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Optimization of Oil Spill Cleanup Using Composites Fibres (ES) Modified Kola Nut POD.

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Abstract

Natural sorbents was chemically and thermally modified by a novel nonwoven bonding with introduction of 10-30% polyethylene/polypropylene sheath-core composites fibres (ES) under different reaction conditions respectively. A product was made using natural fibre (kola nut pod) which were blended with 10-30%ES and placed into a muffle furnace. Three (3) natural sorbent were produced KP/ES ratios of 70/30 80/20 and 90/10. The physical properties (densities, viscosities, surface tension and surface energy) of the Automotive Gas Oil (AGO) were carried out. The sorption capacity and oil-to-water selectivity's of structured sorbent were also determined. The structure of modified kola nut pod was confirmed using Fourier transform infrared (FTIR) and Gas chromatography-mass spectrophotometer (GC-MS). FTIR analysis exhibited characteristics vibrational mode of cellulose and hydrocarbon, while the GC-MS analysis from each retention time (RT) and area percentage (%) suggested of one compound dodecanoic acid . The hydrophobicity of the modified kola nut pod increased after modification, with water contact angles in the range of 112–120.60º (10.33). Scanning electron microscope (SEM) images of the kola nut pod before and after modification were similar with fairly smooth surfaces. The modified kola nut pod absorbed oils and organic solvent but not water due to the hydrophobicity of the kola nut pod. The absorption capacities of the modified kola nut pod were 4.63(0.153), 4.76(0.252), and 5.00(0.361) which was automotive gasoline oil, premium motor spirit and turpentine oil optimize sorption capacities. The results of this study suggest that modified natural sorbent KP/ES of 90/10 have a highest sorption capacity on PMS, AGO and turpentine oil when compared with the modified standard KP/ES. The modified kola nut pod could be reused many times without any loss of sorption capacity and could be used under different pH conditions

Key Words: *Hydrophobic Cellulose Modified Sorbents, Natural Kola Nut Pod, Oil Sorption Capacity, Oil Spill Cleanup, Optimization, Surface Tension.*

INTRODUCTION

In present scenario, the increase in the quantum of agricultural and solid wastes attributes the greater impact on environmental pollution. These wastes can be used as a cheap source to Oil Spill Cleanup thereby reducing the environmental pollution to a greater extent.

Crude oil contaminates water through oil spills, an oil spill is the release of a liquid petroleum hydrocarbon into the environment, especially the marine ecosystem, due to human activity, and is a form of pollution. The term is usually given to marine oil spills, where oil is released into the ocean or coastal waters, but spills may also occur on land. Oil spills may be due to releases of crude oil from tankers , offshore platforms , drilling rigs and wells , as well as spills of refined petroleum products (such as gasoline , diesel) and their by-products, heavier fuels used by large ships such as bunker fuel , or the spill of any oily refuse or waste oil Yakimov, M. M et al (2007). Oil spills penetrate into the structure of the plumage of birds and the fur of mammals, reducing its insulating ability, and making them more vulnerable to temperature fluctuations and much less buoyant in the water. Cleanup and recovery from an oil spill is difficult and depends upon many factors, including the type of oil spilled, the temperature of the water (affecting evaporation and biodegradation), and the types of shorelines and beaches involved. Spills may take weeks, months or even years to clean up. Sorbents are materials that soak up liquids. They can be used to recover oil through the mechanisms of absorption, adsorption, or both. Absorbents allow oil to penetrate into pore spaces in the material they are made of, while adsorbents attract oil to their surfaces but do not allow it to penetrate into the material. To be useful in combating oil spills, sorbents need to be both oleophilic and hydrophobic (water-repellant). Sorbent materials with both oleophilic (oil-attracting) and hydrophobic (water-repellent) characteristics can be used as oil sorbents, and they are classified into three main categories: synthetic, natural inorganic and natural organic (Chol H-M., Cloud R. M 1992, Adebajo M. O *et al* 2003 & Teas Ch *et al* 2001). Synthetic sorbents are artificial polymeric materials such as polyurethane, polyethylene, and polypropylene (Li A *et al* 2011, Choi H-M *et al* 1993, Calcagnile P *et al* 2012 & Zhu Q *et al* 2012)**.** These materials account for most of the commercial sorbents used for oil spill cleanup because of their hydrophobicity and oleophilicity (Li A *et al* 2011, Choi H-M *et al* 1993, Calcagnile P *et al* 2012 & Zhu Q *et al* 2012)**.** Therefore, hydrophobic modification is required for natural organic materials so that they can be used as oil sorbents. Cellulosic materials can be hydrophobically modified physically or chemically. Cellulosic materials can be physically modified by nowoven, coating, and surface crystal growth treatments, among other methods (Okwuego P.O & Okonkwo S.I 2021). Synthetic polymers have also used to improve the hydrophobic and oleophilic characteristic of organic materials (Okwuego P.O & Okonkwo S.I 2021). For instance, the oil absorption capacity of pineapple stem fibres increased significantly after being modified by polypropylene and polyethylene using nowoven process as a catalyst (Okwuego P.O & Okonkwo S.I 2021).

