

# The Modified Polyurethane Foam Using as Sorbents for the Oil Sorbency

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**Abstract:** A comparative study of oil sorbency using modified polyurethane foam as sorbents is performed where Polyurethane type polyester was prepared locally. The objective of the study was to compare the oil spill removal capability of the pure and modified polyurethane where this modification was done by adding both sisal fibers and rice hulls (600  $\mu\text{m}$  size) as reinforcing fillers to the polyurethane matrix. The study also examined the effect of pin holes density .All Experiments were performed on a beaker scale. The obtained results showed the increase in sorption efficiency with the increase of the immersion time according to the difference in the capillary structure of both pure and modified polyurethane. Pin holes have a high effect on the sorption efficiency with a saturation sorption efficiency for each case of pin hole numbers. At small number of pin holes the saturation values is 86.58 while at high pin holes number the saturation value is 448.32. We also have an exponential increment of sorption efficiency with the increase of pin holes which is an indication of high loading capacity according to the transition of surface sorption to three dimensional one.

**Keywords:** modified polyurethane foam; sorbent; oil spill ; OIL SORBENCY; vegetable fibers ;sorption; surface sorption;

## 1. Introduction

Oil is one of the most important sources of energy as well as of raw material sources for synthetic polymers and chemicals worldwide .There has been an increasing demand for oil supply in the modern industrial world. Oil spills can be caused by operation failures, equipment breaking down, accidents, and natural disasters during the production, transportation, storage and use of oil. Oil spills into lands, rivers or ocean impose a major problem on the environment (1-2).

The problem of water pollution with oil and its products has an increasing international conce, p\ [pk9rn because of the importance of the marine environment to the living species including the human beings (3-4). Such spills not only represent a loss of oil but also often have a major negative effect on natural flora and fauna and human health. Physical, chemical, and biological processes can be used to recover/remove the oil or to destroy it in situ among the methods that can remove the oil from a water surface are various sorbents. They include manufactured polymeric materials, naturally occurring minerals, expanded graphite, and naturally occurring organic materials (5-7).

It is found that some synthetic polymeric materials like polyurethane foam and urea formaldehyde have the absorption ability toward Crude oil spilt in the marine (3,8 -10) where the first publication on the use of polyurethane foam (PUF) for sorption processes dates back to 1970(8).

Most commonly used commercial sorbents are synthetic sorbents made of polypropylene or polyurethane (11). They have good hydrophobic and oleophilic properties, but their no biodegradability is a major disadvantage (12-13).

The spilt crude oil environmentally undergo a wide variety of weathering processes, which include evaporation, dissolution, dispersion, photochemical oxidation, microbial degradation, adsorption onto suspended materials, agglomeration etc (4,14).

In recent years, biological surface-active compounds that is biosurfactants, are gaining prominence and have already taken over in a number of important industrial uses, due to their advantages of biodegradability, production of renewable resources and functionality under different conditions (15-16). Biosurfactants are biodegradable and can also enhance the biodegradation of oil by increasing the bioavailability of hydrophobic compounds (17).

This paper covers studying of the use of local rice husk and sisal fibers to modify polyurethane which is prepared locally and examine capability as a sorbing substance for treating oil pollution of Iraqi waters.

## 2. Experimental Work

The sisal fiber is obtained from the leaves of the plant Agave sisalana, which was originated from Mexico and is now mainly cultivated in East Africa, Brazil, Haiti, India and Indonesia It is grouped under the broad heading of the "hard fibers" among which the sisal is placed second to manila in durability and strength. A good sisal plant yields about 200 leaves when each leaf has a mass composition of 4% fiber, 0.75% cuticle, 8% other dry matter and 87.25% moisture. The fiber is composed of numerous elongated fusiform fiber cells that taper towards each end. The fiber cells are linked together by means of middle lamellae, which consist of hemicelluloses, lignin and pectin. Physically, each fiber cell is made up of four main parts, namely the primary wall, thick secondary wall, tertiary wall and the lumen. Chemically the vegetable fibers comprise cellulose, hemicelluloses, lignin, pectin and a small amount of waxes and fat. The mechanical properties of sisal fiber such as initial modulus, tensile, Young's modulus and average modulus increase with test length

The sisal fiber consists of 66-72% cellulose, 12% hemicelluloses and 10 -14% lignin. The superior engineering properties (diameter 50–200  $\mu\text{m}$ ; microfibril angle 10–220, Ultimate Tensile strength of 468–640 Mpa; Modulus of

