

## Oil spill sorption using carbonized pith bagasse: trial for practical application

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**ABSTRACT:** In the present work, an attempt was made to provide an efficient, easily deployable method of cleaning up oil spills and recovering of the oil. Carbonized pith bagasse, a relatively abundant and inexpensive material is currently being investigated as an adsorbent to remove contaminants "oil" from water. Fibers extracted from bagasse and carbonized at 300 °C were found to have a high performance for sorption and recovery of light, heavy oils and even the viscous ones. The physical properties of pith bagasse were investigated using scanning electronic microscope to show the inner and the outer surface and the cross section area of the pith bagasse and thermo gravimetric analyzer to investigate the degradation profile of the pith bagasse. The carbonized pith bagasse was packed into a polypropylene bag and its sorption behavior was studied. A comparison was made between the prepared pad and the commercial sorbents show that the pad containing carbonized pith bagasse has higher sorption capacity in comparison to the commercial sorbents. The pad exhibited high oil retention ability and a high selectivity for the oils over the water. The pad showed a possibility of reuse for eight times. The sorption capacity of the pads containing carbonized pith bagasse was found to increase with increasing the time of sorption till it reaches the maximum value at the time of sorption equal to 60 min.

**Key words:** Carbon fibers, sorption, oil recovery, sorbent

### INTRODUCTION

Oil is one of the most important energies and raw material sources for synthetic polymers and chemicals worldwide. Whenever oil is explored, transported and stored and its derivatives are used, there is risk of spillage with the potential to cause significant environmental impact. Pollution by petroleum oils affects sea life, economy, tourism and leisure activities because of the coating properties of these materials. Oil spills harm the beauty of polluted sites; the strong odor can be felt miles away and the excessive growth of green algae alters sea color and the landscape (Annunciado *et al.*, 2005). Crude oil spilt in the marine environment undergoes a wide variety of weathering processes, which include evaporation, dissolution, dispersion, photochemical oxidation, microbial degradation, adsorption onto suspended materials, agglomeration etc. (Jordan and Payne, 1980). These physico-chemical changes enhance oil dissolution in seawater (Payne and Phillips, 1985). Previous studies show that photo-oxidation of oil in the aquatic

environment leads to the formation of numerous oxygenated products such as aromatic, aliphatic, benzoic and naphthanoic acids, alcohols, phenols and aliphatic ketones (Kawahara, 1969; Frankenfeld, 1973; Larson *et al.*, 1977; Payne and Phillips, 1985). Mechanical recovery is the transfer of oil from the spilled area to some transportable form of temporary storage by the help of oil sorbents or skimmers (Choi and Cloud, 1992). Today, the sorbents in use can be classified as either polymers, natural materials or treated cellulosic materials (Deschamps, *et al.*, 2003). It is recently reviewed the porous materials used for oil-spill cleanup and several studies of different natural, synthetic and mineral sorbents have also been conducted (Choi and Moreau, 1993; Reynolds *et al.*, 2001; Toyoda, 2003). Most commonly used commercial sorbents are synthetic sorbents made of polypropylene or polyurethane (Teas *et al.*, 2001). They have good hydrophobic and oleophilic properties, but their non-biodegradability is a major disadvantage (Choi and Cloud, 1992; Deschamps *et al.*, 2003). Since most oil products are biodegradable, oil could be disposed of

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for example by composting. A biodegradable material with excellent absorption properties would be advantageous in this respect. A number of natural sorbents have been studied for use in oil-spill cleanup, e.g. cotton (Choi and Kwon 1993; Choi, 1996; Johnson *et al.*, 1973), wool (Radetic *et al.*, 2003), bark (Haussard *et al.*, 2003), kapok (Hori *et al.*, 2000, Ghalambor 1995; Rowell, 1998) and rice straw (Sun *et al.*, 2002). These agricultural products and residues are locally inexpensive and available. Some are waste materials and hence their reuse will result in savings in disposal fee. The cellulosic products which exist in fibrous form can be easily formed into mats, pads and non-woven sheets for convenient applications (Fanta *et al.*, 1986). The methods commonly used to remove oil involve oil booms, dispersants, skimmers, sorbents etc. (Wardley-Smith, 1983). In order to apply this extremely high sorption capacity and high rate of activated carbon to a practical recovery process of heavy oils spilled on water, the bulky and fragile nature of carbonized pith bagasse has to be overcome. As a preliminary trial for practical applications for the recovery of heavy oil, carbonized pith bagasse was packed into a polypropylene bag and its sorption behavior was studied. Particular attention was paid to the sorption time, desorption time, weight of sorbent and the reusability of pad. Consequently, the objective of this work is to provide an efficient, easily deployable method of cleaning up oil spills and recovering the oil. It is important to provide a safe system for oil removal and recovery. The main goal in this work is not only to provide an environmentally acceptable method of cleaning up oil spills but also to get an applicable technique which allows its recovery.

