Analysis of Superhydrophobic-Superoleophilic Properties on Modification of Polyurethane Sponge for Selective Oil-Water Separation

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Abstrak. Pada penelitian ini, telah dilakukan modifikasi material spons polyurethane (PU) untuk memperoleh sifat superhidrofobik-superoleofilik. Modifikasi yang dilakukan yakni melapisi spons PU dengan beberapa nanomaterial seperti ZnO, Fe_3O_4+TEOS, dan stearic acid dengan metode *dip-coating* dan *drop-coating*. Pengujian yang dilakukan meliputi pemisahan minyak dan air secara selektif dengan menggunakan respon magnetik. Beberapa jenis minyak dan pelarut organik diuji daya serapnya. Hasil penelitian menunjukkan bahwa spons PU@ZnO@Fe_3O_4@SA memiliki kapasitas penyerapan yang cukup baik, yaitu sebesar 4.37 mL hingga 7.37 mL. Spons PU yang dibuat dapat secara selektif memisahkan minyak dari air dengan efisiensi pemisahan diatas 99%. Spons PU yang dibuat juga dapat digerakkan secara magnetis oleh medan magnet eksternal. Dari hasil karakterisasi menggunakan 3D OM, diperoleh sudut kontak air sebesar 153.38° yang menunjukkan bahwa spons PU@ZnO@Fe_3O_4@SA merupakan superhidrofobik. Dari morfologi permukaan diperoleh ukuran rata-rata diameter pori sebesar 167.475 µm.

Kata Kunci: superhidrofobik-superoleofilik, spons PU, ZnO, Fe_3O_4+TEOS, stearic acid.

Abstract. In this research, a modification of polyurethane (PU) sponge material has been made to obtain superhydrophobic-superoleophilic properties. The PU sponge was coated with several nanomaterials such as ZnO, Fe_3O_4+TEOS, and stearic acid by dip-coating and drop-coating methods. The tests include selective separation of oil and water with a magnetic response. Several types of oil and organic solvents were tested for absorption capacity. The results showed that the PU@ZnO@Fe_3O_4@SA sponge has a good absorption capacity, from 4.37 mL to 7.37 mL. The fabricated PU sponge could selectively separate oil from water with a separation efficiency above 99%. The fabricated PU sponge also could be magnetically driven by external magnetic fields. From the characterization using 3D OM, the water contact angle was 153.38°, which indicates that the PU@ZnO@Fe_3O_4@SA sponge is superhydrophobic. And from surface morphology obtained an average pore size diameter of 167.475 µm.

Keywords: superhydrophobic-superoleophilic, PU sponge, ZnO, Fe_3O_4+TEOS, stearic acid.

INTRODUCTION

Production and consumption of petroleum products have increased worldwide. With the increasing need for petroleum, there is a risk of accidents due to oil spills [1]. The largest case of oil spills occurred in 2010 in the Gulf of Mexico with 779 million liters of oil spilled into the sea [2]. The effects of environmental pollution caused by oil spills and organic pollutants that insoluble in water require an urgent cleaning process. Thus, an oil collector based on sorbent materials with special properties is needed [3]. PU sponge is one of the candidate materials, but commercial PU sponge cannot be used immediately, so surface modification is needed to obtain superhydrophobic-superoleophilic properties [4].

Superhydrophobic

Hydrophobic is a term derived from a Greek term "hydro" meaning water and "phobos" meaning fear. Hydrophobic literally means "the fear of water". So, superhydrophobic is a special property of a surface because of its high ability to repel water with a contact angle above 150°. Superhydrophobicity arises when a molecule does not partake in the hydrogen bonding of water [5]. The surface of a lotus leaf is an example of superhydrophobicity, because of its non-wetting surface and perfection of its water repellency with unique hierarchical micro/nanoscale structures [6]. Superhydrophobicity can be improved by reducing surface tension and by increasing surface roughness [7].

