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Fabrication of a Superhydrophobic RGO Coated-Polyurethan Sponge for Removing Oil, Organic Solvent, and Gasoline from Water

Thi Phuong Nhung Nguyen*, Trung Tien Phan, Quoc Viet Dang, Huu Thang Vuong
PetroVietnam University, Ba Ria-Vung Tau Province, Viet Nam

*Corresponding author. *Email:* nhungntp@pvu.edu.vn

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ABSTRACT

In recent years, the issue of oil and organic spillage caused by human population growth has become increasingly urgent, not only in Vietnam but also worldwide. Researchers are showing great interest in the research and development of materials capable of selectively absorbing oils and organic solvents while repelling water. In this project, an oil-absorbing material was developed using reduced graphene oxide particles incorporated into a polyurethane (PU) foam base. Utilizing PU sponge as the base material enhances the oil absorption capacity of the material. Graphene oxide was initially synthesized using the Hummers method and then reduced with ascorbic acid to form reduced graphene oxide (RGO). RGO was applied to the sponge with varying loading amounts, ranging from 0 to 254%. Subsequently, the porous material was coated with high-density polyethylene (HDPE) to assess its hydrophobicity and its ability to adsorb oil and organic solvents. The results indicate that the oil and organic solvent absorption capacity of RGO and HDPE coating materials is highest at RGO loading percentages exceeding 64%, yielding absorption rates ranging from 35 to 63 times the weight of the material. Additionally, the contact angle of RGO and HDPE coating materials is approximately 150°, demonstrating the high hydrophobicity of the material.

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1. Introduction

The development of superhydrophobic materials has been a prominent focus in both academic studies and practical industries. A superhydrophobic material or surface is one that displays a contact angle exceeding 150°[1]. Drawing inspiration from the natural superhydrophobic properties observed in lotus leaves, researchers have recognized that crafting artificial superhydrophobic surfaces necessitates a combination of surface roughness or structure alongside careful management of surface energy [2], [3], [4]. Over the past decade, these surfaces have found diverse applications across fields such as anti-corrosion coatings [5], anti-wax treatments [6], self-cleaning mechanisms [7], anti-fog solutions [8], anti-adhesion technologies [9], and water/oil separation [10]. Various methods have been employed to achieve artificial superhydrophobic surfaces, with most techniques relying on two primary principles: creating structured surfaces to amplify surface area and chemically modifying the surface to lower its energy [5] - [10].

On the other hand, the increasing demand for fossil fuels has led to the expansion of fossil fuel infrastructures, resulting in more oil spills and leaks of pollutants. Consequently, the removal of oil, organic solvents, and gasoline from water has garnered significant attention over the years. Various techniques have been employed to separate oil from water, including physical methods such as skimmers, booms, meshes, barriers, and absorbents, chemical methods using dispersants and solidifiers, and biological methods.

Among these environmental remediation strategies for oil spills, mechanical remediation using sorbent materials is considered one of the most efficient [11]. However, conventional absorbents like vegetable fibers, wool fibers, and cotton fibers have drawbacks such as low absorption capacity, poor recyclability, and selectivity [12]. Alternatively, a wide range of synthetic polymer fibers and sponge-like carbonaceous materials [12], such as carbon nanotubes (CNTs) [13] or graphene aerogels [14], have been employed. Despite the high performance of polymer fibers, their production has not been cost-effective. Herein, we present a simple method for preparing a superhydrophobic coating on high-density polyethylene (HDPE) and graphene-reduced-coated polyurethane sponge (HDPE-RGO-coated PU sponge) for the separation of oil, gasoline, and organic solvents from water. Initially, graphene oxide (GO) was synthesized using the Hummer modification method, followed by reduction of the GO powder using ascorbic acid in an ultrasonic machine to produce reduced graphene (RGO), which was then deposited onto the PU sponge. After coating the RGO-coated PU sponge with an HDPE layer, the sponge was utilized to remove oil, gasoline, and organic solvents from water.

2. Materials and Methods

2.1. Materials

Polyurethane sponge, high density polyethylene (HDPE), toluen, ethanol, graphit were analytical grades and were purchased from Xilong company. The materials were used as received without any further purification process.

2.2. Preparation of reduced graphene oxide (R-GO)

GO was produced through the reaction of ascorbic acid with GO (graphene oxide), which had been prepared by chemically exfoliating flake graphite using a modified Hummers' method [15], [16]. Utilizing ultrasonication for 1 hour, a uniform RGO suspension was obtained by dispersing RGO in 15mL of ethanol.