**MATERIALS AND METHODS**

*Materials*

Carbonized pith bagasse with a bulk density of 0.0852 g/cm<sup>3</sup> which had been used in our previous papers (Amer and Hussein, 2006) and the fraction particle size between 1 mm and 0.8 mm were selected and then subjected to a carbonization process in a closed carbonized stainless steel tube (with a length of 12.5 cm, inner diameter of 2.5 cm and a small hole at the top for the ventilation of the gases produced during carbonization). It was heated in a muffle furnace at 300 °C for 2 h. and packed in a polypropylene bag with the following specifications (Nonwoven polypropylene permeable to oil but retains the sorbent with average

thickness of 65 mm, shear modulus of 6.25 N/cm<sup>2</sup> and modulus of elasticity (elongation) 32.2%). The commercial sorbents (adsorbe-IT filtration fabric and oil-only sorbent) obtained from Canada and The United States have the specifications as shown in Table 1.

Table 1: Commercial sorbents specifications

Type	Adsorbe-IT filtration fabric	Oil-only sorbent
Company and country of manufacturing	ECO-TECH, Inc, USA	ARCUS absorbent Inc, Toronto, Ontario, Canada
Composition	Geo-textile quality nonwoven filtration fabric manufacture from 100% recycled selected fiber from textile industry.	Hydrophobic polypropylene product available pad
Thickness	0.69 <sup>+</sup>	3.73 mm

*Tested oils*

Different kinds of oils were tested for the application of sorbents to represent a wide variety. Gas oil has a specific gravity of 0.82 at T= 15 °C with a flash point of 55°C obtained from benzene station; heavy Arabian crude oil which has a kinematics viscosity of 11.2 cSt at 40 °C and a specific gravity of 0.8825 at (60/60) was obtained from Medore Refining Company. Fuel oil which has a kinematics viscosity of 445 cSt at 50 °C was obtained from Alexandria Petroleum Company. The gas and fuel oil were used without modification. In early stages of an oil spill, lighter hydrocarbons do evaporate and consequently the oil viscosity increase before any possible cleanup operation can take place (Satish, 2003). Thus, in order to simulate this situation of oil spill and to minimize experimental variation, crude oil samples were put on a tray where oil formed a layer of a 5 mm thick and was situated in open air for one and seven days (Stlver and Meck, 1984). Different types of oil, namely gas oil, one and seven day weathered heavy Arabian crude oil were employed to investigate the oil sorption characteristics of pith bagasse. Gas oil represents low viscosity (74.6118 cSt at 25 °C) oils such as light crude oil, kerosene and gasoline. One day weathered heavy Arabian crude oil is a good surrogate for oils with intermediate viscosity (181.360 cSt at 25 °C) and a density of (0.856 g/cm<sup>3</sup>) such as heavy crude oil and vegetable oils. Seven day weathered heavy Arabian crude oil represents highly viscous oils (512.79 cSt at 25 °C) and a density of (0.8954

g/cm<sup>3</sup>) such as lubricating oils. These oils were investigated in favor of the crude oils or lightweight hydrocarbon oils, because they were less volatile and had better compositional uniformity, which minimized transient change in their chemical and physical characteristics during experiments.

#### *Methodologies of oil sorption experiments*

##### *Determination of dynamic oil retention and oil sorption capacity*

A 500 mL sample of artificial sea water (3.5% NaCl) was placed in a 1 L glass beaker, as described in Technical Manual of the American Association of Textile Chemists and Colorists [AATCC] (Choi and Cloud, 1992). A forty mL of oil was added to the beaker. The beaker containing crude oil and artificial sea water was mounted in a shaking apparatus. Approximately one g of a sorbent material was contained in a (7 cm length and 7 cm width) pad and placed in the system, which was shaking for 15 min at 105 cycles/ min. The wet pad was weighed after being drained for 5 min in the sustainer. Water content of the sorbent was analyzed by the ASTM D4007-81 (ASTM, 1998a). Petroleum ether was used as the carrier solvent. The use of pads makes the application of the pith bagasse fiber easier. The weight of the oil and water sorbed by the non-woven fabric with and without the carbonized pith bagasse was measured; the difference between the two weights was taken to indicate the oil sorption capacity and water pick up.

$$\text{Oil sorption capacity} = [S_T - S_p - S_C - S_A] / S_A$$

where,  $S_A$  is the dry weight of the sorbent (g);  $S_T$  is the total weight (g) of the oil, water and dry sorbent and  $S_C$  is the weight of water (g).  $S_p$  is the amount of the oil sorbed by the empty non-woven polypropylene pad (g).

