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Clean Up and Recovery of Oil from Water Bodies Using Oil Sorbents with High Sorption Capacity, Oil/Water Selectivity and Reusability

O. Oribayo
Department of Chemical and Petroleum Engineering, University of Lagos, Lagos, Nigeria
Email: ooribayo@unilag.edu.ng

Abstract

To enhance the removal of oil contaminants from water, an oil spill clean-up sorbent was prepared by synthesizing a lignin based polyurethane foam (LPU) and modified with graphene and 1H,1H,2H,2H-perfluorodecanethiol (PFD) monomer (LPU-rGO-PFD). The LPU-rGO-PFD sorbent was fabricated by anchoring of reduced graphene oxide (rGO) on the skeleton of a LPU foam using adhesive polydopamine, followed by functionalization with (PFD) monomer. This resulted in the ability to tune the surface properties of the LPU sponge skeleton to superhydrophobic and super-oleophilic, with a contact angle of 140.1°. The LPU-rGO-PFD sorbent was characterized with microscopic and spectroscopic analyses, and it exhibited many outstanding features, including a high sorption capacity (up to 68.2 times its own weight), high selectivity to crude oil sorption, and excellent reusability in comparison to commercial non-woven polypropylene sorbent. Furthermore, the oil sorption capacity remained the same after 20 cycles of oil sorption-squeezing experiments and the absorbed crude oil could be removed and collected by a simple squeezing process before reuse. As a result, LPU-rGO-PFD is considered as a promising oil sorbent for oil spill containment removal and environmental protection.

Keywords: Environmental protection, super-hydrophobic, super-oleophilic, oil absorbent, oil spill clean-up commas.

1.0 INTRODUCTION

Polymeric materials synthesized from renewable resources have been one of the developing research areas in the scientific community (Bernardini *et al.*, 2015; Hassan and Shukry, 2008). Nowadays, due to the environmental and economic concerns with the increasing dependence on depleting petroleum resources, there has been a growing need of utilizing renewable resources as substitute for petroleum-based resources. Bio-based polymers obtained from renewable resources (i.e. plants), particularly those from non-food renewable resources are attracting increasing research attention due to the environmental compatibility, special physical properties and low stable market prices attributed with these derived products (Ahvazi et al., 2011; Cinelli et al., 2013; D'Souza and Yan, 2013). Additionally, renewable resources also possess unique intrinsic properties that can contribute to the synthesis of novel polymeric materials utilized as substrate and offers economical advantage over its petroleum-based derived counterparts (Mahmood *et al.*, 2016). The combination of all these factors constitute a driving force which, promotes the utilization of renewable resources in the synthesis of polymeric materials.

Lignocellulosic biomass referred to as plant dry matter (i.e. wood waste) is an important renewable resource for the production of fine chemical such as bio-based polyol. Lignocellulosic biomass is composed of three major constituents namely: cellulose, hemicelluloses and lignin. It also has other smaller constituent of pectin, protein, extractives and ash, which together form a complex and rigid structure (Bernardini et al., 2015; Hassan and Shukry, 2008).

Lignin is the most abundant phenolic biopolymer obtained in huge quantities as a by-product of the pulp industry and it has been reported that lignin can copolymerize with isocyanates in (PU) producing polyurethane foams (Bernardini et al., 2015; Cinelli et al., 2013; Hassan and

Shukry, 2008; Jasiukaitytė et al., 2010). Based on these interesting functionalities and properties, lignin offers great prospect and higher benefit in the synthesis of polyurethane foam. An approach used in utilizing lignin is to transform the renewable waste to polyol via liquefaction.

PU foam possesses the important characteristics as an absorbent for oil clean-up, with a high hydrophobicity and oleophilicity properties. However, most commercially available PU sponges exhibit hydrophilicity to some extent or even poor hydrophobicity, which compromises their practical use for oil spill clean-up and recovery. Therefore, surface modification to enhance the oil-wettability and hydrophobicity of PU is desired to make it a super-hydrophobic and super-oleophilic oil absorbent.

The fabrication of super-hydrophobic and super-oleophilic sorbent is attracting great attention as potential sorbent materials for oil spill cleanup, due to their excellent sorption capacity and high selectivity (Cojocaru et al., 2011; Fang et al., 2016; Hadji et al., 2020; Said et al., 2009; Witka-Jeżewska et al., 2003). Zhou et al. (2013) developed a vapour phase deposition process to fabricate super-hydrophobic polypyrrole-1H,1H,2H,2H-perfluorooctyltriethoxysilane (PPy-PTES) sponge sorbent from commercial PU sponges for the clean-up of oil spills and organic pollutants. The sorbent was produced by dip coating of PU in a solution of FeCl3 and 1H,1H,2H,2H-perfluorooctyltriethoxysilane, followed by a second coating with polypyrrole (PPy). Their conclusions suggested that this sorbent material may find practical applications for clean-up of oil spills and removal of organic pollutants from water surfaces. Wang et al. (2014) fabricated a super-hydrophobic PU absorbent by coating an ultra-thin silane layer onto a polyurethane foam, and its potential use for oil spill and organic pollutant clean-up was demonstrated. The fabrication involved deposition of an Al_2O_3 transition layer onto the PU foam skeleton, followed by coupling silane molecules onto the foam skeleton through the hydroxyl groups on the surface of the Al_2O_3 layer. Although the modified PU foam sorbent obtained was reported to exhibit excellent oil affinity and water repellence without compromising its elasticity and porosity, the fabrication process requires sophisticated equipment like an atomic layer deposition equipment (Savannah S100, Cambridge NanoTech) for depositing and grafting Al2O3 onto the Pu foam.

