Analysis of Structured Natural Sorbent from Agricultural Waste Materials

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ABSTRACT

The studies of structured natural sorbents produced from kolanutpod(KP), pumpkin stem (PS) and pineapple leaf (PL) fibres were prepared by a novel nonwoven bonding with introduction of 10-30% polyethylene/polypropylene sheath-core composites fibres (ES). The productwere made using different natural fibres which were blended with 10-30%ES and placed into a muffle furnace. Nine (9) natural sorbent were produced KP/ES, PS/ES and PL/ES each at three different ratios of 70/30, 80/20 and 90/10. Scanning electron microscopes (SEM) and Fourier transform infrared (FTIR) were used for the chemical analysis of the materials. Wax contents of KP, PS and PL were determined.The physical properties (densities, viscosities and surface tension) of the two oil premium motor spirit (PMS) and automotive gas oil (AGO)were carried out. The sorption capacity and retention capacity of structured sorbent were also determined. The result of SEM analysis of the three (3) natural fibres KP, PS and PL showed complete different morphological microstructure, FTIR analysis exhibited characteristics vibrational mode of cellulose and hydrocarbon. Wax content of KP,PS and PL fibres are 2.4(%), 1.2(%) and 1.6(%) respectively, this shows that KP contains the highest wax content and PS had the lowest wax contents. The densities, viscosities and surface tension of PMS are 0.716 g/cm^3, 64.73 g/cm^3 and 28.300.826 g/cm^{3}mN/m respectively. While in AGO density is 0.826 g/cm^3, viscosity is 120.65 g/cm^3 and surface tension24.90 mN/m.. This indicates a significant strength of the oil which occupies a specific volume at a defined temperature and pressure. Oil sorption capacity of different ratios of KP/ES, PS/ES and PL/ES using PMS and AGO oil sorption capacity was carried out. The result shows that PS/ES of 90/10 had highest sorption capacity in PMS 6.43(g/g). In AGO PL/ES at ratio of 90/10 has the highest sorption capacity of 9.46(g/g) while KP/ES had 70/30 which is the lowest sorption capacities at 4.53g/g in PMS and 4.63g/g in AGO, PS/ES had highest oil retention capacity 93.5% at ratio of 90/10 in PMS while KP/ES has the lowest of oil retention capacity 57.0% at ratio of 70/30 in PMS. In AGO PS/ES at ratio of 90/10 has the highest oil retention capacity 91.7% while KP/PS/ES at ratio of 58.4(g/g) has the lowest of 53.2%. The results of this study suggest that structured sorbent PL/ES and PS/PL/ES have a highest sorption capacity on PMS and AGO when compared with the standard. KP/ES structured sorbent has the highest efficiency in removing oil from water and enhances oil-to-water selectivity than PL/ES and PS/PL/ES sorbents