2. Materials and methods

2.1. Materials **Sample collection;** 500g of kola nut pod fibres samples were collected from Coke Market in idemili-South Local Government Area, Anambra state. Turpentine oil, Polyethylene and polypropylene chemicals were purchased from Obipetlab Global Link Limited. Premium Motor Spirit (PMS) and Automotive Gas Oil (AGO) collected from North-west fuel station at Nkpor, Anambra state which were used as experimental oils..

Sample Preparation;
The sample kola nut pod (KP) was collected weighed and dried under the sun for six (6) months. After which it was re-weighed and grinded to finest particles with a manual grinder model Colombia product RF. 12100. Physical Properties of the oils (AGO,PMS and Turpentine oil) such as densities, viscosities, surface tensions and surface energy were determined using below method The 50mls dry and empty density bottle were weighed and the 50mls density bottle filled with oils (AGO,PMS and Turpentine oil) respectively, avoiding bubbles. The ground neck was covered to about 1/3. It was placed in thermostatic bath and adjusts the temperature of the bottle and contents to 20 °C. Align the stopper respectively with the thermometer of the density bottle according to the marker and insert carefully. The capillary tube fills up and the displaced liquid comes out. It was carefully dry the outer surfaces of the stopper and the density bottle with tissue. It was carefully done to avoid removing any oil from capillary. The oil samples were exactly leveled with the upper end of the capillary are the weight of the filled density bottle was taken after which the density from the mass (weight) and the volume of the liquid at the reference temperature of 20 °C was calculated(Okwuego P.O & Okonkwo S.I 2021)..

Using the equation; Density = Mass /Volume

Also 100mls of oil samples (AGO,PMS and Turpentine oil) were poured into a digital rotary viscometer model ASTM E2975-15 cup and allowed the torque to rotate the disk bob in a fluid at about 10mins, after that a digital reading for the viscosity was automatically calculated and displayed on a screen to every spindle/ speed combination. There was no further calculation and the results were recorded. Surface energies and their components of fibres were measured by optical contact angle meter by using double-side tape attaching the fibres to a glass slide while paved in the form of plane.
After all were calculated according to equation (1) and (2).

$$\sigma_l(1 + \cos\theta) = 2\left(\sqrt{\sigma^d_s \sigma^d_l} + \sqrt{\sigma^p_s \sigma^p_l}\right) \text{ ---------------------- } (1)$$

$$y = \sqrt{\sigma^p_s} \times x + \sqrt{\sigma^d_s}$$

$$y = (1 + \cos\theta) \times \sigma_l / \sqrt{\sigma^d_l} \text{ -------------------------------------- } (2)$$

$$x = \sqrt{\sigma^p_s / \sigma^d_s}$$

Other modified sorbents were prepared accordingly. Three (3) natural sorbent with different fibres modification ratios were produced PS/ES ratios of 70/30 80/20 and 90/10.

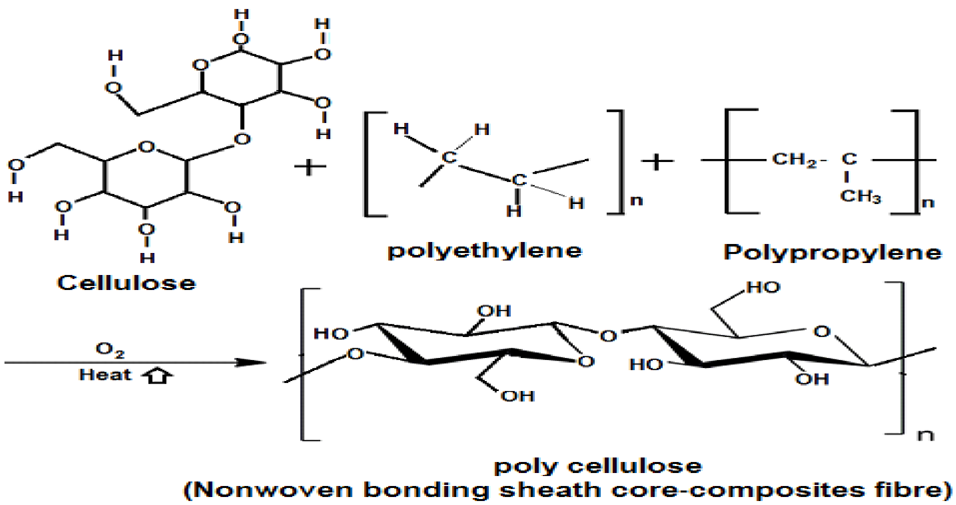


Fig.1 Modification reactions of Natural Sorbents

Chemical Analysis

Chemical and morphological structure of processed kolanut pod fibres were examined using fourier transformed infrared (FTIR) and Gas chromatographic -Mass spectroscopic (GC-MS). The wax content of kolanut pod fibres were analyzed by soxhlet extraction method. The dry kolanut pod fibre of 200grams each were placed in a different soxhlet extractor and extracted with alcohol and benzene in the ratio of 1:2 at 95°C with four to six (4-6) times per hour for 4hrs. After drying in an oven at 105°C, the fibres were re-weighed and there was decrease in weight indicating the wax contents of (KP) fibre.