In the present study, a lignin-based PU (LPU) foam substrate was synthesized and subsequently functionalized to fabricate a super-hydrophobic absorbent for oil spill clean-up. The idea is to synthesize a lignin-based polyurethane (LPU) foam and enhance its hydrophobicity by incorporating long hydrophobic -CH2 chains and alkyl groups from 1H,1H,2H,2H-perfluorodecanethiol (PFD) functionalizing molecules through an adhesive coating of polydopamine reduced graphene oxide (rGO) on the lignin-based polyurethane (LPU) foam. The functionalization of the synthesized LPU foam substrate is to enhance its properties as an oil spill clean-up absorbent. This property is unique when compared to some of the previously reported super-hydrophobic sorbents in which the hydrophobic coatings are attached physically onto the substrate skeletons (Liu et al., 2013; Lü et al., 2016; Zhao et al., 2016) and are vulnerable to detachment by squeezing when reused repeatedly during oil spill clean-up. This is made possible because of the endowed adhesive polydopamine rGO, which undergoes secondary reaction with the PFD molecules via a Michael addition or Schiff base reaction to form covalently-grafted functional layers (Lee et al., 2007b; Lee et al., 2008; Oribayo et al., 2017b; Xu et al., 2010). In addition, the properties and performance of the material as an oil absorbent were also investigated.

2.0 MATERIALS AND METHODS

2.1 Materials

Polyphenylmethane polyisocyanate (PMDI) was purchased from Wanhua Chemical Group, China. Castor oil was purchased from Sangon Biotech (Shanghai) Co., Ltd., and polyethylene glycol (PEG-400, average molecular weight 400) was purchased from Chinasun Specialty Products Co., Ltd, China. Lignin was purchased from Adams Reagent Co., Ltd. 1H,1H,2H,2H-perfluorodecanethiol, Surfactant (polymethylphenylsiloxane), catalyst (dibutyltin dilaurate), graphite, oil red and methylene blue were all purchased from Energy Chemical Shanghai, China. Glycerin, sulphuric acid (99.9%), cyclohexane, tetrahydrofuran (THF), 1,2 dichloromethane, chloroform, toluene, benzene, cyclohexane, acetone, ethanol, carbon tetrachloride, NaOH (99.9%), 1,4-dioxiane and silicone oil were purchased from Shanghai Chemical Reagents Co. Ltd.

2.2 Liquefaction of Lignin

Lignin (6 g) was added to a mixed solvent of (18.9 g) polyethylene glycol (99.9 %) and glycerin (6.6 g) in a 250 mL three-neck flask equipped with a mechanical stirrer (IKA Labortechnik). Sulphuric acid (0.67 g), used as liquefaction catalyst, was subsequently added to the mixture under vigorous mechanical stirring at 300 rpm. The flask was then kept at 160 °C in an oil bath for a period of 1 hr while being constantly stirred, and nitrogen gas purge was used to remove the water generated (Bernardini et al., 2015; D’Souza and Yan, 2013).

2.3 Synthesis of LPU foam and LPU-rGO-PFD foam sorbent

LPU foam was synthesized according to a prepared formulation (Oribayo et al., 2017a). Liquefied lignin was added to polyol (99.9%) and other additives (catalysts, surfactant and blowing agent) at ambient temperature for 5 min, and PMDI (99.9%) was then added and mixed for 30 s. Afterwards, the resultant foaming mixture was quickly transferred into a mould (11.5 cm x 7.5 cm x 4.5 cm), where it was allowed to rise freely. The resulting foam was then allowed to cure fully at ambient conditions for 2days. The LPU foam was cut into blocks and cleaned in ethanol (99%) purity. The foam blocks were then rinsed with distilled water, dried at 50°C in an oven for 1hr, and then immersed in 500 ml of ethanoic graphene oxide (GO) solution (0.2 mg/ml) for 30 min. Dopamine hydrochloride (50 mg) was then added to an ethanoic solution of 10 mM tris-buffer solution (pH 8.5) under continuous mechanical stirring at 70 rpm. The GO was subjected to reduction by polydopamine at 40°C. After the reaction time of 2hrs, the LPU-rGO was removed from the solution and washed with distilled water and drained via squeezing repeatedly until the squeezed water became clear. The LPU-rGO sample was then washed with ethanol to remove the retained water and dried in a vacuum oven at 30°C. After drying to its constant weight, the resulting LPU-rGO foam was reacted in 2mg/ml 1H,1H,2H,2H-perfluorodecanethiol (PFD) in an ethanoic solution of 10 mM tris-buffer solution (pH 8.5) under mechanical stirring at 50 rpm for 24 hrs. Finally, the resultant LPU-rGO-PFD foam sorbent was washed with ethanol and distilled water repeatedly and dried overnight in air.