***Keywords**: Kolanut pod, Pumpkin stem, Pineapple fibre, Structured sorbents, Onitsha (Anambra State).*

INTRODUCTION

Crude oil contaminates water through oil spills. An oil spill is the release of a liquid petroleum hydrocarbon into the environment especially to the marine ecosystem due to human activity Wahi, R. et al, (2013). Oil spills also may be due to release 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 Yakimov, M. M et. al, (2007). This is carried by 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 which includes the type of oil spilled, the temperature of the water (affecting evaporation and biodegradation) 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). Although they may be used as the sole cleanup method in small spills, sorbents are most often used to remove final traces of oil, or in areas that cannot be reached by skimmers Kaku Professional Engineer limited, Nigeria (2012).Once sorbents have been used to recover oil, they must be removed from the water and properly disposed on land or cleaned for re-use. Any oil that is removed from sorbent materials must also be properly disposed or recycled. Sorbents can be divided into three basic categories: natural organic, natural inorganic, and synthetic sorbents. Mineral Adsorbents represent a very large group; these are commonly used as they have a number of advantages such as non-amiability, chemical inertness, relatively low cost and easy availability. These are also known as sinking sorbents, and they are highly dense, fine grained materials natural or processed used to sink coating oil. They can be considered as a group of universal adsorbents. Most mineral adsorbents are raw materials of natural origin which are used in a powder or granular form. Their particle size may range from several nm to several mm (not more than 3 mm). Mineral adsorbents are generally non-combustible and resistant to acids and bases. Usually, their sorption capacity towards petroleum derivatives is in the range of 0.20–0.50 g/g, and their bulk density is 0.45–0.90 kg/dm^3 Tic, W. (2015). Natural Organic Adsorbents used in chemical rescue include peat, needle-cover, moss, dry leaves, straw, sawdust, bark and wood waste, cellulose from paper and cotton products and linen materials. Tic, W. (2015). The literature also describes other sorbents of natural origin from agricultural and/or processing wastes, such as rice husk. Various types of plant shells and plant waste, kapok and many others Wahi, R. et al, (2013) and Li, J.; Luo, et al (2013) . Natural organic adsorbents are considered to be effective, inexpensive (although this is not universally true), easily available and environmentally friendly. In synthetic polymers the group of synthetic polymers includes polypropylene, polyethylene, polyacrylate, polystyrene, and polyurethane, which are used to manufacture special sleeves, mats, cloths, or cushions for the sorption of hazardous liquids. Polymer adsorbents exhibit hydrophobic properties, low bulk density (0.10–0.45 kg/dm3), and large sorption capacity with respect to petroleum derivatives. Depending on the type of material, the sorption capacity differs ranging from few to several tens g/g, and some studies indicated that the capacity can exceed up to 100 g/g. Adebajo et al. (2003) A modern nonwoven with introduction of 10-30% polyethylene/polypropylene sheath – core composite fibre (ES) was used to prepared structured natural fibre assemblies made by kolanut pod, pumpkin stem and pineapple leaf fibres. The background of study is a quest for natural sorption material will continue to receive attention since the material although they have high capacity of oil absorbing almost all of them are made from agricultural by product which is non-renewable and very expensive. Niger Delta region in Nigeria produces 70% of crude oil in the country and then is increasingly serious oil pollution caused by oil spillages which has raised a vast concern all over the country and the world at large. Every year, an average of about 35million barrels of petroleum is transported across the seas around the world and this renders the marine ecosystem vulnerable to pollution Anisuddin et at, (2005).

EXPERIMENTAL

Sample collection;

100g of kola nut pod , pumpkin stem and pineapple leaf fibres samples were collected from Ochanja Market in Onitsha-South Local Government Area, Anambra state.Polyethylene and polypropylene chemicals were purchased from Pomic Company Nigeria Limited. Premium Motor Spirit (PMS) and Automotive Gas Oil (AGO) collected from Nigerian national corperation (NNPC) station at Awka Anambra state which were used as experimental oils..

Sample Preparation;

These were collected as KP,PS and PL respectively weighed and dried under the sun for three 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 (PMS and AGO) such as densities, viscosities and surface tensions were determined using below method The 25mls dry and empty density bottle were weighed and the 25mls density bottle filled with Premium Motor Spirit (PMS) and Automotive Gas Oil (AGO) 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.

Using the equation; Density = Mass /Volume

Also 50mls of the Premium Motor Spirit (PMS) and Automotive Gas Oil (AGO) samples 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 5mins, 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. Other fabricated structured sorbents were prepared accordingly. The nine (9) kinds of sorbents with different fibres blending ratios were made as follows below.

Table.1 Blending ratios of polyethylene/polypropylene sheath core composite (ES) and the natural fibres of kolanut pod (KP), pumpkin stem (PS) and pineapple leaf (PL)

Types	Kolanut pod/ES	Pumpkin Stem/ES	Pineapple leaf/ES
BlendedRatios	70/30	70/30	70/30
	80/20	80/20	80/20
	90/10	90/10	90/10