2.3. Preparation of superhydrophobic HDPE-RGO coated PU sponge

The superhydrophobic HDPE-RGO coated PU sponge was prepared by the procedure outlined Figure 1. Typically, a polyurethane (PU) sponge (2×2×2 cm^3) was immersed in 15 mL of ethanol containing RGO particles and sonicated for one hour. The RGO-coated PU sponge was dried before being immersed in 25 mL of toluene containing 2.5 g of high-density polyethylene (HDPE) for 5 minutes. Finally, the modified PU sponge was dried in an oven at 50^{o}C for 6 hours.

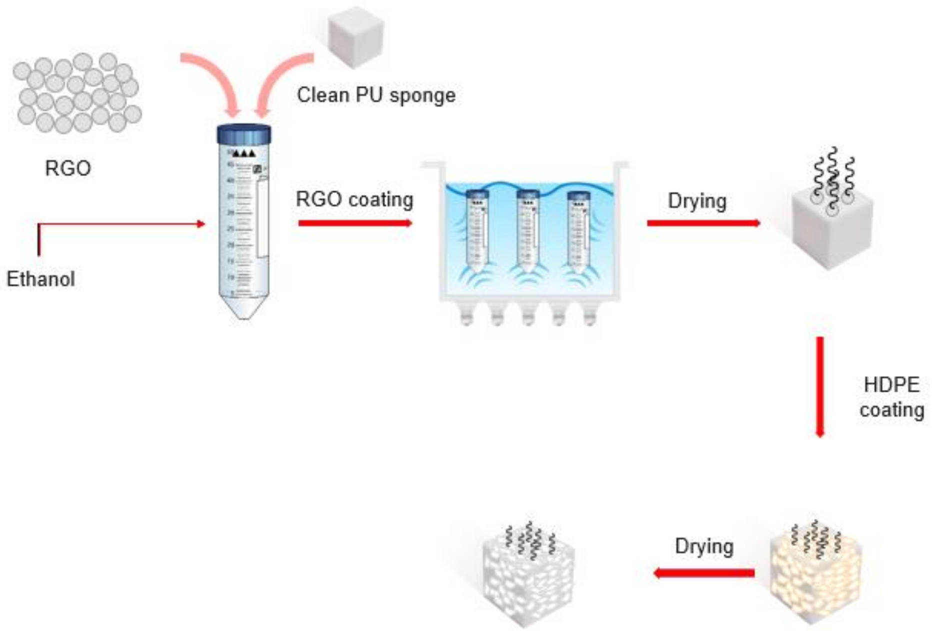


Figure 1. *Process of superhydrophobic sponge preparation*

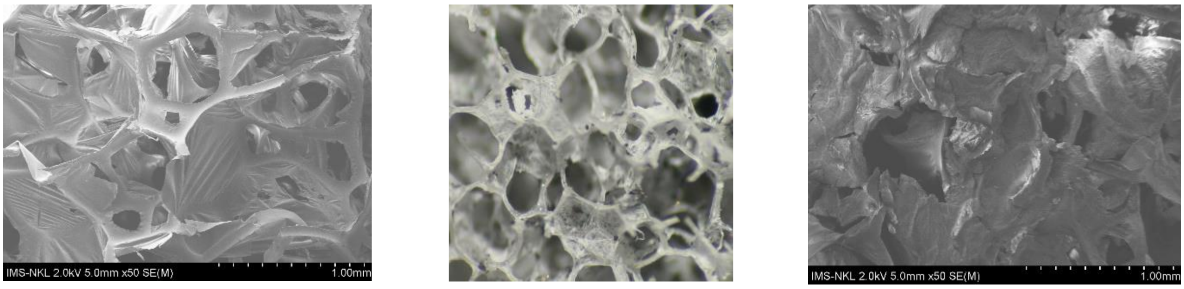
2.4. Sample characterization

The morphology of PU sponge was characterized using a Scanning Electron Microscopy (SEM, JEOL 7600F with EDS, Oxford Instruments). The wetting properties of the RGO particles were evaluated by measuring the static contact angle of water using an OCA-data physics instrument at three different positions on each surface, with a 5 µL distilled water droplet.

