

Date Palm leaves Fiber Utilization as sorbent for Crude Oil Spill Cleanup and the Temperature Effect

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Abstract:

Crude oil spill are a global concern due to the environmental and economic impact as well as harm the beauty of the polluted sites. Date Palm leaves fiber (DPLF) as a natural agricultural fiber, which is environmentally materials, biodegradable, renewable, abundant, and cheap. A hollow cellulosic material like DPLF is a potential sorbent to counter the oil spill pollution. The oil sorption capacity (OSC) of fresh and weathered oils into DPLF as a sorbent was studied. The effects of contact time and temperature on sorption were studied in simulated tap water as well as salty water. The OSC increases with increasing the contact time. The DPLF has given oil sorption capacity of 4.534-7.985 g oil/g sorbent for a contact time of 5-90 min for fresh oil (tap water, at room temperature). This OSC are considered to be good for a sorbent considering it is locally available and not expensive. Fresh oil is having higher OSC at room temperature at all the experimental times (5-120 min). At lower temperature, e.g. 15 °C the adsorption of oil having greater role in increasing OSC, since at low temperature the oil having high viscosity and that will increase the adherence of oil onto the surface of the fibers and within the capillary during drainage. At room temperature and little higher e.g. 25 & 30 °C , the oil will have less viscosity and more diffusion and that will increase the absorption within the internal capillary and lumens of the fibers and that increase the OSC. There is decrease in viscosity at higher temperature e.g. 45 & 60 °C that will increase the diffusion in the oil and increase the segmental mobility of the fibers as well as increasing the penetration of oil into the pores and lumens of the fibers. That will increase the OSC, but much oil will come out during the drainage time (5 min).

Introduction:

Oil is one of the most important energy and raw material source for synthetic polymers and chemicals worldwide. Whenever oil is explored, transported and stored, there is risk of spillage with the potential to cause significant environmental impact. Between 1974 and 1994, there are 175 major oil spills worldwide. The total annual influx of petroleum hydrocarbons is about 10 million metric tons [1-4].

Oil spill is a release of a liquid hydrocarbon into the environment due to human activity, and it is a form of pollution. It has adverse impacts to the ecosystem and human health. Not only is it messy, their effects are long lasting, it harms the flora and fauna that depend on the affected water body for survival. Furthermore, oil spill also hurt the revenue from the tourism and fishery industries. The organic pollutants release from spill can lead to water contamination [5-7].

The most recent oil spills including March 1989 the Exxon Valdez incident spill 11.2 million gallons of crude oil into the costal water of Alaska. The Gulf War oil spill with a spill size of 1.5 million tons and costing an estimated USD 540 million to cleanup. In addition to the British Petroleum (BP) Deepwater Horizon oil spill that happened on 20th April 2010, which saw the release of 205.8 million gallons of oil. Not only did it pose a heavy threat to marine wildlife and ecosystem, it also costs a lot to initiate a cleanup [8-10].

Various processes have been developed to control these spills, e.g., removing oil from polluted areas by the use of booms, dispersants, skimmers, oil water separator and bioremediation (11-13) or sorbent materials. Sorbents can be divided into three basic categories: natural inorganic such as clay, sand, sludge, high calcium fly ash, perlite and exfoliated graphite (14-17). Synthetic organic sorbents are including polypropylene, polyurethane and others (10, 18-20). In addition, organic natural cellulosic materials sorbents many have been studied include, cotton, bark, milkweed, kapok, rice husk, Wheat straw and bagasse (8-10, 21-24).

Efficient methods of cleaning up the oil spill, such as using sorbent, have been widely used to clear up oil spills fast. A viable sorbent to mop up oil spill need to be affordable when employed in huge quantities, readily available, show high affinity for oil, low water retention capacity, high oil retention capability for the ease of transporting and ease of recovery of the oil. In addition, it has to be easily deployed, biodegradable, and resistant to deformation, chemical attacks and photo-degradation [25].