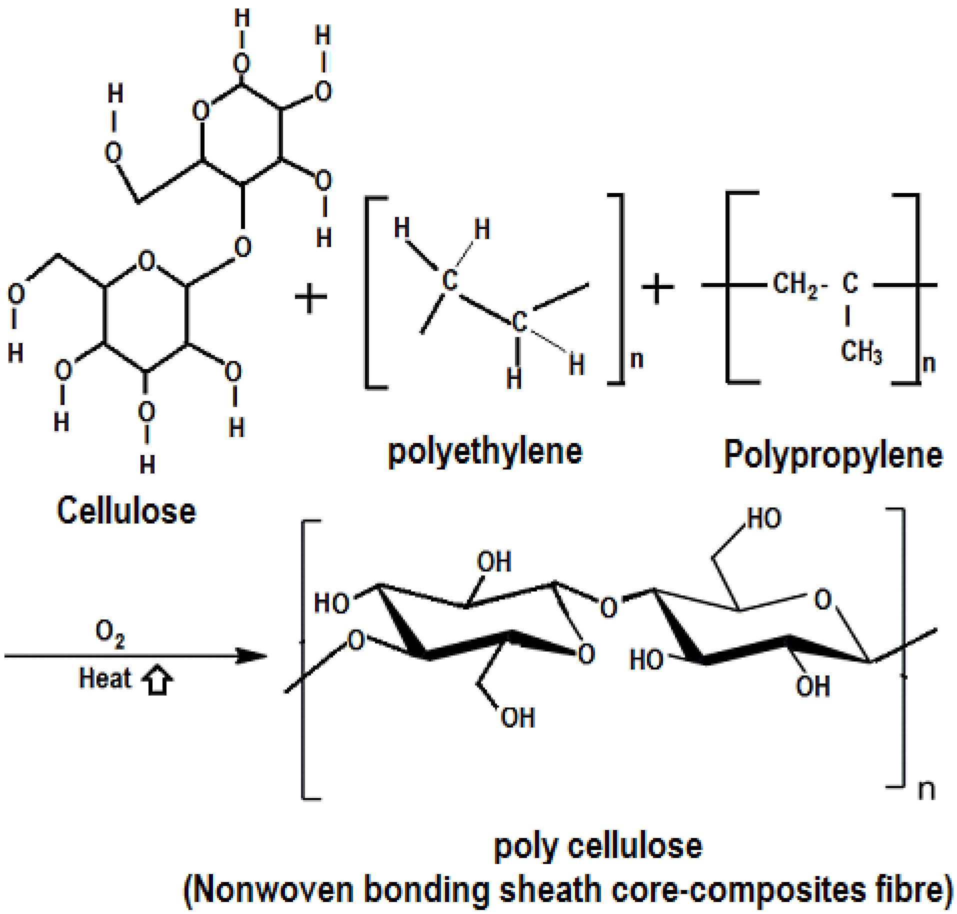


Fig. 1 Fabrication of structured fibre sorbents

Chemical Analysis

Chemical and morphological structure of processed kolanut pod, pumpkin stem and pineapple leaf fibres were examined using fourier transformed infrared (FTIR) and scanning electron microscopy (SEM). The wax content of kolanut pod, pineapple leaf and pumpkin stem fibres were analyzed by soxhlet extraction method. The dry (KP, PL and PS) fibres of 50grams each were placed in a different soxhlet extractor and extracted with alcohol and benzene in the ratio of 1:2 at 95^{o}C with four to six (4-6) times per hour for 4hrs. After drying in an oven at 105^{o}C, the fibres were re-weighed and there was decrease in weight indicating the wax contents of (KP, PL and PS) fibres.

Oil sorption and retention capacity

Oil sorption test was performed as follows; 5g structured fibre assemblies each of the three (3) structured fibres was put in the two (2) oil samples (PMS and AGO). 25minutes was taken as the equilibrium oil sorption time, since no obvious differences were observed for the assemblies after a longer soaking time. The structured 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 (1) and (2)

Oil sorption capacity = $^{m}f_{25} - {}^{m}f / {}^{m}f$ ------------------------------ (1)Dong T. et al (2015).

Oil retention capacity = $^{m}f_{12} - {}^{m}f / {}^{m}f_{25} - {}^{m}f$------------------------- (2)Dong T. et al (2015).

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

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

$^{m}f_{12}$ is the mass of oil wetted sample at 12h dripping (g)

RESULTS AND DISCUSSION

Table 1 Properties of experimental oils Premium Motor Spirit (PMS) and Automotive Gas Oil (AGO).

