. Spectrometer was used to scan over the spectra range of 400 to 4000 cm^{-1} wavenumber. The corn silk morphology was observed using Field Emission Scanning Electron Microscopy (FE-SEM). The samples were fixed on round stainless steel sample holders with double sided conductive tapes and then were coated with gold to provide a conductive coating to make ensure good image generation under FE-SEM. The diameters of internal and external corn silk fiber were measured using FE-SEM. Density and viscosity of experimental oil were determined using a density meter (Anton Paar, Austria) and an EV1000 Viscometer (Anton Paar, Austria), respectively.

Measurement of Oil Sorption Capacity

A batch system was used to measure the oil sorption capacity of raw and acetylated corn silk. 30 m*l* crude oil was added to 300 m*l* of artificial seawater (3.5 wt% NaCl) in a 500 m*l* beaker and mixed for 5 min by constant stirring at room temperature. One gram of sorbent was immersed in the oil/water mixture. The system was kept on an orbital shaker for pre-decided time (5 to 60 min) at 150 rpm. After the required time, the sample was filtered from the beaker using a mesh screen and dried in an oven at 40 °C for 30 min to reach a constant weight. The oil sorption capacity of the sorbent was calculated from the mass of sorbent before (m_1) and after (m_2) sorption using the following equation [14]:

$$Oil\ Sorption\ Capacity = \frac{m_2 - m_1}{m_1}$$

Reusability of Corn Silk

After measurement of oil sorption capacity of corn silk, the sorbent was put into a cylinder and squeezed by putting pressure on the piston to drain any oil remaining in the sample. The test was repeated four times and the average oil sorption capacity of the sample was evaluated.

Results and Discussion

Characterization of Corn Silk as a Sorbent

Fourier Transform Infrared (FTIR) Analysis of Sorbent

FTIR spectra of raw corn silk and acetylated corn silk are shown in Figure 1. Four major differences are noticeable from the two spectra which are: creation of new carbonyl (C=O) band at 1740 cm^{-1} which indicates stretching of ester; enhancement of carbon-hydrogen (C-H) bending at 1374 cm^{-1} in acetyl group; increase in absorbance of carbon-oxygen (C-O) at 1245; and reduction in absorption peak at 3440 cm^{-1} corresponding to the hydroxyl group (O-H). In addition, the presence of three important ester bonds in the acetylated spectrum implies good evidence of acetylation reaction and

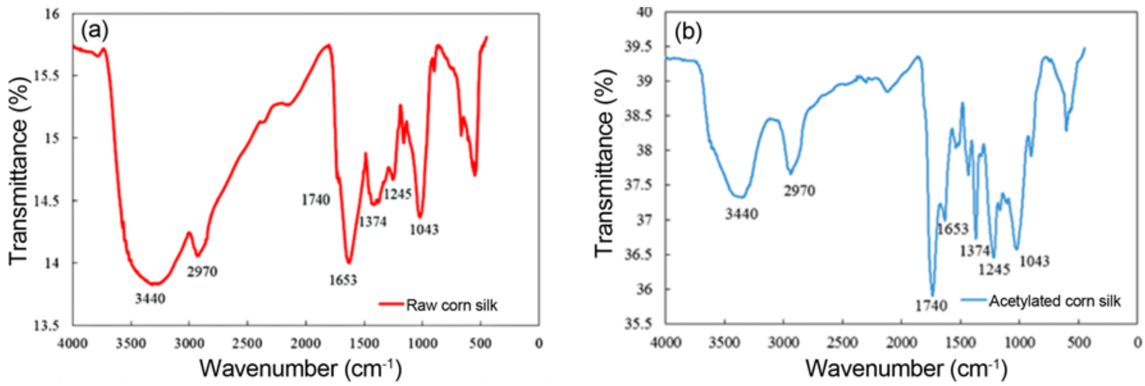

Figure 1. FT-IR spectra of (a) raw and (b) acetylated corn silk.