DPLF, or DPF here after as described by Zaid and Wet [26], the base of the frond is a sheath encircling the palm. This sheath consists of white connective tissue ramified by vascular bundles. As the frond grows upwards, the connective tissue largely disappears leaving the dried, and now brown, vascular bundles as a band of tough, rough fiber attached to the lateral edges of the lower part of the midribs of the fronds and unsheathing the trunk. Varieties differ in the height to which the fiber grows up the central column of unopened fronds and in the texture of the fiber and also somewhat in colour. The upkeep of the date palm trees results in the production of a huge renewable amount of by product such as date palm fibers . So, DPF is a by-product of date palm cultivation and cannot use as feed for animals. It is usually use as fuel for cooking and heating. Little works have been done on palm tree by-products, such as Modified oil palm leaves as adsorbent [7], date stones (pits) and palm trees leaves as biosorbents of copper, lead and nickel ions [27-29]. Date Palm Fibers was used as polyepoxy composites in preparing resin (30). Since there is no work done on using DPF as sorbent for crude oil as the authors know, this study, the use of DPF as sorbent for the removal of crude oil from water surface was investigated. The research objective is to develop a process to convert the by-product fibers into a usable value-added end product.

Materials and Methods:

Materials: The date palm fibers used in this study were obtained from date Palm trees planted in Basrah region of Iraq. Before cutting it to small pieces, the Date palm fibers (DPF) was thoroughly washed with distilled water to remove unwanted dusts and air dried and then cut in to small pieces. The dried cut (DPF) pieces (6-8 mm) were crushed in Willey mill Crusher and sieved to be used. The one which passed the 1.0 mm sieve but did not pass 0.1 mm, (0.1-1.0 mm) was selected for this work. Specification of Date Palm fibers are sized 0.1- 1.0 mm, Density of 0.213 g/cm^3 , the shape of 5-8 mm thin rods and black to grey colour.

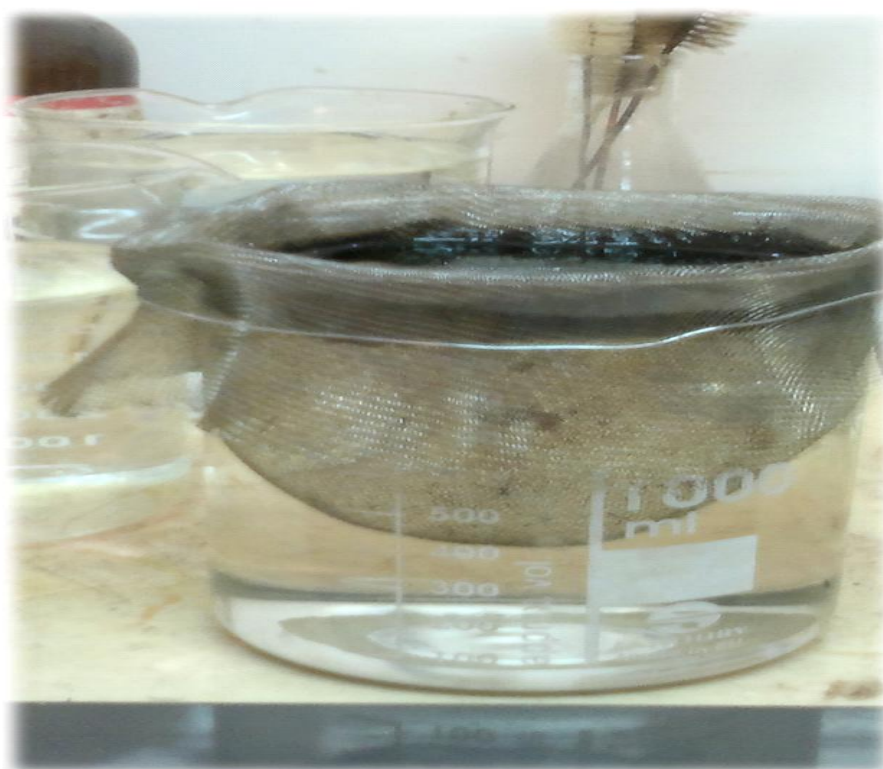


Fig. (1) The sorption process test sitting during this research experiments.

Oil Samples: The Crude oils used through all experiments were from South Oil Company, (mixture of Bazergan and Ben Omer oil fields) of Basrah, Iraq, have

the specification as in Table (1). Weathered oil was made in the Laboratory by holding the crude oil in thin layers at trays for 24 and 44 hrs. in open air , and

lost about 14.65 and 19.87 % of its weight respectively. Sea water was made by Dissolving 37 g of Sodium Chloride in 1000 mL fresh water.

Table (1) Specifications of crude oil samples from Bazergan + Ben Omar oil Fields.