9.40–15.80 Gpa and elongation of 3–7%) make it an excellent material for manufacturing the high strength textile and reinforcing in composites for various applications<sup>(18-20)</sup>

Rice hulls have a very low bulk density (118 kg/m<sup>3</sup>). Rice hulls are a hygroscopic material, i. e. they change their equilibrium moisture content depending on temperature and relative air humidity. The explanation for the observed unique properties of rice hulls should be sought in their considerable silicon content. It is indicative that the amorphous SiO<sub>2</sub> is 93.54 %, potas-sium oxides are 3.12 %, iron oxides 1.11 %, and the remaining oxides are in minimal amounts<sup>(21)</sup>.

Pure polyurethane type polyester foams are prepared by two types pure and modified polyurethane where pure polyurethane is prepared by reacting a liquid isocyanate with a liquid blend of polyols. The modified polyurethane is prepared as mentioned above which adding sisal fibers and rice hulls to the reacting materials .

Crude oil was brought from Qurna west oil field with A.P.I. equal to 22.2 and hydrolic oil are used in the sorbent evaluation procedure.

An uncovered glass jar of 2- liters capacity and a diameter of 14.8 cm is used. In each experiment 2 liters of water and 250 ml of an oil sample was placed in the jar. The dry weights of polyurethane cubes are taken before immersing them into the jar. The samples are periodically removed from the test jar .The wet surface of the cubes are dried between filter paper and weighed immediately to the nearest + 0.1 g .The samples are placed back immediately into the test jar and the experiments are carried out in progress. The experiments are repeated at the same conditions using modified polyurethane

### 3. Results and Discussions

The results are obtained as a function of two variables which are the time of immersion and the pin holes density (pin holes / surface area of polyurethane sample) where we used both perpendicular and horizontal pin holes due to sample surface .We used five different densities of pin holes (0,0.5, 1, 1.5 and 2.5 hole/ cm<sup>2</sup>) . Pin holes with 100 µm in diameter are made in order to increase the sorption efficiency of the polyurethane foam. The sorption efficiency is calculated on the basis of the weight of oil absorbed per kilogram of the sorbent

Figure (1) shows the variation of sorption efficiency of pure and modified polyurethane foam as a function of immersion time. Modified polyurethane shows an obvious increase in sorption efficiency along with the increase of the immersion time. Another result is obtained where the sorption efficiency of crude oil is less than that of hydrolic oil made from modified polyurethane while we have almost the same efficiency for both pure polyurethane. This can be explained in terms of the amount of oil sorption by a sorbent which is mainly affected by the capillary structure, the spreading of the oil on the sorbent, adhesive energy of the oil on the sorbent, and cohesive energy of the oil<sup>(22)</sup> .

Figure (2) shows the effect on sorption efficiency of modified polyurethane with the increase of pin holes numbers for both crude and hydrolic oil . The sorption of modified polyurethane is much related to both immersion time and pin holes numbers. The saturation value for crude oil is increasing with the increase of the pin holes number where at 5 and 25 pin holes the saturation values are 86.58 and 448.32 respectively. The above figure shows that the saturation value at 25 pin holes is higher for light oil (hydrolic oil) than that of viscous oil (crude oil) which means higher sorption efficiency due to increase of hydrolic oil sorbed by modified polyurethane . These results can be explained in term of the volume of penetration which is proportional to the square root of the time of soaking and the square root of the ratio of the surface tension to the viscosity ratio<sup>(23)</sup> .

Figure (3) shows the variation of the sorption efficiency as a function of pin holes density at a constant immersion time which is 5 minutes. It is obvious that the exponential increment of the sorption efficiency is an indication of the high loading capacity. The increase in loading capacity can be related to transition from surface sorption to the volume sorption, deep inside the modified polyurethane. This result is very important due to the necessity of treating polluted waters during the early hours of oil leakage or spillage especially where the pollutants are light oils.

