Article

Not peer-reviewed version

Facile Fabrication of High Performance Superhydrophobic Reusable Oil Absorbing Sponge

Rabiga Kudaibergenova , Erzhigit Sugurbekov , Gulnar Sugurbekova * , Gulzat Demeuova

Posted Date: 12 September 2023

doi: 10.20944/preprints202309.0684.v1

Keywords: polyurethane sponge; reduced graphene oxide; silicone oil; magnetic; superhydrophobic/superoleophilic; oil/water separation

Article

Facile Fabrication of High Performance Superhydrophobic Reusable Oil Absorbing Sponge

Rabiga Kudaibergenova [1], Erzhigit Sugurbekov [2], Gulzat Demeuova [2] and Gulnar Sugurbekova [2,*]

[1] Taraz Regional University named after M.Kh. Dulaty, Faculty of Technology, Department of Chemistry and Chemical Technology, 60 Tole Bi Street, 080000 Taraz, Kazakhstan 1; rabi_07@bk.ru
[2] Eurasian National University named after L.N. Gumilyov, 010000 Astana, Kazakhstan 2; sugurbekova.g.55@gmail.com
* Correspondence: sugurbekova.g.55@gmail.com

Abstract: Wastewater treatment from oils and oil products, organic mixtures are a very relevant topic that can be successfully used to solve problems of serious environmental pollution, such as oil spills, industrial oily wastewater discharges and water treatment in the water treatment process. In this work, we have developed new superhydrophobic magnetic polyurethane (PU) sponges functionalized with reduced graphene oxide (RGO), $MgFe_2O_4$ nanoparticles, and silicone oil (SO) as a selective and reusable sorbent for purification and separation of wastewater from oils and organic solvents. The surface morphology and wettability of the sponge surface were characterized by scanning electron microscopy (SEM) and a contact angle analysis system, respectively. The results showed that the obtained PU sponge PU/RGO/$MgFe_2O_4$/SO had excellent mechanical and water-repellent properties, reusable properties (more than 20 cycles), as well as fast (immersion time 20 sec) and excellent adsorption capacity (16.61- 44.86 g / g), and good magnetic properties made it easy to separate the sponge from the water with a magnet. And the presence of RGO in the composition of the nanomaterial improves the separating and cleaning properties of materials, and also leads to an increase in the absorption capacity of oil and various organic solvents. The synthesized PU sponge has great potential for practical applications due to its facile fabrication and excellent oil-water separation property.

Keywords: polyurethane sponge; reduced graphene oxide; silicone oil; magnetic; superhydrophobic/superoleophilic; oil/water separation

1. Introduction

In recent years, there has been an increase in the number of accidental oil spills during oil production, transportation and storage, as well as industrial discharges of oils/organic solvents, which pose a significant threat to marine ecosystems [1,2]. In this regard, the separation of oil-water mixtures is the actual theme, and plays an important role in the industry to deal with very serious environmental pollution, such as oil spills, industrial oily wastewater discharges and oil recovery [3]. To reduce the impact of oil pollution, the main challenge for researchers is to develop low cost and high-performance oil absorption materials. The preferred oil spill treatment method is absorption [4], which has high efficiency, easy operation and high absorption capacity [5]. It is very important for an oil absorbent to be hydrophobic as it will selectively absorb oils while repelling water [6–8].

In recent years, a number of traditional materials such as activated carbon [9,10], carbon nanotubes [11], fibers [12], zeolites [13,14], silica [15], as well as synthetic films [16], meshes and fabrics [17,18] have been explored for the removal and collection of spilled oil. However, these materials have a number of disadvantages such as low absorbency, low selectivity, poor reusability.

To date, much research has been focused on developing nanomaterials that have great advantages in oil and organic solvent absorption and high porosity, low density, and recyclability,

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 12 September 2023 doi:10.20944/preprints202309.0684.v1

such as membranes [19], carbon nanotubes [20], polymer gels [21], and nanoporous polymers [22]. Unfortunately, the complexity of the preparation process, high cost and environmental hazards do not allow the use of these materials in practical applications. Therefore, it is necessary to develop absorbent nanomaterials with better characteristics for efficient removal of oils/organic solvents. Superhydrophobic magnetic nanomaterials and their outstanding absorption characteristics of oils and organic solvents have recently been investigated. Zhu others [23] coated polysiloxane on polyurethane sponge, which exhibit high oil/organic solvent absorption capacity, their use is still solely due to some limitations such as expensive materials and complex processes.

Currently, much attention is paid to the production of superhydrophobic and superoleophilic PU sponges, as they are inexpensive, porous, elastic three-dimensional materials with a large internal surface area, which is widely used for oil and water separation [24].

Among various superhydrophobic materials, adsorbents coated with reduced RGO have unique hydrophobic properties due to chemical stability and hydrophobic interactions [25]. In this study, we aim to use graphene oxide to produce superhydrophobic materials with superior oil-water separation. Graphene oxide (GO) is a 2D material - it is a single-atomic layered material, made by the powerful oxidation of graphite, which is cheap and abundant [26]. Graphene-based superhydrophobic composite nanomaterials have become widely used due to their excellent characteristic properties such as self-cleaning, excellent mechanical/superhydrophobic properties, good absorption of oil and organic liquids [27].

In this study, a highly absorbent PU sponge based RGO was fabricated using the dipping method. The resulting sponge has excellent potential for practical applications due to its ability to completely absorb oil within a few seconds. In addition, the new super hydrophic magnetic sponge has excellent oil selectivity, high absorbency. This study proposes a simple and inexpensive method for making a hydrophobic and lipophilic sponge that can be used to separate oil and water.

2. Materials and Methods

2.1. Chemicals and apparatus

Silicone oil (viscosity 500 cSt (25 °C)) and hexane (laboratory reagent, ≥95%) were purchased from Sigma-Aldrich. Polyurethane sponge (PU, density 22 Kg/m^3) was purchased at a local hardware store. The new superhydrophobic magnetic sponge was characterized using various analysis techniques listed below. Scanning electron microscopy (SEM) images were recorded using a Carl Zeiss Crossbeam 540 with GEMINI II Scanning Electron Microscope. Water contact angles (CA) of the initial PU and prepared PU/$MgFe_2O_4$/RGO/SO sponges were measured with a Dataphysics Instrument OCA 15EC contact angle analysis system.

2.2. Preparation of GO and RGO

GO was synthesized according to the modified Hummers method [28], as described in [29]. The resulting GO is chemically reduced with hydrazine monohydrate [29].

2.3. Preparation of magnetic $MgFe_2O$ nanoparticles

Magnetic $MgFe_2O_4$ NPs were obtained by the sol-gel method [30], which is described in detail in the work [29].