S. #	Sp. Gr. (60 ° F)	API (60 ° F)	Salt Cont. (ppm)	Water Co (%)	Wt. Loss %	
					After 24 hrs	After 44 hrs
1	0.8773	29.83	10.0	0.025	N/A	
2	0.8665	31.80	26.70	0.025	14.65	19.87

*** 2 oil samples were used during the research period, only # 2 used as weathered oil.**

ASTM D-1298 (API Gravity), IP 358/82 (water Cont.), IP 77 (salt Cont.)

Sorption Study: For the evaluation of the oil sorption behaviors of the sorbent materials (fibers 0.1-1.0 mm size), oil spill has been simulated in a 1000 mL glass beaker by add 40 g of Crude oil to about 800 ml to Fresh water (sea water also tested) flowing the procedure of Hussein *et. al.* [5] with little modification. The test sitting of sorption showed in Fig(1).

For the sorption of the oil spill 1.0 g of sorbent material was spread gently over the surface of the oil in 1000 mL. The beaker was little gaited by hand gently for particular times (2- 120 min). The temperature of the water in the beaker was kept at close to crude oil temperature. Sorbent were moved up vertically with Wire net and the sorbent was let to drain by hanging the net over the beaker. The Sample weight was determined and recorded. Each test was run at least in duplicate and the average was taken.

The OSC of the sorbents were obtained with the formula:

$$\text{OSC} = \frac{\text{New weight gain}}{\text{Initial weight of Sorbent}}$$

Result and Discussion

Oil sorption capacities of DPF of selected size e.g. 0.1-1.0 mm at different times with weathered and fresh oils are shown in table (2).

Table (2) Crude oils sorption capacities for DPF size 0.1-1.0 mm and effect of Contact time on weathered and fresh oils at room Temp. using 1 gm. Fibers and 40 gm. crude oil.

S. No.	Sorption time (min)	Oil Sorbet (gm) WO*	Oil Sorbet (gm) FO**
1	5	4.219	4.534
2	10	4.441	4.723
3	15	4.455	4.846
4	20	4.472	5.268
5	30	4.552	5.397
6	45	4.793	5.724
7	60	4.848	6.269
8	90	4.968	7.985
9	120	5.13	6.658

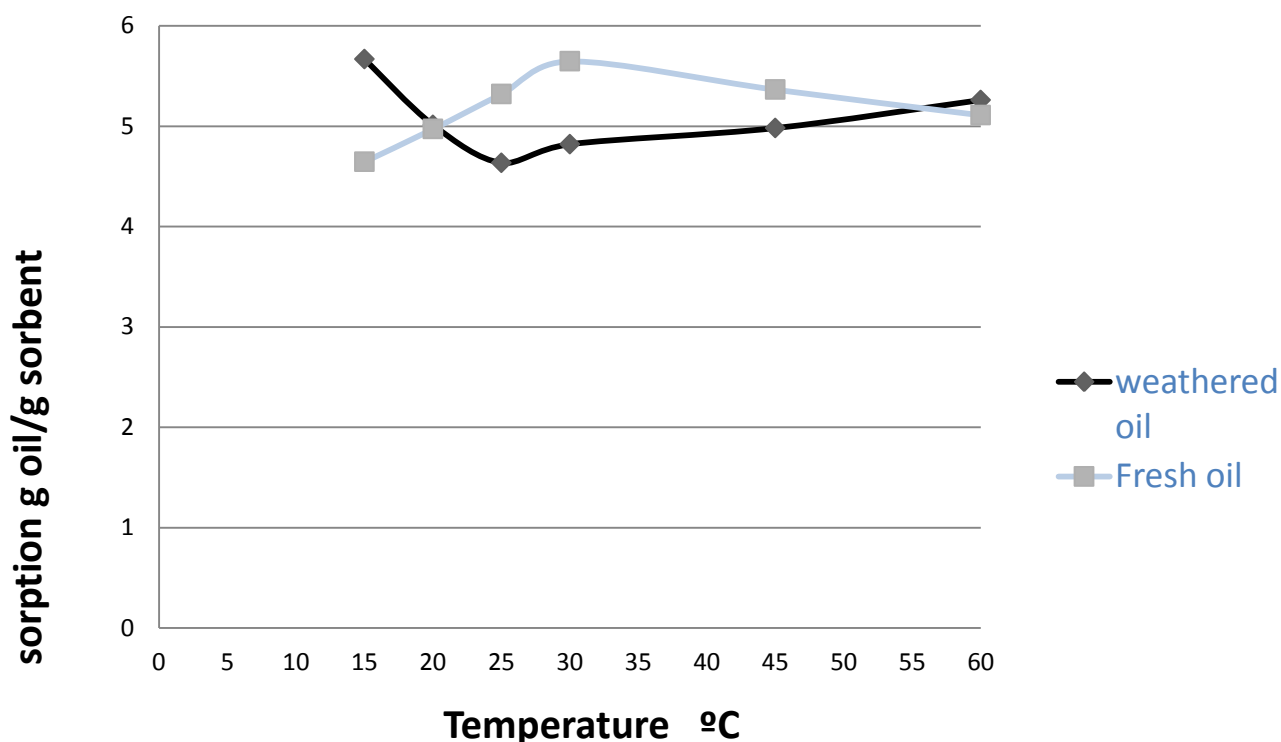
*** WO = Weathered Oil, ** FO = Fresh Oil**

