



Acetylation of banana fibre to improve oil absorbency

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ABSTRACT

Oil spill leaves detrimental effects on the environment, living organisms and economy. In the present work, an attempt is made to provide an efficient, easily deployable method of cleaning up oil spills and recovering of the oil. The work reports the use of banana fibres which were acetylated for oil spill recovery. The product so formed was characterized by FT-IR, TG, SEM and its degree of acetylation was also evaluated. The extent of acetylation was measured by weight percent gain. The oil sorption capacity of the acetylated fibre was higher than that of the commercial synthetic oil sorbents such as polypropylene fibres as well as un-modified fibre. Therefore, these oil sorption-active materials which are also biodegradable can be used to substitute non-biodegradable synthetic materials in oil spill cleanup.

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1. Introduction

Oil is one of the most important energy and raw material sources for synthetic polymers and chemicals worldwide (Annunciado, Sydenstricker, & Amico, 2005). During production, transportation, storage and usage of oil there is always a risk of oil spillage. Oil spill occurs over the seas, water bodies and land surfaces due to ship breakage, tanker disasters, wars, operation failures, equipment breaking down, accidents and natural disasters. Oil spills into land, river or ocean impose a major problem on the environment (Azzam & Madkour, 2008; Wei, Mather, Fotheringham, & Yang, 2003). Under favorable conditions, oil in water body continues to spread over the water surface and forms a monomolecular layer and affects the natural habitat. Oil film which is formed on the surface of water due to spills impairs the exchange of energy, heat, moisture, and gases between the water reservoirs and the environment. This leads to considerable harm to environment and marine life. Oil spills harm the beauty of polluted sites; give strong odour and the excessive growth of green algae, alter sea colour and the landscape (Annunciado et al., 2005). Viscosity of the oil also plays an important role in deciding the severity of such spill. Viscous oils spread more slowly than less viscous ones and therefore, water temperature, along with wind speed and sea conditions have tremendous effect on the extent of oil spreading. It is reported that spreading is important in determining the fortune of spilled oil (Reed et al.,

1999; Wei et al., 2003) through evaporation, emulsification and neutral dispersion.

One of the ways to clean up the oil spills is to make use of proper sorbents. The sorbents presently in use can be classified as polymers, natural materials or treated cellulosic materials. Most commonly used commercial sorbents are synthetic sorbents made of polypropylene or polyurethane (Deschamps, Caruel, Borredon, Bonnin, & Vignoles, 2003). They have good hydrophobic and oleophilic properties, but their non biodegradability is a major disadvantage (Choi & Cloud, 1992; Deschamps et al., 2003). A number of natural sorbents have been studied for use in oil-spill cleanup, e.g. cotton (Choi, 1996; Johnson, Manjrekar, & Halligan, 1973), wool (Radetic, Jovic, Jovancic, Petrovic, & Thomas, 2003), bark (Haussard et al., 2003) and rice husk (Nwankwere, Omolaoye, Nwadiogbu, & Nale, 2011). These agricultural products and residues are locally available and inexpensive. Some are waste materials and hence their reuse will result in savings in disposal fee. Cellulose is an abundant and naturally occurring polymer that can be obtained from numerous resources. Its structure is organized into fibrils, which are surrounded by a matrix of lignin and hemicellulose (Rosa et al., 2010). The cellulosic products which exist in fibrous form can be easily formed into mats, pads and non-woven sheets for convenient applications (Fanta, Burr, & William, 1986).

One such cellulosic fibre is banana fibre obtained from banana plants. These banana plants are of the family Musaceae and are cultivated primarily for their fruit. As such, after harvesting the fruit, the matured pseudostems are generally disposed as a landfill or left to decompose slowly in a plantation field (Bilba, Arsene, & Ouensanga, 2007). Banana fibre can also be extracted from the "pseudostems" which is clustered, cylindrical aggregation of leaf

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stalk bases. Banana fibre is a ligno-cellulosic fibre which has relatively good mechanical properties. The extraction of fibre however is not a common practice.

The objective of this work is to provide an environmentally acceptable method of cleaning up oil spills and also to get an applicable technique which allows its recovery using banana fibre as a substrate. This work evaluates the use of banana fibre for sorption of spilled oil from aqueous media. Since banana fibre tends to also absorb water, its oil sorption capacity may be drastically reduced. Thus, esterification is carried out to increase the hydrophobicity of the fibres and also to enhance oleophilicity.