2.4. Preparation of superhydrophobic magnetic PU sponges

First, the polyurethane sponge was cut into pieces (1.5×1.5×1 cm) and sonicated with acetone and deionized water, respectively, for 30 minutes to remove surface stains and oils. The sponges were then placed in an oven at 80°C for 3 h to dry completely [29].

The dried sponge was immersed in 50 ml of a homogeneous solution containing $MgFe_2O_4$ NPs (130 mg), RGO (0 or 40 mg), SO (40 mg) in hexane under the influence of ultrasound for 7 hours. Finally, the sponge was repeatedly washed with distilled water to remove unreacted solutions, and

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 12 September 2023 doi:10.20944/preprints202309.0684.v1

then dried at 60°C for 12 hours. Mass loading of $MgFe_2O_4$/SO or $MgFe_2O_4$/RGO/SO ranged from 0 to 40 wt.%. The resulting superhydrophobic magnetic sponges were named PU/$MgFe_2O_4$/RGO/SO with RGO and PU/$MgFe_2O_4$/SO without RGO.

The presence of $MgFe_2O_4$, SO and RGO nanoparticles in the prepared superhydrophobic magnetic sponge improves superoleophilic, self-cleaning properties, as well as oil/water separation. With increasing mass loading of $MgFe_2O_4$/RGO/SO and $MgFe_2O_4$/SO, wt.%, the higher was the absorption capacity of the superhydrophobic magnetic sponge. Therefore, all absorption studies were conducted with a maximum load of 40%.

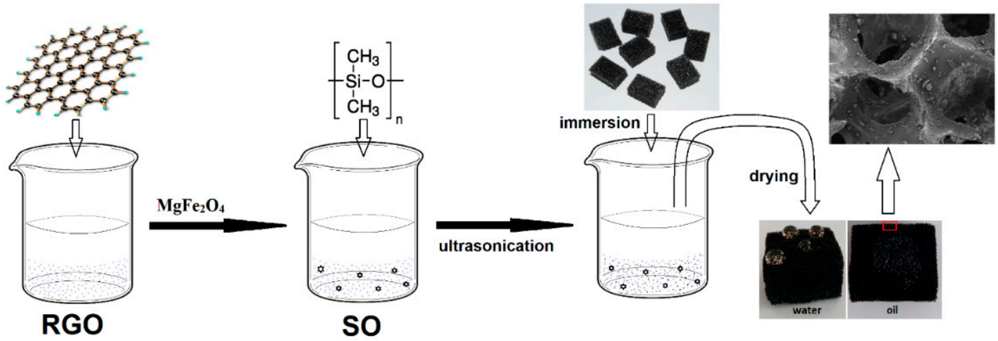

Figure 1. Scheme for obtaining superhydrophobic magnetic materials

2.5. Studies of superhydrophobic/superoleophilic properties

To study the hydrophobic properties of the prepared PU/$MgFe_2O_4$/RGO/SO and PU/$MgFe_2O_4$/SO (loading 40 wt.%) sponge pieces 1.5×1.5×1 cm in size with a known weight were immersed with tweezers in distilled water at room temperature for 10 min. To study the hydrophobic properties of the prepared PU/$MgFe_2O_4$/RGO/SO and PU/$MgFe_2O_4$/SO (loading 40 wt.%) sponge pieces 1.5×1.5×1 cm in size with a known weight were immersed with tweezers in distilled water at room temperature for 10 min.

2.6. Testing oil/water separation property and oil absorption capacity

To study the oil/water separation property, a modified PU/$MgFe_2O_4$/RGO/SO and PU/$MgFe_2O_4$/SO sponge was immersed in an crude oil/water mixture until completely filled with oil. The sponge was then removed from the surface of the water using a magnetic field to check the weight.

The separation efficiency (R(%)) of the superhydrophobic magnetic sponge for various mixtures of oils and organic solvents was calculated by measuring the weight of the oil before and after absorption according to equation (1):

$$R(\%) = \left[\frac{n2-n1}{n0}\right] * 100\% \qquad (1)$$

where, n1, n2 - total mass of oil/water mixed before and after separation, and n0 - the mass of oil before absorption. In total, 20 cycles were carried out and all experiments were performed in triplicate and the mean experimental value reported.

To study the absorption capacity, the modified sponge was immersed in oil or an organic solvent for 20 seconds. After that, each piece of sponges PU/$MgFe_2O_4$/RGO/SO and PU/$MgFe_2SO_4$/SO (40 wt%) was weighed and the oil absorption amount (Q(g/g)) was calculated by the following formula (2):

$$Q\ (g/g) = \frac{m2-m1}{m1} \qquad (2)$$

where m2 and m1 are the masses of the sponge before and after oil absorption. All experiments on the absorption capacity of the sponge were carried out 3 times and the average absorption value was recorded.

3. Results and discussion

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 12 September 2023 doi:10.20944/preprints202309.0684.v1

3.1. SEM morphology analysis of new superhydrophobic magnetic sponges PU/$MgFe_2O_4$/RGO/SO

The morphology of the new superhydrophobic magnetic sponge before and after modification was studied using SEM. On figure 2 shows SEM images of a new PU/$MgFe_2O_4$/RGO/SO sponge prepared with loadings of 20 and 40 wt.%. As seen in figure 2a, the sponge has a three-dimensional porous structure which is advantageous for liquid absorption. At the same time, the prepared superhydrophobic magnetic sponge had the same porous structure after modification [31], which means that the modification does not destroy the porous structure of the sponge (figure 2b, c). Also, compared with the smooth surface of the original sponge, it is clearly seen that the 3D skeleton of the sponge modified with PU/$MgFe_2O_4$/RGO/SO has become uneven, rough, and has a rougher structure. In turn, as the content of $MgFe_2O_4$/RGO/SO increases from 0 to 40 wt %, the 3D sponge skeleton becomes more uneven and rough. The unevenness and roughness of the surface is of great importance for the preparation of an excellent hydrophobic and oleophilic surface. The results showed that the superhydrophobic $MgFe_2O_4$/RGO/SO magnetic NPs are well and uniformly distributed over the entire surface of the PU sponge.

