



## Superhydrophobic poly (dimethylsiloxane-co-alkylmethylsiloxane)-SiO<sub>2</sub>-coated polyurethane sponge sorbent for oil spill treatment

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### Abstract

Pollution caused by an oil spill has been identified as one of the major environmental problems with a serious impact on both humans and the ecosystem. The development of hydrophobic oil sorbents for the removal of spilled oil and organic solvent seeping is very important to ecological preservation. In this respect, a facile procedure was used to prepare commercial polyurethane sponge sorbent coated by Poly(dimethylsiloxane-co-alkylmethylsiloxane)-silica nanoparticles (PDMS/AMS-SiO<sub>2</sub>) through dip-coating accompanied by polymerization in situ. The obtained materials are characterized by various physico-chemical tools; such as DLS, Raman, XRD, SEM, and contact angles (CA). The PDMS/AMS-SiO<sub>2</sub>-P.U shows superhydrophobicity with water contact angle 145° with obtained selectivity for oil-water separation. Moreover, the oil sorption capacity was studied using different oils and organic solvents including crude oil, motor oil, diesel, and toluene. High sorption capacity exceeded 130 g/g and fast swelling kinetics rate is achieved. Furthermore, the sorbed organic solvent or oils can be recovered simply by squeezing the coated P.U, and the used sorbent can be reused up to 10 times without obvious deterioration in its swelling capacity or losing its hydrophobicity. The results indicating that the prepared sorbent has potential application in oil-water separation.

*keywords:* Polyurethane sponge, superhydrophobic sorbent, dip-coating, in situ polymerization, swelling capacity, and reusability.

### 1. Introduction

The leaking of crude oil and petroleum products remains one of the most serious environmental problems during the exploration and production of crude oil. The treatment of oil spilled into the whole environment and marine ecosystem especially has been a major ecological challenge.[1] A growing quantity of oily wastewater, as well as the seeping of organic solvents (such as xylene, chloroform, toluene, and others), pose a danger to public health and the environment.[2,3] Many techniques, such as in situ burning, mechanical extraction, oil spill dispersant, and oil sorbent, have been used to mitigate oil spill emissions to protect our environment.[4,5] The use of sorbent materials is thought to be one of the most important methods for removing oil and organic pollutants due to its removal efficiency, facile process, and avoiding subaltern contamination.[6–8] Sorbent materials are divided into three main categories: structure assembly fibers, porous materials, and aerogels. Porous materials with 3D structures have sparked a lot of

interest in oil recovery from water due to their hydrophobic characters with exceptional oil selectivity, high swelling capacity, rapid swelling kinetics, flexibility, and recyclability. Unfortunately, the high cost and complex preparation process of these sorbents continue to limit their use. As a result, it is urgently to produce sorbent material with high swelling capacity, low cost, practical applicability, and ease of preparation.[9,10]

Polyurethane (PU) foam is a commercially available 3D porous material with decreased density, elevated sorption capacity, large surface area, low price, excellent elasticity, and easy fabrication that can be used in the spilled oil removal.[11,12]

Pristine P.U foams have hydrophilic nature making them ineffective for selective oil removal from water because its poor selectivity they absorb both water and oil at the same time. The selectivity and oil swelling capacity of P.U require hydrophobic modification with materials contains special wetting characters.[13] Various research groups in the literature developing synthetic procedures for the

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production of modified P.U sponge including, in-situ polymerization, dip-coating, polymer grafting, solution immersion, vapor phase polymerization, graphen /polydimethylsiloxane based coating, and modification with various materials such as ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{ZnO}$ , carbon nanomaterials).[14,15] Dip-coating procedure considers one of the most commonly used techniques for fabrication of P.U sponge to obtain a superhydrophobic polyurethane sponge, it's only takes a few hours to produce the modified sponge and suitable for oil-water separation.[16] Polydimethylsiloxane– $\text{TiO}_2$  coated superhydrophobic polyurethane sponge was reported by Shuai et al.[12] Several modifying agent/hydrophobic coating such as carbon-based materials (for example carbon nanotube, graphene, and others) have been used. The instability of most polymeric sponges is one of their drawbacks. Because of its oleophilicity, hydrophobicity, and commercial availability, poly(dimethylsiloxane) (PDMS) has recently been discovered to be a promising candidate for oil sorption applications, and porous PDMS has been used to selectively separate oils or organic solvents from water.[9,17] Poly(dimethylsiloxane-co-alkylmethylsiloxane) (PDMS/AMS) pre-polymer is an alkyl-rich silicon compound that contains long-chain alkyl group and siloxane groups, it has the properties of PDMS and contains a long alkyl chain length and siloxane group supporting higher oil sorption capacity. However, up to our knowledge, this is the first time using PDMS/AMS in the hydrophobic modification of P.U sponge. In this study, we first prepared silica nanoparticles  $\text{SiO}_2$  by sol-gel method and deposited them on P.U sponge surface. Then the commercial polyurethane sponge (P.U) is dipped into PDMS/AMS solution without damaging the P.U sponge structure and no extra treatment procedures. Meanwhile, the hydrophobicity of the modified P.U sponge may be increased by the PDMS/AMS- $\text{SiO}_2$  coated on the sponge surface, which may increase the surface roughness and lower the P.U sponge's surface energy. As a result, the modified P.U sponge's hydrophobic nature and high porosity guarantee high oil swelling capacity. The prepared sorbent will be characterized using various tools and evaluated in different types of oils with the investigation of swelling and network parameters. Moreover, this work provides a cost-effective, facile procedure to prepare a modified sponge for saving our environment from oil spills and organic pollutants.