As show in table (2), there are gradual increases in OSC as the contact time's increase in both weathered and fresh oils. Fresh oil sorption are higher than that of weathered oil all over the testing times due to less viscosity and small molecules

contents of the fresh oil which can penetrate into sorbent pores easy. In weathered oil the light molecules were evaporated and only heavy molecules remain. High molecular weights in weathered oil were constraining the oil from penetrating into the pore and hollow of the fibers [9,11] this lead to lower OSC.

In fresh oil small molecules absorb fast into the pores of sorbent while the large molecules will not be able to inter the pores of sorbent in same speed. That happened to weather oil and so its OSC lowers than the fresh oil as show in table (2).

Increase of oil sorption at low temperature as result of increase in oil viscosity at this temperature e.g. 15 ° C. That will increase the adherence action of oil onto the surface of the fibers and within capillary of the sorbent fibers that specially for weathered oil as shown in figure (2).



Fig(2). Temperature effect on sorption of weathered and fresh oils in to date palm leaves fibers (1 gm sorbent, 40gm crude oil, 20 min sorption)

Increase temperature will reduce oil viscosity and that will increase the oil diffusion through internal capillary movement and lumens. This leads to increase in oil absorption at higher Temperature e.g. 30⁰ C, especially of fresh oil. Moreover the present of oleophilic lignin layer on the fiber surface will increase the adsorption of crude oil in contact with fiber surfaces [30, 31]. Farther increase in temperature e.g 45-60⁰ c will reduced viscosity and that increase the diffusion of oil into pores and lumens of fibers but also increase its loss during draining time.

In addition the sorption of crud oil is very fast. For 2 min sorption , the OSC was 4.960 g/g with 2 min draining time . Moreover, the experiment, with salt water give lower OSC. e.g. 4.220 g/g , for 5 min sorption time and 5 min. draining. That may be due to interaction between salt and oil reduce the sorption .

Table (3) shows some of sorbents studied with its sorption capacities along with this study. Although the sorbent we used is a raw material (not modified) that shows good OSC. DPF having good sorption capacity due to the present of large lumens as well as the oleophilic lignin layer which contributed to enhance the oil sorption of DPF, comparing with others sorbents which have lower sorption capacities [22,31– 32]. Recycled wool-toasted nonwoven material having higher oil sorption capacity than this research work may be due to higher surface area which increase the oil adsorbed onto the material as will as higher contact time.e.g.10 min.[33]. For that, DPF could be a promising sorbent especially for small-scale crude oil spill. In addition it is OSC can be farther increase with modification.

Testing oil sorption of DPF over sea water gave lower OSC of 4.22 (g oil/g sorbent) that may be due to interaction of salty water with crude oil.

Table (3): Comparison of oil sorption capacity of various sorbents

S. N	Sorbent	Sorption Capacity (g/g)	Temp °C	contact time (min)	Ref.
1	Date Palm Fibers	4.53	26	5	This work
2	Hydrophobized vermiculite with carnauba wa	1.1+0.1	---	60	7
3	Hydrophobic aquaphyte- Salvinia sp. (HAS)	1.39	25	180	7
4	Hydrogel of chitosan based on polyacrylamid	2.3	25	200	7
5	Carbonized rice husks (CRH)	6	25	10	7
6	Black rice husk ash (BHRA)	6.22	20	3	7
7	Lauric acid treated oil palm leaves	1.2+0.12	30	20	7
8	Miscanthus Floridulus stem	2.23	26	720	31
9	Coniferous barks	1.3	20	3	22
10	Peat moss thermal treated	4.14			32
11	Chemically treated sludge	2	30	1.5	15
12	Recycled wool-based nonwoven material	11.5	---	10	33

Conclusion :

That DPLF is economical and solving environmental problems.