##### *Evaluation of cyclic sorption/desorption characteristics*

This experiment evaluated reusability of the pith bagasse fiber for cyclic oil sorption/desorption. As the cyclic sorption/desorption characteristics of a fibrous sorbent depend on its packing density, the influence of packing density on these characteristics were investigated. The experiments were carried out under simulated field conditions, as described previously. The procedure was similar to that adopted by Inagaki (Inagaki *et al.*, 2002) with modification on their oil recovery method. Using filtration under mild suction

(by using a vacuum pump) of the sorbed carbonized pith bagasse, oil could be recovered without serious disruption of the bulky morphology of carbonized pith bagasse. The sorption/desorption cycle was repeated for the desired number of cycles until oil sorption capacity was less than 50% of the sorbed oil in the first cycle.

## RESULTS AND DISCUSSIONS

### *Electro scanning of pith bagasse*

Pith bagasse is a three dimensional, biopolymer composite anisotropic, amorphous and porous which has a high aspect ratio (length/width) and a rough surface. The fiber structure is hollow tubular structure (or lumen) with external diameter of 111.764  $\mu\text{m}$ , internal diameter of 88.23  $\mu\text{m}$  and length of 220  $\mu\text{m}$ ., laminated and randomly oriented, with molecular layers and an integrated matrix, as seen from the electronic scanning microscope in Fig. 1 a and b. The figure also shows the roughness of the surface and the projections which enhance the adsorption properties of pith bagasse. Also, they show the anisotropic structure of pith bagasse, the amorphous orientation of the fibers and the big fiber lumen which enhances the capillary action and the diffusion of oil through the cuticle to the inner fibers. Finally, they show the hollow tubular structure (or lumen) which enhances the absorption properties of pith bagasse.

### *Studying the thermal gravimetric analysis of pith bagasse*

The thermal gravimetric analysis of the bagasse sample is shown in Fig. 2. The fiber mass decreased from about 97.242% (at 100 °C) to 51.939 % (at 250 °C) and to 28.153% (at 350 °C). Different regions can be associated with the loss of retained water at 100 °C, hemicellulose degradation in the 200-260 °C regions, cellulose degradation at 240-350 °C and lignin degradation at 280-500 °C. Between 100 and 250 °C, degradation turns the lignocellulosic fiber into a brownish color material, losing its strength though this was not quantified. At higher temperatures, up to 500 °C, carbonization occurs with accentuated loss of material. Being one of the oldest thermal analytical procedures used for the study of polymeric systems, the thermogravimetry analysis is a technique of evaluating the thermal decomposition kinetics of materials by monitoring the weight loss of the sample in a chosen atmosphere (usually nitrogen or air) as a