## 2. Experimental

### 2.1. Materials:

Poly(dimethylsiloxane-co-alkylmethylsiloxane) (PDMS/AMS), curing agent (Sylgard 184B), Tetraethyl orthosilicate (TEOS,  $\text{SiO}_2$  content 28.5 wt %) were purchased from Sigma Aldrich Co. ammonia solution (25 % ammonia content), n-hexane, ethanol, toluene, xylene, from PIOCHEM. commercial polyurethane sponge (P.U), motor oil, and diesel from a local store. Crude oil from Khalda petroleum company, Egypt.

### 2.2. Preparation of PDMS/AMS–P.U:

P.U sponge was pretreated firstly by washing in ethanol and hexane consecutively, sonicated, dried at 70 °C for 4 h, and finally cut into dimension (1.5x1.5x1.5 cm). PDMS/AMS-P.U is prepared by dissolving a mixture of PDMS/AMS and sylgard 184B curing agent with different weight percentage (wt%) in 30 mL of n-hexane, then sonicated for 30 min named solution (A). After that PDMS/AMS – P.U coated sponge was prepared by dip-coating the pretreated sponge into the solution (A) for several minutes followed by polymerization of PDMS/AMS in-situ on P.U sponge surface. The dip-coating process was controlled by repeating the immersion cycles of P.U in PDMS/AMS solution. Finally, the PDMS/AMS –P.U was cured in an oven at 80 °C for 12 h. The constituents and designation are shown in Table 1.

### 2.3. Preparation of PDMS/AMS– $\text{SiO}_2$ –P.U:

The nano-silica ( $\text{SiO}_2$ ) was synthesized by hydrolysis of TEOS with minor modifications.[18] Briefly, TEOS (6.9 ml), ethanol (15 ml) was stirred, and then a mixture of distilled water and ammonia solution was added and kept stirring for 4 hours until the mixture turned into milky solution. The resulting a milky solution then was filtered washed with ethanol and then dried at 60 °C for 5 hrs, after that calcinated at 600°C for 2hr to obtained white silica nano powder. PDMS/AMS- $\text{SiO}_2$ -P.U modified sponge was prepared as follows: different wt% of silica nanoparticles (1, 2, 3, 4 wt %) was firstly dispersed in n-hexane and sonicated on pretreated P.U sponge and air-dried. Then  $\text{SiO}_2$ -P.U sponge was dip-coated in solution A and cured at 80 °C to finally obtain PDMS/AMS- $\text{SiO}_2$ -P.U modified sponge. The constituents and designation of the as-prepared sponge using different weight ratios from PDMS/AMS, curing agent, and  $\text{SiO}_2$  are shown in Table 1.

Table 1. Preparation conditions of P.U-modified sponge oil sorbent

Designation	P. U (g)	PDMS/AMS(g)	Sylgard 184B (wt%)	SiO <sub>2</sub> (wt%)
PDMS/AM S -P.U	1	1	5	0
	1	1	10	0
	1	1	12	0
PDMS/AM S -P.U	1	0.5	10	0
	1	1	10	0
	1	2	10	0
	1	3	10	0
PDMS/AM S -SiO <sub>2</sub> -P.U	1	2	10	1
	1	2	10	2
	1	2	10	3
	1	2	10	4

#### 2.4. Characterization:

The particle size of the synthesized nanoparticles can be measured by dynamic light scattering (DLS), the hydrodynamic diameter and polydispersity index can also be determined by DLS. The samples were dispersed in ethanol, placed into quartz cuvette, and measured at 25 °C using a Zetasizer nano-ZS instrument, Malvern, U.K. The average particle size analysis of SiO<sub>2</sub> powder was conducted and the ethanol was used as the dispersant medium.

Raman measurements were performed using Raman spectrometer, Sentra, Bruker Corporation, Germany. The measurement obtained at a laser source 532 nm, laser output power 2 mW, and aperture setting 50x1000 μm.

X-ray diffraction (XRD) patterns were recorded using XRD which was performed by using PANalytical X'Pert PRO diffractometer with Cu Ka = 1.5418 Å over the angular range from 4° to 70° with a scanning rate of 4° min<sup>-1</sup>. The surface morphology of the sponge before and after modification was examined by a field emission scanning electron microscope (FESEM) model (ZEISS, Gemini, Sigma 300 VP, Germany); the accelerating voltage of electron beam is 30 keV. For better conductivity all of the samples were coated with a thin layer of gold.

The hydrophobicity of the prepared PDMS/AMS-SiO<sub>2</sub>-P.U was measured using a spinning drop interface tensiometer (Theta optical tensiometer, Bioline scientific Co., Finland), the measurement was performed at room temperature using a droplet (5 μL) of water or oil as the indicator.