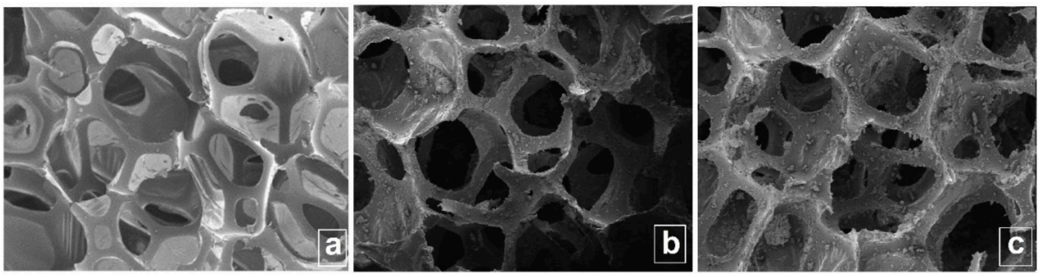

Figure 2. SEM images of a) unmodified PU sponge, b) 20 wt.% and c) 40 wt% modified with $MgFe_2O_4$/RGO/SO sponges.

3.1. Hydrophobic and oleophilic properties of new superhydrophobic magnetic sponges PU/$MgFe_2O_4$/SO, PU/$MgFe_2O_4$/RGO/SO

The separation of oil and water usually touches the interface, and the development of new materials with special wettability is an effective strategy. To assess the wettability of the surface of the sponges, the water contact angle (WCA) was measured by placing drops of oil and water on the surface of an unmodified PU sponge (figure 3a), 20% wt. (figure 3b) and 40% wt. (figure 3c) modified with $MgFe_2O_4$/RGO/SO sponges [32]. The results showed that the unmodified PU sponge had high hydrophilic properties based on the shape of the water drop (figure 3a). Also, on the surface of the 20% wt. and 40% wt. modified with $MgFe_2O_4$/RGO/SO sponges, the waterdrop remained stable, which proves that they exhibit good hydrophobic properties. The WCA were about 90° (unmodified PU sponge, figure 3a) 148.5° (20 wt%, figure 3b) and 157° (40 wt%, figure 3c).

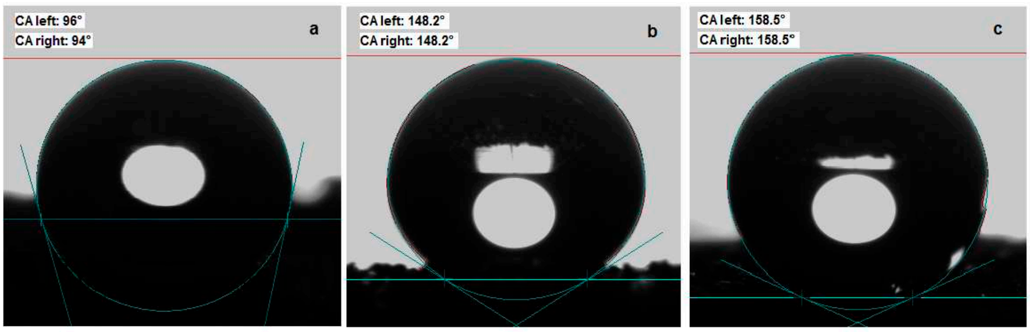

Figure 3. Water contact angle on the a) unmodified PU sponge, b) 20 wt.% and c) 40 wt% modified with $MgFe_2O_4$/RGO/SO sponges.

Also, photographs were taken to determine the hydrophobicity and oleophilic wettability of the modified with $MgFe_2O_4$/RGO/SO sponge. As seen in figure 4, a drop of water on the surface of the

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 12 September 2023 doi:10.20944/preprints202309.0684.v1

modified sponge stands in the form of a ball and can easily roll off the surface, showing superhydrophilic property [33]. On the contrary, when a drop of crude oil was dropped onto the surface of the sponge, the drop of oil very quickly completely absorbed and penetrated into the interior of the modified sponge, which in turn indicates excellent oleophilic properties. The contact angle of the oil was about 0°. The results also showed that with an increase in the loading of $MgFe_2O_4$/RGO/SO, an increase in the hydrophobic and oleophilic properties of the sponges occurs.

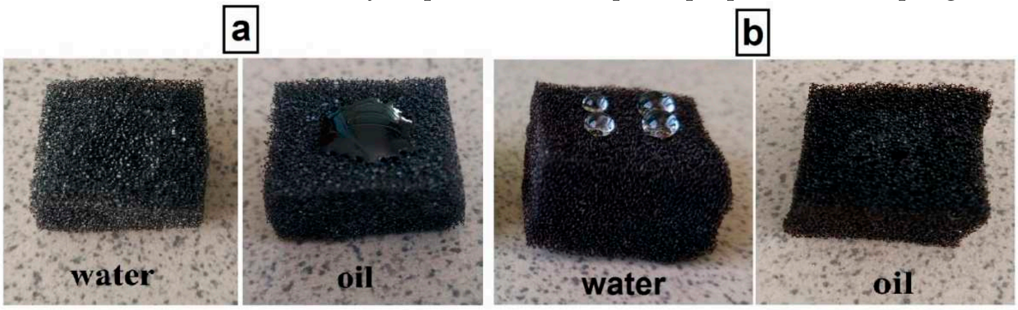

Figure 3. Photographs of drops of water and oil on a) unmodified PU sponge; b) modified sponge PU/$MgFe_2O_4$/RGO/SO (load $MgFe_2O_4$/RGO/SO 40 wt %).

Also, to determine the hydrophobicity, the modified sponges PU/$MgFe_2O_4$/SO, PU/$MgFe_2O_4$/RGO/SO were immersed in water for 10 minutes at room temperature with the action of an external force with tweezers. The figure shows a modified sponge immersed in water, as a result of a homogeneous air gap between the hydrophobic surface and water, had a typical silver mirror surface [34]. In addition, before immersion, it floated on the water surface due to its light weight and hydrophobic property (figure 5). Also, after the action of the external force was stopped, the modified sponge immediately floated to the surface of the water again, in addition, the water was not absorbed into the sponge. The studies were carried out three times and the results indicate a positive effect of RGO on the superhydrophobic properties of the modified sponges PU/$MgFe_2O_4$/SO, PU/$MgFe_2O_4$/RGO/SO.

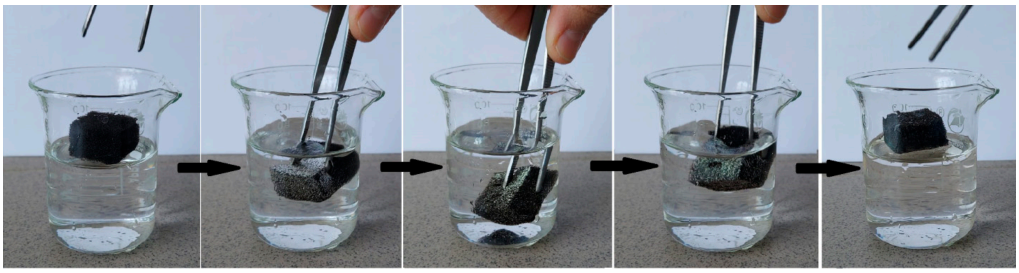

Figure 5. Photographs of a modified PU/$MgFe_2O_4$/RGO/SO sponge (40 wt% $MgFe_2O_4$/RGO/SO loading) immersed in water using tweezers, showing the silver mirror surface (left to right).