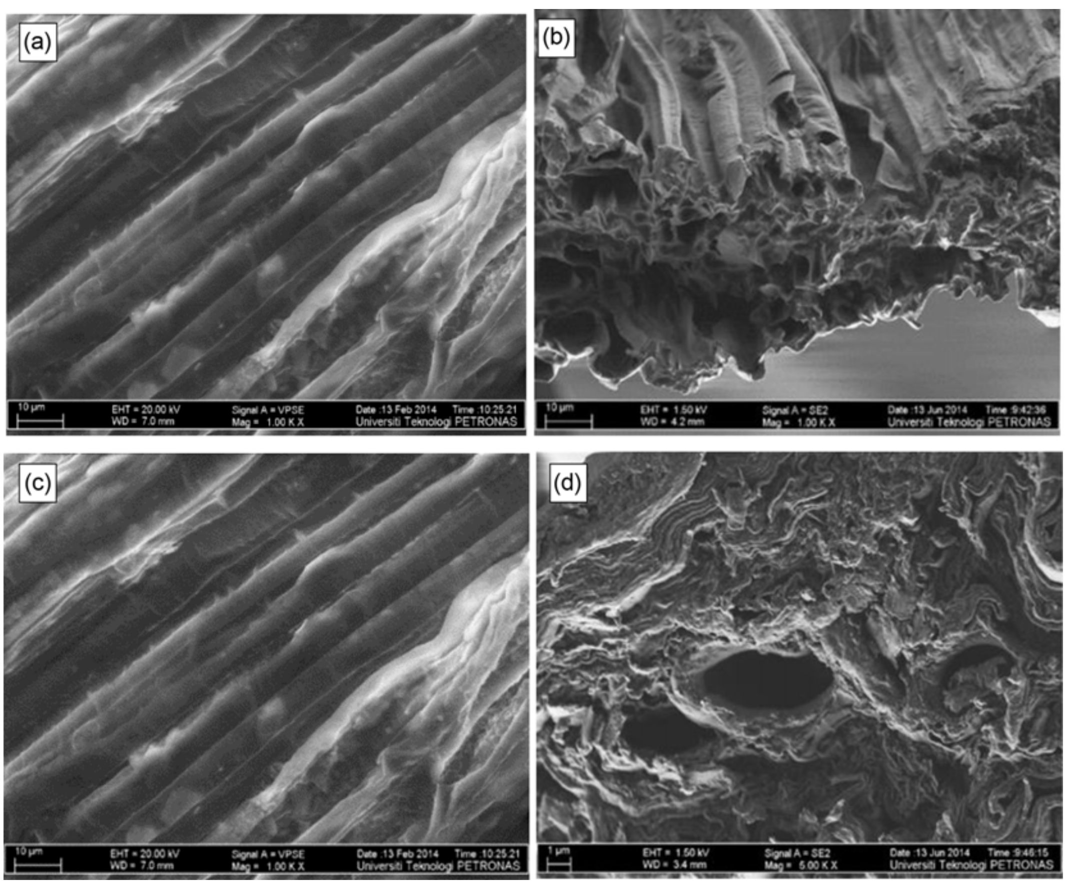

Figure 2. FE-SEM of the surface of (a) untreated corn silk and (b) treated corn silk, (c, d) the cross section of corn silk.

enhancement of the acetylation level. It is noted that the presence of ester bonds reduces the hygroscopic nature of the cell wall of corn silk. The absence of peaks for absorption at 1700 cm^{-1} (carboxylic group) and in the region 1760-1840 cm^{-1} of the acetylated sample shows the product is free of the unreacted acetic anhydride and the byproduct of acetic acid [6].