#### 2.5. Sorption capacity and recyclability for Oil /organic solvent:

The oil swelling capacity (Q) of the prepared sorbent for different oil and organic solvents

(including crude oil, motor oil, diesel oil, and toluene) at room temperature was measured by weight gain method using the equation;

$$Q = (m_t - m_0) / m_0$$

where  $m_0$  and  $m_t$  are the weights of sorbent before and after swelling test, respectively.[19] The swelling kinetic rate was evaluated by weight measurement of modified sponges absorbed oil at different times.

To study the recyclability of modified sponges, the oil-saturated sponge sorbent was squeezed simply then dried to constant weight in an oven. The dry P.U sponge was cooled down to room temperature and used in the next swelling-drying process; this reused process was performed for 10 cycles.

### 3. Results and discussion:

Commercial polyurethane sponge didn't have any selectivity for water or oil it's absorbed both of them, in this respect to prepare the PDMS/AMS-SiO<sub>2</sub>-P.U modified sponge, SiO<sub>2</sub> nanoparticles were deposited on the sponge surface, then PDMS/AMS polymerizations in-situ, scheme 1 illustrates the preparation process in detail. The deposition of nanosilica on the P.U sponge surface may depend on two interactions: one is the hydrogen bond interaction between the H-bond acceptor on the P.U sponge surface of carbonyl group and the H-bond donor on the SiO<sub>2</sub> surface of hydroxyl group, and the other is the van der Waals' force between P.U and SiO<sub>2</sub> nanoparticles. Then, PDMS/AMS pre-polymer and curing agent occurs polymerization reaction at 80 °C on the sponge surface, yielding a polymer layer coated on the SiO<sub>2</sub> coated sponge surface.

#### 3.1. Characterization of the prepared materials:

DLS is a well-established and widely used technique for determining the size and polydispersity of nanoparticles within a sample. The size distribution for silica nanoparticles SiO<sub>2</sub> are in Figure 1, the average particle size of nanosilica is 112.6 nm, and polydispersity index (PDI) is 0.14 which means the average size is a very narrow and uniform.

To understand the formation of silica on coated P.U sponge, we traced the reaction process with Raman techniques and X-ray diffraction (XRD). Raman spectra of the prepared materials are reported in Figure 2. Untreated P.U structural network has represented the existence of aromatic and urethane linkage consist of different functional groups based on amide I (1720 cm<sup>-1</sup>), amide-II (1538 cm<sup>-1</sup>), and amide-III (1533 cm<sup>-1</sup>) and 1619 cm<sup>-1</sup> (Figure 2a), some of those peaks merged as broad peak.[20,21] In Figure 2b the absence of the stretching mode  $\nu(\text{Si-}$

OH) at  $945\text{ cm}^{-1}$ , which is usually assigned to the hydrophilic residual silanol group, indicated that the precursor polymerization is complete. S-C=S bending vibration is responsible for the well-defined band seen at  $385\text{ cm}^{-1}$ , while the D1 band appears at  $490\text{ cm}^{-1}$  due to siloxane ring breathing mode (with SiO units). The band at  $502\text{ cm}^{-1}$  is attributed to C-C-C and C-C-N bending. The stretching of C-S bond is apparent at  $606$  and  $701\text{ cm}^{-1}$ . The modified PDMS/AMS-SiO<sub>2</sub>-P.U sponge (Figure 2c) appears the characteristics peaks for both P.U at range (1500-1740) and siloxan groups peaks for silica and PDMS/AMS at range (380-700) for Si-O-Si & Si-C & Si-OH groups.

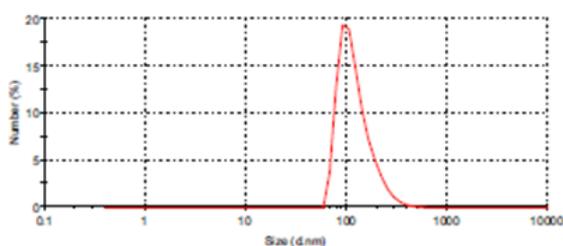


Figure 1: Particle size measurement for SiO<sub>2</sub>

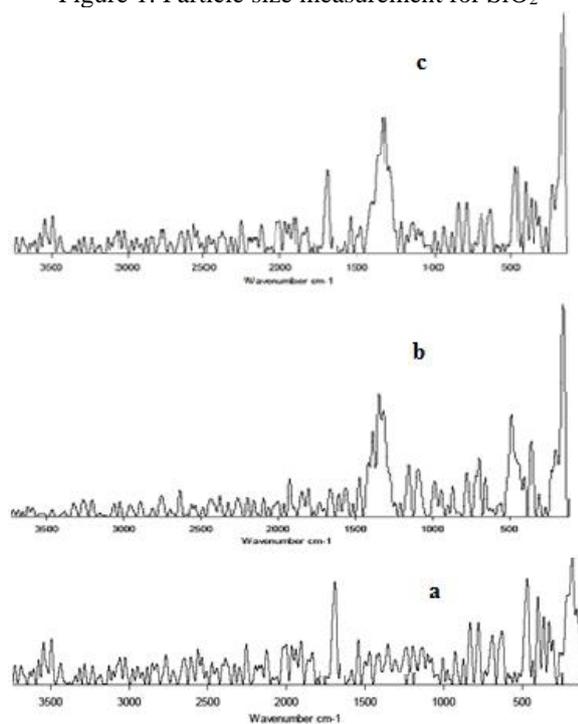


Figure 2: Raman spectra of a) P.U b) SiO<sub>2</sub> c) PDMS/AMS-SiO<sub>2</sub>-P.U