2. Experimental

2.1. Materials

Banana fibre was purchased from a local market (Mumbai, India) and was dried in sunlight. Acetic anhydride, N-Bromosuccinimide (NBS) and all other chemicals were supplied by S.D. Fine Chemicals Mumbai India. High density oil used for the testing purpose was purchased from local market.

2.2. Methods

2.2.1. Acetylation in a solvent free system

A fixed quantity of banana fibre (10 g) was placed in a 500 ml round bottom flask containing required ml of acetic anhydride and N-Bromosuccinimide (NBS) (2%) as a catalyst. The flask was then placed in an oil bath set at the required temperature (120 °C) using atmospheric pressure with a reflux condenser fitted. After the reaction for the required time (1 h) the flask was removed from the oil bath and the hot reagent was decanted-off. The banana fibre was then thoroughly washed with ethanol and acetone to remove the un-reacted acetic anhydride and acetic acid by-products. The modified fibres were then dried in an oven at 60 °C to constant weight. The oven-dry materials were weighed to determine the weight gains on the basis of initial oven-dry weight (Sun, Sun, & Sun, 2004). To confirm the results, each experiment was repeated thrice under the same conditions and the weight percent gain (WPG) values were estimated which were well within the acceptable standard deviation of 0.2%. Weight percent gain of the banana fibre due to acetylation was calculated using the formula:

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

wherein, W_1 and W_2 are the weights of banana fibre and acetylated banana fibre, respectively.

2.2.2. Oil absorptivity

Oil absorptivity was determined by using method reported in literature (Sun et al., 2004). A fixed quantity of machine oil (50 g) was suspended in water in a beaker. The acetylated banana fibre (1 g) was added at room temperature and allowed to absorb oil for 1 h. The banana fibre was then picked up and held to drain-off the excess amount of oil. The banana fibre was then reweighed to determine the oil absorptivity.

2.2.3. Recovery of sorbed oil and reusability of sorbents

In order to examine the reusability of these sorbents, methods described elsewhere were followed, with the limitation that this method gives only an approximate value of oil sorption. The method is briefly summarized. Machine oil (50 g) was suspended in water in a beaker. The acetylated banana fibre (1 g) was added and mixed for 1 min at room temperature and allowed to absorb oil for 1 h. The sorbent with oil was weighed and then squeezed between two rollers at a pressure of 10kgf/cm before it was reweighed to

determine the amount of recovered oil. The squeezed sorbent was again used in the sorption process as before (Choi & Moreau, 1993). The efficiency of sorbent reusability was determined by oil sorption capacity of each sorbent after repeated sorption and mechanical desorption cycles (Ansari, East, & Johnson, 2003).

3. Chemical characterization

3.1. IR spectra

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

3.2. TGA

Thermal gravimetric analysis (TGA) of the unmodified and acetylated banana fibres was carried out by regular method. The thermograms of samples were recorded on Shimadzu 60H DTG machine using aluminum pan between temperature range 30–550 °C and under the inert atmosphere of N_2 at a flow rate of 50 ml/min.

3.3. Degree of acetylation

The percent acetylation (acetyl %) was determined using titration method. Acetylated banana fibre (1 g) was placed in a 250-ml flask, and to this, 50 ml of 75% ethanol in distilled water was added. The loosely stopper flask was agitated, warmed to 50 °C for 30 min, cooled, and 40 ml of 0.5 M KOH was added to it. The excess of alkali was back titrated with 0.5 M HCl with phenolphthalein as an indicator. The solution was allowed to stand for 2 h 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.

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

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).

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

3.4. Scanning electron microscopy (SEM)

Analysis of the morphology of dried and modified sample was carried out using scanning electron microscope (JEOL, Japan), from Institute of Chemical Technology. The samples were sputter coated with gold layers and images were recorded using scanning electron microscope.

3.5. Chemical analysis

An accurately weighed 2 g of banana fibre sample was boiled in ethanol (4 times) for 15 min, washed thoroughly with distilled water and kept in oven for drying at 80 °C for overnight. It was again weighed and then divided into two equal parts in which one part is considered as A fraction. Second part of residue was treated with 24% KOH for 4 h at 25 °C, washed thoroughly with distilled water and dried at 80 °C over night and the dry weight was taken as B fraction. The same sample was further treated with 72% H_2SO_4 for 3 h to hydrolyse the cellulose and then refluxed with 5% H_2SO_4 for 2 h.

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