3.0 RESULTS AND DISCUSSION

In this study 1H,1H,2H,2H-perfluorodecanethiol monomer (PFD) with a long -CH_2- chains having a good affinity for oil or solvents with lower surface free energy than water and rGO was used to create wetting difference between oil and water on the LPU foam substrate for spill cleanup application. This surface property tuning of LPU foam from hydrophilic to super-hydrophobic and super-oleophilic LPU-rGO-PFD sorbent was achieved by incorporating rGO on LPU foam, with subsequent functionalization with PFD monomer as illustrated in Figure 1.

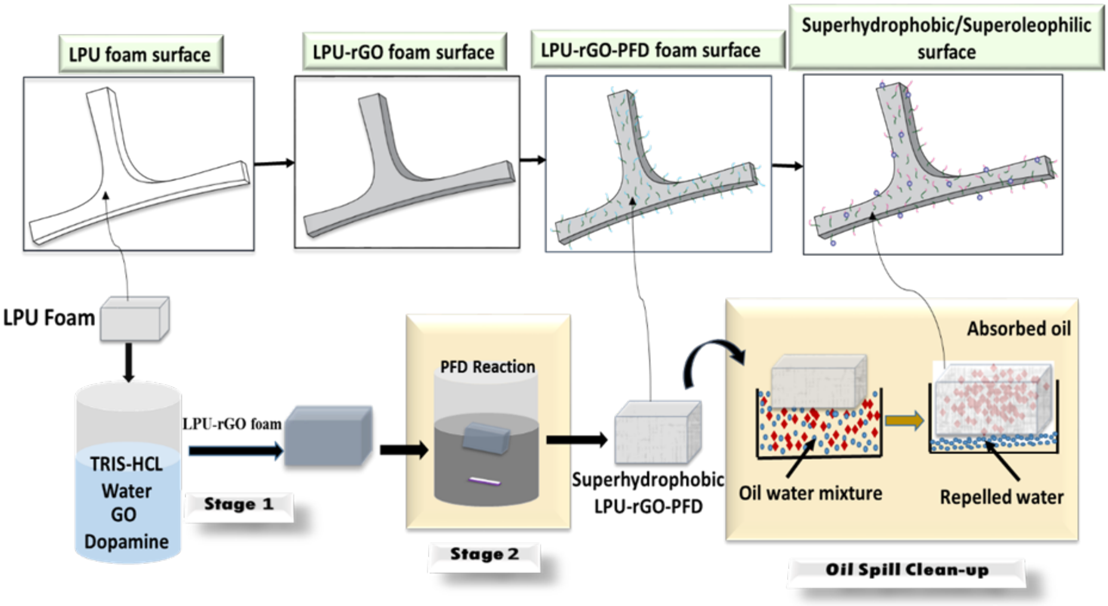

Figure 1: Photographic and schematic Illustration for the fabrication process and application of LPU-rGO-PFD foam sorbent for oil spill clean-up.

Hydrophilic GO was covalently attached to the LPU foam and reduced to hydrophobic rGO, through the oxidative self-polymerization of dopamine to polydopamine. Dopamine, a commonly known neurotransmitter or hormone, is a unique molecule which mimics adhesive proteins secreted by mussels. It self-polymerizes at a weak alkaline pH to form adherent polydopamine coating on a wide range of surfaces (Jayalakshmi *et al.*, 2013; Lee *et al.*, 2007a; Lee *et al.*, 2007b; Pham and Dickerson, 2014; Wang *et al.*, 2013). This adherent polydopamine is a coupling agent that binds rGO to the LPU foam skeleton. This compound, which contains catechol and thiol functional groups, has been reported to exhibit excellent affinity to most organic and inorganic substrate surfaces, including polymers, metals and metal oxides (Lee et al., 2007a). Furthermore, the oxidized quinone form of catechol adhered on the LPU-rGO foam during self-polymerization reaction of dopamine to polydopamine, undergoes secondary reaction with the thiol functional groups of PFD via a Schiff base reaction or Michael addition reaction to form covalently grafted functional layers (Lee *et al.*, 2007a; Lee *et al.*, 2011; Oribayo *et al.*, 2017b).