The pristine P.U sponge was amorphous in nature. XRD pattern of untreated P.U (Figure 3a) shows a broad peak at  $2\theta=20^\circ$  and didn't show any other characteristics peak indicating its amorphous nature, while the XRD pattern for silica nanoparticles shown

in Figure. 3b reveals that the silica nanoparticles are mainly amorphous having the broad peak at  $22^\circ$  with average particle size ranging between 65.2-100 nm using Debye-Scherrer equation. XRD for PDMS/AMS-P.U (Figure 3c) shows a sharp peak at  $2\theta=22^\circ$  due to meso porous siloxane polymer in PDMS/AMS and gives polymer crystallinity. After deposition of silica nanoparticles and formation of the nanocomposite, the crystallinity increases as we can see from the intensity of peak at  $22^\circ$  of PDMS/AMS-P.U with additional crystalline peaks at  $30-40^\circ$  (Figure 3d).

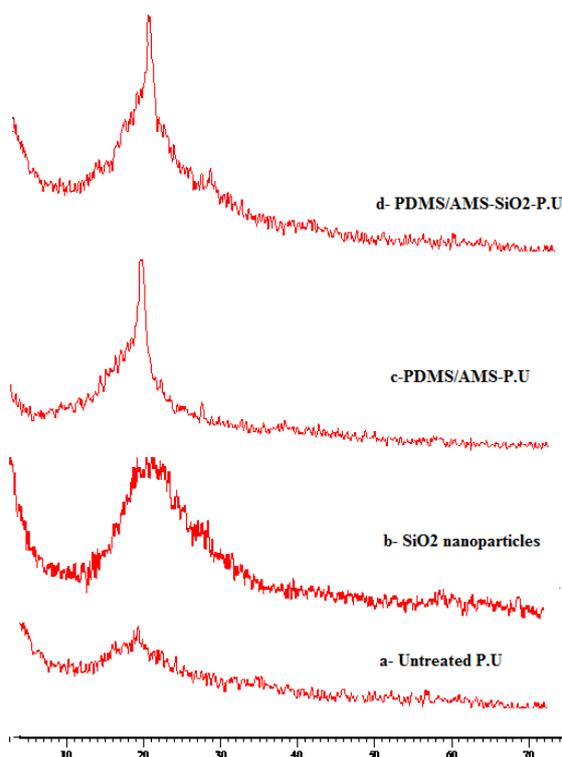


Figure 3: XRD patterns of a) untreated P.U b) SiO<sub>2</sub> nanoparticles c) PDMS/AMS-P.U d) PDMS/AMS-SiO<sub>2</sub>-P.U

Figure 4 shows the SEM images of the prepared coated P.U sponges at two magnifications. The pristine P.U sponges have a smooth skeleton and flat surface, with no obvious microscale protrusions or spherical structures distributed on the surfaces (Figure 4a,b) respectively. The PDMS/AMS-P.U surface, on the other hand, had a random rough skeleton surface, as shown in Figure 4c,d. Furthermore, there are several spherical particles distributed on the P.U sponge surface, as a result of the introduction of PDMS/AMS-SiO<sub>2</sub> composite film on the P.U sponge as shown by SEM image Figure 4e,f. The spherical particles were critical to

the sponges' hydrophobicity, just as surface protrusions are to lotus leaves' hydrophobicity.[1,22] Furthermore, these spherical particles were a major contributor to the spontaneous absorption of oil. There were dense interspaces between different spherical particles, as shown in Figure 4f. These interspaces could be thought of as a network of tiny capillaries.[23–25]

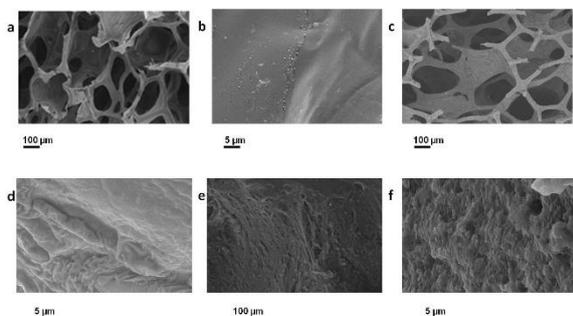


Figure 4: SEM images of untreated P.U (a,b), PDMS/AMS-P.U (c,d), PDMS/AMS-SiO<sub>2</sub>-P.U (e,f) with different magnifications.

