SUPERHYDROPHOBIC/SUPEROLEOPHILIC POLYURETHANE FOAMS MODIFIED SILICA NANOPARTICLES AS AN ABSORBENT FOR OIL-WATER SEPARATION

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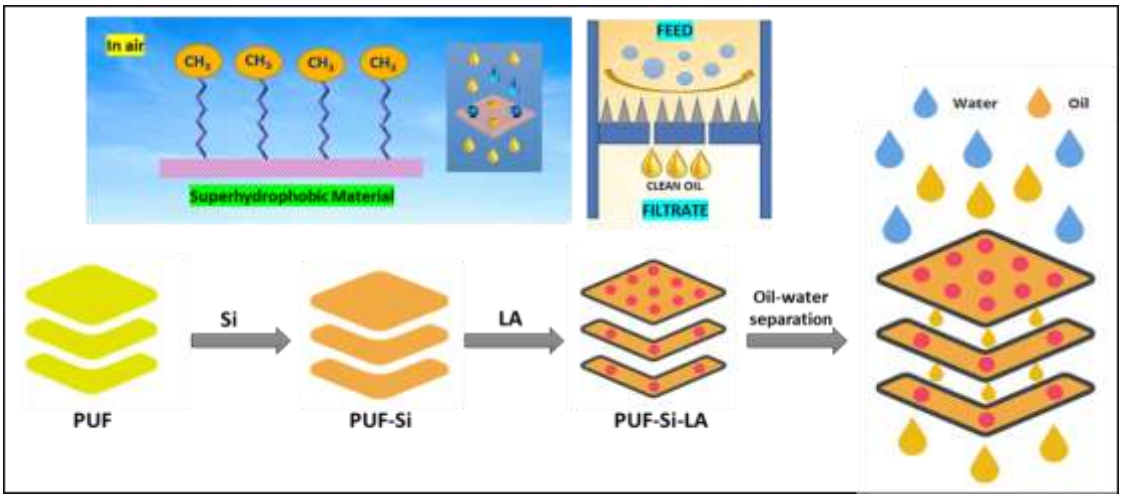
Abstract

Due to the technology development, the commercial polyurethane foam (PUF) modified with silica nanoparticles (Si-NPs) and lauric acid (LA) was used to synthesis the superhydrophobic/superoleophilic absorbent to remove the oily contaminant from oil/water mixture in the oil industry. The facile dip-coating method has been used to generate PUF-Si-LA through ultrasonication and relux at 70 °C for 12 h. Additionally, the FTIR, SEM, and EDX, characterization results displayed that the raw materials were identically distributed throughout the PUF surface as can be observed from the strong chelating bond between the carboxylates, hydroxide, and silica active surface. The water contact angle (WCA) was observed up to 158° presenting powerful superhydrophobicity. The absorption capacity results of the PUF-Si-LA for the tested oils and organic solvents are high ranging from 23.00 to 40.00 g/g after 20 consecutive cycles varied from the samples. The oil removal from water-oil mixture revealed a quick absorption of oil contaminant within few seconds. These features presented that the PUF-Si-LA nanocomposite is expected to be a future promising absorbent in a wide range of applications due to long-term performance, high mechanical, and thermal stability in various environmental treatments.

Keywords: Polyurethane, superhydrophobic, nanocomposites, oil/water separation, and emulsion

GRAPHICAL ABSTRACT



1. INTRODUCTION

Nowadays, one of the world challenges which has negative environmental implications is water pollution. Chemical leakages have posed a serious environmental threat to aquatic life that causes high water demand in the world. The oil separation from water is a very crucial treatment due to its repeatable accidents in the oil industry, such as Exxon Valdez disaster in 1989 (Alaska), Prestige oil spill in 2002 (Spain), and deep-water horizon oil spill in 2010 (Mexico).[1] It has the possibility of increasing due to the increase in various industrial activities. Therefore, the development of environmental technologies to treat industrial water is essential for facing stringent environmental regulations and reusing the water. Conventional oil/water separation methods such as skimming, booming, and chemical dispersant has several disadvantages including poor efficiency, high energy consumption, and low yield.[2,3] For solving these crucial problems, several technologies are available for water treatment management that have been studied by many previous reports. One of them, membrane technology has been recently used in many industrial fields, such as; ultrapure water production, product recycling, seawater desalination, and wastewater treatment. All of these methods utilized porous materials with 3D structures such as commercial sponges as an absorbent. Commercial sponges have various prominent properties such as the ability to hold oil within their matrix and subsequent recovery of oils from their pores.[4,5]