3.1 Liquefaction of Lignin

A method for obtaining polyols from renewable resources is through liquefaction. Liquefaction of lignin is a chemical process in which the macromolecular components of lignin are depolymerized and converted into a multi-functional liquid. The liquefied lignin contains highly reactive aromatic and aliphatic hydroxyl groups and is used as polyol substitute to that obtained from crude oil in the preparation of PU foams. In the liquefaction process, lignin was degraded into smaller fragments of lower molecular weight at 160 °C with sulphuric acid as catalyst. After the liquefaction step, the chemical structure of liquefied-lignin was characterized using size-exclusion chromatography (HP-AGILENT) and Fourier transform infrared spectrometer (Thermo Scientific Nicolet IS10). The weight-average molecular weight (Mw) of lignin was 3021 g/mol and decreased to 1411 g/mol for the liquefied-lignin. This implies that the linkages in the lignin macromolecules were fractured and degraded during liquefaction. Furthermore, the Fourier-transform infrared spectroscopy (FTIR) spectrum of the liquefied lignin was compared to that of the un-liquefied lignin as shown in Figure 2. In the FTIR spectrum, the absorption intensity of OH functional group (3404 cm^{-1}) for the liquefied lignin polyol increased remarkably in comparison to that of un-liquefied lignin. Moreover, the stretching vibration peaks of methyl and methylene at 2881–2932 cm^{-1}, the symmetric distortion vibration peaks of methylene at 1462 cm^{-1} and the antisymmetric distortion vibration peaks of methyl for the liquefied lignin also increased significantly in comparison to the un-liquefied lignin. The strong absorption peaks of methylene might be due to the structure of polyethylene glycol (PEG) and glycerol and the increase of the absorption peaks of methyl groups is due to the degradation of lignin in the presence of sulphuric acid during the liquefaction process (Cinelli *et al.*, 2013).

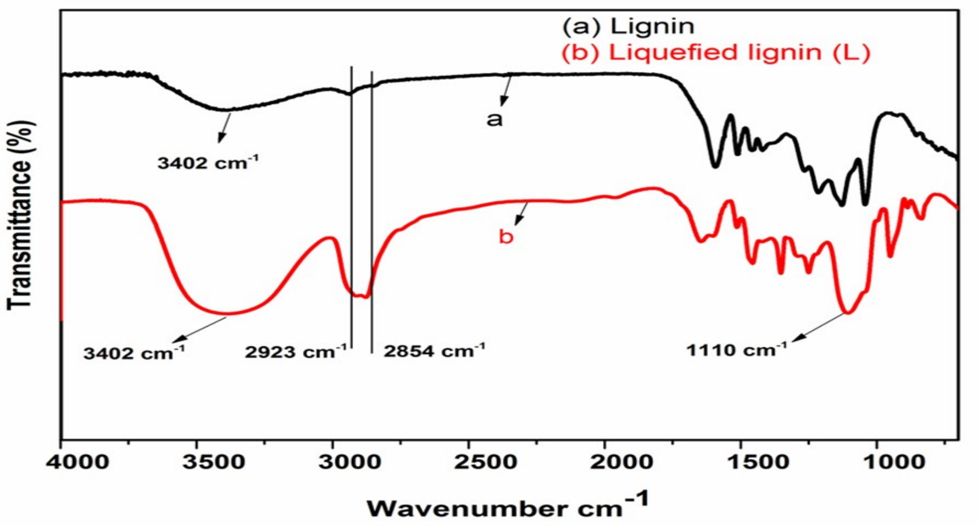

Figure 2: FTIR comparison between lignin and liquefied lignin

3.2 FTIR and Thermogravimetric Analysis (TGA)

The FTIR analysis was also carried out to identify the characteristic peaks of the LPU foam before and after functionalization with nucleophilic groups, and the results are shown in Figure 3. The FTIR spectrum of the LPU foams (Figure 3a) confirmed the presence of urethane linkages, as represented by the prominent peaks at 2920 and 2853 cm^{-1} that are attributed to C−H stretching of $-CH_3$ and $-CH_2$ and –NH asymmetric stretching in the vibration region (3200 - 3500 cm^{-1}). The peaks at 1721, 1606, and 1223 cm^{-1} are associated with C=O stretching in the amide, urea and ether groups, respectively, and the peak at 1526 cm^{-1} is attributed to the amide II band (Liu *et al.*, 2013). After grafting with polydopamine reduced graphene oxide (rGO) and subsequent functionalization with 1H,1H,2H,2H-perfluorodecanethiol (PFD), the intensities of the peaks at 2853 and 2920 cm^{-1} were strengthened significantly, which are ascribed to the C−H stretching in the $-CH_2$ and $-CH_3$ of the functionalized PFD monomer (Figure

3 b). Also, the peak at about 3357 cm^{-1} for the LPU-rGO-PDF foam was broadened and increased in intensity as compared to the LPU foam, which may be due to an overlap of the N−H and O-H stretching vibrations of ODA and rGO respectively (Ahn *et al.*, 2012; Cinelli *et al.*, 2013; Donald *et al.*, 2009). In general, the FTIR spectra showed that the rectified property of LPU-rGO-PFD foam originated from RGO and PFD and that the functionalization of LPU foam was indeed achieved.