Oil sorption and retention capacity

Oil sorption test was performed as follows; 200g of modified fibre assemblies each of the three (3) modified fibres was put in 50mls of an oil samples (AGO,PMS and Turpentine oil). 25minutes was taken as the equilibrium oil sorption time, since no obvious differences were observed for the sorbents after a longer soaking time. The modified samples were lifted and placed them on a wire mesh with free oil dripping out for a period of 12h. Each sample was tested severally. Their oil sorption and oil retention capacities were calculated according to equaton (3) and (4)

Oil sorption capacity = $^{m}f_{25} - {}^{m}f / {}^{m}f$ ------------------------------ (3).

Oil retention capacity = $^{m}f_{12} - {}^{m}f / {}^{m}f_{25} - {}^{m}f$------------------------- (4).

Where; $^{m}\mathbf{f}$ is the mass of sample before sorption (g)

$^{m}\mathbf{f}_{25}$is the mass of the oil wetted sample at 25min dripping (g)

$^{m}\mathbf{f}_{12}$ is the mass of oil wetted sample at 12h dripping (g) Dong T. et al (2015)

Selectivity of oil absorbed from water

50ml of oil samples (AGO, PMS and Turpentine oil) was poured into 150ml water and the oils got separated from the water and were floating; 25g of each structured fibre assemblies were put in beaker. After 25minutes of oil absorbing, the sorbents was lifted and placed on a wire mesh with free oil dripping out for 15minutes. The sorbents were then put in a graduated cylinder previously filled with 75mls of n-hexane in which the absorbed oil was dissolved and the water sank to the bottom of graduated cylinder due to its higher density. The mass of absorbed water was then calculated according to its volume in graduated cylinder. Each sample was tested for 3times. The oil–to-water selectivity and oil removal efficiency were all calculated according to equation (5) and (6).

Oil – to-water selectivity = $^{m}f_{25} - {}^{m}f - {}^{m}w / {}^{m}w_{15}$-- (5)

Oil – removal – efficiency = $^{m}f_{25} - {}^{m}f - {}^{m}w / {}^{m}o$ ------------------------------ (6)

Where; ^{m}f is the mass of sample before sorption (g)

$^{m}\mathbf{f_{25}}$ is the mass of the oil wetted sample at 25minutes dripping (g)

$^{m}\mathbf{w_{15}}$ is the mass of water absorbed by the sample at 15minutes dripping (g)

$^{m}\mathbf{o}$ **is** the mass of the oil in the beaker before sorption (g) Dong T. et al (2015)

RESULTS AND DISCUSSION

Table 1.0 Properties of experimental oils Premium Motor Spirit (PMS), Automotive Gas Oil (AGO) and Turpentine oil (TO).

Liquid medium	**Density (g/cm^3)**	**Viscosity (mPas)**	**Surface Tension (mN/m)**
Premium motor spirit (PMS)	0.716	64.73	28.30
Automotive gas oil (AGO)	0.826	120.65	24. 90
Turpentine oil	0.795	95.50	25. 10

Table 2.0 Wax content of kolanut pod, pumpkin stem and pineapple leaf fibres

Fibres	Wax content (%)
Kolanut pod	2.4

Table 3.0 Surface Energy with their Contact Angles of Kolanut pod fibres

Contact angles (0)						Surface energy (mN/m)		
Fibres		Water	Turpentine oil	PMS	AGO	Polar components	Dispersion components	Total components
Kolanut pod	Max	120.60	87.50	78.30	89.50	2.78	38.10	40.88
	Min	116..50	73.80	65.90	84.60			
	Ave	118.55	80.65	72.10	87.05			
	Std	(10.33)	(8.40)	(7.85)	(8.67)			

Table 3.1 Selective sorption performance of modified natural sorbents to Premium Motor Spirit (PMS), Automotive Gas Oil (AGO), premium motor spirit (PMS) and Turpentine oil (TO)