In this recent years, nanomaterial composites have attracted much attention due to their tuneable, chemical, physical, thermal, and mechanical features.[6] Polyurethane foam (PUF) is becoming a great absorbent due to its various interesting properties including excellent mechanical properties, porous structure, low density, and high contact surface.[7] It can be used for oil or water removal in water-oil separation after surface modification treatment to make it more hydrophobic or hydrophilic. Silica nanoparticle (Si-NPS) was selected to be connected to the PUF surface to enhance the capacity storage of PUF due to its larger surface area.[7] It will provide numerous of the alcohol (-OH) and amine (-NH) groups on the PUF surface to be incorporated with the long organic hydrophobic chain, such as lauric acid (LA). LA was chosen due to its inexpensive, non-toxic chemical, biodegradable, and highly hydrophobic acid which can help the reaction to be easily completed.

The proposed research aims are to synthesize functionalized silica nanoparticles with the long organic branch to produce superhydrophobic material. From the latest reports, several desirable materials have been observed and investigated for oil/water separation application. In this study, PUF will be embedded with Si-NPs and LA which can be incorporated on the PUF top surface to produce a hierarchical roughness structure. This work will be proposed by the facile layer-to-layer dip-coating method as a novel material which is cost-effective, easy prepared, high mechanical stability, and durability. Some data will be evaluated by several tests toward the developed material, such as water contact angle, oil absorption capacity, reusability, efficiency, and oil removal as an eco-friendly absorbent.

2. MATERIALS AND METHODS

2.1 Material

In this work, all the used chemicals were already analytical grade without any purification method. Chemicals such as TEOS (tetra ethylene orthosilicate), ethanol 98%, lauric acid powder, acetone 99%, methylene blue (MB), methyl orange (MO), deionized water, heptane, dichloromethane, tetrachloromethane, and toluene were obtained from Sigma Aldrich. Commercial polyurethane foam (PUF) and olive oil were obtained from the local market.

2.2 Synthesis of Polyurethane Foam (PUF)-Silica-Lauric Acid

a. Preparation of Activated-PUF

Typically, the pristine PUF were cut into 1 x 1 x 1 cm^3 in size for 8 pieces, then the 1:1 ethanol-acetone mixture was poured to wash the foams until clean. After drying, the 50 mL HNO_3 0.2 M was also poured into the foams to activate the PUF surface for 2 h at RT. After all, the foams were dried overnight at 60 °C.

b. Loading NPs into pristine PUF

The Si-NPs was prepared by sol-gel method. Around 5 mL of TEOS was dissolved in 20 mL of ethanol analytical grade under stirring at room temperature and mixed for 1 h to make a homogeneous solution. A mixture of NH_4OH catalyst and water (pH 10.0) was added drop-wise into the reaction mixture. The reaction mixture was gradually stirred from 25-35 °C for 5 h. The reaction mixture was then cooled to room temperature again to form a transparent silica sol upon aging. After that, the prepared PUF was gradually inserted to the Si-NPS solution to form PUF-Si which reacted for another 5 h at 70 °C under refluxing step to avoid solvent evaporation.

c. Preparation of PUF-Si-LA by in-situ dip-coating method

The obtained PUF-Si then will be incorporated with 3.0 % lauric acid solution with ethanol in a beaker glass and sonicated for 1 h at 50 °C. After sonication, the foams were slowly stirred overnight to let the long organic branch will be properly attached inside the foams. Then, the modified foams were dried at 60 °C to get PUF-Si-LA as a result.