3. Results and Discussion

3.1. Morphology of HDPE-RGO coated PU sponge

In this study, a PU sponge is used as the 3D skeleton material to coat RGO, preparing the superhydrophobic sponge. Figure 2 (A) shows the pristine PU sponge with a smooth surface on each "bone," high porosity, and the appearance of tiny membranes between the holes. When RGO is introduced into the PU sponge (Figure 2(B), the original 'bone' surface of the sponge is seen to be uniformly covered by many RGO particles, resulting in a rough surface of RGO-coated PU sponge. However, as shown in Figure 2 (C), it is noted that the addition of HDPE layer coating not only helps to increase the roughness of the skeleton PU sponge but also contributes to decreasing the surface energy of the PU sponge. Both facts are introduced to make the PU sponge more hydrophobic.



(A) (B) (C)

Figure 2. (A) *SEM images of pristine PU sponge, (B) Optical image of RGO coated PU sponge, and (C) SEM images of HDPE-RGO coated PU sponge.*

3.2. Wettability of HDPE-RGO-coated PU sponge

Before applying RGO and HDPE coating, the original PU sponge was superhydrophilic (highly attracted to water). After coating with HDPE or loading RGO onto the PU sponge, it became more resistant to water or hydrophobic, with contact angles of approximately 140° and 135°, respectively. Additionally, both RGO and HDPE coating increased the hydrophobic capacity from hydrophobic to superhydrophobic, with contact angles exceeding 150°. However, varying amounts of RGO powder on the PU sponge affected its hydrophobic properties. This study aimed to understand how different RGO amounts impacted the PU sponge's ability to repel water.

The RGO powder was applied to the PU sponge using a repetitive dipping and drying process, allowing control over the amount of RGO. The amount of RGO was calculated as the ratio of RGO powder weight to sponge weight, expressed as a percentage. After coating both the original PU sponge and the RGO-coated sponge with HDPE, the relationship between RGO amount and water contact angle was examined. According to Figure 3, the water contact angle of the original PU sponge was zero, while for RGO-loaded sponges with less than 64% RGO, the contact angle remained below 150°. At 64% RGO loading, the contact angle exceeded 150°, indicating superhydrophobic surfaces. Further increases in RGO loading did not significantly affect the contact angle, indicating saturation. Consequently, the PU sponge treated with RGO and HDPE exhibited significant resistance to water, with high contact angle values. Thus, the PU sponge with a 64% RGO loading was chosen for further investigation.

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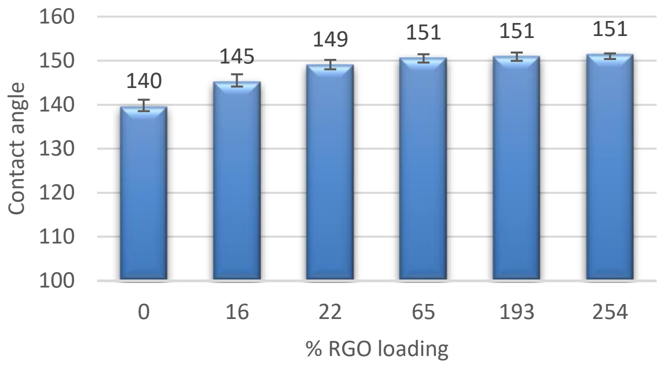
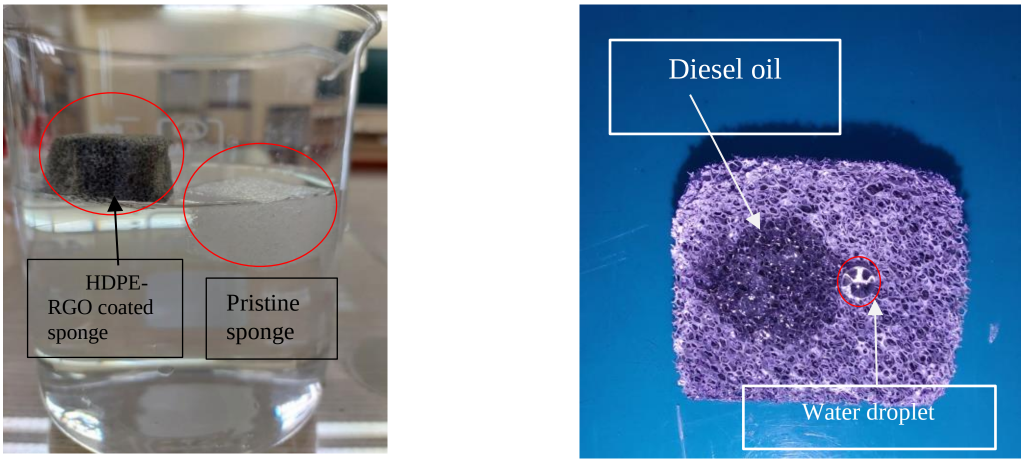