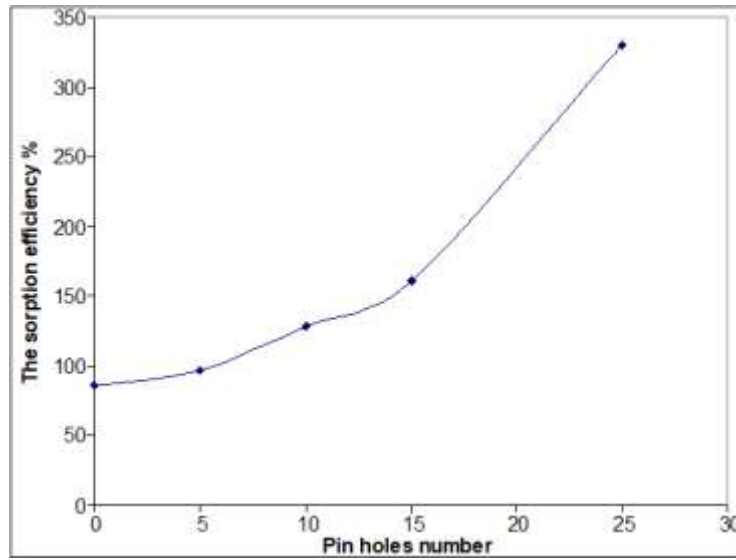
### 4. Conclusion

The sorption capacities of modified polyurethane are more enhanced than those of pure polyurethane due to the capillary structure changes made to the polyurethane after adding rice hulls and the sisal fibers .These two materials are readily and normally available as well as affordable . All obtained results suggest that that modified polyurethane has a Considerable potential as an oil sorbent specially during the first hour of oil leakage or spillage especially when the pollutants are light oils. The 5 minutes period is sufficient for both viscous oils such as heavy crude oil and light oil. A comparison between PUF and other sorbents reveals that this solid phase has obvious advantages due to the light weight, ease of fabrication and handle,high ability to be shaped in any form and its reusability as sorbent substance . The pin holes have a huge effect on sorption efficiency due to the transition from the surface sorption to three dimensional one.

### References

- [1] Yunhua\_Cui, Guanbiao\_Xu, Yijie\_Liu ,Oil sorption mechanism and capability of cattail fiber assembly, journals.sagepub, Volume: 43 issue: 3, page(s): 330-337,Article first published online: July 3, 2012; Issue published: January 1, 2014 , <https://doi.org/10.1177/1528083712452902>.
- [2] Albert Matlack, Introduction to Green Chemistry, Second Edition, 24, 14 ,2010
- [3] <https://books.google.iq/books?isbn=1439882118> .
- [4] Edward H. Lundquist, Maritime Domain Awareness(MDA) : Port and Coastal Security for the Homeland Is Evolving. Partnerships, priorities, force protection, and a common operating picture. Air