Surface Tension

Surface tension is the energy required to increase the surface area of a liquid due to intermolecular forces [5]. The cohesion force acts to separate the two different materials in the same intervention medium. If the cohesion force on a solid is higher than a liquid, then the two materials will not stick together and tend to form the smallest possible surface area. That's why the water droplets are spherical because the spherical shape is the most stable geometry and can minimize surface tension [8]. Thus, it is necessary to reduce surface tension to obtain wetting properties such as superhydrophobic.

Surface Roughness

In general, the surface roughness will make hydrophobic surfaces superhydrophobic. The concept of superhydrophobic was introduced by Wenzel (1936). Wenzel proposes a modification to Young's equation based on the Wenzel state [6], [9].

$$\cos \theta_W = r_s \times \cos \theta, \tag{1}$$

where θ_W is the contact angle at the Wenzel state and r_s is the roughness factor. This Wenzel equation predicts that the contact angle can be increased by roughing the surface [7].

The Wenzel theory was further developed by Cassie and Baxter (1944). The Cassie-Baxter model shows the angle of contact depends on the percent of solids in contact with the droplets. On heterogeneous (porous) surfaces it decreases with increasing part of the wettable surface [10]. The Cassie-Baxter equation:

$$\cos \theta_{CB} = f_s \times \cos \theta - (1 - f_s), \tag{2}$$

where θ_{CB} is the angle of contact in the Cassie-Baxter state, and f_s is the fraction of the surface area in contact with the liquid droplet [6].

Superoleophilic

Oleophilic comes from the word "oleo" meaning oil and "philic" meaning love. As the wettability properties of the others, oleophilic is a property of some materials due to its ability to attract oil [11]. Oleophilic refers to materials that have a strong affinity for oils. A surface is oleophilic if it has a contact angle to the oil less than 90°. Meanwhile, surfaces that are superoleophilic have a contact angle to the oil of less than 10° even 0° [12]. Superoleophilic is a surface whose energy is dominated by London dispersion forces, exceeding the surface tension of hydrocarbons [13].

Porous surfaces with superoleophilic properties (good permeability to oil) are commonly used as oil-water separation devices [14]. Because such surfaces are easily wet with oil but can completely repel water, they are effective in the separation process of water and oil mixtures.
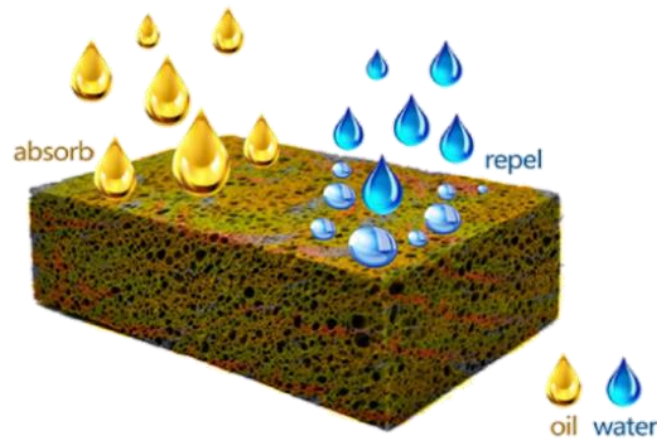

Figure 1. superhydrophobic-superoleophilic on the surface of the sorbent material

The maximum oil absorption capacity (k) for a porous sorbent material can be calculated by weight gain ratio,

$$k = \frac{W_a - W_b}{W_b} \ (g/g), \tag{3}$$

where W_a and W_b are the weight of the sorbent after and before oil absorption, respectively. Meanwhile, to calculate the separation efficiency of a mixture of oil and water (50%, v/v) or an oil-in-water emulsion (e) can be determined as:

$$e = \frac{V_a}{V_b} \times 100\%, \tag{4}$$

where V_a is the volume of water remaining on the surface and V_b is the initial volume of water in the water-oil mixture [15].