Figure 3. *Effect of RGO loading on the contact angle of PU sponge*

3.3. Application of superhydrophobic HDPE-RGO coated-PU sponge for oil, gasoline, and organic solvent absorption

To compare the hydrophobic properties between the pristine sponge and the modified sponge, both samples were deposited on the water surface, as shown in Figure 4(A). The results show that the sponge coated with modified HDPE-RGO layers floating on the surface of water, whereas the pristine sponge is completely submersion. This is because the sponge becomes superhydrophobic with a contact angle of approximately 151° degrees when coated with modified HDPE-RGO. On the other hand, when a diesel oil droplet is deposited on the superhydrophobic sponge, the diesel oil completely spreads, as shown in Figure 4 (B). The result is opposite with colored water droplet, which stay o the surface of the sponge due to the superhydrophobic properties. Therefore, after coating with modified RGO and HDPE, the sponge becomes both superhydrophobic and superoleophilic. This implies that the modified sponge exhibits high selectivity for oil, gasoline, and organic solvent adsorption.



(A) (B)

Figure 4. *Photograph of sponge to test the hydrophobic and oleophilic behavior:*
(A) Sponge coated with modified HDPE-RGO coating (64%) vs. Pristine sponge on the water surface;
(B) Water droplet and diesel oil droplet on the sponge coated with modified HDPE-RGO coating

Figure 5 illustrates the results of the oil adsorption experiment conducted on the water surface. Remarkably, when 20 mL of oil is spread on the water surface, the HDPE-RGO coated PU sponge exhibits rapid oil adsorption within a mere 2 seconds. Additionally, this modified PU sponge possesses sufficient capacity to store oil droplets at the bottom. Importantly, despite its ability to retain oil, the sponge effectively prevents water droplets from infiltrating the storage space.

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Figure 6 (A) presents the findings regarding the adsorption capacity of the HDPE-RGO coated PU sponge towards oil, gasoline, and organic solvents. The absorption capacities recorded range from 32 to 64 g/g, indicating an exceptional ability of the modified PU sponge to absorb these substances. Interestingly, the results reveal that the HDPE-RGO coated PU sponge exhibits the highest absorption capacity for oil and the lowest for hexane. This variance in absorption capacity may stem from the intricate absorption process, influenced by factors such as surface tension, density, and viscosity of the absorbates. Moreover, Figure 6 (B) depicts the investigation into the absorption recyclability of the modified sponge. Impressively, the absorption capacity remains largely unchanged even after 5 cycles, underscoring the excellent reusability and sustainability of the modified PU sponge. These findings highlight the potential of the HDPE-RGO coated PU sponge as a promising solution for efficient and environmentally friendly oil and organic solvent cleanup applications.