2.3 Characterization

Some characterization measurements were placed to analyze the modified PUF nanocomposites and pristine PUF. Field-emission Scanning Electron Microscope (FESEM) which is equipped with Energy Dispersive X-ray spectrometer (EDX) was utilized at a voltage of 10-20 kV to observe its morphology and roughness structure with higher magnification. A thin layer of gold was coated into the modified PUF to make electrical conductivity upon analysis. Furthermore, hydrophobicity and surface wettability of the materials were investigated by using Water Contact Angle (WCA) measurement (Attension Theta Optical Tensiometer). Around 5 µL droplet of distilled water at ambient temperature was pipetted and placed on the material surface. Finally, Fourier Transform Infrared (FTIR) spectra (Smart iTR NICOLET iS10) were also conducted to study material functional groups in 400–4000 cm^{-1} wavelength range. The data were analysed from the directly modified foams without making any pellet.

2.4 Oil Absorption Capacity Test

In the field, oil contamination can be classified into many categories including dispersed, emulsified, dissolved, and also free oil spills. This oil absorption capacity data will be evaluated in oil-water mixture and different types of the used oil/organic solvents, such as heptane, toluene, olive oil, dichloromethane, and tetrachloromethane based on the increase of their density. Experimentally, 50 mL of each oil was poured into a 100 mL beaker containing 30 mL deionized water, then the specific mass t of the modified PUF cube was introduced to the system to let the foam absorb the oil contain. After absorbing around 2 minutes, then the absorbent was taken out directly to measure the current PUF mass using balance. The mass of the absorbed oil was considered as (M_t), foam initial mass (M_o), and oil absorption capacity (C_o), then the calculation was expressed as shown in **Eq. 1**. The desorption treatment was also carried out to return the oil to the beaker by squeezing the foams. The overall test was considered as one cycle, then the test will be repeated for another 19 cycles to generate the oil absorption capacity data for each oil.

The ability to maintain the almost same data until 20 cycles were named reusability process/regeneration.

$$C_o = \frac{Mt - Mo}{Mo} \quad (1)$$

3. RESULTS AND DISCUSSION

3.1 Surface Functionalization

PUF was selected due to its 3D porous structure which leads to easy modification and functionalization toward many functional groups at the molecular level to enhance the surface wettability or repellence. The common functional groups presenting a great surface wettability of the foams such as -OH, COO-, $-NH_2$, $-NH_3^+$, $-OSO_3^-$, $-OSO_3H$, and any ionizable functional group.[8] The surface energy was increasing when these kinds of functional groups are presenting to generate the hydrophilicity behavior.[9] On the other hand, to obtain the superhydrophobic features, the typical functional groups like fluorocarbon, long hydrocarbon chain, and silicon-based polymer can decrease the surface energy then promote the WCA > 150° and OCA ~ 0º (not wetted in water).[10-11] Until now, one of the common synthesis methods of the particular material is dip-coating with facile treatment by immersing into the coating solution with 1– 100 μm thickness at an optimum temperature.[12] The complete reaction to generate a coating material (Si NPs-LA) nanocomposite can be described in **Figure 1**.

In **Fig. 1a**, the sol-gel method is operating for converting TEOS to become $Si-(OH)_4$ after treating with basic solution NH_4OH which has many alcoholic groups to connect to the PUF and LA branches. Since it was produced by reaction diisocyanate and polyol substances, PUF has many functional groups to be connected with silica nanoparticles such as (amines, carbonyl, amide, and ether).[13] The chemical interaction between Si-NPs with lauric acid (LA) in ethanol solution as depicted in **Fig 1b**. The esterification reaction was taking place since LA containing carboxylic group reacted with silica gel containing alcohol group in an acid environment. The functional groups and temperature would be important parts during the reaction step to control the surface energy after putting LA.