3.3. Testing oil/water separation property and oil absorption capacity

New $MgFe_2O_4$ /RGO/SO modified (40 wt% loading) sponge is being tested as an oil-absorbing and recyclable sorbent for wastewater treatment (figure 6), which are important factors for its practical application. Also, in order to investigate the positive effect of RGO on the absorption capacity of the new modified sponge, absorption and recycling experiments were also carried out with a sponge without RGO (e.g. PU/$MgFe_2O_4$/SO sponge, 40 wt.% load) [29].

First, we are investigating the possibility of reusing $MgFe_2O_4$/RGO/SO and $MgFe_2O_4$/SO modified sponges for the selective recovery of crude oil from water by repeated absorption-desorption processes. It is worth noting that the new superhydrophobic sponge had great elasticity and strength, as evidenced by its high absorption capacity after 20 cycles, which gives it a high potential for practical applications [35].

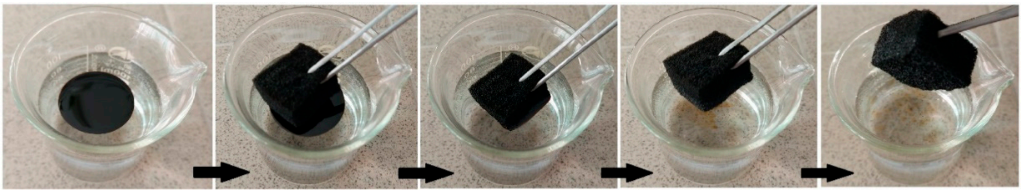

Figure 6. Separation process of oil and water using a superhydrophobic magnetic sponge PU/$MgFe_2O_4$/RGO/SO (load 40 wt.%) and collecting crude oil from the surface of the water.

The dependence of the water contact angle on the absorption cycle of PU/$MgFe_2O_4$/RGO/SO (40 wt %) was also studied (figure 7). The results showed that the received PU/$MgFe_2O_4$/RGO/SO (40 wt %) sponge exhibited a superhydrophobic state after 20 cycles (after 1 cycle 155,5°, 5 cycles 147,5°, 10 cycles 145,6°, 15 cycles 143,8°, 20 cycles 141,9°).

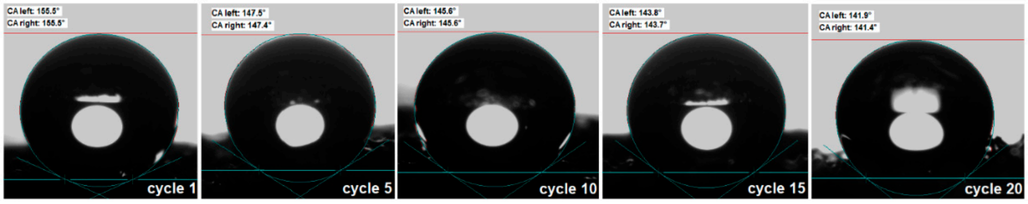

Figure 7. Dependence of water contact angle on absorption cycle of PU/$MgFe_2O_4$/RGO/SO (load 40 wt.%).

And the separation efficiency of the superhydrophobic magnetic sponge was investigated by separating crude oil/water, olive oil/water, toluene/water, ethanol/water mixtures and calculated by equation 1. Figure 6 shows the successful separation of crude oil/water mixture with high efficiency and almost imperceptible oil remaining in water after separation. Also, the magnetic properties of the modified sponge make it easy to move it to the contaminated water area and easy to remove out of the water with a magnet. Calculations of the separation efficiency of the resulting superhydrophobic sponge for various mixtures are shown in Figure 8. It can also be seen that the resulting superhydrophobic magnetic sponge exhibits excellent and efficient crude oil and water separation capability. In particular, the separation efficiency of the prepared superhydrophobic sponges of crude oil/water, olive oil/water, toluene/water mixtures was 97.5%, 89.3%, and 96.7%, respectively. The high separating properties of the obtained sponges can be associated with high porosity, since the small pore size creates strong capillary effects [36].

These claimed superior properties of the new $MgFe_2O_4$/RGO/SO and $MgFe_2O_4$/SO modified PU sponges make them promising candidates for oil/water separation.

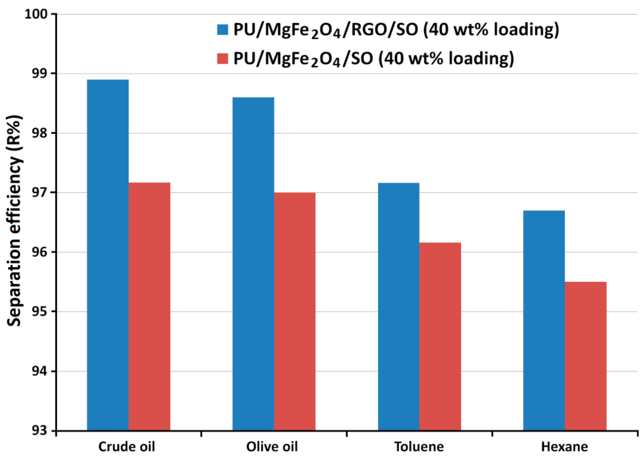

Figure 8. Separation efficiency of prepared superhydrophobic magnetic PU/$MgFe_2O_4$/RGO/SO and PU/$MgFe_2O_4$/SO (40 wt% loading) sponges for various oil/water mixtures.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 12 September 2023 doi:10.20944/preprints202309.0684.v1

Secondly, the absorption capacity of the new modified with $MgFe_2O_4$/RGO/SO and $MgFe_2O_4$/SO (load wt. 40%) PU sponges for olive oil and organic solvents was investigated by the immersion method for 20 seconds. The amount of absorbed olive oil and organic solvents was determined by the mass method according to equation 2. The absorbency of superhydrophobic sponges containing PU/$MgFe_2O_4$/RGO/SO and PU/$MgFe_2O_4$/SO (load 40 wt.%) was tested on various organic solvents with different densities such as hexane, ethanol, acetone, toluene and chloroform, as well as on olive oil. On figure 9 shows the absorption capacities of sponges containing PU/$MgFe_2O_4$/RGO/SO and PU/$MgFe_2O_4$/SO (load 40% by weight) during 5 absorption cycles, each cycle repeated three times. The results show that the resulting superhydrophobic sponge exhibits excellent absorbency (10-20 times its weight in 20 seconds immersion) and after 5 cycles, the absorbency of the sponges for all solvents and oils was almost unchanged. In addition, the absorption capacity also depends on the density, surface layer and viscosity of the absorbed solvent or oil [37].