Morphology Identification of Sorbent

The sorption mechanism of sorbent can be adsorption, absorption, or a combination of both. The amount and rate of oil which is sorbed into a sorbent are closely related to the chemical property of the sorbent, the molecular arrangement, and the physical configuration of the sorbent such as surface roughness, hollow lumen, porosity, twist, and crimp. Oleophilicity and surface energy of the sorbent are mainly dependent upon the chemical property and the surface wax, which are significant properties in the absorption mechanisms, though the main factor in the adsorption mechanism and capillary action is the physical configuration of the sorbent [20]. FE-SEM images of surface and cross sections of corn silk fiber are showed in Figure 2. As illustrated in Figure 2(a), the surface of the untreated sample is completely smooth with tiny ripples. Figure 2(b) presents the surface and cross section of treated corn silk showing a tubular structure with holes and voids. The acetylation process changed the physical configuration of the untreated corn silk, and thus the fineness properties of the surface of untreated corn silk transformed and became rough with high crimp. This is helpful in the adsorption and adhesion of oil on the fiber surface. The tubular structure with holes and voids of diameter of 3 to 15.79 μm can be seen in Figure 2(c) and (d). These sizes indicate the presence of the macro porous structure. That causes the low bulk density of corn silk. It is believed that high percentage of oil can be trapped into the porous interior of the sample by capillary mechanism. The macro porous interior fiber enhances the capillary action and the diffusion of oil through the fiber and improves the sorption properties of corn silk. Thus, two main factors which cooperate to enhance sorption are surface configuration and porosity of interior fiber. Oil is first adsorbed by physical trapping on the rough fiber surface and then fills the porous interior of the sorbent via capillary action. The absorbency of sorbent is increased by chemical change in the structure. Thus, the sorption mechanism of acetylated corn silk is a combination of absorption and adsorption.

Effect of Different Parameter on WPG

Table 1 shows the effect of reaction time, temperature, and

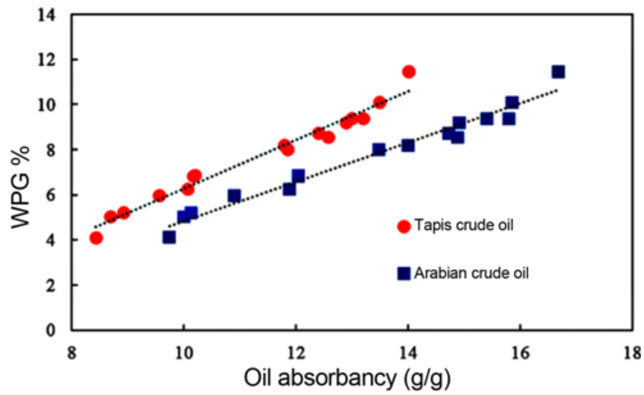

Figure 3. Relations between Oil absorbency and WPG.

catalyst concentration on WPG and oil sorption capacity of Tapis and Arabian crude oil. It is observed that WPG has a direct relation with oil sorption capacity (Figure 3). The best oil sorption capacity and optimum WPG were achieved by acetylation using 3 % NBS (3 g NBS in 100 m*l* acetic anhydride) as a catalyst at 120 °C for 6 h reflux time. The results were 14.02 and 16.68 g/g sorption by for Tapis and Arabian crude oil, respectively (Table 1). The data shows that the oil sorption capacity increases with the increase of NBS for the same reaction time. This suggests that NBS increases the rate of reaction. However, the role of NBS is not certain but it is believed that NBS could activate the carbonyl group of acetic anhydride to yield reactive acylating agent. This acylating agent reacts with hydroxyl groups of corn silk [19]. WPG is influenced by time and temperature.

Table 1. Effect of reaction time, temperature and catalyst concentration on acetylation and oil absorbency

No	Reaction time (h)	Temperature (°C)	Catalyst (%)*	WPG (%)**	Oil absorbency (g oil/g acetylated sample)	
					Tapis crude oil	Arabian crude oil
1	1	90	1	4.10	8.43	9.74
2	1	90	3	5.01	8.70	10.00
3	1	120	1	5.21	8.93	10.13
4	1	120	3	5.95	9.56	10.90
5	3	90	1	6.26	10.07	11.89
6	3	90	3	6.87	10.20	12.05
7	3	120	1	6.81	10.18	12.05
8	3	120	3	8.00	11.86	13.48
9	6	90	1	8.72	12.40	14.73
10	6	90	3	9.38	13.0	15.41
11	6	120	1	10.10	13.5	15.86
12	6	120	3	11.45	14.02	16.68
13	9	90	1	8.17	11.79	14
14	9	90	3	8.56	12.58	14.88
15	9	120	1	9.18	12.90	14.91
16	9	120	3	9.37	13.20	15.80

*Catalyst (%) represents1-3 % by weight of corn silk and **WPG represents the weight percent gain of corn silk due to acetylation and it was measured according to: WPG (%)=[(weight gain/original weight)]×100.