EXPERIMENT

Materials

Commerical polyurethane sponges (PU sponge D.24), ZnO, Fe_3O_4 nanoparticles, TEOS, NH_4OH, and stearic acid were used to modify surfaces. Palm oil, olive oil, castor oil, lubricating oil, kerosene, and gasoline were used to test the oil absorption capacity of the fabricated sponge. Deionized water was used for all experiments and tests.

Methods

The research was done with an experiment to make superhydrophobic-superoleophilic sponges. But, before that, Fe_3O_4 was first coated with TEOS precursor solution.

Preparation of Fe_3O_4 Nanoparticles

The magnetic Fe_3O_4 nanoparticles were prepared by coating the material with a TEOS precursor solution. Briefly, 4 g Fe_3O_4 were stirred with ethanol and deionized water for 30 minutes. After that, 4 mL of TEOS were poured, and 10 mL of NH_4OH were slowly added to the solutions containing Fe_3O_4, the mixture was stirred for 6 h. The mixture was repeatedly separated by a magnet and washed with deionized water. Then, Fe_3O_4 dried at 80° for 18 hours.

Preparation of Superhydrophobic-Superoleophilic Sponge

The pristine PU sponge was cut into cubes ($2 \times 2 \times 2$ cm^3) and cleaned with deionized water and ethanol several times and dried at 60°C for 6 h. Several pieces of clean sponges were immersed in a uniform suspension contains 0.2 g ZnO and 30 mL ethanol by ultrasonication for 30 min, and dried at 80℃ for 2 h. PU@ZnO sponges were uniformly coated with Fe_3O_4+TEOS by drop-coating method and dried. But, it was found that the interaction between the sponge and the Fe_3O_4 particles was weak. Then, the PU@ZnO@Fe_3O_4 sponges were dipped into 0.1 g stearic acid solution overnight at room temperature. Stearic acid was used as the top layer, to decrease the loss of Fe_3O_4 and also to obtain superhydrophobicity. The PU@ZnO@Fe_3O_4@SA were annealed at 80℃ for 4h to obtain the superhydrophobic-superoleophilic PU sponge.
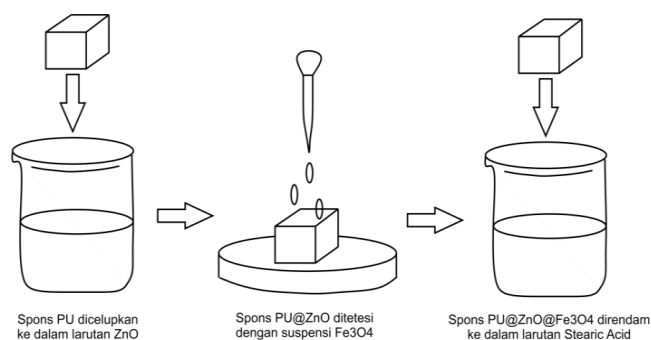

Figure 2. Schematic steps involved in the synthesis of superhydrophobic-superoleophilic PU sponge

RESULTS AND DISCUSSIONS

Testing results of the surface-modified PU sponges
Wetting Properties

To determine the surface properties of each sponge, a comparison was made between pristine PU sponge, PU@ZnO sponge, PU@Fe_3O_4@SA sponge, and PU@ZnO@Fe_3O_4@SA sponge, as shown in the following image and table.
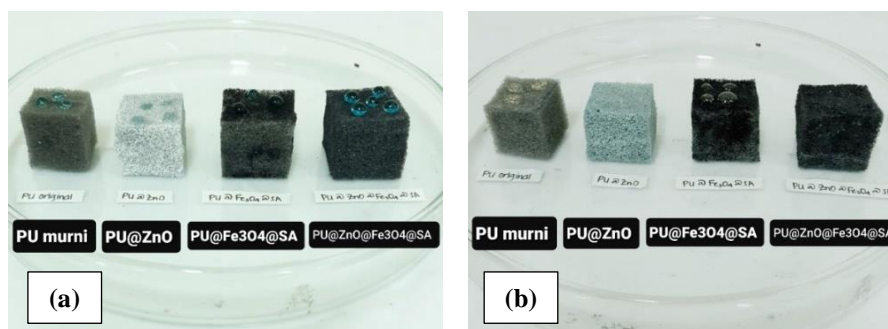