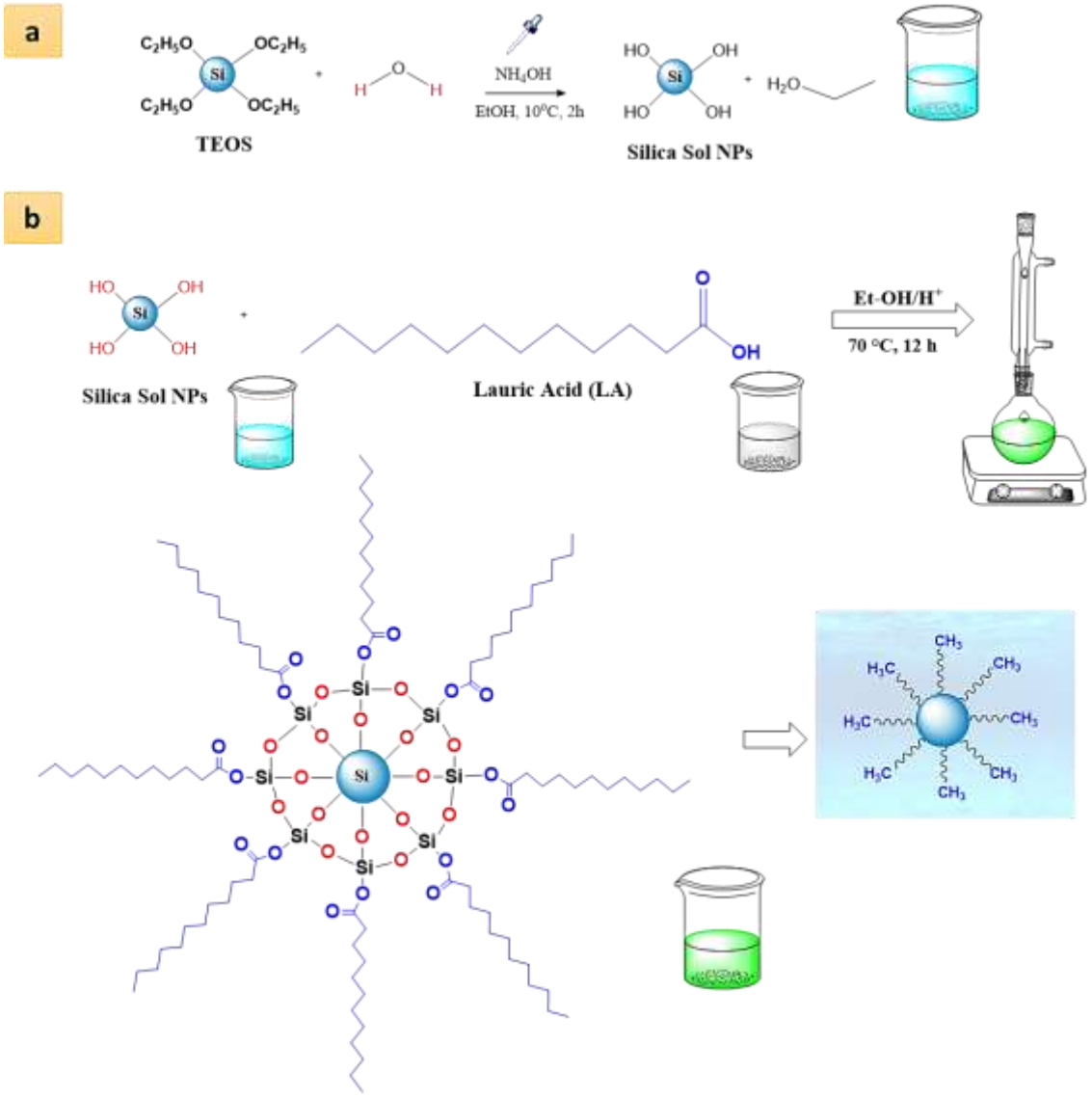
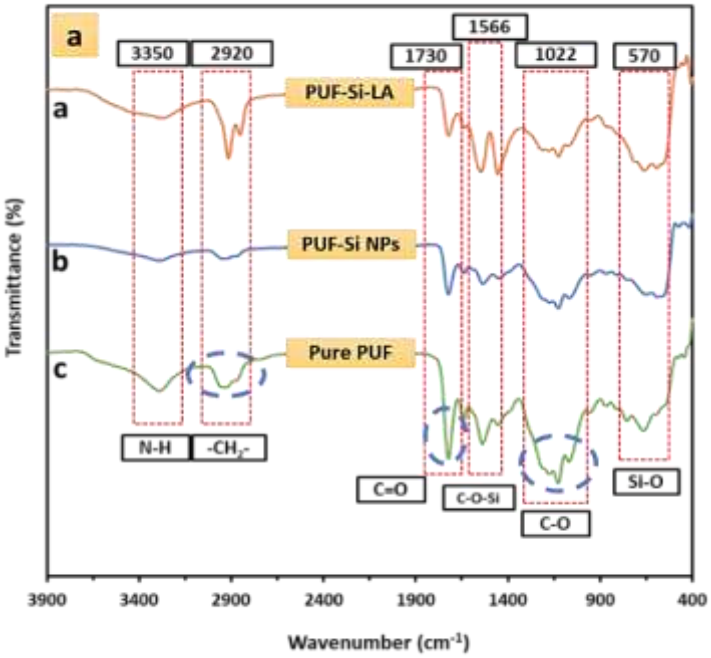