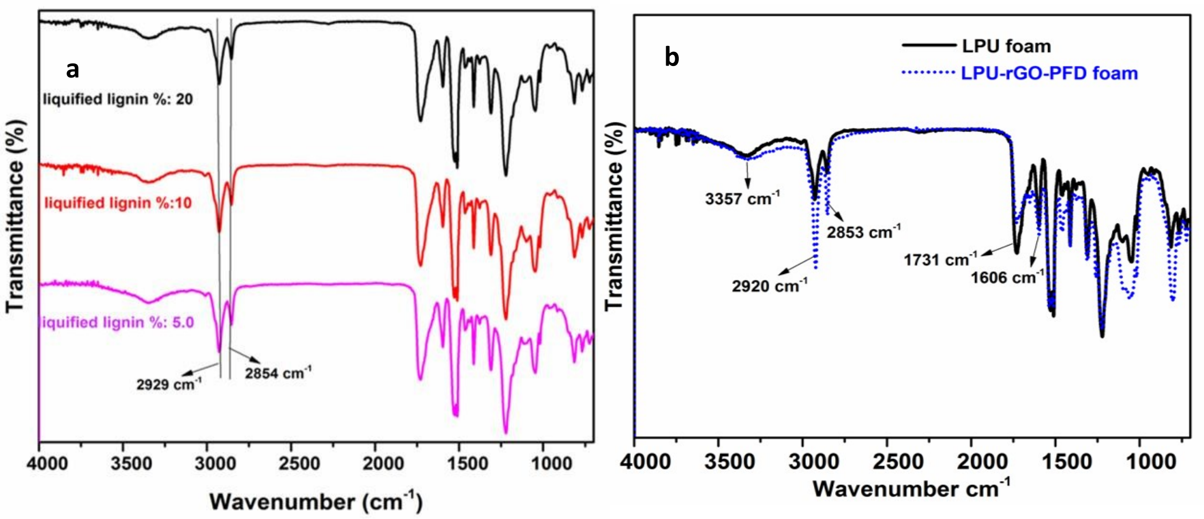

Figure 3: (a) FTIR of synthesized LPU foams, (b) FTIR spectra comparison between LPU and LPU-rGO-PDF foam (reaction time 10 hrs).

3.3 Surface morphology, spectroscopic and thermogravimetric analyses

LPU foam and the LPU-rGO-PFD foam sorbent morphology were also examined under scanning electronic microscopy (SEM), as shown in Figure 4. The LPU foam exhibit smooth skeletons as shown in Figure 4(A1, A2, A3 and A4). The resulting LPU-rGO-PFD foam sorbent revealed rougher morphology as shown in Figures 4 (B1, B2, B3, B4) after attachment and reduction of GO onto the skeletons of the LPU foam by adhesive polydopamine and subsequent functionalization with the nucleophilic groups from PFD. The LPU-rGO-PFD foam sorbent exhibited the same porous structure and skeleton dimensions as the LPU foam substrate, indicating the cell structure of the foam was not damaged or altered after its functionalization reaction as shown in Figure 4. The attachment of rGO onto the LPU foam backbone by the adhesive polydopamine increased the surface roughness of the foam and the transformation into LPU-rGO-PFD led to a super-hydrophobic absorbent (Miwa *et al*., 2000; Yang *et al*., 2016). This introduced roughness by reduced graphene oxide and the PFD functional layer enhances the surface properties of the foam and thus the wettability of the LPU foam changes. The roughness of a surface affects its interaction with a wetting or non-wetting liquid, due to an enlargement or amplification of the solid-liquid interactions (Lee et al., 2007b; Zhu et al., 2014).

Moreover, due to the secondary reaction between the low surface free energy PFD monomer and quinone (oxidized form of catechol produced during dopamine self-polymerization reaction) the self-assembly resulted in the desired enhancement in the super-hydrophobic and super-oleophilic properties (Lee *et al.*, 2007a). In addition, the skeletons of the LPU-rGO-PFD foam were covered by a large number of micro-scale protrusions, an indication that rGO and PFD were successfully anchored onto the LPU-rGO-PFD foam skeletons. Thus, the nucleophilic groups with low surface energy introduced into the LPU foam by the hydrophobic long alkyl chains from the PFD monomer and the rGO, altered the chemical composition of the surface layer to make the foam super-hydrophobic and super-oleophilic.