Figure 3. Surface properties between the coated PU sponges (a) with water and (b) with oil

Table 1. Surface properties to water and oil

PU sponge	Surface Properties to Water	Surface Properties to Oil
Pristine PU sponge	Hydrophobic	Oleophobic
PU@ZnO sponge	Superhydrophilic	Superoleophilic
PU@Fe_3O_4@SA sponge	Hydrophobic	Oleophobic
PU@ZnO@Fe_3O_4@SA sponge	Superhydrophobic	Superoleophilic

Based on Figure 3 and Table 1, it's known that the PU@ZnO@Fe_3O_4@SA sponge is superhydrophobic-superoleophilic. Because the surface has good abilities to repel the water and can completely absorb oil. Sample with the composition of ZnO 0.2g, Fe_3O_4 0.3g, and SA 0.1g was made to test the capacity

Absorption Capacity

Several types of fluids include oil and organic solvents used to test the time and absorption capacity of the PU@ZnO@Fe_3O_4@SA sponge.

Table 2. Test results of PU@ZnO@Fe_3O_4@SA sponge with several types of oils and organic solvents

Types of Oil	Density of Oil (g/cm^3)	Absorption Capacity (g/g)	Absorbed Volume (mL)
Palm Oil	0.92	12.5845	6.6332
Olive Oil	0.91	14.0268	6.7053
Castor Oil	0.95	13.7361	6.8732
Lubricating Oil	0.90	11.5483	6.4594
Gasoline	0.73	10.4116	7.3745
Kerosene	0.82	10.5448	6.3682

Types of Organic Solvent	Density of Organic Solvent (g/cm^3)	Absorption Capacity (g/g)	Absorbed Volume (mL)
Ethanol	0.80	11.1777	5.0908
Aceton	0.78	10.2260	6.2078
n-Hexane	0.65	9.4568	6.6361
Toluene	0.86	11.7350	6.2125
Tetrachloromethane	1.59	12.8844	4.3774
Trichlorethen	1.32	13.0129	5.1864

Oil-Water Separation

Tetrachloromethane was used to test the ability of the oil-water separation of PU@ZnO@Fe$_3$O$_4$@SA sponge. In this case, oil has a density lower than water is hard to use, so tetrachloromethane acts as a substitute for oil. Tetrachloromethane and water are both clear liquids. So the water must be given a dye to facilitate visual observation.
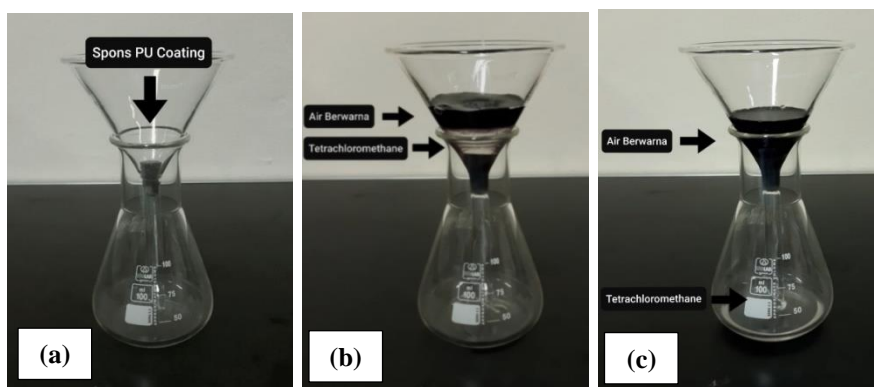

Figure 4. (a) PU sponge in a funnel (b) A mixture of dyed water and tetrachloromethane (50%/50%) poured into the funnel (c) Selective separation of water from organic solvent by PU@ZnO@Fe$_3$O4@SA sponge

From the results, it's known that the PU@ZnO@Fe$_3$O$_4$@SA sponge can selectively separate water from organic solvents. Tetrachloromethane can completely absorb the oil with small pieces of coated PU Sponge, showing its superoleophilic properties. Meanwhile, water is held above the surface and repelled because of its superhydrophobic properties. The modified PU sponge can selectively separate oil-water with separation efficiency above 99%.