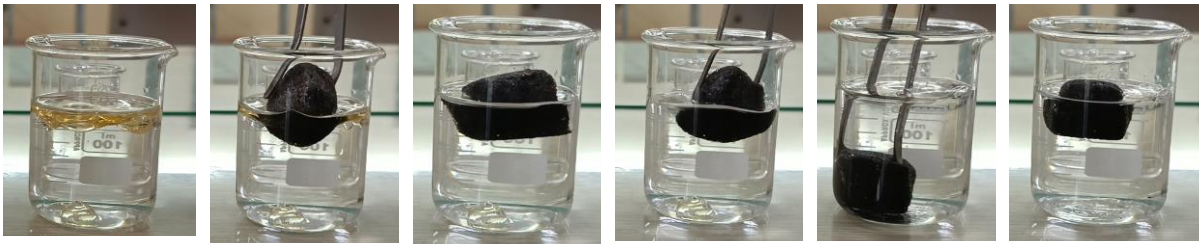

Figure 5. *The sequence image of oil removing from water*

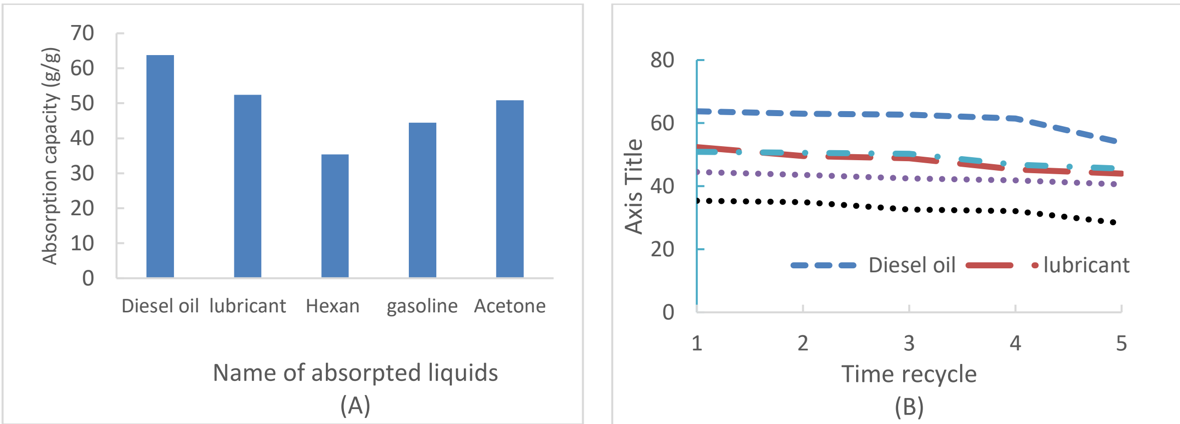

Figure 6. *Absorption capacity of HDPE-RGO coated sponge toward 5 different types of liquids (A), absorption recyclability of HDPE-RGO coated sponge toward 5 different types of liquids (B)*

4. Conclusions

We've successfully created a superhydrophobic HDPE-RGO coated PU sponge using a straightforward and economical synthesis method. Initially, we synthesized graphene oxide (GO) using the Hummer modification approach. Next, we reduced the GO powder with ascorbic acid in an ultrasonic machine to produce reduced graphene (RGO), which we then applied onto the PU sponge. Coating the RGO-coated PU sponge with an HDPE layer rendered it superhydrophobic, boasting a contact angle surpassing 151° and enabling efficient oil/water separation. The absorption capacities observed ranged from 32 to 64 g/g, with swift absorption rates. Additionally, even after undergoing 5 cycles, the absorption capacity remained largely consistent. We anticipate that the HDPE-RGO coated PU sponge holds significant promise for novel applications in sustainable remediation of petroleum contamination.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

REFERENCES

[1] T. Iline-Vul *et al.*, "Engineering of superhydrophobic silica microparticles and thin coatings on polymeric films by ultrasound irradiation," *Mater. Today Chem.*, vol. 21, Aug. 2021, doi: 10.1016/j.mtchem.2021.100520.

[2] J. T. Simpson, S. R. Hunter, and T. Aytug, "Superhydrophobic materials and coatings: A review," *Reports Prog. Phys.*, vol. 78, no. 8, p. 86501, 2015, doi: 10.1088/0034-4885/78/8/086501.

[3] E. C. Cho *et al.*, "Robust multifunctional superhydrophobic coatings with enhanced water/oil separation, self-cleaning, anti-corrosion, and anti-biological adhesion," *Chem. Eng. J.*, vol. 314, pp. 347–357, 2017, doi: 10.1016/j.cej.2016.11.145.

[4] T. Phuong, N. Nguyen, T. V. Nguyen, and P. A. Nguyen, "Micro and nanostructured ZnO-based superhydrophobic steel surface with enhanced corrosion protection."

[5] T. P. N. Nguyen, T. N. T. Nguyen, H. L. Nguyen, T. H. Tran, V. K. Nguyen, and P. A. Nguyen, "Micro/nanostructured ZnO-based superhydrophobic steel surface with enhanced corrosion protection," *Petrovietnam J.*, vol. 6, pp. 59–66, 2022, doi: 10.47800/pvj.2022.06-07.

[6] Z. Wang, L. Zhu, H. Liu, and W. Li, "A conversion coating on carbon steel with good anti-wax performance in crude oil," *J. Pet. Sci. Eng.*, vol. 112, pp. 266–272, 2013, doi: 10.1016/j.petrol.2013.11.013.

[7] S. Yu and H. Li, "Fabrication of superhydrophobic and oleophobic zinc coating on steel surface," *Mater. Sci. Technol. (United Kingdom)*, vol. 33, no. 11, pp. 1290–1297, 2017, doi: 10.1080/02670836.2017.1288675.