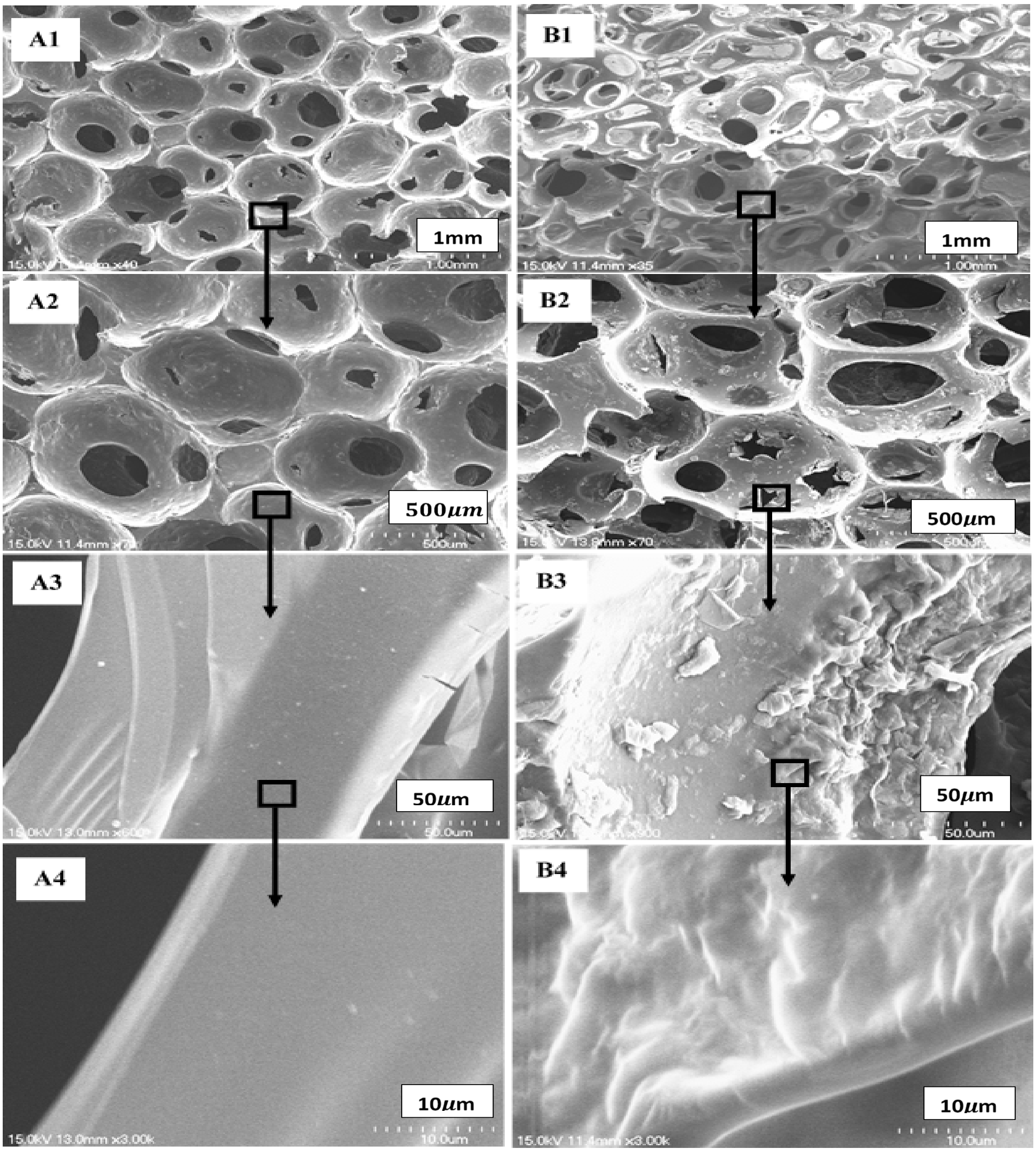

Figure 4: Surface morphologies of pristine LPU foam (A1, A2, A3, A4) and LPU-rGO-PFD foam sorbent (B1, B2, B3, B4).

3.4 Surface wettability of LPU-rGO-PFD sorption material

The surface wettability of the synthesized LPU-rGO-PFD sorbent is shown in Figure 5. It can be observed that the LPU-rGO-PFD sorbent displayed a significantly hydrophobic surface.