Magnetic Response

Adding a magnetic component such as Fe$_3$O$_4$ is a simple way to drive the PU@ZnO@Fe$_3$O$_4$@SA sponge using an external magnetic field. Oil adsorption for cleaning the water surface by a magnet can be seen in the figure below.
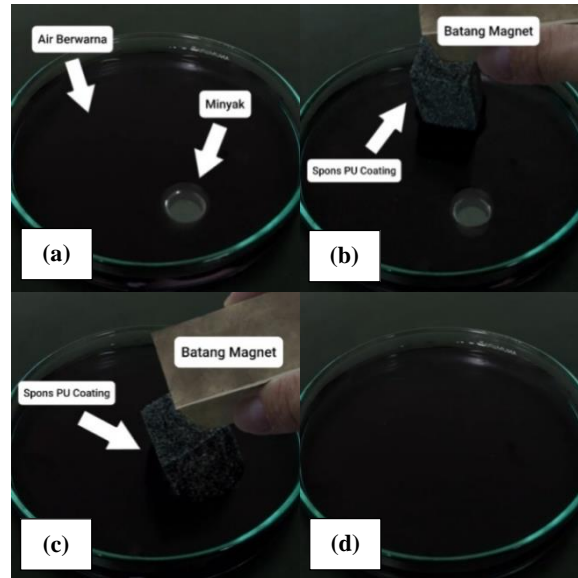
Figure 5. (a) Petri dish containing oil droplet on the dyed water surface (b, c) cleaning oil with magnetically PU@ZnO@Fe$_3$O$_4$@SA sponge (d) cleaned water surface

The modified PU sponge has a magnetic response that is good enough. So that is easy to use in the selective separation of oil-water.

Characterization results of the surface-modified PU sponges
Water Contact Angle

There were 4 samples observed, including pristine PU sponge, PU@ZnO sponge, PU@Fe$_3$O$_4$@SA sponge, and PU@ZnO@Fe$_3$O$_4$@SA sponge. The 3D OM characterization was carried out by using the sessile drop method. The results of measuring the water contact angle on the surface can be seen in the image below.
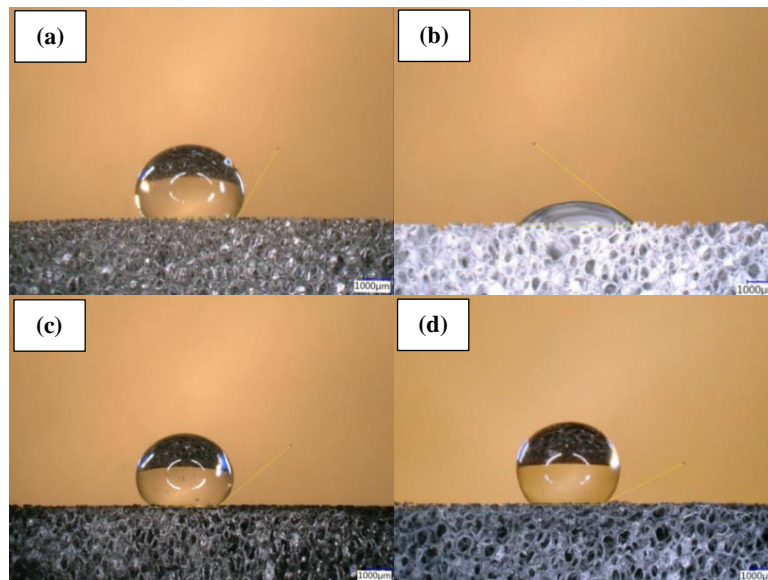

Figure 6. Water contact angle measurement (a) pristine PU sponge, (b) PU@ZnO sponge, (c) PU@Fe$_3$O$_4$@SA sponge, and (d) PU@ZnO@Fe$_3$O$_4$@SA sponge

The water contact angle is affected by surface tension. Contact angle on the surface occurs because the cohesion force between water droplet molecules is greater than the adhesion force between water molecules and molecules on the surface. Water droplets tend to be attracted to a sphere due to the forces between molecules.