Fibres	Modified ratio	Oil sorption capacity(g/g)	Water sorption capacity(g/g)	Oil-to-water selectivity(g/g)	Oil retention Capacity(g/g)	Oil removal efficiency(%)
Kolanut pod/ES PMS	70/30 80/20 90/10	4.53(0.252) 4.56(0.153) 4.60(0.4)	0.13(0) 0.13(0.01) 0.15(0.01)	18.33(0.306) 18.80(0.1) 19.03(0.153)	57.0(3.386) 58.2(3.082) 58.3(2.823)	46.6(0.557) 47.2(0.709) 47.9(1.901)
Kolanut pod/ES Gas Oil (AGO)	70/30 80/20 90/10	4.63(0.153) 4.76(0.252) 5.00(0.361)	0.10(0.006) 0.12(0.01) 0.13(0.01)	15.70(0.964) 15.86(1.201) 16.57(1.001)	58.4(1.808) 61.0(2.042) 61.0(2.658)	47.9(1.901) 48.4(1.557) 48.7(1.457)
Kolanut pod/ES TURPENTINE OIL	70/30 80/20 90/10	5.50(0.153) 5.76(0.404)	0.50(0.01) 0.51(0.020) 0.52(0.015)	24.96(0.306) 25.30(0.361)	91.1(1.266) 92.8(1.682) 93.5(3.966)	98.6(0.252) 98.8(0.153) 98.9(0.153)

		6.43(0.321)		**25.60(0.265)**		

***Values within parentheses indicate the standard deviations for three repeats.**

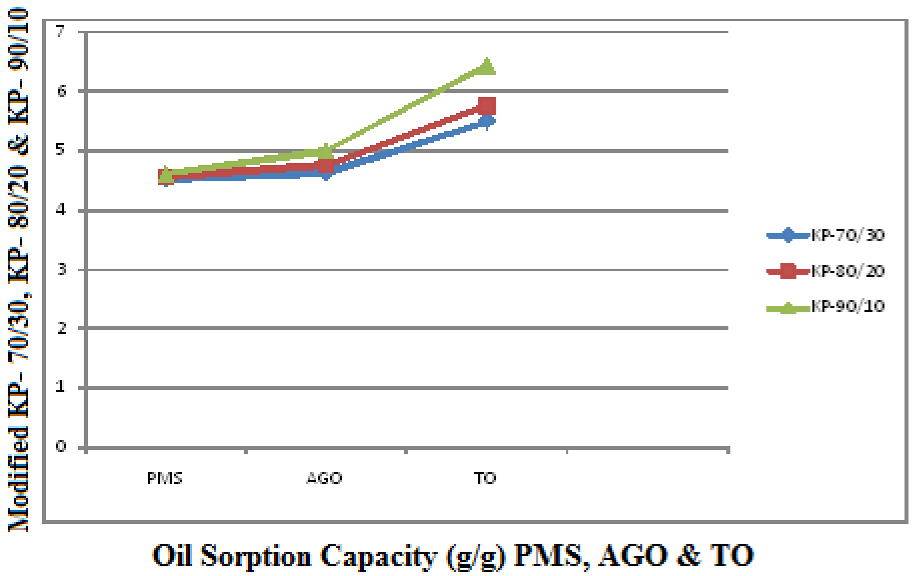


Fig. 1.0 A graph of Oil sorption capacity(g/g) of modified natural sorbents to Premium Motor Spirit (PMS), Automotive Gas Oil (AGO), premium motor spirit (PMS) and Turpentine oil (TO)

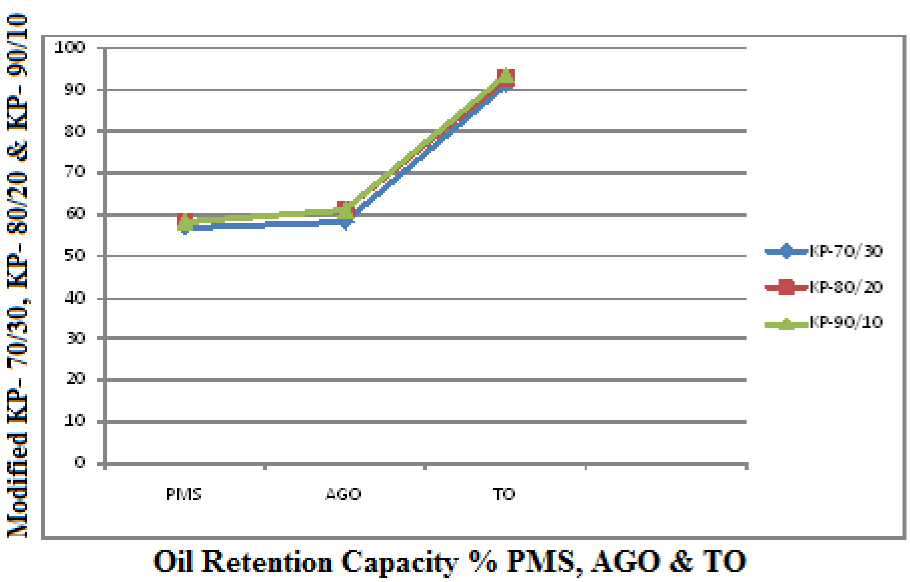


Fig. 2.0 A graph of Oil retention Capacity(g/g) of modified natural sorbents to Premium Motor Spirit (PMS), Automotive Gas Oil (AGO), premium motor spirit (PMS) and Turpentine oil (TO)