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

Table 2 Wax content of kolanut pod, pumpkin stem and pineapple leaf fibres

Fibres	Wax content (%)
Kolanut pod	**2.4**
Pumpkin stem	**1.2**
Pineapple leaf	**1.6**

Table 3: Oil sorption and retention capacities of single fibre assemblies

Fibres	Blended ratio	Premium Motor Spirit (PMS)	Automotive Gas Oil (AGO)

		Oil sorption Capacity(g/g)	Oil retention Capacity(g/g)	Oil sorption Capacity(g/g)	Oil retention Capacity(g/g)
Kolanut pod/ES	**70/30**	**4.53(0.252)**	**57.0(3.386)**	**4.63(0.153)**	**58.4(1.808)**
	80/20	**4.56(0.153)**	**58.2(3.082)**	**4.76(0.252)**	**61.0(2.042)**
	90/10	**4.60(0.4)**	**58.3(2.823)**	**5.00(0.361)**	**61.0(2.658)**
Pumpkin stem/ES	**70/30**	**5.50(0.153)**	**91.1(1.266)**	**7.80(0.200)**	**85.6(3.092)**
	80/20	**5.76(0.404)**	**92.8(1.682)**	**8.50(0.361)**	**88.9(2.082)**
	90/10	**6.43(0.321)**	**93.5(3.966)**	**8.93(0.404)**	**91.7(6.424)**
Pineapple leaf/ES	**70/30**	**5.56(0.321)**	**88.8(1.498)**	**8.93(0.252)**	**89.0(2.701)**
	80/20	**5.86(0.451)**	**88.9(2.434)**	**9.33(0.306)**	**89.8(1.015)**
	90/10	**6.26(0.351)**	**90.2(2.261)**	**9.46(0.252)**	**91.2(1.320)**

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

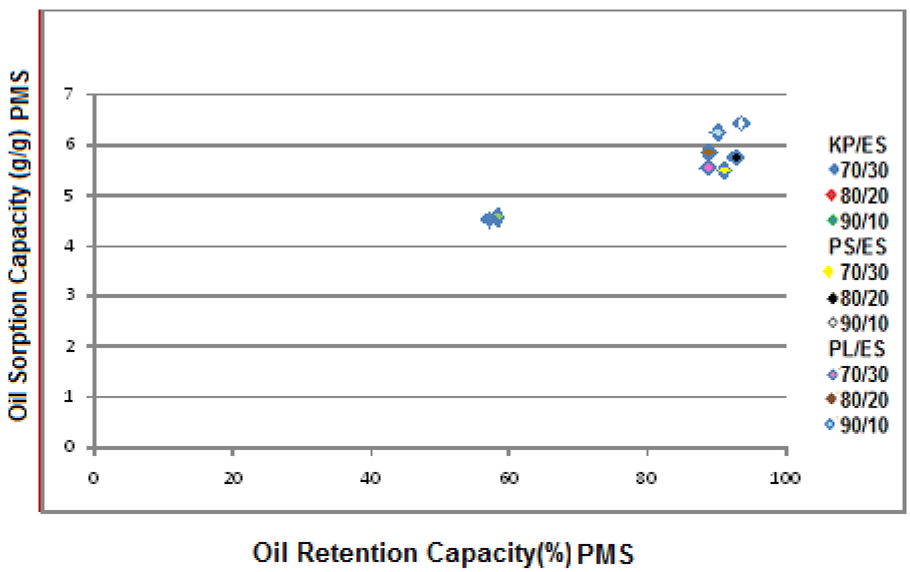


Fig. 1 A graph of Oil sorption and retention capacities of single sorbents in Premium Motor Spirit (PMS)