Water droplets on the surface were observed with 3D OM to measure the contact angle. Measurements performed 10 times to get a definite value and reduce human error. Measurement of the average contact angles shown in the following table.

Table 3. Measurement of the average contact angle

Sample	Average Contact Angle	Surface Properties
Pristine PU sponge	120.34°	Hydrophobic
PU@ZnO sponge	37.14°	Hidrophilic
PU@Fe$_3$O$_4$@SA sponge	140.40°	Hydrophobic
PU@ZnO@Fe$_3$O$_4$@SA sponge	153.38°	Superhydrophobic

From **Table 3**, it is known that the modified PU Sponge has increased the contact angle. This increased contact angle occurs due to the role of each component. Such as Fe$_3$O$_4$ and stearic acid increases surface roughness, and ZnO acts as an amphiphilic surfactant. All of those can change the surface wettability to become superhydrophobic and proves the theory of Wenzel also Cassie-Baxter which states that surface roughness and low surface tension can increase the water contact angle.

Surface Morphology

To determine how surface roughness affects the surface properties, it can be seen in the surface morphology image below.
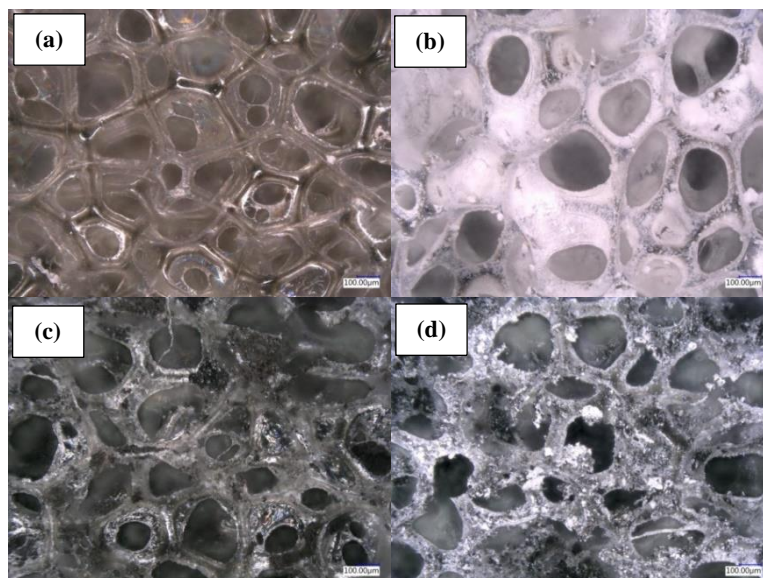

Figure 6. Images of surface morphology using 3D OM with 200x magnification (a) pristine PU sponge, (b) PU@ZnO sponge, (c) PU@Fe$_3$O$_4$@SA sponge, (d) and PU@ZnO@Fe$_3$O$_4$@SA sponge