The porous structure, super hydrophobicity and oleophilicity, as well as excellent mechanical properties provide excellent absorbency for organic solvents and oils, as well as high recyclability [38]. Accordingly, it can be concluded that sponges containing PU/$MgFe_2O_4$/RGO/SO and PU/$MgFe_2O_4$/SO (load 40 wt.%) can presumably become a promising and inexpensive material for practical use in the purification of water contaminated with oil and organic solvents.

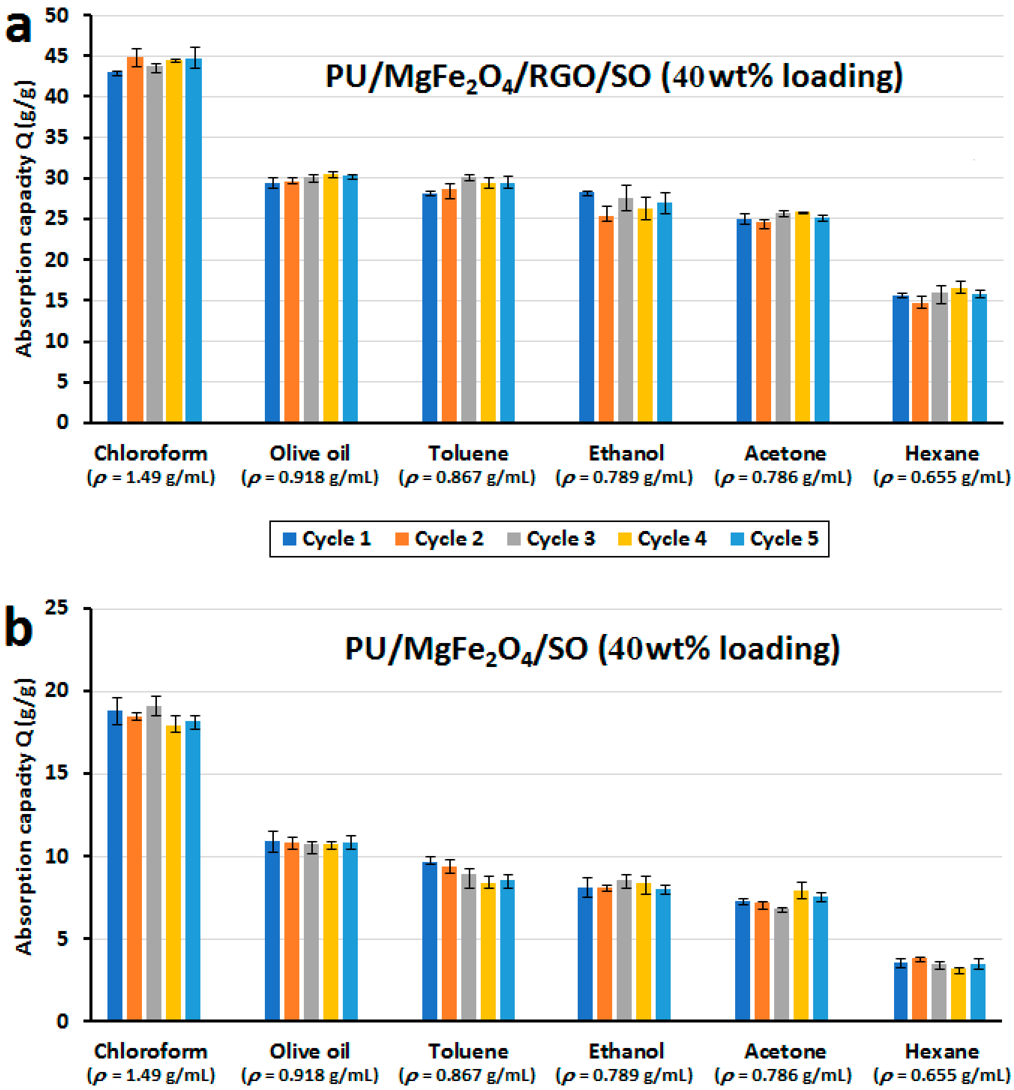

Figure 9. Absorption capacity of superhydrophobic magnetic PU/$MgFe_2O_4$/RGO/SO and PU/$MgFe_2O_4$/SO (40 wt% loading) sponges for oil and various organic solvents.

 doi:10.20944/preprints202309.0684.v1

Third, to further evaluate the performance of a sponge containing PU/$MgFe_2O_4$/RGO/SO (40 wt% loading), we investigated the efficiency of continuous separation of oil/water mixtures using a diaphragm vacuum pump, a rubber tube and a sponge (figure 10a) [39]. With the help of a diaphragm vacuum, a tube connected with a modified sponge, when placed at the oil / water interface, quickly sucks in oil and forms an oil flow in the tube due to its continuous suction, then the oil flows through the tube into a connected glass flask, and the thickness of the oil layer in the glass gradually decreases (figure 10c).

Figure 10b shows that no oil remains on the surface of the water and no water was found in the collected oil, and the separation efficiency is about 99.4%. Separation efficiency was evaluated based on the difference between the mass of oil and water before and after separation. All experiments were carried out three times.

Experimental results showed that the sponge containing PU/$MgFe_2O_4$/RGO/SO (load 40 wt%) has excellent separation efficiency and high selectivity due to its admirable hydrophobicity and lipophilic capacity.

Figure 10. Continuous separation of oil and water of a superhydrophobic PU/$MgFe_2O_4$/RGO/SO magnetic sponge (40 wt %) sponge using a diaphragm vacuum pump, a) before separation; (b) after separation; c) during separation.

The absorption capacity of absorbents mainly depends on the physical properties of the absorbed substance, such as density and surface tension, as well as on the time it is immersed in these liquids. The new modified with $MgFe_2O_4$/RGO/SO (40 wt % loading) sponge exhibits excellent and fast (immersion time 20 seconds) absorbency for oil and organic solvents (16,61 to 44,86 g/g) while repelling water (water absorption of about 0.5%), as well as a very high separation efficiency of oil and organic solvent/water mixtures (up to 98,9%). The absorption capacities of PU/$MgFe_2O_4$/RGO/SO are quite high compared to other magnetic composites found in the literature (Table 1), indicating competitiveness and high potential interest in the new PU/$MgFe_2O_4$/RGO/SO sponge as a promising candidate for separation of oil and water.