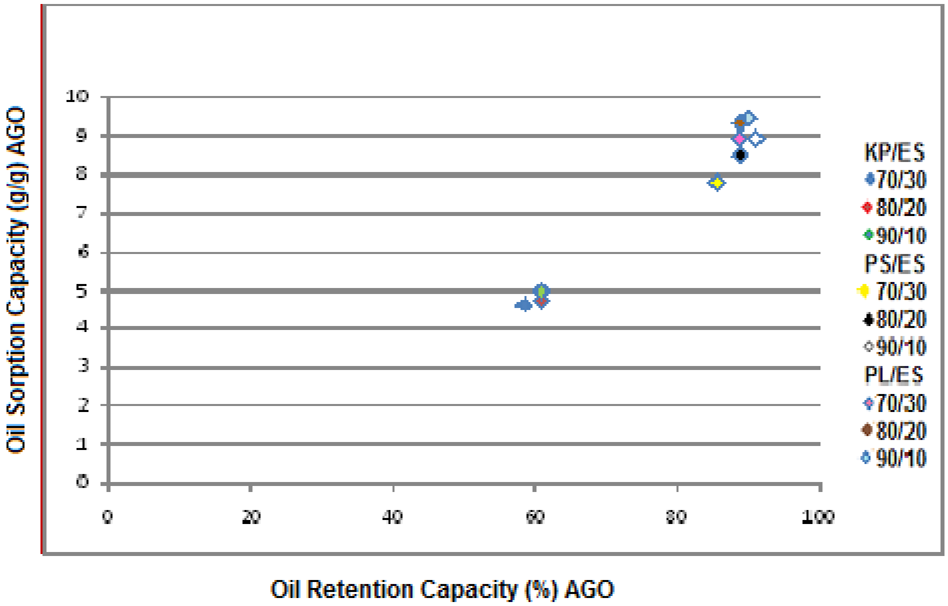


Fig.2 A graph of Oil sorption and retention capacities of single sorbents in Automotive Gas Oil (AGO)

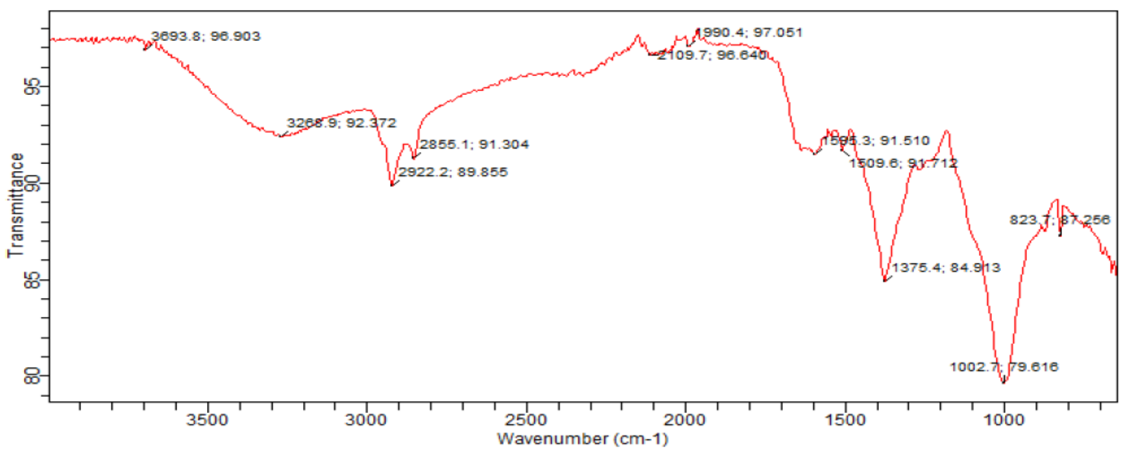
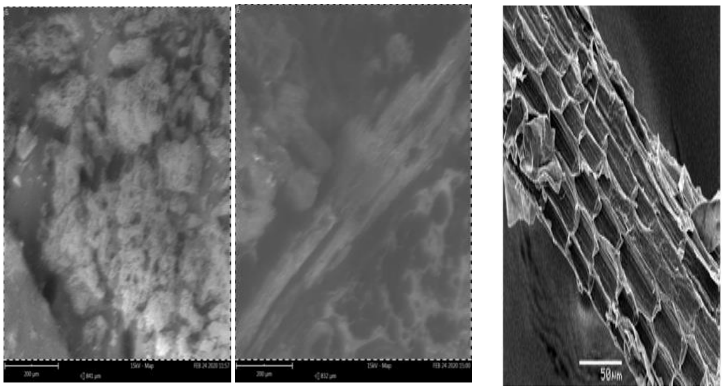