Figure 1. Preparation for Si nanoparticles (NPs) surface activation (a), and reaction with lauric acid (LA) to produce Si-LA composite (b).

3.2 FTIR, SEM, and EDX Characterization Results

The various functional groups inside the modified PUF, PUF-Si NPs, and pristine PUF were investigated by using FTIR measurement to confirm material functional groups of each nanocomposite. Each sample was collected to observe its absorption bands characteristic indicating the change of the material structure after adding some chemicals. In **Figure 2a**, the pristine PUF exhibited some absorption bands such as stretching vibration band for (-NH) at 3350 cm^{-1}, two weak peaks (C-H) at 2920 cm^{-1}, carbonyl (C=O) at 1730 cm^{-1}, and (C-O) at 1022 cm^{-1}. When the PUF was functionalized, some absorption bands were strengthened and weakened due to the new chemical interaction. For modified PUF, two peaks on -CH_2- bands at 2920 cm^{-1} were sharply displaying due to (-CH_2-C-) from the additional long organic chain, and (-CH_2-O-) from polyurethane. Carbonyl stretching vibration at 1730 cm^{-1} was weakened due to the strong connection between (C=O) and (N-H) from PUF.[14] At the peak of 1020 cm^{-1}, the modified PUF was attributed a weak band denoting nanoparticle (Si-O) and long organic chain (-CH_2-) in the plane mode from lauric acid. The spectrum at 570 cm^{-1} corresponded to the stretching vibration of the (Si-O) bond showed on the nanocomposite spectra. In short, all the bands showed that the

nanocomposite was successfully functionalized into the surface of the PUF which produces superhydrophobicity.



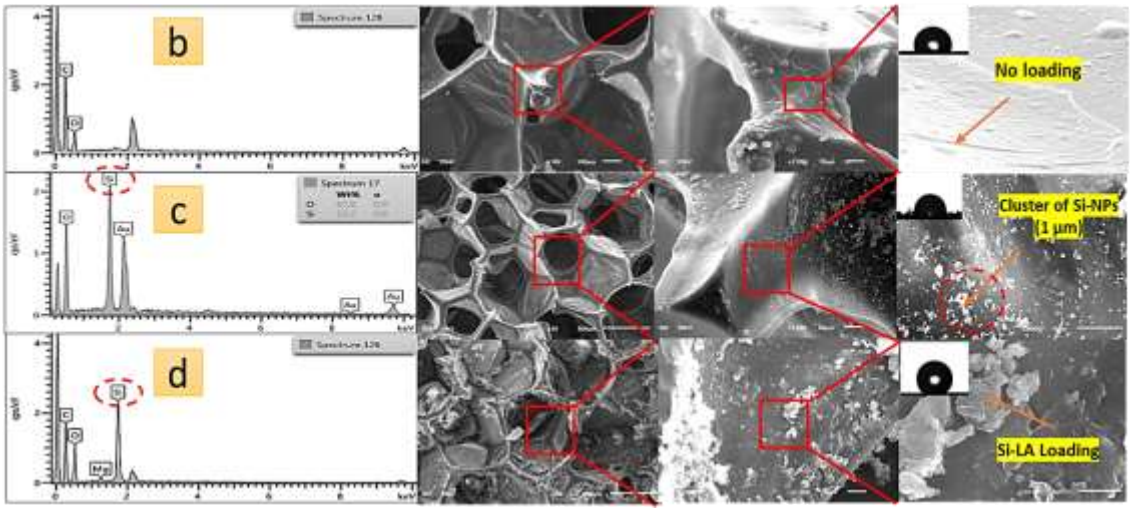


Figure 2. FTIR spectrum (a), and SEM/EDX images (b-d) of the pure PUF and PUF-Si-LA nanocomposite.