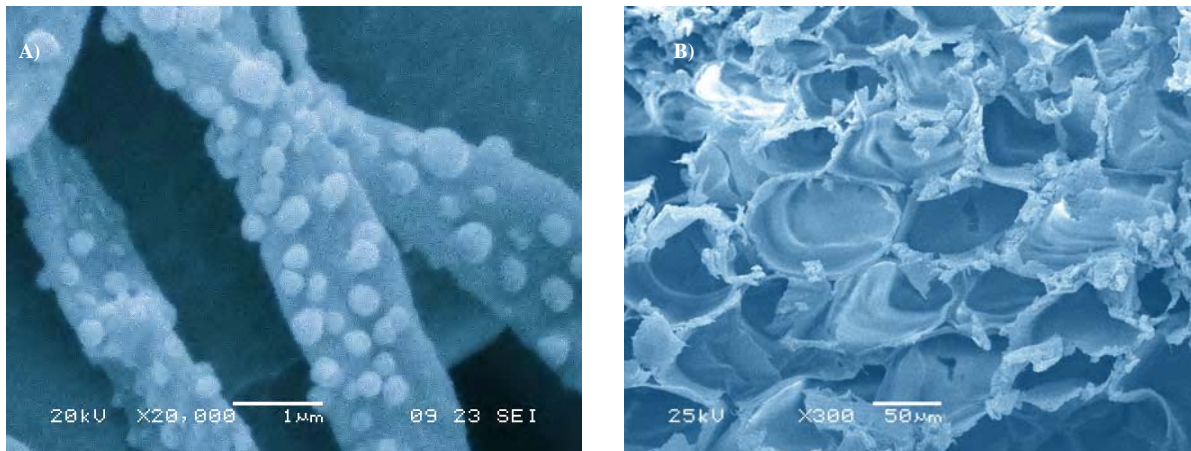


Fig. 1: Scanning electron micrographs of the longitudinal and cross section of pith bagasse before carbonization

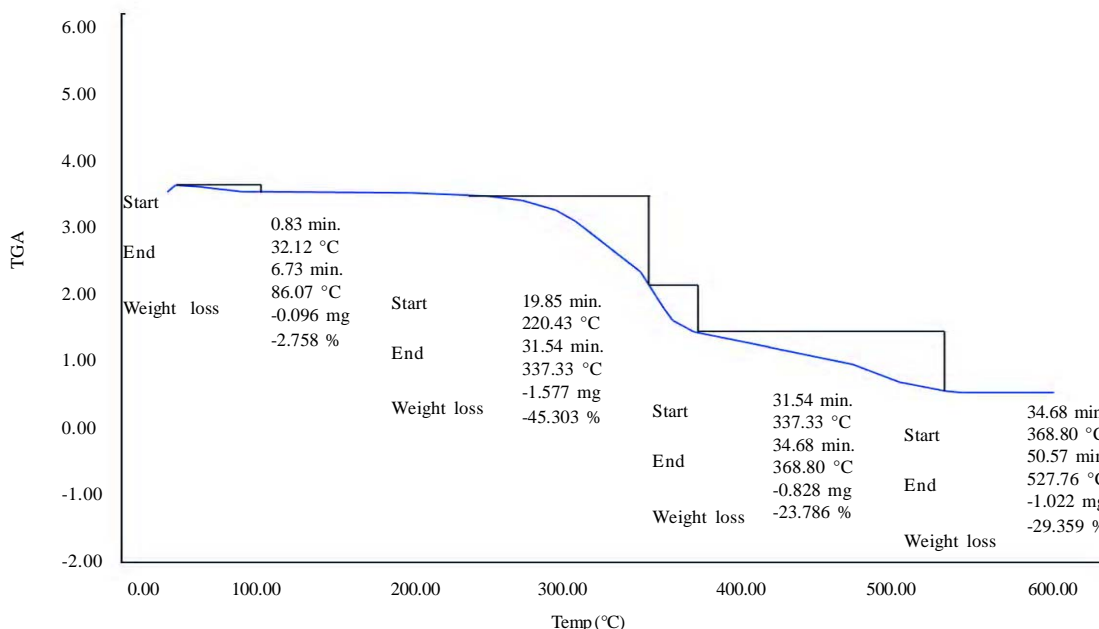


Fig. 2: Thermal gravimetric analysis of the bagasse sample

function of temperature (Description, 2003). Not all thermal events result in a change of the sample mass: melting, crystallization and glass transition do not exhibit a mass change, whereas desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition do. TGA is the best known for its ability to provide information on the bulk composition of compounds. The usefulness of TGA for analyzing complex systems is greatly enhanced by the ability to record simultaneously the first derivative of the weight loss, that is, the derivative of the thermo gravimetric curve.

*Sorption time under simulated field condition*

Fig. 3 indicates that the sorption capacity of the pads containing carbonized pith bagasse increases with an increase in the time of sorption till it reaches the maximum value at a time of sorption equal to 60 min. It also indicates that the seven-day weathered crude oil has the maximum sorption capacity of 32 g/g fiber. Then, the one-day weathered crude oil (30 g/g fiber) and finally the gas oil has the lowest value of sorption capacity of 23 g/g fiber. The results confirm (Tavisto *et al.*, 2003; Gerald *et al.*, 2003) that the oil sorption