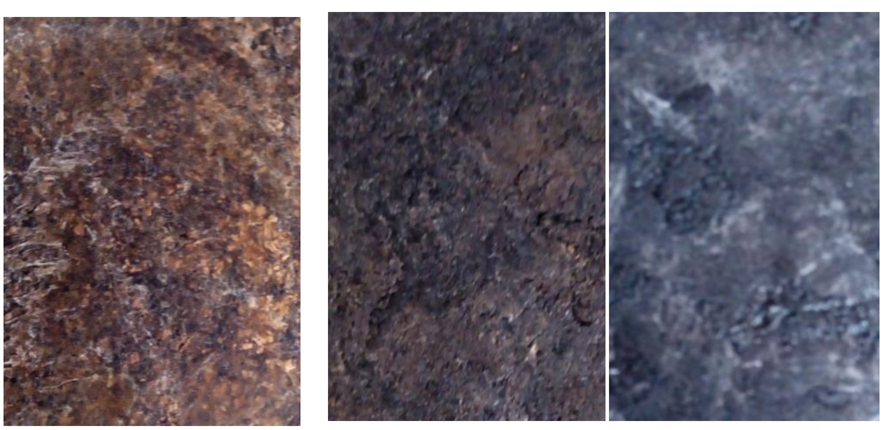
Fig. 3 Infrared spectrum of pumpkin stem(PS) fibres



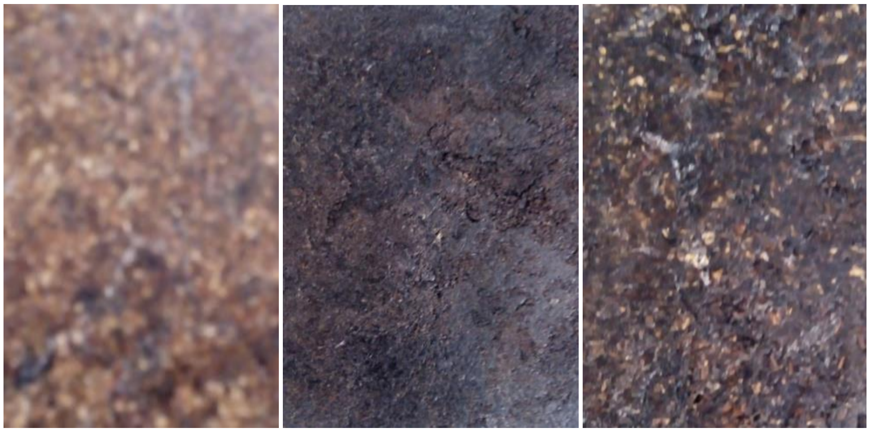
(a)KP/ES-90/10% (b) PS/ES-90/ES% (c) PL/ES90/10%

Fig.4 (a-c) SEM image of (a) KP-90/10%ES (b) PS-90/10%ES (c) PL 90/10%ES

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



PS/ES – 70/30% PS/ES – 80/20% PS/ES –90/10%



PL/ES – 70/30% PL/ES – 80/20% PL/ES –90/10%

Fig. 5 Fabricated structured fibre Sorbents of KP/ES – 70/30%, KP/ES – 80/20%, KP/ES – 90/10%,PS/ES – 70/30%, PS/ES – 80/20%, PS/ES – 90/10%, PL/ES – 70/30%, PS/ES – 80/20%, PS/ES – 90/10%.