The further morphological surface and elemental investigation, the pristine PUF and modified PUF were analyzed by EDX and SEM at various magnifications to identify the elemental material information attached to the foam. In **Figure 2b**, the pristine PUF was displayed a smooth surface area and 3D dimensional porous structural size ranging at 500-700 µm without any coating and attached nanoparticle. When Si NPs were introduced, the EDX result appeared a strong signal of silica and formed the cluster of the nanoparticle with 1-2 µm in size (**Figure 2c**). Moreover, the aggregation and roughness surface were shown after lauric acid incorporation with PUF-Si NPs. The appearance of the relevant NPs during EDX analysis indicated that was a successful synthesis of the 3D PUF nanocomposites (**Figure 2d**). A higher magnification confirmed that the nanoscale particles were compactly dense.

3.3 Oil Absorption Capacity Test

To verify the reusability of the modified PUF, 20 absorption-desorption cycles were conducted to observe its oil absorption capability by using five different oils and organic solvents which are available in the laboratory and local market (heptane, toluene, olive oil, dichloromethane, and tetrachloromethane). After each cycle, the adsorbed oil and organic solvent were separated by manual squeezing. The recyclable absorption capacity curves for 20 cycles of PUF-Si-LA for the oils and organic solvents are shown in **Figure 3**. The absorption capacity of PUF-SI-LA for different oils and organic solvents has not significantly changed even after 20 cycles conforming to the strong superhydrophobic properties. The modified PUF could increase its absorption capacity after 20 cycles again. The absorption capacity retentions of PUF-Si-LA for the tested oils and organic solvents are high ranging from 23.00 to 40.00 g/g after 20 cycles. Heptane was observed as the smallest capacity which was around 23 times as much as its weight caused rapid solvent evaporation.[1] Whereas the largest capacity was tetrachloromethane, which was around 40 times as much as the foam's weight.

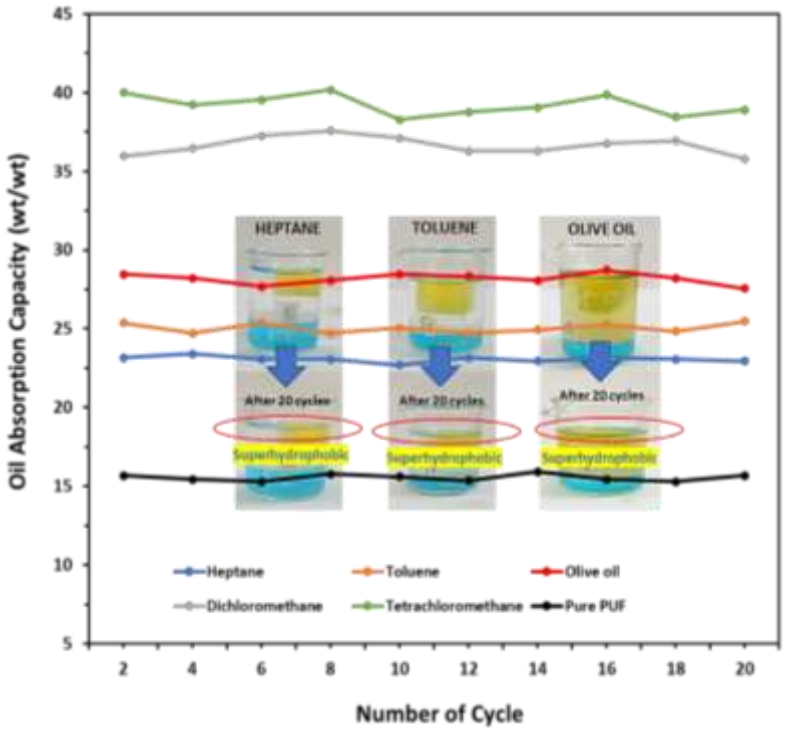


Figure 3. The comparison of the oil absorption capacity data of the pristine PUF using heptane, and PUF-Si-LA nanocomposite using various organic solvents in 20 cycles.