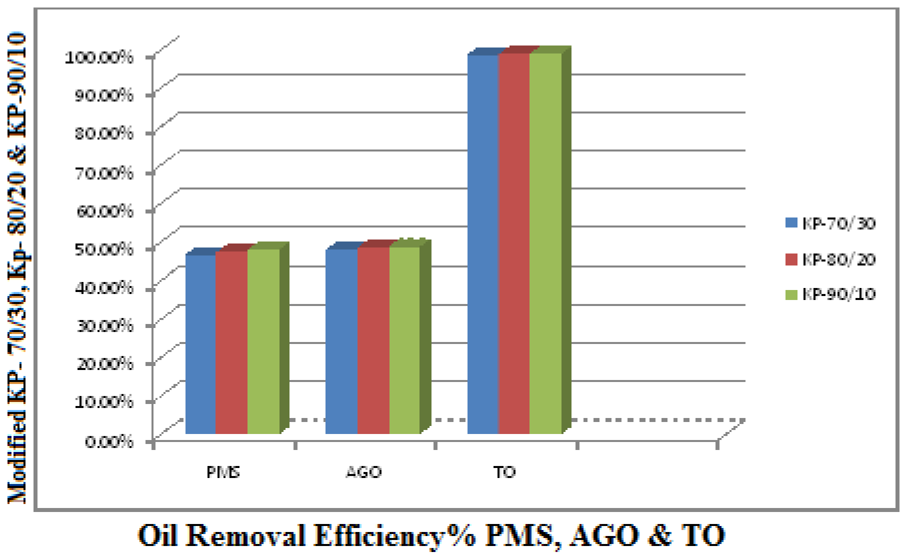
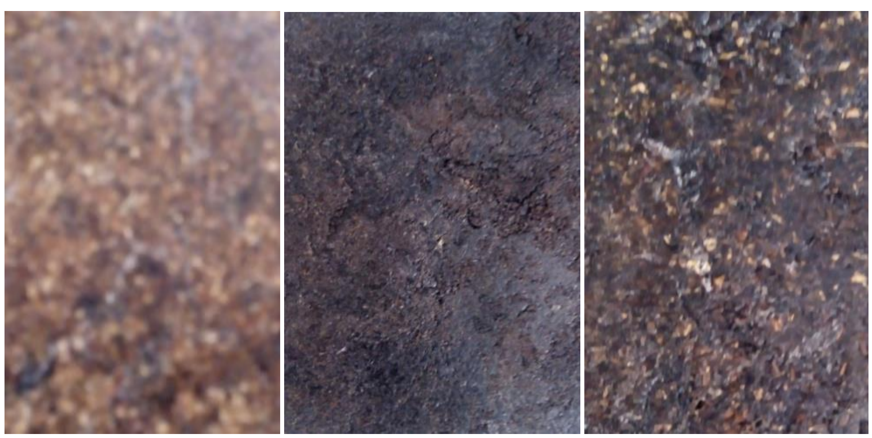


Fig. 3.0 A graph of Oil removal efficiency (%) of modified natural sorbents to Premium Motor Spirit (PMS), Automotive Gas Oil (AGO), premium motor spirit (PMS) and Turpentine oil (TO)



KP/ES – 70/30% **KP/ES – 80/20%** **KP/ES –90/10%**

Fig. 4.0 Modified Natural Sorbents of KP/ES – 70/30%, KP/ES – 80/20%, KP/ES – 90/10%,