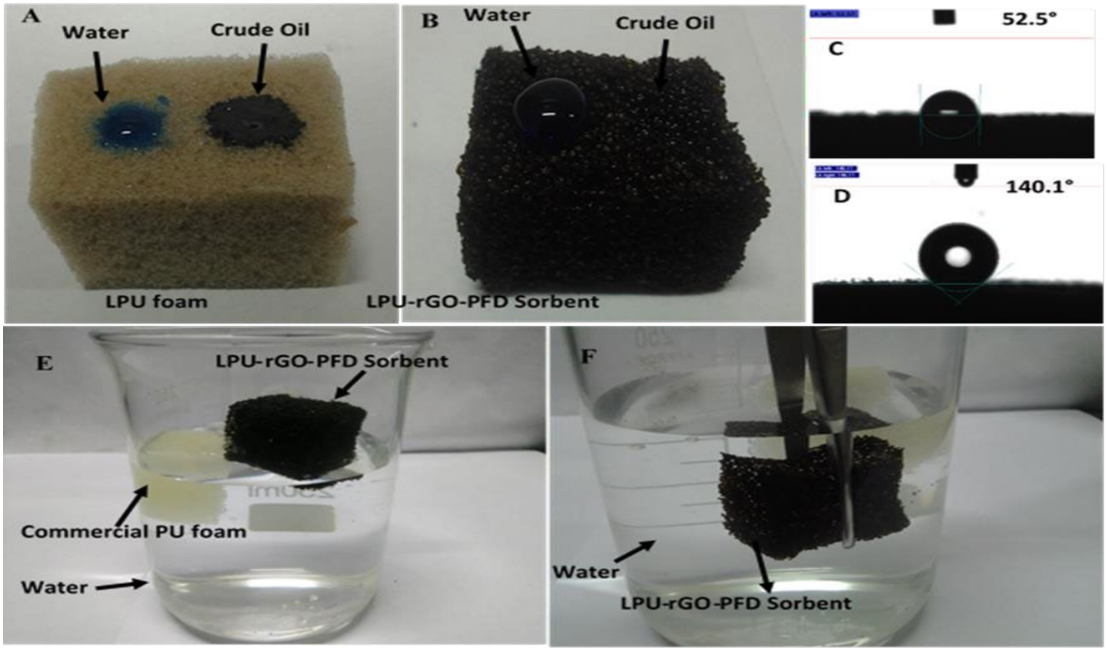

Figure 5: Surface wettability of the LPU-rGO-PFD sorbent. Crude oil and water (coloured in blue with methylene blue) were spotted on the surface of the LPU-rGO-PFD foam sorbent (A, B); Shapes of water droplet on LPU foam(C) and LPU-rGO-PFD sorbent (D) samples; LPU-rGO-PFD foam and commercial PU foam placed on the water surface (E), LPU-rGO-PFD sorbent immersed in water under an external force (F)

As shown in Figure 5, when crude oil and water droplets dyed with methylene blue was deposited on the top surface of LPU foam and LPU-rGO-PFD, both could easily penetrate into the LPU foam (Figure 5A), showing amphiphilic characteristics. On the other hand, the crude oil immediately penetrated into the LPU-rGO-PFD sorbent, whereas water remained on the surface, confirming the super-hydrophobic and super-oleophilic properties as shown in Figure 5B. Figures 5C and 5D show the water contact angles and water droplet images on the LPU and LPU-rGO-PFD foams, respectively. The hydrophobicities of the LPU foam and the LPU-rGO-PFD sorbent were determined by contact angle measurements using a Dataphysics OCA20 contact-angle (CA) meter (Stuttgart, Germany). The original LPU sponge exhibited hydrophilic surface with a contact angle of 52.5°, while the LPU-rGO-PFD foam showed a super-hydrophobic surface with a water contact angle of 140.1°.

When the LPU-rGO-PFD foam sorbent was placed on the surface of water (Figure 5E), the sorbent sample floated on water surface due to its water-repelling properties. The commercial PU foam submerges in water due to the hydrophilic pore walls of its 3D structure. In addition, when the LPU-rGO-PFD foam sorbent floating on the water surface was forced to enter into water under an external force, a mirror-like surface was observed on the sorbent because of the interface formed between entrapped air residing along the surfaces of the sorbent and the surrounding water (Figure 5F). This phenomenon is due to its non-wetting water behaviour. Upon release of the applied external force, the foam immediately returned to the water surface, without absorption of any water as confirmed gravimetrically afterward, indicating its excellent water repellence.

3.5 Oil Absorption Performance

With appropriate surface morphology, super-hydrophobic and super-oleophilic properties, the LPU-rGO-PFD appears to be an excellent sorbent candidate for oil spill remediation. Thus, the absorption performance of the LPU-rGO-PFD sorbent for various oils and organic solvents with different densities and viscosities in absence of water was investigated. Five independent samples were measured to obtain the average value. The viscosity of the organic solvents and oils used are important as they influence the sorption uptake rate of the LPU-rGO-PFD sorbent. The sorption uptake time varied from as short as only a few seconds for low viscosity solvents (e.g., carbon tetrachloride) to a few minutes for high viscosity oils (e.g., engine oil) for the LPU-rGO-PFD sorbent to reach sorption equilibrium. This may be attributed to the slow mobility of highly viscous oil/solvent in the matrix of the LPU-rGO-PFD sorbent. Figures 6a show the sorption capacities of the LPU-rGO-PFD sorbent for various organic solvents and oils in the absence of water. The LPU-rGO-PFD exhibited very high sorption capacity, from 26.4 ± 0.9 to 68.2 ± 1.5 times its own weight, depending on the density and viscosity of the oil and organic solvents used. It was also observed that the contact angle of water on the LPU-rGO-PFD sorbent, before and after the sorption test with the solvents, remained the same. This is confirmation of excellent water repellence of the LPU-rGO-PFD sorbent. For comparison, the absorption capacities of a commercial oil clean-up sorbent, non-woven polypropylene sorbent was compared with that of the LPU-rGO-PFD sorbent. The absorptive properties of LPU-rGO-PFD was far superior to that of commercial polypropylene sorbent PP sorbent (6.9 ± 0.7 to 16.2 ± 1.0 times its own weight, Figure 6a).