Oil uptake is rapid even at 2 min where OSC was 4.960 g oil/ g sorbent for 2 min draining time and retains oil for long time.

It's a low-cost, higher biodegradability as it is a natural cellulosic fiber and cost effectiveness compared to synthetic organic sorbent [34].

It is abundant and locally available sorbent with a good oil sorption capacity.

References:

1. Annunciado, T.R.; Sydenstricker, T.H.D. and Amico, S.C., (2005), Experimental investigation of various vegetable fibers as sorbent materials for oil spills; *Marine Pollut. Bull.*, 50 (11), 1340-1346.
2. Hussein, M.; Amer, A.A.; El-Maghraby, A. and Taha, N.A.,(2009), Availability of barley straw application on oil spill clean up, *International J. Environ. Sci. Technol.*, **6** (1), 123-130 .
3. Abdullah, M.A.; Ur Rahmah, A. and Man, Z., (2010), Physicochemical and sorption characteristics of Malaysian *Ceiba pentandra (L.)* Gaertn as a natural oil sorbent, *J. Hazard. Mater.*, 177, 683-691.
4. Suni, S.; Kosunen, A.L.; Hautala, M.; Pasila, A. and Romantschuk, M., (2004), Use of a by-product of peat excavation, cotton grass fibre, as a sorbent for oil-spills, *Marine Pollut. Bull.*, 49, 916-921 .
5. Hussein, M.; Amer, A.A. and Sawsan, Is.Ib.,(2009), Oil spill sorption using carbonized pith bagasse. Application of carbonized pith bagasse as loose fiber, *Global NEST J.*, 11(4), 440-448 .
6. Wei, Q.F.; Mather, R.R. and Fotheringham, A.F., (2005), Oil removal from used sorbents using a biosurfactant, *Bioresour. Technol.*, 96, 331-334
7. Sidik, S.M.; Jalil, A.A.; Triwahyono, S.; Adam, S.H.; Satar, M.A.H. and Hameed, B.H., (2012), Modified oil palm leaves adsorbent with enhanced

- hydrophobicity for crude oil removal, Chem. Eng. J., 203, 9-18.
8. Tan, K.S.L.; Abdul Razak, M.M. and Tan, J.H., (2011), Use of a natural fibrous sorbent for oil spill cleanup, Stockholm Junior Water Prize Competition, pp 20 .
 9. Choi, H.M. and Cloud, R.M.,(1992), Natural sorbent in oil spill cleanup, Environ. Sci. Technol., 26, 772-776.
 10. She, D.; Sun, R.C. and Jones, G.L.,(2010), Chemical Modification of Straw as Novel materials for industries. In Cereal straw as a resource for Sustainable biomaterials and biofuels: Chemistry, Extractive, Lignins, Hemicelluloses, and cellulose, R. C. Sun (Editor), 1st Edition, Elsevier (Oxford, U .K), Chapter 7, 209-217.
 11. Trindade, P.O.V.; Sobral, L.G.; Rizzo, A.C.L.; Leite, S.G.F. and Soriano, A.U.,(2005), Bioremediation of a weathered and recently oil- Contaminated soils from Brazil: a comparison study, Chemosphere, 58, 515-522 .
 12. Suni, S.; Kosunen, A.L. and Romantschuk, M., (2006), Microbially Treated Peat -Cellulose Fabric as a Biodegradable oil-collection cloth, J. Environ. Sci. Health- A, 41, 999-1007.
 13. Biswas, S.; Chaudhari, S.K. and Mukherji, S.,(2005), Microbial uptake of Diesel oil sorbed on soil and oil spill clean-up sorbents, J Chem. Technol. Biotechnol., 80, 587-593.