### 3.2. Hydrophobicity and contact angle measurement (CA):

The contact angles of the sponges were measured to determine their hydrophobicity and hydrophilicity.[26,27] Figure 5 shows the contact angles of the treated and untreated P.U sponges. The weight ratios of silica nanoparticles deposited on the P.U sponge surface and the PDMS/AMS layer coated on the SiO<sub>2</sub>-P.U sponge may affect the hydrophobic characteristics of the fabricated coated P.U. As a result, the effects of PDMS/AMS and SiO<sub>2</sub> nanoparticle concentrations on the hydrophobic properties of the prepared materials were optimized. The water contact angles (CAs) of P.U treated with PDMS/AMS at weight ratios (0.5, 1, 2, 3) were 85°, 120°, 138°, and 134°, respectively as shown in Figure 5a. When the PDMS/AMS weight ratio was fixed at 2:1 (PDMS/AMS: P.U), the water contact angles (CAs) of the prepared PDMS/AMS-SiO<sub>2</sub>-P.U sponges with SiO<sub>2</sub> concentrations of 1, 2, 3, 4 wt%, was 140°, 142°, 145°, and 143°, respectively Figure 5b. To attain the highest water CA, a SiO<sub>2</sub> nanoparticles concentration of 3 wt% and a PDMS/AMS-P.U with a wt% of 2:1 were chosen to prepare the PDMS/AMS-SiO<sub>2</sub>-P.U modified sponge. The water CA is 145° and the oil CA is about 0° (Figure 5c,d) for the optimized PDMS/AMS-SiO<sub>2</sub>-P.U sponge, respectively. On the other hand, the pristine sponge's water contact angle was around 60° as shown in Figure 5 e, indicating its intrinsic hydrophilicity. These findings show that both

unmodified P.U sponge and modified P.U sponge are hydrophobic and oleophilic. The PDMS/AMS-SiO<sub>2</sub>-P.U sponge, displays superhydrophobicity attributed to the rough surface and the hydrophobic group formed by SiO<sub>2</sub> particles and PDMS/AMS layer. The water CA (Figure 5a) for PDMS/AMS coated P.U sponge without deposition of SiO<sub>2</sub> (PDMS/AMS-P.U) was only 138°. The addition of SiO<sub>2</sub> to the P.U surface increases surface roughness, resulting in the PDMS/AMS-SiO<sub>2</sub>-P.U sponge's superhydrophobicity.

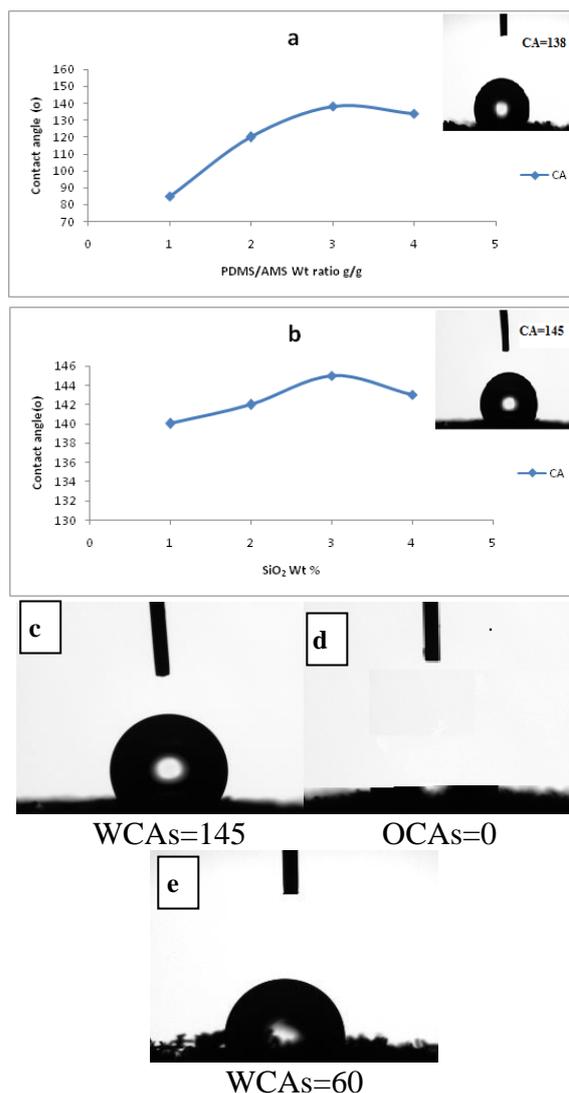


Figure 5: Effect of concentrations of a) PDMS/AMS b) SiO<sub>2</sub> on sponge hydrophobicity c) Water contact angle measurement for optimized PDMS/AMS-SiO<sub>2</sub>-P.U d) Oil contact angle measurement e) water contact angle for pristine P.U sponge.

### 3.3. Evaluation of the selective absorption for oil and organic solvents from water:

The practical application of the prepared coated sponge was investigated for selective oil sorption

from the water surface under normal conditions. As shown in Figure 6a,b the prepared sponge has superhydrophobic-superoleophilic characters so, the water droplet remains on the surface of the modified sponge with a sphere shape rather than permeating or spreading on the sponge surface. Thereafter, in less than a second, the oil droplet permeated the prepared sponge. When the as-prepared sponge is placed on the surface of crude oil (10%)/ water mixture it's floated on the surface of the oil/water mixture and spontaneously wetted with oil, this may be attributed to capillary action. The coated sponge continued to drift on the residual region of the oil film until the oil was fully absorbed due to its hydrophobic and oleophilic properties. Moreover, the sponge consists of many holes through which the oil moved upward. The oil-water separation process was depicted in Figure 6c. when the oil-water mixture was dropped on the sponges surface, the oil was easily absorbed in seconds, while the water quickly departed. The absorbed oil was collected by a simple squeezing process, the absorption and squeezing process was continued until oil completely separated without leaking, exhibiting excellent oil-keeping performance. This separation procedure is more eco-friendly than other reported methods such as in situ burning.[28]

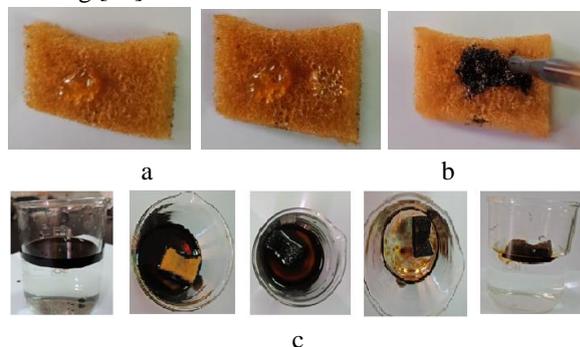


Figure 6: photo image of a) water droplet standing on the treated sponge surface b) oil droplet permeating the sponge surface c) removal of oil from oil/water mixture by a piece of treated sponge.