DISCUSSION

The results of the properties of the oils Premium Motor Spirit (PMS) and automotive gas oil (AGO) used are shown in table 1, the densities, viscosities and surface tension of two oils (PMS and AGO) have their values like density 0.716g/cm^3 and 0.826g/cm^3 while in viscosity 64.73g/cm^3 and 120.65g/cm^3 also in surface tension 28.30mN/m and 24.90mN/m. This indicates a significant strength of the oil substance capacity occupies within a specific volume at a defined temperature and pressure. Table 3, lists oil sorption and retention capacity of nine (9) sorbents and their broad performances are illustrated in Fig.1 and fig.2. No much significant differences were observed in the same ratio sorbents absorbing Primium motor spirit (PMS) and automotive gas oil (AGO). In general, they absorbed slightly more automotive gas oil than Primus motor spirit. This could be explained by the fact that automotive gas oil is heavier than Primus motor spirit within the same unit volume. On the other side, automotive gas oil was more readily to drip out from the assemblies than Primium motor spirit. The draining occurs when the capillary pressure is insufficient to hold the weight of the oils Cherian, B. M et al (2011). The heavy nature of automotive gas oil will combined with its lower viscosity than Primium motor spirit was favorable for the dipping process. Comparing with assemblies made by different natural sorbents, pumpkin stem fibre sorbents showed the highest oil sorption and retention capacities which absorbed over 15 times the mass of oils over its own weight and retained more than 84.7% of absorbed oil after 12 h dripping. Although KP fibre sorbents were less preferred in terms of oil sorption capacity, it would retain around 79.5% of absorbed oils, about 7% higher than that of kolanut pod fibre assemblies which was around 67.4%. Pumpkin stem fibre had a distinct shaped microstructure unlike pineapple leaf fibres and kolanut pod fibres, which was reported to make up of 65–75 % of the fibre volume. Due to its low surface energy and excellent oleophilicity, the oil droplets were not only absorbed on the fibre surface but entered into the distinct parts of the fibre, as observed in fig 7 and 8. The excellent oil retention of pineapple leaf sorbents can be explained by unique block shaped structure of pineapple fibre, which was angled divided in the middle part of the image and at top side like triangle structures. This morphological structure was obviously favorable for oil to be retained in pores within assemblies Hyung-MlnChol (1992. For fibre assemblies with different ES contents, it was found that 90/10 of natural fibre/ES sorbents was preferable to obtain a reasonable bonding structure and meanwhile guarantee the sorbents's best oil sorption performance, since more amount introduction of ES would otherwise decrease the oil sorption and retention capacity of the assembly. Fig. 4(a-c) shows completely different morphological structures. The pulling stable of KP fibres ranged between 2.2mm to 3.2mm and PS fibres ranged between 4.8mm to 5.8mm while PL fibres ranged between 6.3mm to 7.5mm respectively. The SEM of structured sorbents, showed a stable and porous structured sorbent is not only favorable for oil sorption and retention during oil absorbing but also could be easily collected after used. Their mechanical interlocking due to its fibres surface roughness which can promote adhesion interaction, mainly of the van danwaals type between the fibre and its polymer matrix. From the chemical analyses, the chemical composition of KP, PS and PL 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 1.6% kolanut pod, 1.2% pumpkin stem and 2.4% pineapple leaf of their fibres as shown in 2. In fig. 3, the two absorption signals was observed in the intensity O-H bond at 3888cm^{-1} and 3288cm^{-1} corresponds to the non-free O-H stretching vibration, indicating that the hydroxyl groups contents in pumpkin stem fibre, showed strong band at 3288cm^{-1}. The strong peak at 2922cm^{-1} and 2855cm^{-1} corresponds to the aliphatic CH_3 stretching vibration, indicating the presence of the plant fibre wax which generally consists of long chain alkanes and alkenes Chrian, B. M, et a. (2011). An absorbance peak at 1395cm^{-1} corresponding to aromatic skeletal vibration breathing with C-O, the absorptions of a strong sharp peak at 1027cm^{-1} and 823cm-1 attributed to C-O stretching in cellulose, hemicelluloses and lignin arises from ά-glucosidic linkage between the pumpkin stem fibre units hemicelluloses and cellulose.

CONCLUSION

A modern nonwoven with introduction of 10-30% polyethylene/polypropylene sheath – core composite fibre (ES) was used to prepare structured natural fibre assemblies made by kolanut pod, pumpkin stem and pineapple leaf fibres. It was found that KP sorbent was comparatively less preferred in terms of oil sorption capacity (4.53- 4.63g/g) to PS/ES (5.50 – 7.80g/g) and PL/ES (5.56 -8.93g/g) sorbents when compared in PMS and AGO. They showed excellent oil (PMS and AGO) retention capacity (within 84.7% after 12h dripping). The twisted gravel-like shaped microstructure of KP fibre which provided advantageous gap for oil retained in pores within sorbents was considered as the main reason for oil (PMS and AGO) retention. The sorbents with different blended ratio of 10%ES was considerable to obtain a reasonable bonding structure and meanwhile, guarantee the assembly's best oil sorption performance. It was observed that KP fibre had extreme chemical similarities in IR and also contained significantly higher wax content (2.4g/g).Finally, when three (3) sorbents were compared it was confirmed that two natural (PS/ES and PL/ES) sorbents out of three sorbents showed highly corresponding to oil (PMS and AGO) sorption with addition of 10%ES significantly increasing oil sorption capacity and retention capacity than KP sorbent. This research has contributed to knowledge in the PS/ES and PL/ES structured sorbent since it has the highest oil retention capacities than KP/ES sorbents which was actually enriched the academic knowledge of the researchers and the world at large for they are rich in nature, environmental friendly and cost-effectives.

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