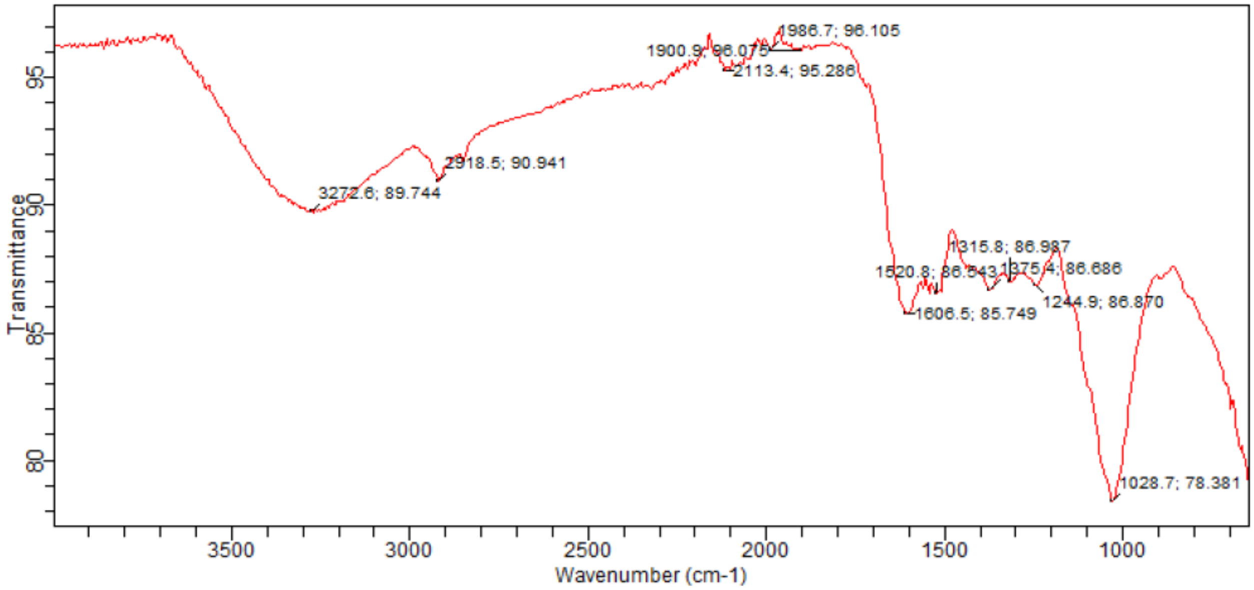


Fig. 5.0 Infrared spectrum of kolanut pod fibres.