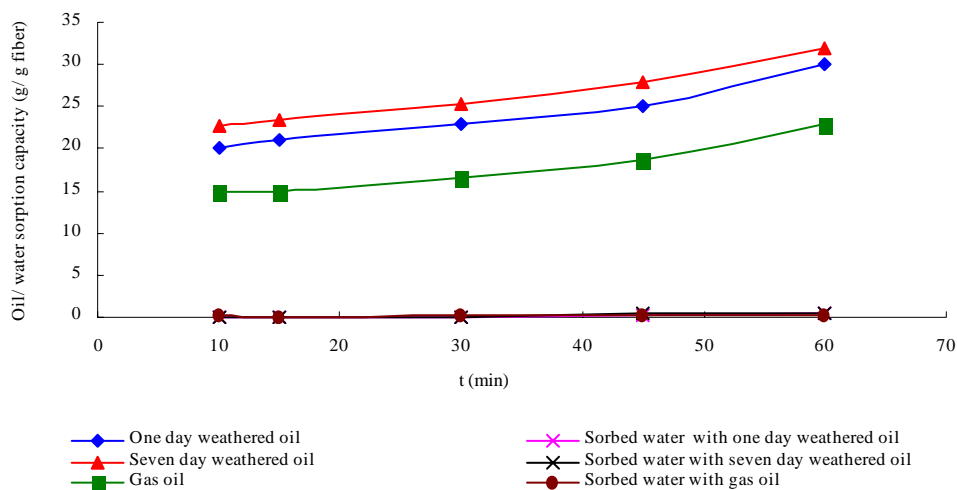


Fig. 3: Effect of sorption time on the oil sorption capacity (g/g of fiber)

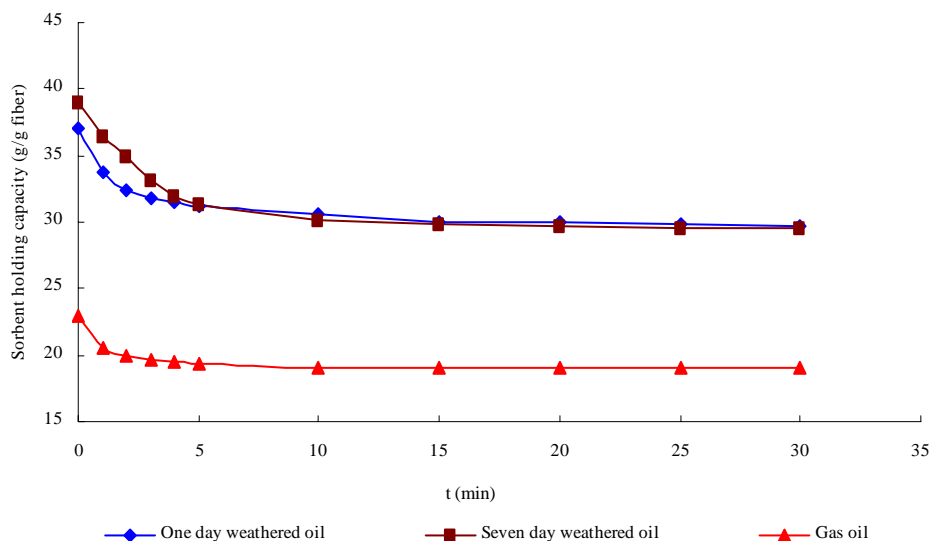


Fig. 4: Effect of desorption time on the holding capacity (g/g of fiber)

capacity increases with increasing the sorption capacity till it reaches a maximum value.

*The effect of desorption time on the holding capacity*

Fig. 4 shows that the dripping of oil from the surface of the carbonized pith bagasse is fast during the first 5 min and then it approximately stops. These results are in agreement with those reported by Choi and Kwon (1993) as they investigated the kinetics of oil desorption. They found that the rate of desorption for both fabrics was

rapid during the initial 2 min and then began to level off. Also, the results are in agreement with Wei (2003). The results show that the retention behavior of all sorbents follows almost the same trend. There are at least two distinct zones in each retention curve. The first zone is the initial stage of release, which occurs over 5 min. The rate of release is very high during this period. The second zone represents the steady-state period. During this period, the sorbent tends to begin a descent towards a steady state. Through this zone, additional time will