3.4 Surface Wettability and Water Contact Angle (WCA) Measurement

Another crucial test to confirm the superhydrophobicity is the surface wettability of the fabricated material. **Figure 4a** showed the trend of the WCA value from the pristine and modified PUF nanocomposite. The pristine PUF and PUF-Si NPS could be sunk on the water with WCA values at 83° and 62° respectively due to their hydrophilicity with many alcohol (-OH) functional groups on their surface area. After being functionalized with LA, the PUF-Si-LA was completely floated with WCA value at 158° due to the superhydrophobicity from the long organic chain (superhydrophobic WCA > 150°). LA will contribute to provide the low surface energy and the roughness produced during the surface modification. At the same time, **Figure 4b** also depicted the surface wettability toward various daily liquids (lemon, juice, tea, milk, and coffee) which are stable in spherical shapes after testing on the material surface. The results were plotted into the

graph indicating strong superhydrophobicity in the air (WCA > 150º). Additionally, an interesting superhydrophobic feature was also presented when the 5 µL water droplet was refused to contact the modified PUF surface, then returned the complete spherical droplet to the mount pipette (**Figure 4c**).

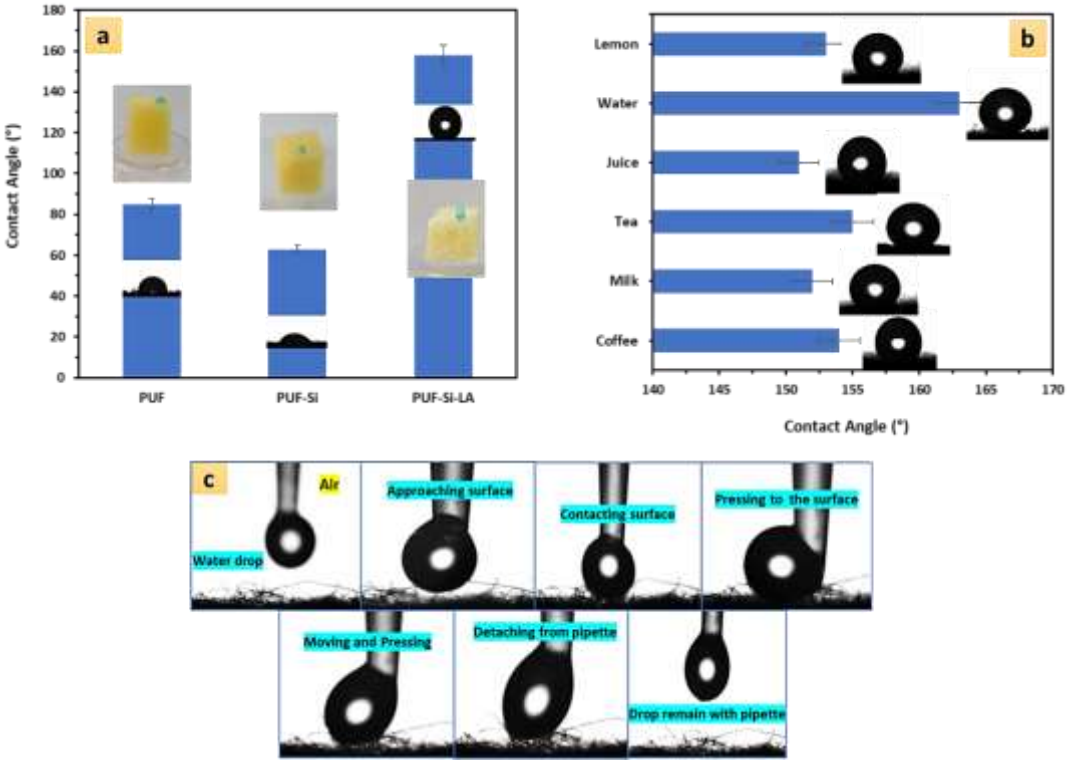


Figure 4. The water contact angle transformation from PUF to PUF-Si-LA nanocomposite to observe its wettability (a), water contact angle for different daily liquid (b), and pendant drop test to evaluate the superhydrophobicity on the material surface (c).