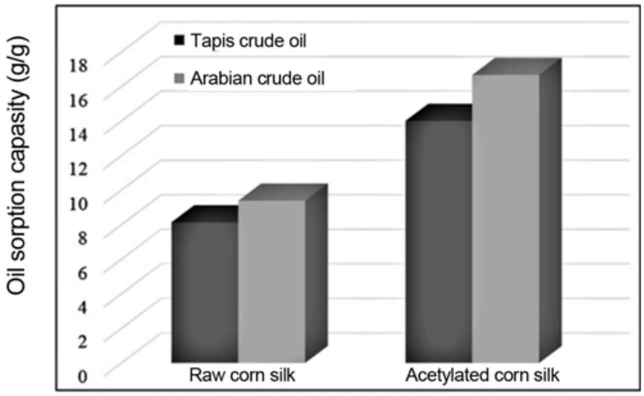

Figure 4. Maximum oil sorption capacity of sorbents for Tapis and Arabian crude oil.

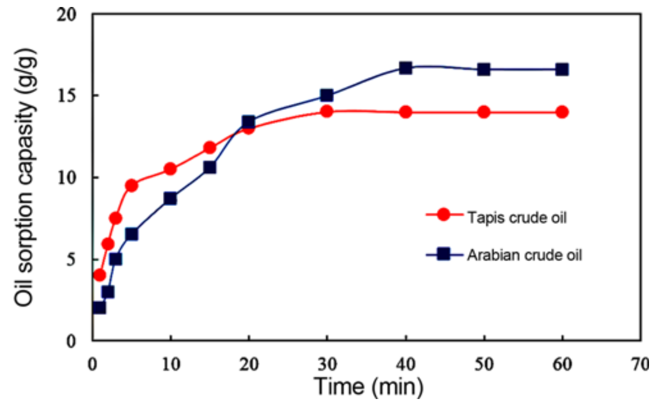

Figure 5. Effect of contact time on oil sorption capacity.

Two different temperatures were investigated as shown in Table 1. WPG increased with the increase in acetylation temperature. In acetylation process, hydrogen bonding network in hydroxyl group is broken to diffuse the acylating agent. When temperature is increased, the hydrogen bonding network swells and breaks and the hydrogen bonds make reactive chemical sites for accepting the acylating agent. Therefore the WPG at 120 ^{o}C was higher than at 90 ^{o}C.

Time is another factor that affects acetylation. The WPG was enhanced with the increase in reaction time. As shown in Table 1, the WPG was 5.65 %, 8.31 %, 11.15 %, and 9.37 % for 1, 3, 6, and 9 h, respectively. This increment of WPG by extending the reaction time was in direct relation with the process of diffusion and absorption of the reactants between the acetic anhydride and the corn silk molecules. Similar trend of absorption process was also reported earlier [21]. Table 1 also indicates that there is a slight decrease in WPG at 9 h reaction time. This is probably due to acetic acid produced during the reaction, which decreased the concentration of acetic anhydride and then decreased the reaction rate [22]. These results conclude that the highest WPG (11.15 %) and higher oil sorption capacity were achieved at 120 ^{o}C for 6 h reflux time with 3 % NBS.

Oil Sorption Experiment

The oil sorption of raw and acetylated corn silk was examined using Tapis crude oil and Arabian crude oil which represent low-viscosity and medium viscosity oils, respectively. The physical properties of Arabian and Tapis crude oil are shown in Table 2. Tapis crude oil was immediately absorbed by the sorbent in the first few minutes of contact but Arabian crude oil took a longer time to reach the same level of sorption (Figure 5). This difference could be due to the higher viscosity of the Arabian crude oil compared to Tapis. Viscous oils need longer time to reach the porous interior of sorbents through capillary action. The rate of oil sorption is inversely proportional to the oil viscosity [20].