### 3.4. Swelling capacity measurement for PDMS/AMS-SiO<sub>2</sub>-P.U

The swelling capacities of the PDMS/AMS-SiO<sub>2</sub>-P.U sponges for different types of oils including crude oil, motor oil, diesel, and toluene were investigated and presented in Table 2. To investigate the effect of curing agent and PDMS/AMS pre-polymer contents on the swelling capacity the PDMS/AMS-P.U (1/1) foam sponge was prepared with different contents of sylgard 184 curing agent (crosslinker). The content of the sylgard 184 was

fitted (5-12 %) based on the sum weight of PDMS/AMS and untreated P.U sponge. The effect of curing agent on the swelling capacity of PDSM/AMS-P.U sponge is shown in Table 2. As we can see the swelling capacity increases clearly with increasing sylgard content, while the highest sorption capacity for PDMS/AMS-P.U was attained at 10 Wt% and can be achieved at 95.6, 83.6, 63.4, and 112.6 g/g for diesel, crude oil, motor oil, and toluene respectively. The effect of PDMS/AMS content on swelling capacity was studied by fixing the curing agent contents to 10% and using different concentrations of PDMS/AMS (0.5-3 wt%). Table 2 showed increasing the swelling capacity with increasing PDMS/AMS contents from 0.5 wt% to 3wt%, while the maximum swelling capacity obtained at a weight ratio (2:1 PDMS/AMS: P.U) and achieved 102, 90, 68.9, and 119 g/g for diesel, crude oil, motor oil, and toluene respectively. The optimum PDMS/AMS contents is 2 wt%. Hydrophobic modification by PDMS/AMS leads to high oil sorption capacity; this may be attributed to the strong lipophilicity of the functional siloxan, alkyl chain of PDMA/AMS attached to the sponge, and the capillary force of the sponge pores. Hence the absorption capacity of the treated sponge is better than that for pristine P.U and other reported compounds. We also noticed that the ordering of oils as follows: toluene, diesel, crude oil, and motor oil. To understanding, these behavior two forces controlled this sorption capacity one is the viscosity of oils and the second is adhesion force, in the case of solvents toluene having lower viscosity then diesel. On the other hand, crude oil has a higher viscosity than motor oil so the adhesion forces increasing the crude oil sorption.

The effect of hydrophobic SiO<sub>2</sub> nanoparticles at different concentrations namely (1, 2, 3, or 4 wt %) was represented in Table 2. The data shows that as the SiO<sub>2</sub> nanoparticle concentrations increase, the sorption capacity increased and reached to its maximum values at 3 wt%. The swelling capacity of PDMS/AMS-P.U at 3 wt% SiO<sub>2</sub> is 118, 106, 81.8, and 135 g/g for diesel, crude oil, motor oil, and toluene respectively. This may be attributable to the wide surface area created by inserting SiO<sub>2</sub> nanoparticles to coated polyurethane foam, which causes the polymeric network to swell further.[29] The sorption capacity for toluene, diesel was elevated and for crude, motor oil was reduced due to the viscosity difference between toluene and crude oil, where the crude oil cannot simply diffuse from the

outside surface of foam into the inside networks due to its higher viscosity than toluene. Furthermore, crude oil's higher viscosity may have opposing effects: decreased sorption during permeation through the network's interior and improved sorption when the oil is well adhered to the compounds.[30,31]

The prepared sorbent PDMS/AMS-SiO<sub>2</sub>-P.U sponge exhibits excellent sorption capacities compared to typical oil absorbents reported in the literature such as PDMS sponge, Porous PDMS, PDMS-TiO<sub>2</sub>-PU sponge, and PDMS@SiO<sub>2</sub>@WS2 sponge with maximum sorption capacity 11, 34, 44, and 112 g/g, respectively.[9,12,32,33]