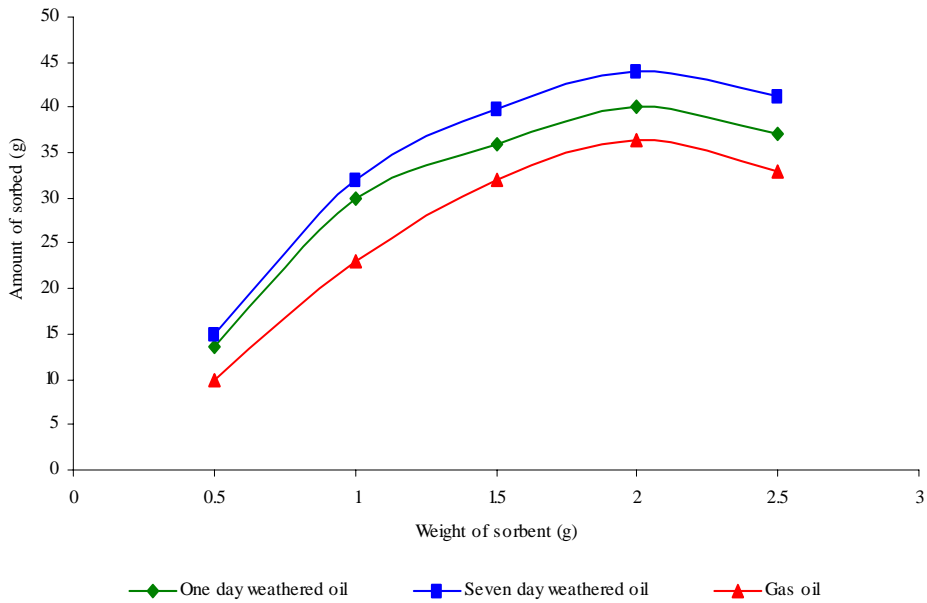


Fig. 5: Effect of sorbent weight on oil sorption capacity (g/ total weight of fiber)

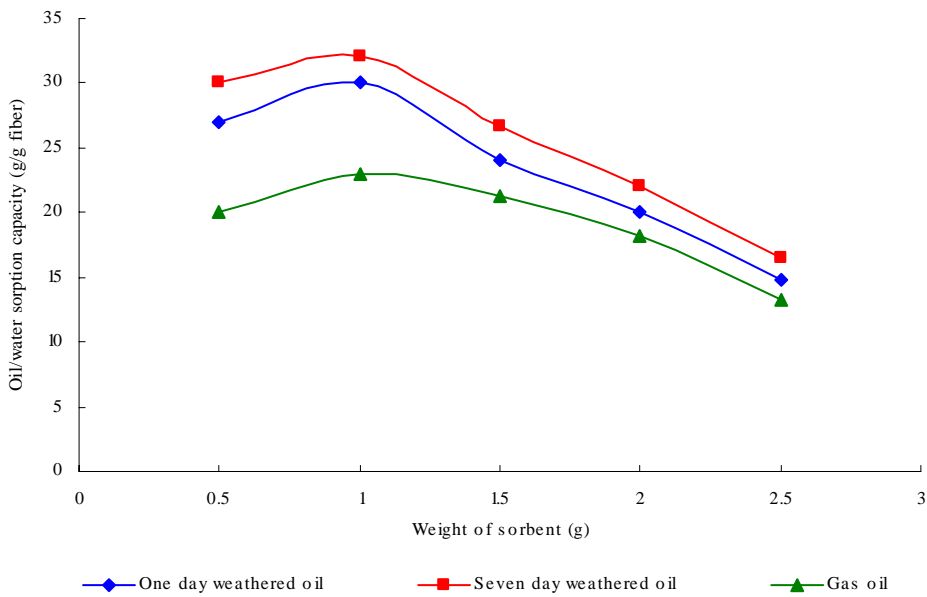


Fig. 6: Effect of sorbent weight on oil sorption capacity (g/ g of fiber)

not release any significant amount of oil. However, although the sorption retention curves for all sorbents show similar trends, they also exhibit many varied phenomena. Light oil tends to be released from sorbent fast with high release rate compared to the heavy oil.