- and Marine Operations Center. The Air and Marine Operations Center at March Air Reserve Base in Calif. , defensemedianetwork , JANUARY 11, 2014.
- [5] <https://www.defensemedianetwork.com/.../maritime-domain-awarene>.
- [6] Hegazi, A., N. R. Samra, E. E. El-Baz. T .Bahan, M. Khalil and S. Gawish , American-Eurasian J. Agric. Environ. Sci., 7: 312-319,2014.
- [7] <https://www.agrsaba.alexu.edu.eg/images/2017>.
- [8] V. Jensen Hans, V Mulin Joseph, MORICE (2003), New technology for mechanical oil recovery in ice infested waters, Marine pollution Bulletin 47 : 453-469,2003.
- [9] Sherif S. Z. Hindi ,International Journal of Science and Engineering Investigations, Characteristics of Some Natural Fibrous Assemblies for Efficient Oil Spill Cleanup, vol. 2, issue 16, May 2013 .
- [10] Toyoda, M., Aizawa, J., Inagaki, M., Sorption and recovery of heavy oil by using exfoliated graphite. Desalination,115, pp. 199–201, 1998.
- [11] V.A. Lemos a , M.S. Santos a , E.S. Santos a , M.J.S. Santos a , W.N.L. dos Santos b,h, A.S. Souza b , D.S. de Jesus c , C.F. das Virgens d , M.S. Carvalho e , N. Oleszczuk f , M.G.R. Vale f , B. Welz b,g, S.L.C. Ferreira b,
- [12] Application of polyurethane foam as a sorbent for trace metal pre-concentration , Spectrochimica Acta Part B 62, 4–12, 2007.
- [13] Sonja Arpadjan, Lili Vuchkova and Elena Kostadinova. Sorption of Arsenic, Bismuth, Mercury, Antimony, Selenium and Tinon Dithiocarbamate Loaded Polyurethane Foam as a Preconcentration Methodfor Their Determination in Water Samples by Simultaneous Inductively Coupled Plasma Atomic Emission Spectrometry and Electrothermal AtomicAbsorption Spectrometry, Analyst 122 ,243–246, 1997.
- [14] Ismail M. M. Rahman, , Zinnat A. Begum , Hiroshi Hasegawa , Selective separation of elements from complex solution matrix with molecular recognition plus macrocycles attached to a solid-phase: A review, The research article is originally published at Microchemical Journal An Elsevier Journal <http://www.journals.elsevier.com/microchemical-journal/> The original publication is available at: <http://dx.doi.org/10.1016/j.microc.2013.06.006,2013>.
- [15] Jintao Wang , Yian Zheng, Aiqin Wang , Effect of kapok fiber treated with various solvents on oil absorbency, Industrial Crops and Products, 40 ,178–184, 2012 .
- [16] H. O. Nwabueze, P.K. Igbokwe, E. U. Amalu and S.E. Okoro , A study on the equilibrium and kinetics of oil spill cleanup using acetylated corn cobs, INTERNATIONAL JOURNAL OF ENVIRONMENTAL SCIENCES Volume 5, No 6, 2015.
- [17] G.Alaa El-Din , A.A.Amer ,G.Malsh , M.Hussein, Study on the use of banana peels for oil spill removal, Alexandria Engineering Journal,Available online, open access, 3 June 2017.
- [18] M. HUSSEIN, A.A. AMER and Is.Ib. SAWSAN, OIL SPILL SORPTION USING CARBONIZED PITH BAGASSE. APPLICATION OF CARBONIZED PITH BAGASSE AS LOOSE FIBER, Global NEST Journal, Vol 11, No 4, pp 440-448, 2009.
- [19] Tania Hubert Ribeiro, Ross W. Smith, and Jorge Rubio, Sorption of Oils by the Nonliving Biomass of a *Salvinia* sp., *Environ. Sci. Technol.*, 34 (24), pp 5201–5205 , 2000.
- [20] Q.F. Wei, F.L. Huang, R.R. Mather, A.F. Fotheringham, Factorial Design Evaluation of Oil Removal from Fibrous Sorbents by Biosurfactant, Oil & Gas Science and Technology – Rev. IFP, Vol. 62 ,No. 3, pp. 407-413 ,2007 .
- [21] Qingyi Xu , Mitsutoshi Nakajima , Zengshe Liu and Takeo Shiina , Biosurfactants for Microbubble Preparation and Application, *Int. J. Mol. Sci.* , 12(1), 462-475, 2011.
- [22] Sandeep Bhardwaj and Rupali Sharma ,Natural Fibre Composites- An Opportunity for Farmers, Int. J. Pure App. Biosci. 5(5): 509-514 ,2017 .
- [23] M. Chandrasekar ,M. R. Ishak ,S. M. Sapuan ,Z. Leman and M. Jawaid , A review on the characterisation of natural fibres and their composites after alkali treatment and water absorption, journal Plastics, Rubber and Composites Macromolecular Engineering ,Volume 46, Issue 3, 2017.
- [24] K.Setswalo, M. Namoshe, S. Kutua , O.P. Oladijo, and B. Samson, Effect of Thermal and Alkali Treatment on Pterocarpus Angolensis (Mukwa) Wood Flour, International Conference on sustainable Materials Processing and Manufacturing,SMPM 2017, Procedia Manufacturing,7,205-210,2017.
- [25] Nguyen Thi Kim Tuyen , Do Nguyen Thanh Nhan , Trieu Thi Nhat , Ngo Thanh An , and Nguyen Quang Long , Removal of copper (II) ion from aqueous solution using zeolite Y synthesized from rice husk ash: Equilibrium and kinetic study, AIP Conference Proceedings 1878, 020016 ; <https://doi.org/10.1063/1.5000184> ; 2017.
- [26] Akshay Jain, Oil Sorption Behavior of Fibrous Substrates, M.Sc. Thesis In Industrial Engineering , Texas Tech University, May, 2017.
- [27] O. S. H. Santos, M. Coelho da Silva ,and M. I. Yoshida, Synthesis and performance of different polyurethane foams as oil sorbents, Journal of Applied Polymer Science, Volume134, Issue41 , 2017 modified polyurethane foam; sorbent; oil spill ; OIL SORBENCY; vegetable fibers ;sorption; surface sorption



**Figure 3:** The variation of sorption efficiency as a function of pin holes number