Table 1. Adsorption capacity of various sorbent materials described in the literature.

Material	Adsorbed organics	Q(g/g)	References
PU/$MgFe_2O_4$/RGO/SO sponge	Crude oil, olive oil, chloroform, toluene, ethanol, acetone, hexane		Present work
PU/$MgFe_2O_4$/SO sponge	Olive oil, chloroform, toluene, ethanol, acetone, hexane	3,5-19	Present work

Fe_3O_4-PDMS/MWNTs sponge	Dichloromethane, petroleum ether, hexane, chloroform, tetrahydrofuran, toluene, gasoline	8,5-20	[39]
PDMS sponge	Dichloromethane, toluene, transformer oil	4,3-11	[40]
PU Sponge@Fe_3O @SiO_4 @Fluoropolymer sponge	Petrol, Toluene, Chloroform	17–23	[41]
PU Sponge@Magnesium Stearate@Phenol formaldehyde Resin	Motor oil, Food oil, Paraffin, Gasoline,n-Hexane, Toluene	19–38	[42]
3D macroscopic superhydrophobic magnetic porous carbon aerogel	engine oil, chloroethane and corn oil	10,02–10,83	[43]
TiO_2–PVA sponge	Polyethylene glycol, CCl_4, liquid paraffin, *N*, *N*-dimethylformamide, ethanol, edible oil, and *n*-hexane	4,3 -13,6	[44]
CNT/PDMS-coated PU sponge	Soybean oil, used motor oil, diesel oil, n-hexadecane, gasoline, n-hexane	15-25	[45]

* Tables may have a footer.

4. Conclusions

Superhydrophobic sponges have significant potential for separating oil and water. The disadvantages of most of the methods used for superhydrophobic modification of sponges are environmental hazards, high cost, difficulty in use, and easy destruction of the hydrophobic layer on the surface of the sponge. This article has described an easy and simple method to develop a high performance super hydrophobic sponge with excellent recyclability. The SEM images showed high porosity and roughness of the sponge, confirming that the surface of the sponge was successfully modified with PU/$MgFe_2O_4$/RGO/SO and PU/$MgFe_2O_4$/ SO. The wettability of PU/$MgFe_2O_4$/RGO/SO was studied, and WCAs of sponges increased when loaded up to 20 wt. % (148.5°), as well as when loading up to 40 wt. % (157°), which proves its superhydrophobic properties. And also, experiments on adsorption and cycling showed that sponges with a loading of 40 wt. % PU/$MgFe_2O_4$/RGO/SO and PU/$MgFe_2O_4$/SO showed excellent absorption capacity for various organic solvents and oils (16.61- 44.86 g / g), with an oil-water separation efficiency of up to 97.5%, and the structure of the obtained sponges remains stable after 20 cycles. In addition, PU/$MgFe_2O_4$/RGO/SO and PU/$MgFe_2O_4$/ SO sponges have shown excellent recyclability, and due to their magnetic properties, the sponges can be controlled by a magnet. It is expected that in the future superhydrophobic and superoleophilic sponges containing PU/$MgFe_2O_4$/RGO/SO and PU/$MgFe_2O_4$/SO will be widely used to clean water from oil and organic pollutants.

Author Contributions: Conceptualization, R.K. and G.S.; methodology, R.M.; software, E.S.; validation, R.K. and G.S.; formal analysis, R.K.; investigation, E.S.; resources, G.D.; data curation, R.K.; writing—original draft preparation, R.K.; writing—review and editing, R.K.; visualization, E.S.; supervision, R.K. and G.S.; project administration, R.K.; funding acquisition, R.K. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to acknowledge the support of the Ministry of Science and Higher Education of the Republic of Kazakhstan under Grant No. AP15473575 "A facile method to fabricate graphene-based superhydrophobic magnetic material for oil-water separation".