*Weight of sorbent under static conditions*

Fig. 5 shows that as the weight of carbonized pith bagasse fiber increases the sorption capacity (g oil/ total weight of fiber) till it reaches a maximum value at 2 g of carbonized pith bagasse fiber and then it

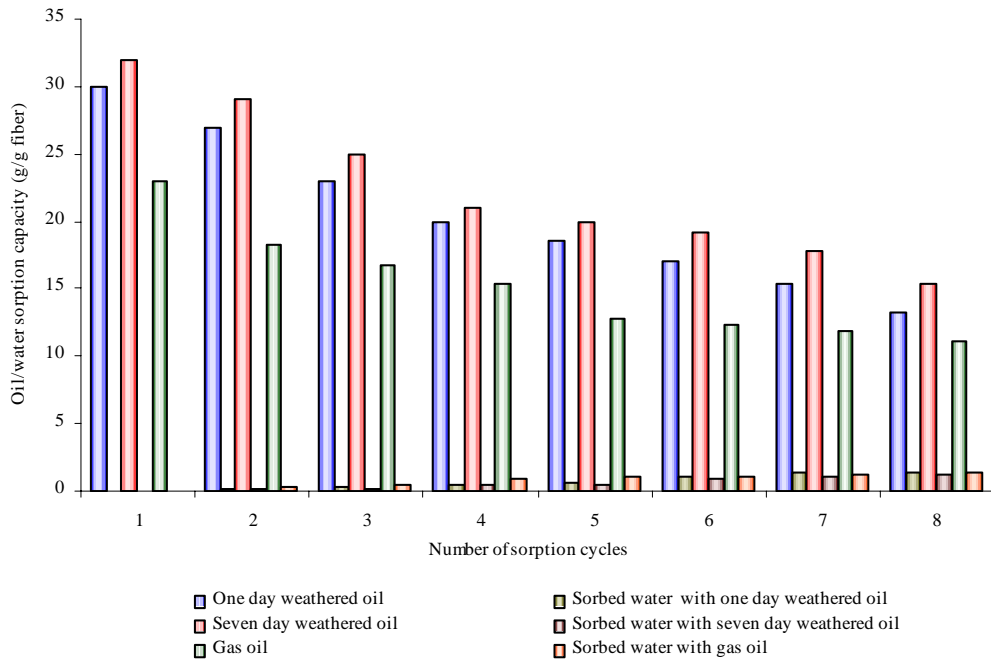


Fig. 7: Effect of reusability on oil sorption capacity (g/g of fiber)

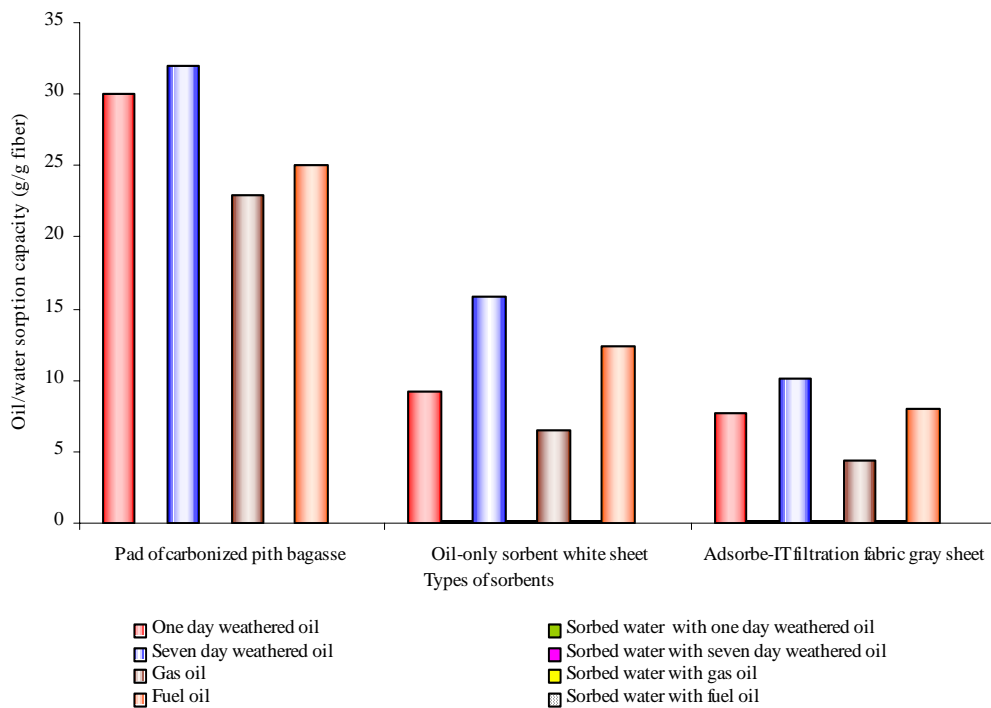


Fig. 8: Comparison between the prepared carbonized pith bagasse and the commercial sorbent