### 3.5. Swelling kinetics and recyclability:

The sorption kinetics curve for PDMS/AMS at different concentrations of SiO<sub>2</sub> in toluene is shown in Figure 7, with the sorption capacity plotted as a function of immersion time. According to Figure 7, the sorption capacity increases rapidly at the start of the swelling tests (0-30 sec) and attains a plateau thereafter. Interactions and van der Waals forces between toluene and the prepared sponge's hydrophobic groups absorbed the oil first. Toluene was then absorbed into the PDMS/AMS-SiO<sub>2</sub>-P.U sponge via internal capillary movement, allowing for greater oil sorption. Toluene saturated swelling can be achieved in 30 seconds. In practical applications, the material's sorption regeneration and recyclability are an extremely important indicators for evaluating the superiority of the sorption materials. There are two common recycling techniques: solvent evaporation and squeezing. The sponge can be quickly regenerated by simple squeezing, and the dissolved oils can be extracted in the meantime. The recyclability of the optimized PDMS/AMS-SiO<sub>2</sub>-P.U sponge in toluene and crude oil for example is shown in Figure 8. The residual oil within the foams, which cannot be completely removed by a simple manual squeezing operation, is responsible for the slight reduction in absorption ability. The PDMS/AMS-SiO<sub>2</sub>-P.U sponge sorbent during the 10 recycle phase, the sponge will uptake these liquids at 5–10 times its weight, and there is no apparent decrease in recycling sorption ability after 9 cycles, suggesting that the sponge has a stable sorption and recycling efficiency. The fact that 10% of residual organic solvents remained in the treated sponge after each cycle may explain the lower sorption power. The prepared foam

sorbent with good reusability and stability is the perfect material for oil absorption, according to the recyclability experiments.

Swelling parameters of the investigated coated sponge crosslinked by sylgard 84B with different wt%. The  $Q_{max}$ ,  $Q$ , equilibrium toluene or crude oil (ETC) or (ECC), characteristic time required for the swelling (T) and swelling kinetic constant (k) for the prepared samples were determined according to our previous work[31], The swelling parameters were determined and listed in Table (3).  $Q_{max}$  values were discussed previously in swelling behavior section. Characteristic swelling degree (Q) of the tested samples in toluene or 10% crude oil at room temperature, the data of Q show the same trend as  $Q_{max}$  as it is about 2/3 of  $Q_{max}$ . Regarding ETC and ECC for the prepared samples both characters increase with increasing PDMS/AMS content of the tested samples. They also show higher values upon using high contents of SiO<sub>2</sub> nano particles and with increasing the alkyl hydrophobic functionality.

### Conclusion

Superhydrophobic oleophilic polyurethane sponge sorbent was fabricated by facile dip-coating method with a hydrophobic mixture of Poly(dimethylsiloxane-co-alkylmethylsiloxane) and silica nanoparticles (SiO<sub>2</sub>). The prepared coated sponge showed a flexible, porous structure with a high sorption capacity for oils and organic solvents. The SEM results revealed a random rough skeleton with several small spherical particles distributed on the treated sponge surface, which was a major reason for the hydrophobicity oil uptake. Contact angle measurements demonstrated the superhydrophobicity of the prepared sorbent with high water contact angles exceeds 140°. Swelling capacity and recyclability tests indicated that the prepared sorbent has a high swelling capacity for different types of oils and good recyclability in separation of oil-water mixture. The swelling capacity of the coated sponge sorbent is 135 g/g and can be reused up to 10 cycles. All the outstanding results indicated that the prepared sorbent is a promising candidate for the fast removal of oil spills and chemical leakages.

### Conflicts of interest

“There are no conflicts to declare”.

Table 2. The maximum swelling capacity ( $Q_{max}$ ) for pristine P.U sponge and PDMS/AMS-SiO<sub>2</sub>-P.U in diesel, crude oil, motor oil, and toluene at room temperature

Designation	Composition (wt/wt)	Sylgard 184B wt%	SiO <sub>2</sub> wt%	$Q_{max}$ (g/g)			
				Diesel	Crude oil	Motor oil	Toluene
Pristine P.U	-	-	-	28	33	29	30.90
PDMS/AMS -P.U	1/1	5	0	90	78	60.1	107
		10	0	95.6	83.6	63.4	112.6
		12	0	92	80	61.7	109
PDMS/AMS -P.U	0.5/1	10	0	90.3	78.3	59.6	107.3
	1/1			95.1	83.1	63.4	112.1
	2/1			102	90	68.9	119
	3/1			98	86	67.5	115
PDMS/AMS -P.U	2/1	10	1	104	92	71.4	121
			2	112	100	75	129
			3	118	106	81.8	135
			4	115	103	80	132