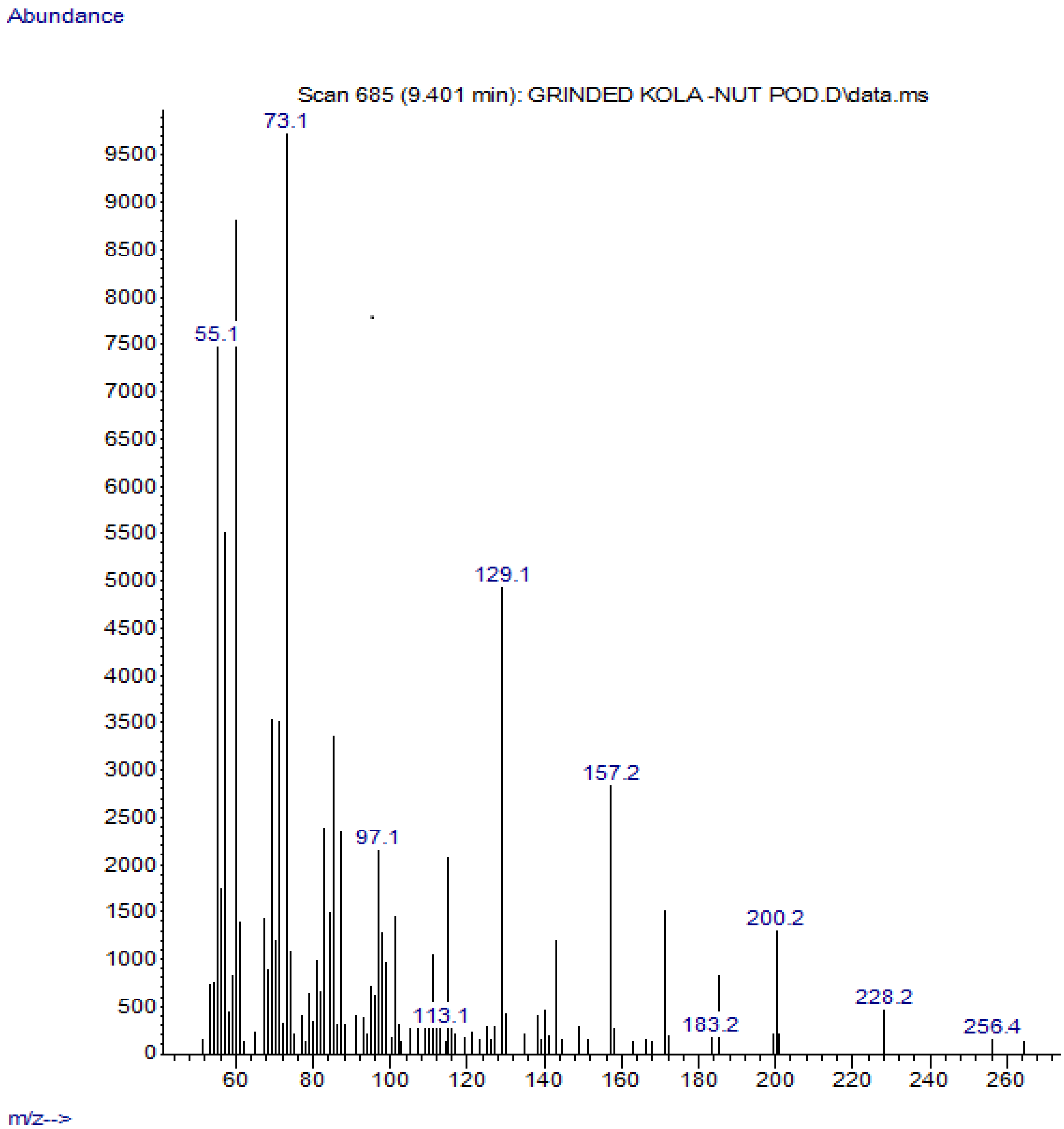


Fig. 6.0 GC-MS analysis of kolanut pod fibres

DISCUSSION

The results of the properties of the oils Premium Motor Spirit (PMS), automotive gas oil (AGO) and turpentine oil (TO) used are shown in table 1, the densities, viscosities and surface tension of two oils and one oily chemical (PMS, AGO and TO) have their values like density 0.716g/cm^{3,} 0.826g/cm^3 and 0.795 g/cm^3 while in viscosity 64.73g/cm^{3,}120.65g/cm^3 and 95.50g/cm^3 also in surface tension 28.30mN/m and 24.90mN/m and 25.10mN/m respectively. This indicates a significant strength of the oil substance capacity occupies within a specific volume at a defined temperature and pressure. The selective oil sorption performances of three (3) kinds of modified sorbents in oil-over-water bath containing 50% of premium Motor Spirit, automotive gas oil and turpentine oil are illustrated in Table 3.1. Huge differences were observed in oil-to-water selectivity and oil removal efficiency of different modified natural sorbents of kolanut pod/ES fibre (70/30, 80/20 and 90/10) among the three (3) oils. The oil sorption capacities and oil removal efficiencies of kolanut pod/ES modified sorbent showed higher in TO which was approximately 6g/g and 99% while in PMS and AGO 5g/g and 49%, respectively. The modified natural sorbents also showed higher oil retention in turpentine oil which was around (91.1g/g, 92.80g/g, 93.50g/g) than other counterpart PMS and AGO which were (57.0g/g, 58.2g/g, 58.3g/g) and (58.4g/g, 61.0g/g, 61.0g/g) and respectively..The reason for this was obviously the higher sorption performance of turpentine oil than other two oils associated with the chemical characteristic of kolanut pod fibres, including its distinctively high wax coating, low surface energy and high ratio between dispersion component and polar component. Compared 90/10 kolanut pod/Es modified natural sorbents with 70/30 and 80/20 kolanut pod/Es modified natural sorbents showed complementary selective oil sorption with more quantity introduction of kolanut pod fibres significantly increasing modified natural sorbent oil sorption capacities and oil removal efficiencies, and also significantly enhancing oil-to-water selectivity's. From the chemical analyses in fig 5.0, the chemical composition of kp fibres showed the typical bands of lignocellulosic fibre, cellulose and lignin are the components for stretching vibrations. The wax content was also analyzed given as 2.4% kolanut pod and the fibres as shown in table 2.0. In fig.5.0, the broad strong peak at 3280cm^{-1} corresponds to the hydroxyl group content that is O-H stretching vibration of alcohol and phenol. The strong peaks at 2922cm^{-1} and 2855cm^{-1} correspond to the symmetric and asymmetric aliphatic CH_3 and CH_2 stretching vibration, indicating the presence of the plant fibre wax which generally consists of long chain alkanes and alkenes. The absorption bands at 2074cm^{-1} and 1871cm^{-1} are attributed to the C=O stretching vibration of aldehydes , carboxylic ,fatty acids ,acetyl esters, ketones and esters in lignin.(Lim and Huang 2007). The four absorptions signals around are 1587cm^{-1}, 1375cm^{-1}, 1244cm^{-1} and 1155cm^{-1} are related with the C-O and C=C stretching vibration of alcohol and ether in lignin. The absorption band at 1028cm^{-1} belongs to the stretching of C-O in cellulose, hemicelluloses and lignin (Likon et al 2013). From the GC-MS result of kolanut pod oil shown in fig. 6.0, it was found that the suggested compounds dodecanoic acid even after various retention time and area percentage it still maintained the same compound . The various ranges of retention time fall within 5.692-7.141RT of the same dodecanoic acid and 0.02 -0.15% of area percentage of the dodecanoic acid. The highest retention time from the result is 7.141RT while the least among them is 5.692RT. Also the highest area percentage is 0.15% and the least among them is 0.02%, from the result possibly suggested compound should be dodecanoic acid. Finally, the RT and area (%) of kp ranges from 5.692-7.141RT and 0.02 -0.15%, from the above GC-MS results the compound dodecanoic acid is suggested compound.