14. Carmody, O.; Frost, R.; Xi, Y. and Kokot, S.,(2008), Selected adsorbent materials for oil-spill cleanup – a Thermoanalytical study, *J. Thermal Analysis and Calorimetry*, 91(3), 809-816 .
15. Sayed, S.A. and Zayed, A.M., (2006), Investigation of the effectiveness of some adsorbent materials in oil spill clean-up, *Desalination*, 194, 90-100.
16. Karakasi, O.K. and Moutsatsou, A., (2010), Surface modification of high calcium fly ash for its application in oil spill clean up, *Fuel*, 89 , 3966-3970.
17. Toyoda, M. and Inagaki, M., (2000), Heavy oil sorption using exfoliated graphite: New application of exfoliated graphite to protect heavy oil pollution, *Carbon*, 38, 199-210.
18. Ceylan, D.; Dogu, S.; Karacik, B.; Yakan, S.D.; Okay, O.S. and Okay, O., (2009), valuation of butyl Rubber as sorbent material for the removal of oil and polycyclic aromatic hydrocarbons from seawater, *Environ. Sci. Technol.*, 43 (10), 3846-3852.
19. Gao, Y.; Zhou, Y.; Zhang, X.; Zhang, L. and Qu, P., (2012) Synthesis and characteristics of graft copolymers of poly(butyl acrylate) and cellulose fiber with ultrasonic processing as a material for oil absorption, *Bioresources*, 7 (1), 135-147.
20. Langley, K. D.; Kim, Y. K. and Lewis, A.F., (2000), Recycling and Reuse of Mixed-Fiber Fabric Remnants, Chelsea Center for Recycling , Chelsea Center for Recycling and economic Development Technical Research Program, Technical Report # 17, University of Massachusetts, April 2000.

21. Adebajo, M. O. and Frost, R.L., (2004), Acetylation of raw cotton for oil spill cleanup application- An FTIR and ^{13}C MAS NMR Spectroscopic Investigation, *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy*, 60, 2315-2321.
22. Haussard, M.; Gaballah, I.; de Donato, P.; Barres, O. and Mourey, A., (2001), Removal of Hydrocarbons from Wastewater Using Treated Bark, *J. Air & Waste Management Assoc.*, 51, 1351-1358.
23. Thompson, N.E.; Emmanuel, G.C.; Adagadzu, K.J. and Yusuf, N.B., (2010), Sorption studies of crude oil on acetylated rice husks, *Archives of Applied Sci. Research*, 2, 142-151.
24. Said, A.E.A.; Ludwick, A.G. and Aglan, H.A., (2009) Usefulness of raw bagasse: A comparison of raw and acylated bagasse and their components, *Bioresource Technol.*, 100, 2219-2222.
25. Adebajo, M. O.; Frost, R.L.; Kloprogge, J.T. and Carmody, O., (2003) Porous Materials for Oil Spill Cleanup: A Review of Synthesis and Absorbing Properties, *J. Porous Materials*, 10, 159-170.
26. Zaid, A. and Wet, P.F., (1999), Botanical and Systemical Description of Date Palm, In, *FAO Plant Production and Protection Papers*, Issue 156, Roodveldt Import BV, Rome, Italy, Chapter 1, pp. 1-28.
27. Belala, Z.; Jeguirim, M.; Belhachemi, M.; Addoun, F. and Trouve, G., (2011), Biosorption of copper from aqueous solution by date stones and palm - trees waste, *Environ. Chem. Lett.*, 9, 65-69.

28. Abdulkarim, M. Abu Al-Rub, F.A., (2004), Lead ions from aqueous solution on Activated carbon and chemically modified activated carbon prepared from date and pits, *Ads. Sci. Technol.*, 22, 119-134.
29. Allaboun, H. and Abu Al-Rub, F.A.,(2008), Dynamics, Mechanistic and equilibrium studies for the Biosorption of nickel on Palm Tree Leaves, *Jordan J. Civil Eng.*, 2, 124-138.
- 30-. Sbiai, A.; Maazouz, A.; Fleury, E.; Sautereau, H.and Kaddami, H., (2010), Short Date Palm tree Fibers / polyepoxy composites prepared using RTM process: Effect of TEMPO mediated oxidation of the Fibers, *Bioresource*, 5, 672-689.
31. Liao, W.; Lai, Y. C.; Huang, C. L. and Lien,C. Y., (2012), Characterization of Physicochemical properties of Miscanthus Floridulus stems and Study of their oil absorption ability using gold nanoparticles, *Bioresources*, 7(3), 4056-4066.
32. Baltrenas, P. and Vaisis, V., (2005),Experimental investigation of thermal modification influence on sorption qualities of biosorbents, *J. Environ. Eng. Landscape Management*, 13 (1), 3-8.
33. Radetic, M. M.; Jovic, D. M.; Jovancic, P. M.; Petrovic, Z. LJ. and Thomas, H. F., (2003). Recycled wool-based nonwoven material as an oil sorbent, *Environ. Sci. Technol.*, 37, 1008-1012
- 34- John, M. J. and. Anandjiwala, R. D., (2008), Recent Developments in Chemical Modification and Characterization of Natural Fiber-Reinforced Composites, *Polymer Composites*, 29, 187-207.