The color difference in the image above shows the difference in the material coated on the PU sponge. But at this magnification, the material can't be identified obviously, so done again with a magnification of 500x. Pores morphology observations were shown in the following figure.
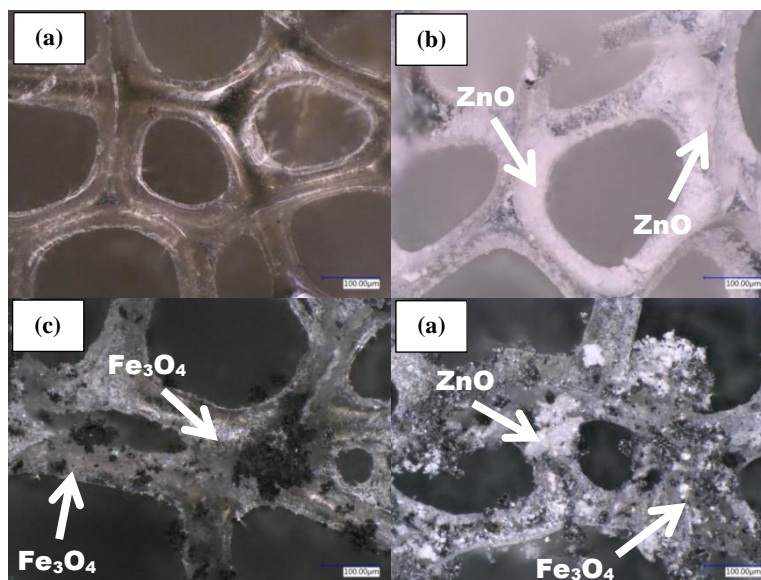

Figure 7. Images of surface morphology using 3D OM with 500x magnification (a) pristine PU sponge, (b) PU@ZnO sponge, (c) PU@Fe$_3$O$_4$@SA sponge, (d) and PU@ZnO@Fe$_3$O$_4$@SA sponge

In **Figure 7a**, pores of the pristine PU sponge still refined because they haven't coated yet. But, in **Figure 7b** there was a thin white layer due to the addition of ZnO. Meanwhile, in **Figure 7c**, there were black lumps due to the addition of Fe$_3$O$_4$. In **Figure 7d**, it can be seen how the ZnO and Fe$_3$O$_4$ materials are mixed and make the pore diameter smaller. The addition of stearic acid could affect the roughness of the PU sponge pores. This proves that surface roughness affects its wettability.

Along with the increasing number of component materials, the rougher the surface, the better surface will repel water. So the PU@ZnO@Fe$_3$O$_4$@SA sponge has better wettability compared to other samples.

Surface roughness is evidenced by a change in the average pore diameter of PU sponges. ImageJ software is used to processing images obtained from 3D OM observations with a magnification of 200x (Fig 6) to determine the size distribution of the average diameter of the coated PU sponge. The data performed 50 times with various diameter sizes. The results are shown in the table below.

Table 4. Average diameter of PU sponges pore size using ImageJ

Sample	Average Diameter (μm)	Minimum (μm)	Maximum (μm)	Standard Deviation (μm) ± (*n*)
Pristine PU sponge	209.76	116	343.913	56.077 ± (50)
PU@ZnO sponge	203.23	92.65	336.149	57.098 ± (50)
PU@Fe$_3$O$_4$@SA sponge	198.841	84.095	297.469	51.241 ± (50)
PU@ZnO@Fe$_3$O$_4$@SA sponge	167.475	78.409	290	52.11 ± (50)

The more the material is added, the smaller the pore diameter. It will increase the surface roughness, thus affecting its superhydrophobic properties.

CONCLUSIONS

The PU@ZnO@Fe3O4@SA sponge has superhydrophobic-superoleophilic properties because it can selectively separate oil and water with a separation efficiency above 99% and has an absorption capacity of oil and organic liquids of 4.37 mL to 7.37 mL. The fabricated PU sponge also has a magnetic response guided by external magnetic fields to adsorb oil. The addition of ZnO, Fe3O4, and stearic acid nanomaterials can reduce surface tension and increase surface roughness, both of them can affect the increase in contact angle. The contact angle formed on the PU@ZnO@Fe3O4@SA sponge is 153.38° with a pore size diameter of 167.475 μm. Hopefully, this research can be applied in the continuous separation of oil-water mixtures in large scales for application in the cleanup of oil spills and removal of organic solvents from water.

ACKNOWLEDGMENT

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