CONCLUSION

A modern modification of 10-30% polyethylene/polypropylene sheath – core composite fibre (ES) was used to modified a natural sorbent made from kolanut pod fibres. It was found that 90/10 of KP/ES sorbents 19.03(0.153)g/g was comparatively highly preferred than 80/20 of KP/ES and 70/30 of KP/ES sorbents 18.80(0.1)g/g, 18.33(0.306)g/g in terms of PMS oil-to-water selectivity and 90/10 of KP/ES sorbents 16.57(1.001)g/g and 25.60(0.265)g/g is also preferred than 80/20 of KP/ES and 70/30 of KP/ES sorbents 15.86(1.201)g/g, 15.70(0.964)g/g and 25.30(0.361)g/g ,24.96(0.306)g/g respectively in terms of AGO and TO oil-to-water selectivity. While in oil removal efficiency 90/10 of KP/ES sorbents 47.9(1.901)% was comparatively highly preferred than 80/20 of KP/ES and 70/30 of KP/ES sorbents 47.2(0.709)%, 46.6(0.557)% in terms of PMS oil removal efficiency and 90/10 of KP/ES sorbents 48.7(1.457)% and 98.9(0.153)% are also preferred than 80/20 of KP/ES and 70/30 of KP/ES sorbents 48.4(1.557)% , 47.9(1.901)% and 98.8(0.153)% , 98.6(0.252)% respectively in terms of AGO and TO oil removal efficiency. The natural sorbents (KP/ES) with the modified ratio of 10%ES was considerable to obtain a reasonable bonding structure and meanwhile, guarantee the assembly's best spill cleanup in performance. It was observed that the modified kolanut pod fibres had extreme chemical similarities in IR and also contained significantly higher wax content (2.4g/g). GC-MS analysis from each retention time (RT) and area percentage (%) suggested dodecanoic acid compounds. Finally, when three (3) sorbents ratios were compared it was confirmed that one natural (90/10 of KP/ES) sorbents out of three sorbents showed highly corresponding to oils (PMS, AGO and TO) sorption with addition of 10%ES significantly increasing oil removal efficiency and oil-to-water selectivity. This research has contributed to knowledge that the lesser ES modified sorbent has the highest oil removal efficiency and oil-to-water selectivity than higher ES modified which was actually enriched the academic knowledge of the researchers and the world at large since they are rich in nature, environmental friendly and cost-effectives.

References

Adebajo, M.O.,Frost, R.L.; Kloprogge, J.T.; Carmody, O.; Kokot, S (2003). Porous materials for oil spill cleanup: A review of synthesis and absorbing properties. *Journal of Porous Materials* 10, 159–170.

Anisuddin, S., Al-Hashar, N., Tasheen, S. (2005): Prevention of oil spill in seawater using locally available materials. –Arabian Journal of Science and Engineering 30(2B): 143-152.

Calcagnile P., Fragouli D., Bayer IS., Anyfantis GC., Martiradonna L., Cozzoli PD., Cingolani R., Athanassiou A. *ACS Nano* 6 (2012) 5413.

Cherian, B. M, Leão, A. L., de Souza S. F. (2011) Cellulose nanocomposites with nanofibres isolated from pineapple leaf fibres for medical applications,"Carbohydrate Polymers, vol. 86, no. 4, pp. 1790–1798, 2011.

Choi H-M., Kwon H-J., Moreau J. P., *Textile. Resource. Journal*. 63 (1993) 211.

Chol H-M., Cloud R. M. *Environ. Sci. Technol*. 26 (1992) 772.

Dong. T, Guangbiao X., Fumei W. (2015) Oil spill cleanup by structured natural sorbents made from cattail fibres. College of Textiles, Donghua University, Shanghai 201620, China Key Laboratory of Textile Science and Technology Ministry of Education, Donghua University, Shanghai 201620, China. Industrial Crops and Products 76 : 25–33.

Li, J.; Luo, M.; Zhao, C.J.; Li, C.Y.; Wang, W.; Zu, Y.G.; Fu, Y.J (2013).Oil removal from water with yellow horn shell residues treated by ionic liquid. Bioresource. Technol. 128, 673–678

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Sun X-F., Sun R., Sun J-X. *Journal. Agricultural. Food Chemistry.* 50 (2002) 6428.

Teas Ch., Kalligeros S., Zanikos F., Stoumas S., Lois E., Anastopoulos G. *Desalination* 140 (2001) 259.

Teli M. D., Sanket P. V. *International Journal of Applied Sciences, Engineering and Technology* 3 (2014) 1.

Wang, J., Zheng, Y., and Wang, A. (2013).“Investigation of acetylated kapok fibres on the sorption of oil water,” Journal Environmental. Scicience. 25(2), 246-253.

Yakimov, M. M.; Timmis, K. N.; Golyshin, P. N. (2007). "Obligate oil-degrading marine bacteria". Curr.Opin.Biotechnol. 18 (3): 257–266.

Zhu Q., Chu Y., Wang ZK., Chen N., Lin L., Liu FT., Pan QM. *Journal. Materal Chemistry A.* 1 (2013) 5386.