[8] J. Zimmermann, F. A. Reifler, U. Schrade, G. R. J. Artus, and S. Seeger, "Long term environmental durability of a superhydrophobic silicone nanofilament coating," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 302, no. 1–3, pp. 234–240, Jul. 2007, doi: 10.1016/j.colsurfa.2007.02.033.

[9] A. K. Kota, G. Kwon, and A. Tuteja, "The design and applications of superomniphobic surfaces," *NPG Asia Mater.*, vol. 6, no. 6, pp. 1–16, 2014, doi: 10.1038/am.2014.34.

[10] J. Huang, M. Yang, H. Zhang, and J. Zhu, "Solvent-Free Fabrication of Robust Superhydrophobic Powder Coatings," *ACS Appl. Mater. Interfaces*, vol. 13, no. 1, pp. 1323–1332, Jan. 2021, doi: 10.1021/acsami.0c16582.

[11] N. T. Duc, N. T. Tung, N. T. Mien, P. Thi, T. Ha, and N. V. Khoi, "Oil-absorbent Materials from graft copolymer of bamboo fiber and alkyl acrylates," (in Vietnamese), vol. 2, no. 1, pp. 10–14, 2015.

[12] S. Gupta and N. H. Tai, "Carbon materials as oil sorbents: A review on the synthesis and performance," *J. Mater. Chem. A*, vol. 4, no. 5, pp. 1550–1565, 2016, doi: 10.1039/c5ta08321d.

[13] C. F. Wang and S. J. Lin, "Robust Superhydrophobic/superoleophilic sponge for effective continuous absorption and expulsion of oil pollutants from Water," *ACS Appl. Mater. Interfaces*, vol. 5, no. 18, pp. 8861–8864, 2013, doi: 10.1021/am403266v.

[14] Y. Luo, S. Jiang, Q. Xiao, C. Chen, and B. Li, "Highly reusable and superhydrophobic spongy graphene aerogels for efficient oil/water separation," *Sci. Rep.*, vol. 7, no. 1, pp. 1–10, 2017, doi: 10.1038/s41598-017-07583-0.

[15] S. Pei and H. M. Cheng, "The reduction of graphene oxide," *Carbon N. Y.*, vol. 50, no. 9, pp. 3210–3228, 2012, doi: 10.1016/j.carbon.2011.11.010.

[16] B. Li, X. Liu, X. Zhang, W. Chai, Y. Ma, and J. Tao, "Facile preparation of graphene-coated polyurethane sponge with superhydrophobic/superoleophilic properties," *J. Polym. Res.*, vol. 22, no. 10, 2015, doi: 10.1007/s10965-015-0832-1.

Nguyen Thi Phuong Nhung is currently a Lecturer at PetroVietnam University. She received a PhD degree from the Lille University in France in 2011. She has published about 20 research articles. Her research focuses on advanced materials, including superhydrophobic and superoleophobic surfaces, corrosion resistance, and chemical surface engineering.

Email: nhungntp@pvu.edu.vn. ORCID: https://orcid.org/0009-0006-5796-7185

Phan Trung Tien is currently Chemical Engineer at Hyosung Vina Chemicals in Vietnam. He is conducting her research under guidance of Dr. Nguyen Thi Phuong Nhung. His research interest focuses on research and manufacture of graphene and high density polyethylene (HDPE) coatings to create hydrophobic materials on Polyurethane (PU).

Email: phantrungtien2001kg@gmail.com. ORCID: https://orcid.org/0009-0006-0460-9413

Dang Quoc Viet, a final-year student majoring in Oil Refining-Petrochemicals at PetroVietnam University in Ba Ria City, Vietnam. He has been conducting research into creating 3D superhydrophobic, oil-absorbent materials, under the supervision of Dr. Nguyen Thi Phuong Nhung.

Email: vietdq10@pvu.edu.vn. ORCID: https://orcid.org/0009-0009-6183-9225

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Vuong Huu Thang is currently final-year undergraduate student in major of Chemical Engineering, PetroVietnam University, Ba Ria City, Vietnam. He is conducting her research under guidance of Dr. Nguyen Thi Phuong Nhung. His research interest focuses on research and manufacture of graphene and high density polyethylene (HDPE) coatings to create hydrophobic materials on Polyurethane (PU).

Email: thangvh10@pvu.edu.vn. ORCID: https://orcid.org/0009-0004-9990-5121