The excellent reusability and retention of sorption capacity, which are important considerations for practical applications, were demonstrated with 20 cycles of sorption-squeezing tests with crude oil. The results are shown in Figure 6b, and highly stable absorption performance and good reusability are demonstrated. The water contact angle after each sorption-squeezing cycle remained in the range of 136° - 140.1°, indicating that the modified LPU-rGO-PFD sorbent can withstand mechanical squeezing repeatedly without losing its super hydrophobicity.

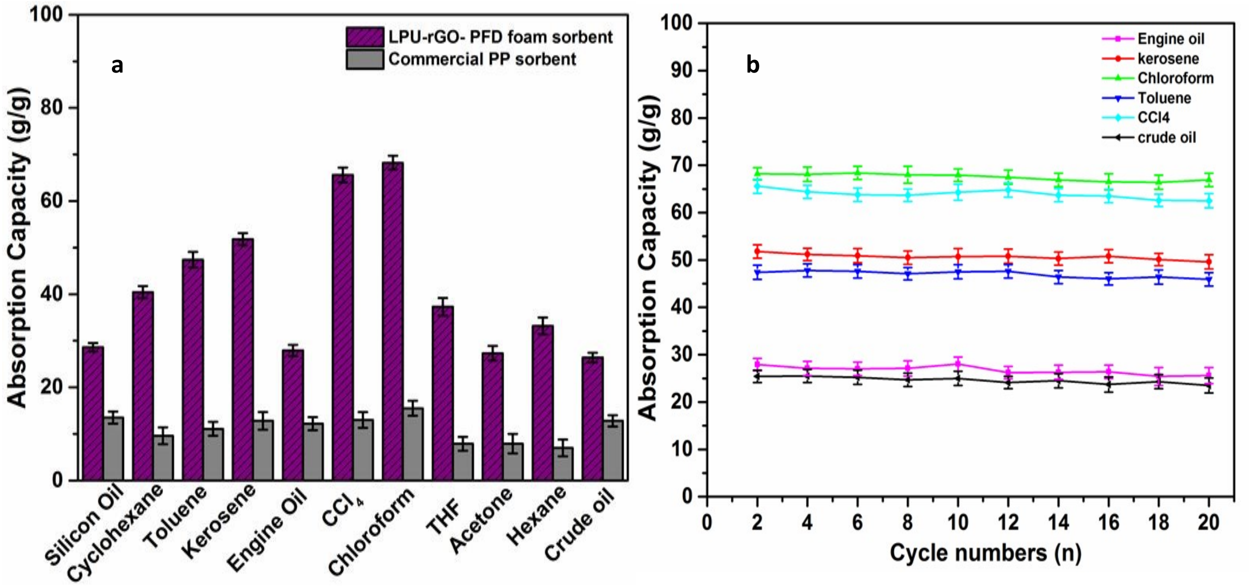

Figure 6: (a) Absorption capacity of LPU-rGO-PFD and a commercial PP sorbent to oil and various organic pollutants, (b) Reusability of LPU-rGO-PFD foam sorbent and commercial PP sorbent to oil and various organic pollutants

4.0. CONCLUSION

Super-oleophilic and super-hydrophobic LPU-rGO-PFD sorbent was successfully fabricated by anchoring of rGO on the skeleton of the LPU foam using adhesive polydopamine, followed by functionalization with PFD monomer. This process led to the transformation of the three-dimensional LPU foam substrate to become super-hydrophobic and super-oleophilic while retaining its open-cell porous structure. The fabricated LPU-rGO-PFD sorbent exhibited many outstanding features as an oil sorbent for oil spill clean-up and recovery, including a high sorption capacity (up to 68.2 times its own weight), high selectivity to crude oil sorption, and excellent reusability. The oil sorption capacity remained the same up to 20 cycles of oil sorption-squeezing experiments. Furthermore, the absorbed crude oil could be removed and collected by a simple squeezing process before reuse. Therefore, the LPU-rGO-PFD sorbents hold great promise for clean-ups of oil spills. It may be worthwhile to state that future works will investigate the cost of production of the absorbent and compare with others currently available in the market.

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