decreases again. The seven-day weathered crude oil has the highest sorption capacity of 44 g oil/ total weight of fiber at a weight of sorbent of 2 g and then one day weathered oil has a sorption capacity of 40 g oil/ total weight of fiber at a weight of sorbent of 2 g and the gas oil has the lowest sorption capacity of 36.5 g oil/total weight of fiber at a weight of sorbent of 2 g. In earlier stage, i.e. from 0.5-2 g the sorbent surface area contact to oil was the maximum. Due to sorbent surface area, pores of pith bagasse particles and channel produce between particle due to random distribution of particle and irregular surface shape. Fig 6 shows that as the carbonized fiber weight increases, the sorption capacity (g/g, fiber) also increases till it reaches a maximum value at 1 g of carbonized pith bagasse. By increasing the weight of sorbent, the sorption capacity decreases, because when the sorbent weight increases at limited area (pad), the sorbent particle, which is not in contact with oil, increases (there will be sorbent accumulation in the limited area pad) so the sorption capacity decreases.

#### *The effect of the reusability*

The results of the experiments are presented in Fig. 7. The figure indicates that the pads containing carbonized pith bagasse fibers could be reused for eight cycles with a fairly good efficiency for eighth sorption cycles. The recovery of oil was found to decrease and the results suggest that pith bagasse can be reused several times for oil spill clean-up with the aid of a suitable mechanical device (vacuum pump). The figure also shows that the seven-day weathered crude oil has the highest sorption capacity; the one-day has the second highest sorption capacity and finally the gas oil has the lowest sorption capacity. The sorption capacity decreases till it reaches the lowest value at the eighth cycle. In practical oil spill clean-up operation on the water, oil is removed from the sorbent by a simple mechanical action, where the vacuum is used and the sorbent is reapplied several times. If the carbonized pith bagasse was squeezed after sorbing heavy oil up to its maximum capacity, a large amount of the oil would come out by simple compression. However, the characteristics of bulky morphology of the carbonized pith bagasse would be destroyed. As a consequence, there was no possibility of recycling the carbonized pith bagasse by compression. Therefore, a much more milder procedure for the recovery of sorbed oil needs to be developed in

order to recycle carbonized pith bagasse as well as the oil. Through a vacuum pump, using filtration under mild suction of the sorbed carbonized pith bagasse, oils could be recovered without serious disruption of the bulky morphology of carbonized pith bagasse. The filtration process seemed to be practical because of the possibilities for recycling both oil and carbonized pith bagasse with reverse to the compression of the carbonized material as it couldn't be used again. These results are in agreement with those introduced by Toyoda and Inagaki (2000). They investigated the efficiency of recovery.

#### *Comparison between the prepared sorbent from bagasse and commercial sorbents.*

The results of these experiments are presented in Fig. 8. The results show that the prepared carbonized pith bagasse has higher sorption capacity (of 25, 32, 30 and 23 g/g fiber) for fuel oil, seven-day weathered oil, one-day weathered oil and gas oil, respectively, when compared with the commercial sorbents which have maximum values for seven-day weathered oil of 15.8125 and 10.15 g/g fiber for oil-only sorbent white sheet and adsorbe-IT filtration fabric gray sheet, respectively.

The present results reveal that the use of carbonized pith bagasse packed into a non-woven polypropylene bag and is found out to be effective in recovering different kinds of oil spilled on water. In order to achieve an extremely high sorption capacity of carbonized pith bagasse, the following points have to be taken into consideration: sorption time, desorption time, weight of sorbent and finally the effect of reusability on the sorption capacity.

The following deductions were proved:

- 1) The carbonized pith bagasse in the form of a pad studied is an excellent sorbent for oils, both under static conditions (oil-only) and under simulated field conditions (artificial water with oil layer).
- 2) The holding capacity of the pad was found out to be good for the different oil type which means that the pad can be left without dripping the sorbed oil.
- 3) The recovery of heavy oils sorbed into carbonized pith bagasse was performed using filtration under mild suction at room temperature which seems to be a more practical process because carbonized pith bagasse can be recovered without serious disruption of its characteristically bulky morphology for 8 times. The sorption capacity was, however, found to decrease with its recycling.



4) Comparative studies with a commercial sorbent material (adsorbe-IT filtration fabric, oil-only sorbent) demonstrated various advantages of the carbonized pith. The carbonized pith bagasse has a greater sorption capacity for oils and it is inexpensive.  
5) Based on the total results obtained, the pad containing carbonized pith bagasse has an excellent commercial potential as a sorbent for oil.

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