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Barbier, E.B.; Moreno-Mateos, D.; Rogers, A.D.; Aronson, J.; Pendleton, L.; Danovaro, R.; Henry, L.-A.; Morato, T.; Ardron, J.; Van Dover, C.L. Ecology: Protect the Deep Sea. *Nature* **2014**, *505*, 475–477, doi:10.1038/505475a.
2. Tian, Q.; Liu, Q.; Zhou, J.; Ju, P.; Waterhouse, G.I.N.; Zhou, S.; Ai, S. Superhydrophobic Sponge Containing Silicone Oil-Modified Layered Double Hydroxide Sheets for Rapid Oil-Water Separations. *Colloids Surf A Physicochem Eng Asp* **2019**, *570*, 339–346, doi:10.1016/j.colsurfa.2019.03.031.
3. Wang, J.; Chen, Y.; Xu, Q.; Cai, M.; Shi, Q.; Gao, J. Highly Efficient Reusable Superhydrophobic Sponge Prepared by a Facile, Simple and Cost Effective Biomimetic Bonding Method for Oil Absorption. *Sci Rep* **2021**, *11*, 11960, doi:10.1038/s41598-021-91396-9.
4. Ge, J.; Zhao, H.-Y.; Zhu, H.-W.; Huang, J.; Shi, L.-A.; Yu, S.-H. Advanced Sorbents for Oil-Spill Cleanup: Recent Advances and Future Perspectives. *Advanced Materials* **2016**, *28*, 10459–10490, doi:10.1002/adma.201601812.
5. Liu, Q.; Meng, K.; Ding, K.; Wang, Y. A Superhydrophobic Sponge with Hierarchical Structure as an Efficient and Recyclable Oil Absorbent. *Chempluschem* **2015**, *80*, 1435–1439, doi:10.1002/cplu.201500109.
6. Guselnikova, O.; Barras, A.; Addad, A.; Sviridova, E.; Szunerits, S.; Postnikov, P.; Boukherroub, R. Magnetic Polyurethane Sponge for Efficient Oil Adsorption and Separation of Oil from Oil-in-Water Emulsions. *Sep Purif Technol* **2020**, *240*, 116627, doi:10.1016/j.seppur.2020.116627.
7. Yu, T.; Halouane, F.; Mathias, D.; Barras, A.; Wang, Z.; Lv, A.; Lu, S.; Xu, W.; Meziane, D.; Tiercelin, N.; et al. Preparation of Magnetic, Superhydrophobic/Superoleophilic Polyurethane Sponge: Separation of Oil/Water Mixture and Demulsification. *Chemical Engineering Journal* **2020**, *384*, 123339, doi:10.1016/j.cej.2019.123339.
8. Nandwana, V.; Ribet, S.M.; Reis, R.D.; Kuang, Y.; More, Y.; Dravid, V.P. OHM Sponge: A Versatile, Efficient, and Ecofriendly Environmental Remediation Platform. *Ind Eng Chem Res* **2020**, *59*, 10945–10954, doi:10.1021/acs.iecr.0c01493.
9. Yang, L.; Wu, S.; Chen, J.P. Modification of Activated Carbon by Polyaniline for Enhanced Adsorption of Aqueous Arsenate. *Ind Eng Chem Res* **2007**, *46*, 2133–2140, doi:10.1021/ie0611352.
10. Diaz De Tuesta, J.L.; Roman, F.F.; Marques, V.C.; Silva, A.S.; Silva, A.P.F.; Bosco, T.C.; Shinibekova, A.A.; Aknur, S.; Kalmakhanova, M.S.; Massalimova, B.K.; et al. Performance and Modeling of Ni(II) Adsorption from Low Concentrated Wastewater on Carbon Microspheres Prepared from Tangerine Peels by FeCl3-Assisted Hydrothermal Carbonization. *J Environ Chem Eng* **2022**, *10*, 108143, doi:10.1016/j.jece.2022.108143.
11. Huang, S.; Shi, J. Monolithic Macroporous Carbon Materials as High-Performance and Ultralow-Cost Sorbents for Efficiently Solving Organic Pollution. *Ind Eng Chem Res* **2014**, *53*, 4888–4893, doi:10.1021/ie5003558.
12. Zhang, M.; Wang, C.; Wang, S.; Shi, Y.; Li, J. Fabrication of Coral-like Superhydrophobic Coating on Filter Paper for Water–Oil Separation. *Appl Surf Sci* **2012**, *261*, 764–769, doi:10.1016/j.apsusc.2012.08.097.
13. Wen, Q.; Di, J.; Jiang, L.; Yu, J.; Xu, R. Zeolite-Coated Mesh Film for Efficient Oil–Water Separation. *Chem. Sci.* **2013**, *4*, 591–595, doi:10.1039/C2SC21772D.
14. Maria, A.; Zhuldu, K.; Serge, B. Use of Sorbents to Improve Water Quality in the Production of Reconstituted Dairy Products. *Emir J Food Agric* **2022**, doi:10.9755/ejfa.2022.v34.i1.2821.
15. Wang, T.; Bao, Y.; Gao, Z.; Wu, Y.; Wu, L. Synthesis of Mesoporous Silica-Shell/Oil-Core Microspheres for Common Waterborne Polymer Coatings with Robust Superhydrophobicity. *Prog Org Coat* **2019**, *132*, 275–282, doi:10.1016/j.porgcoat.2019.03.051.
16. Wang, S.; Li, M.; Lu, Q. Filter Paper with Selective Absorption and Separation of Liquids That Differ in Surface Tension. *ACS Appl Mater Interfaces* **2010**, *2*, 677–683, doi:10.1021/am900704u.
17. Zhu, X.; Zhang, Z.; Ge, B.; Men, X.; Zhou, X.; Xue, Q. A Versatile Approach to Produce Superhydrophobic Materials Used for Oil–Water Separation. *J Colloid Interface Sci* **2014**, *432*, 105–108, doi:10.1016/j.jcis.2014.06.056.
18. Kim, H.J.; Han, S.W.; Kim, J.H.; Seo, H.O.; Kim, Y.D. Oil Absorption Capacity of Bare and PDMS-Coated PET Non-Woven Fabric; Dependency of Fiber Strand Thickness and Oil Viscosity. *Current Applied Physics* **2018**, *18*, 369–376, doi:10.1016/j.cap.2018.01.017.
19. Drelich, J.; Chibowski, E.; Meng, D.D.; Terpilowski, K. Hydrophilic and Superhydrophilic Surfaces and Materials. *Soft Matter* **2011**, *7*, 9804, doi:10.1039/c1sm05849e.
20. Piperopoulos, E.; Calabrese, L.; Mastronardo, E.; Abdul Rahim, S.H.; Proverbio, E.; Milone, C. Assessment of Sorption Kinetics of Carbon Nanotube-based Composite Foams for Oil Recovery Application. *J Appl Polym Sci* **2018**, 47374, doi:10.1002/app.47374.
21. Wu, J.; Chen, J.; Qasim, K.; Xia, J.; Lei, W.; Wang, B. A Hierarchical Mesh Film with Superhydrophobic and Superoleophilic Properties for Oil and Water Separation. *Journal of Chemical Technology & Biotechnology* **2012**, *87*, 427–430, doi:10.1002/jctb.2746.