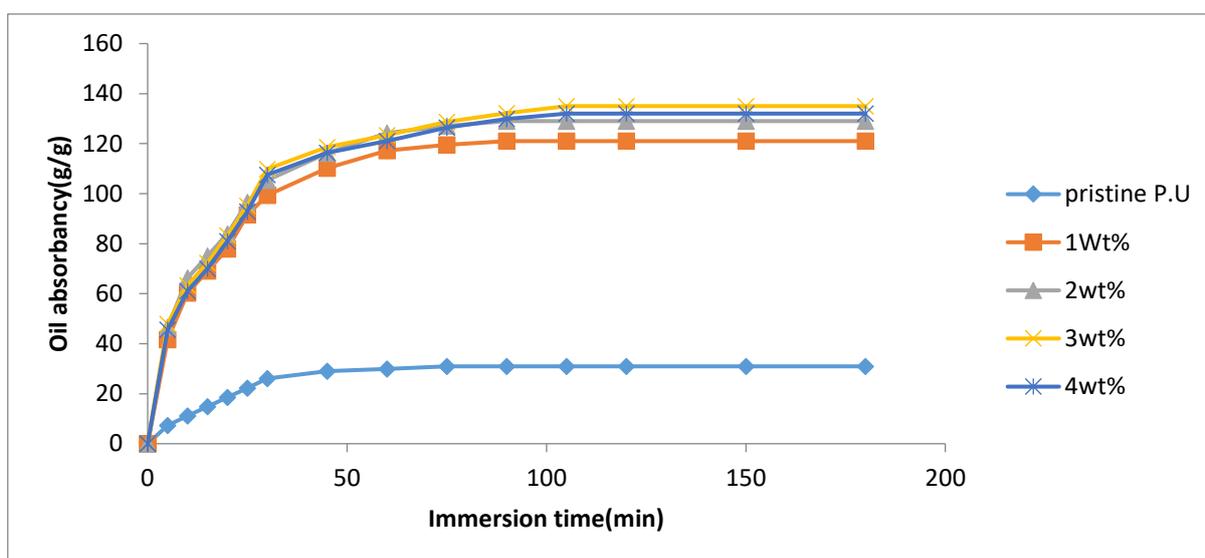


Figure 7: Swelling kinetics behaviors for PDMS/AMS-SiO<sub>2</sub>- P.U at different concentrations of SiO<sub>2</sub> in toluene.

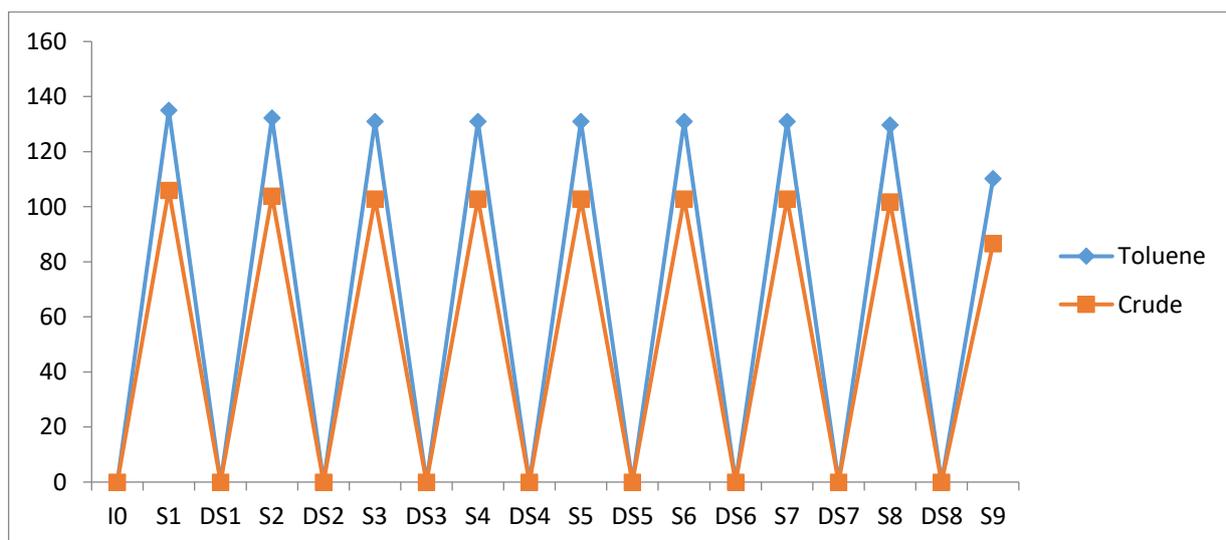


Figure 8: Recyclability of the optimized PDMS/AMS-SiO<sub>2</sub>-P.U in toluene and crude oil.

Table (3): Absorption and Swelling parameters for pristine P.U sponge and PDMS/AMS-SiO<sub>2</sub>-P.U at 25 °C in Crude oil and Toluene.

Designation	Composition (wt/wt)	Sylgard 84 wt%	SiO <sub>2</sub> wt%	Q <sub>max</sub> (g/g)		Q (g/g)		T (h)		K (h <sup>-1</sup> )		ECC	ETC
				Crude oil	Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil	Toluene	Crude oil	Toluene
Pristine P.U	-	-	-	33	30.9	20.856	19.5288	0.33	0.35	3.03	2.86	96.97	96.76
PDMS/AMS –P.U	1/1	5	0	78	107	49.296	67.624	0.31	0.31	3.22	3.22	98.72	99.07
		10	0	83.6	112.6	52.8352	71.1632	0.30	0.32	3.33	3.12	98.80	99.11
		12	0	80	109	50.56	68.888	0.31	0.32	3.22	3.12	98.75	99.08
PDMS/AMS –P.U	0.5/1	10	0	78.3	107.3	49.4856	67.8136	0.33	0.31	3.03	3.22	98.72	99.07
	1/1			83.1	112.1	52.5192	70.8472	0.33	0.32	3.03	3.12	98.80	99.11
	2/1			90	119	56.88	75.208	0.32	0.33	3.12	3.03	98.89	99.16
	3/1			86	115	54.352	72.68	0.31	0.31	3.22	3.22	98.84	99.13
PDMS/AMS –P.U	2/1	10	1	92	121	58.144	76.472	0.34	0.33	2.94	3.03	98.91	99.17
			2	100	129	63.2	81.528	0.34	0.32	2.94	3.12	99.00	99.22
			3	106	135	66.992	85.32	0.35	0.31	2.86	3.22	99.06	99.26
			4	103	132	65.096	83.424	0.33	0.32	3.03	3.12	99.03	99.24

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