3.5 Oil Removal and Separation in Oil/Water System (Mixture and Emulsion)

To evaluate the oil absorption capacity of the developed PUF nanocomposite, oil removal on the oil/water mixture and emulsion are required to be demonstrated. In **Figure 5a and 5b**, the low and high oil densities (heptane, olive oil, lubricating oil, and tetrachloroform) were successfully removed by using the modified PUF within 2-3 seconds.

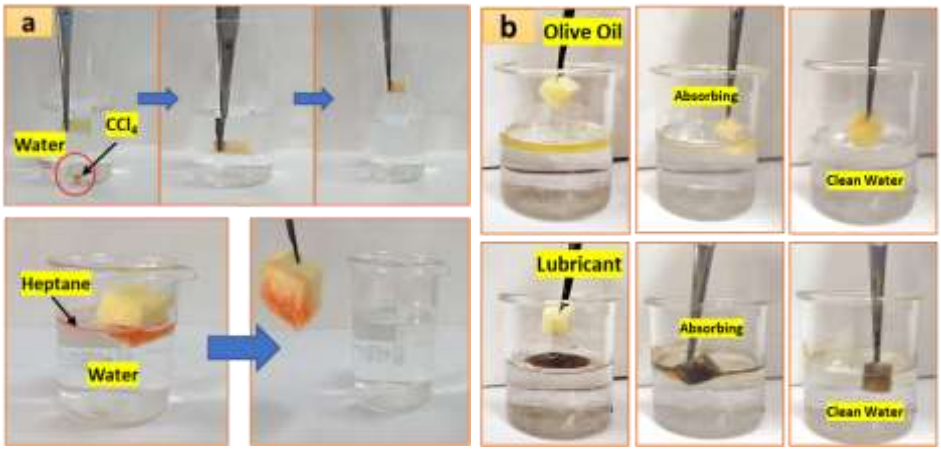


Figure 5. Oil removal and water repellency in the oil/water system using tetrachloromethane and heptane (a), and oil removal for olive oil and lubricant (b).

The oil absorption capacity, water contact angle, and separation efficiency of the modified PUF from the various oil and organic solvents were compared in **Table 1**. The cumulative data reflected that the recent work (PUF-Si-LA) could be an efficient result compared to the previous reports which is low-cost, environmentally friendly, and excellent efficiency.

Table 1. The capacity and WCA values of other recent superhydrophobic absorbents based PUF.

Absorbent	Oil Studied	WCA (º)	Capacity (g/g)	Ref.
NDs-PDA-PFDT	Diesel	151	31	15
	Pump oil		25	
	Gasoline		21	
NC-PUF	Light crude oil	148	18	16
PUF-g-LMA	Kerosene	152	21	17
	Diesel		38	
PUF-Fe-SA	Light crude oil	154	32	18
	Kerosene		28	
	Gasoline		24	
	Soybean Oil		27	
PUF-Fe-NDM	Cyclohexane	145	48	19
ODTCS–SiO_2–PP–PUF	Toluene	154	34	20
PU–CNT–PDA–ODA	Lubricant	158	27	21
	Hexane		35	
Al_2O_3-PUF	Chloroform	144	37	6
PUF-Zn-SA	Food oil	170	30	22
PUF-GN	Toluene	152	34	23
	Acetone		46	
PUF-Si-LA	Toluene	158	26	**This work**
	Dichloromethane		40	

4. CONCLUSION

All in all, the superhydrophobic-superoleophilic PUF-Si-LA nanocomposite which is cost-effective, biodegradable, and durable has been produced by a simple ultrasonic layer dip-coating method. The PUF was reacted with Si NPs and long organic chain lauric acid (LA) to generate a 3D porous size material for the highly efficient water-oil separation application in the oil industry. Several characterizations were conducted displaying a great correlation which the Si NPs and LA. The WCA has been detected at 158° with a strong affirmation of the superhydrophobic property. The oil removal from water-oil mixture revealed a quick absorption of oil contaminant within few seconds. The absorption capacity retentions of PUF-Si-LA for the tested oils and organic solvents are high ranging

from 23.00 to 40.00 g/g after 20 cycles varied from the oil samples. All of these results indicated that the developed absorbent was able to be applied in the larger industrial field.

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