22. Wang, C.; Yao, T.; Wu, J.; Ma, C.; Fan, Z.; Wang, Z.; Cheng, Y.; Lin, Q.; Yang, B. Facile Approach in Fabricating Superhydrophobic and Superoleophilic Surface for Water and Oil Mixture Separation. *ACS Appl Mater Interfaces* **2009**, *1*, 2613–2617, doi:10.1021/am900520z.
23. Zhu, Q.; Chu, Y.; Wang, Z.; Chen, N.; Lin, L.; Liu, F.; Pan, Q. Robust Superhydrophobic Polyurethane Sponge as a Highly Reusable Oil-Absorption Material. *J Mater Chem A Mater* **2013**, *1*, 5386, doi:10.1039/c3ta00125c.
24. Kong, S.M.; Han, Y.; Won, N.-I.; Na, Y.H. Polyurethane Sponge with a Modified Specific Surface for Repeatable Oil–Water Separation. *ACS Omega* **2021**, *6*, 33969–33975, doi:10.1021/acsomega.1c05301.
25. Nguyen, D.D.; Tai, N.-H.; Lee, S.-B.; Kuo, W.-S. Superhydrophobic and Superoleophilic Properties of Graphene-Based Sponges Fabricated Using a Facile Dip Coating Method. *Energy Environ Sci* **2012**, *5*, 7908, doi:10.1039/c2ee21848h.
26. Stankovich, S.; Dikin, D.A.; Piner, R.D.; Kohlhaas, K.A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S.T.; Ruoff, R.S. Synthesis of Graphene-Based Nanosheets via Chemical Reduction of Exfoliated Graphite Oxide. *Carbon N Y* **2007**, *45*, 1558–1565, doi:10.1016/j.carbon.2007.02.034.
27. Ali, I.; Basheer, A.A.; Mbianda, X.Y.; Burakov, A.; Galunin, E.; Burakova, I.; Mkrtchyan, E.; Tkachev, A.; Grachev, V. Graphene Based Adsorbents for Remediation of Noxious Pollutants from Wastewater. *Environ Int* **2019**, *127*, 160–180, doi:10.1016/j.envint.2019.03.029.
28. Hummers, W.S.; Offeman, R.E. Preparation of Graphitic Oxide. *J Am Chem Soc* **1958**, *80*, 1339–1339, doi:10.1021/ja01539a017.
29. Kudaibergenova, R.; Ualibek, O.; Sugurbekov, E.; Demeuova, G.; Frochot, C.; Acherar, S.; Sugurbekova, G. Reduced Graphene Oxide-Based Superhydrophobic Magnetic Nanomaterial as High Selective and Recyclable Sorbent for Oil/Organic Solvent Wastewater Treatment. *International Journal of Environmental Science and Technology* **2022**, *19*, 8491–8506, doi:10.1007/s13762-021-03722-3.
30. Zampiva, R.Y.S.; Kaufmann Junior, C.G.; Pinto, J.S.; Panta, P.C.; Alves, A.K.; Bergmann, C.P. 3D CNT Macrostructure Synthesis Catalyzed by MgFe2O4 Nanoparticles—A Study of Surface Area and Spinel Inversion Influence. *Appl Surf Sci* **2017**, *422*, 321–330, doi:10.1016/j.apsusc.2017.06.020.
31. Zhu, Q.; Pan, Q.; Liu, F. Facile Removal and Collection of Oils from Water Surfaces through Superhydrophobic and Superoleophilic Sponges. *The Journal of Physical Chemistry C* **2011**, *115*, 17464–17470, doi:10.1021/jp2043027.
32. Liang, L.; Dong, Y.; Liu, Y.; Meng, X. Modification of Polyurethane Sponge Based on the Thiol–Ene Click Reaction and Its Application for Oil/Water Separation. *Polymers (Basel)* **2019**, *11*, 2072, doi:10.3390/polym11122072.
33. Kim, H.J.; Han, S.W.; Kim, J.H.; Seo, H.O.; Kim, Y.D. Oil Absorption Capacity of Bare and PDMS-Coated PET Non-Woven Fabric; Dependency of Fiber Strand Thickness and Oil Viscosity. *Current Applied Physics* **2018**, *18*, 369–376, doi:10.1016/j.cap.2018.01.017.
34. Wang, N.; Deng, Z. Synthesis of Magnetic, Durable and Superhydrophobic Carbon Sponges for Oil/Water Separation. *Mater Res Bull* **2019**, *115*, 19–26, doi:10.1016/j.materresbull.2019.03.007.
35. Liu, D.; Wang, S.; Wu, T.; Li, Y. A Robust Superhydrophobic Polyurethane Sponge Loaded with Multi-Walled Carbon Nanotubes for Efficient and Selective Oil-Water Separation. *Nanomaterials* **2021**, *11*, 3344, doi:10.3390/nano11123344.
36. Liang, L.; Xue, Y.; Wu, Q.; Dong, Y.; Meng, X. Self-Assembly Modification of Polyurethane Sponge for Application in Oil/Water Separation. *RSC Adv* **2019**, *9*, 40378–40387, doi:10.1039/C9RA05855A.
37. Jamsaz, A.; Goharshadi, E.K.; Barras, A.; Ifires, M.; Szunerits, S.; Boukherroub, R. Magnetically Driven Superhydrophobic/Superoleophilic Graphene-Based Polyurethane Sponge for Highly Efficient Oil/Water Separation and Demulsification. *Sep Purif Technol* **2021**, *274*, 118931, doi:10.1016/j.seppur.2021.118931.
38. Sultanov, F.R.; Daulbayev, Ch.; Bakbolat, B.; Mansurov, Z.A.; Urazgaliyeva, A.A.; Ebrahim, R.; Pei, S.S.; Huang, K.-P. Microwave-Enhanced Chemical Vapor Deposition Graphene Nanoplatelets-Derived 3D Porous Materials for Oil/Water Separation. *Carbon Letters* **2020**, *30*, 81–92, doi:10.1007/s42823-019-00073-5.
39. Turco, A.; Malitesta, C.; Barillaro, G.; Greco, A.; Maffezzoli, A.; Mazzotta, E. A Magnetic and Highly Reusable Macroporous Superhydrophobic/Superoleophilic PDMS/MWNT Nanocomposite for Oil Sorption from Water. *J Mater Chem A Mater* **2015**, *3*, 17685–17696, doi:10.1039/C5TA04353K.
40. Choi, S.-J.; Kwon, T.-H.; Im, H.; Moon, D.-I.; Baek, D.J.; Seol, M.-L.; Duarte, J.P.; Choi, Y.-K. A Polydimethylsiloxane (PDMS) Sponge for the Selective Absorption of Oil from Water. *ACS Appl Mater Interfaces* **2011**, *3*, 4552–4556, doi:10.1021/am201352w.
41. Wu, L.; Li, L.; Li, B.; Zhang, J.; Wang, A. Magnetic, Durable, and Superhydrophobic Polyurethane@Fe_3O_4@SiO_2@Fluoropolymer Sponges for Selective Oil Absorption and Oil/Water Separation. *ACS Appl Mater Interfaces* **2015**, *7*, 4936–4946, doi:10.1021/am5091353.
42. Parsaie, A.; Mohammadi-Khanaposhtani, M.; Riazi, M.; Tamsilian, Y. Magnesium Stearate-Coated Superhydrophobic Sponge for Oil/Water Separation: Synthesis, Properties, Application. *Sep Purif Technol* **2020**, *251*, 117105, doi:10.1016/j.seppur.2020.117105.

 doi:10.20944/preprints202309.0684.v1

43. Dai, J.; Zhang, R.; Ge, W.; Xie, A.; Chang, Z.; Tian, S.; Zhou, Z.; Yan, Y. 3D Macroscopic Superhydrophobic Magnetic Porous Carbon Aerogel Converted from Biorenewable Popcorn for Selective Oil-Water Separation. *Mater Des* **2018**, *139*, 122–131, doi:10.1016/j.matdes.2017.11.001.
44. He, Z.; Wu, H.; Shi, Z.; Kong, Z.; Ma, S.; Sun, Y.; Liu, X. Facile Preparation of Robust Superhydrophobic/Superoleophilic TiO_2 -Decorated Polyvinyl Alcohol Sponge for Efficient Oil/Water Separation. *ACS Omega* **2022**, *7*, 7084–7095, doi:10.1021/acsomega.1c06775.
45. Wang, C.-F.; Lin, S.-J. Robust Superhydrophobic/Superoleophilic Sponge for Effective Continuous Absorption and Expulsion of Oil Pollutants from Water. *ACS Appl Mater Interfaces* **2013**, *5*, 8861–8864, doi:10.1021/am403266v.