Increase in acetyl groups after acetylation made the corn silk more hydrophobic. Figure 4 illustrates the maximum sorption capacity of the sorbents for Tapis and Arabian crude oil. The oil sorption capacity of raw corn silk for the two types of oils are 8.15 and 9.4 g/g, respectively. These values are much lower than the sorption capacity of the treated silk (obtained by 6 h reflux time at 120 ^{o}C by 3 % NBS) which are 14.02 and 16.68 g/g for the corresponding oils. The effect of contact time on the uptake of oil is shown in Figure 5. The results revealed that maximum sorption capacity of Arabian crude oil was achieved at 40 min contact time, whereas the time for Tapis was 30 min. This observation could be due to the difference in viscosity of the oils. After this time, no significant sorption was observed, indicating that the porous interior of sorbents was almost saturated with oil.

Table 2. Physical properties of Arabian and Tapis crude oil at 25 ^{o}C

Experimental oil	Density (g/cm^3)	Viscosity (c.p)
Tapis crude oil	0.80	2.32
Arabian crude oil	0.89	44.9

Reusability

The reusability of corn silk and recovery of the oil sorbed by sorbent materials was examined by simple squeezing method. This method is a common, practical, and economical method of recovering the oil [23]. The amount of oil sorbed by raw and acetylated fiber after five sorption cycles is shown in Figure 6. The result indicates that a total of 7.3, 8.1 g/g Tapis and Arabian crude oil for raw and 12.5 and 14.8 g/g Tapis and Arabian crude oil for acetylated corn silk could be recovered by simple squeezing in first cycle. The sorbents could be reused for five cycles. The results, however, show that the oil sorption in the first cycle was higher and in the subsequent cycles it is reduced gradually until it reaches the lowest value. After fifth cycle of sorption, the oil sorption capacity of acetylated corn silk for Tapis and Arabian crude oil is 4.8 g/g and 6.9 g/g, respectively. This probably was

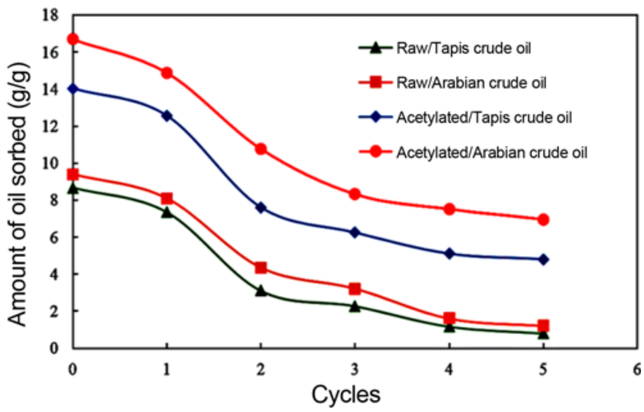

Figure 6. Reusability of raw and acetylated corn silk.

due to the disruption and collapsing of tubular and porous structure of interior fiber during the mechanical squeezing.

It can be inferred that the acetylated corn silk shows good reusability up to five cycles. This is probably because of presence of acetyl group on the sample surface which is very effective to increase its reusability due to more stable liquid bridge between acetylated samples compared with the raw fiber [17].

Conclusion

Sorption of Tapis and Arabian crude oil in water by corn silk is around 8.6 and 9.4 g/g, respectively. These capacity could be improved by acetylation process due to more hydrophobic characteristic and acetylation of the hydroxyl groups in the molecular structure of corn silk. The best condition for acetylation is 3 % catalyst for 6 h reflux at 120 ^{o}C, which showed maximum WPG and oil sorption capacity of 14.02 and 16.68 g/g for Tapis and Arabian crude oil, respectively. The optimum contact time for Tapis and Arabian were 30 and 40 min, respectively. The acetylated corn silk is reusable up to five cycles. FTIR spectrum results of acetylated corn silk showed acetylation reaction and enhancement of acetylation level corresponding to the increase at 1740 cm^{-1}. The FE-SEM images of corn silk showed that high probability of oil trapped on the rough surface and then diffuse in the porous interior fiber. Acetylated corn silk as a low cost and easily available material may be used as alternative to commercial sorbent such as polypropylene for oil spill cleanup.

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