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STUDY OF A MODIFIED MELAMINE SPONGE AND ITS LIPOPHILIC AND HYDROPHOBIC PROPERTIES

ŠTUDIJ MODIFICIRANE MELAMINSKE GOBE IN NJENE LIPOFILNE IN HIDROFOBNE LASTNOSTI

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In this study, silicone rubber and silicone oil were used to modify melamine sponge to obtain lipophilic and hydrophobic properties. The result showed that the modification had no effect on the intrinsic properties of sponges such as the structure and elasticity. After modification, the melamine sponge changed from hydrophilic to superhydrophobic, and the contact angle could reach 155.7°. In addition, this sponge also maintained its good oil-absorption performance and showed its excellent selective oil absorption in an oil-water mixture. Using xylene to simulate pollutants, the oil-absorption rate of the modified sponge could reach 44 g/g while the contact angle and oil-absorption rate of the sponge showed no significant changes after 20 cycles of oil-absorption experiments. The sponge showed a reliable and stable oil-absorption effect after repeated extrusion cycle experiments. The above experiments proved that the modification method and modified sponge have broad application prospects in oil-water separation.

Keywords: superhydrophobicity, oil-water separation, melamine sponge, oily pollutants

V članku avtorji opisujejo uporabo silikonske gume in silikonskega olja za modifikacijo melaminske gobe in analizo njenih lipofilnih in hidrofobnih lastnosti. Rezultati analiz so pokazali, da modifikacija ni imela vpliva na intrinsične lastnosti gobe, kot sta naprimer struktura in elastičnost. Po modifikaciji se je melaminska goba spremenila iz hidrofilne (topne v vodi) v superhidrofobno (močno netopno v vodi) in njen kontaktni kot oz. kot omakanja je lahko dosegel vrednosti do 155,7°. Ne samo to, takšna modificirana goba je tudi ohranila svojo dobro sposobnost absorpcije (vpijanja) olja in imela odlično selektivno sposobnost vpijanja olja v mešanem sistemu voda-olje. Z uporabo ksilena so simulirali onesnaževanje vode in pokazalo se je, da je dosežena hitrost absorpcije olja modificirane gobe 44 g/g in da sta hitrost absorpcije olja in kontaktni kot ostala nespremenjena še po 20 ciklih preizkusov vpijanja olja. Preizkusi z modificirano gobo so pokazali, da ima le-ta zanesljive in stabilne učinke na vpijanje olja tudi med preizkusi ponavljanja z njenim ožemanjem. Opisani preizkusi dokazujejo, da sta metoda modifikacije in modificirana goba potencialno uporabni za ločevanje olja od vode.

Ključne besede: superhidrofobnost, ločitev olja od vode, melaminska goba, oljni onesnaževalci

1 INTRODUCTION

The production and life of human society often produce a large amount of oily wastewater that needs to be treated timely. Whether it is sea water polluted by marine accidents and crude-oil mining, or domestic and industrial wastewater, these wastewaters will destroy human water resources, affect human health and damage the ecological environment of the planet.[1] In the current study, the adsorption-separation method is considered to be the most convenient and effective method for cleaning oily wastewater, which is widely used in production and people's life.[2,3] This method uses the material's selective adsorption of oil and water to achieve a wastewater treatment.[4–6] The lipophilic and hydrophobic sponge is one of the most common materials known for its light weight and compression-resilience property, so it has the potentials of high oil absorption and recyclability.[7–10] The selectivity of oil and water and their stability are important parameters that define the performance of materials.

There are two main methods for improving the hydrophobic ability of sponge materials. One is surface modification with inorganic materials, forming a rough micro/nano-surface, which is similar to the bionic structure of the lotus-leaf surface, thus becoming hydrophobic.[11,12] With a prolonged use of the materials prepared with this method, the presence of interfacial stress will cause the modified layer to fall off and the material properties to deteriorate. The other mechanism is used to modify the surface of a sponge material with hydrophobic and lipophilic groups with low surface energy.[13,14] This method is based on the point of view of atoms or molecules, so the sponge material made in this way has excellent stability. At present, the two natural materials with the lowest surface energy known to mankind are the siloxane- and fluorine-containing materials.[15,16] However, in terms of synthesis, cost and environmental protection,

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the application prospects of the siloxane material is more promising.

In this study, the performance characteristics of room-temperature vulcanized silicone rubber are used to modify the melamine sponge materials in order to prepare sponges with excellent hydrophobic-lipophilic properties and good cycle stability; in this way, a simple and effective method for preparing hydrophobic and lipophilic sponges is developed.

2 EXPERIMENTAL PART

A nano-sponge was modified with the immersion method. Firstly, the sponge base material was obtained by cutting the sponge into square blocks of (20 × 20 × 20) mm (about 0.12 g). They were cleaned with ultrasonic cleaning using pure water and anhydrous ethanol and dried. Then the sponge base material was immersed for 12 h in a modifying solution, made by dissolving uniformly 20 mL of polydimethylsiloxane and 1 g of 107 silicone rubber in 100 mL of toluene. Finally, the soaked sponge was taken out of the modifying solution. The adsorbed modifying solution was removed with centrifugal separation. The sponge was then dried and cured in an oven at 60 °C for 6 h to obtain a modified nano-sponge material.

The morphology of the sample was observed with a scanning electron microscope (Hitachi, SU8010), and its elements were analyzed with a matched energy dispersive spectrometer (EDS).The contact angle of the sample was examined with a contact-angle meter (Kruss DSA30).

For the oil-absorption performance test, xylene was used as the adsorbed oil, and the oil-absorption rate and recycling performance of the modified sponge were examined with immersion and centrifugation. The calculation[17] of oil-adsorption rate n was done with Equation (1):

$$n = \frac{m_1 - m_0}{m_0} \tag{1}$$

In the above formula, m_0 represents the mass of the modified sponge (g) when xylene is not adsorbed; m_1 represents the mass of the modified sponge (g) after xylene is fully adsorbed.

3 RESULTS AND DISCUSSION

Figures 1a and **1b** show the sponge before the modification, and **Figures 1c** and **1d** show the sponge after the modification. The melamine sponge is composed of fibers with a diameter of 5–10 μm. These fibers are interlocked to build a 3D skeleton structure, forming large holes of 50–100 μm so that the melamine sponge has excellent resilience and adsorption capacity. Comparing the electron micrographs before and after the modification, it can be found that the modification process did not cause any significant changes to the overall structure of the material; besides, the surface was covered with colloids after the modification and there was no rough micro/nano-structure on the surface.

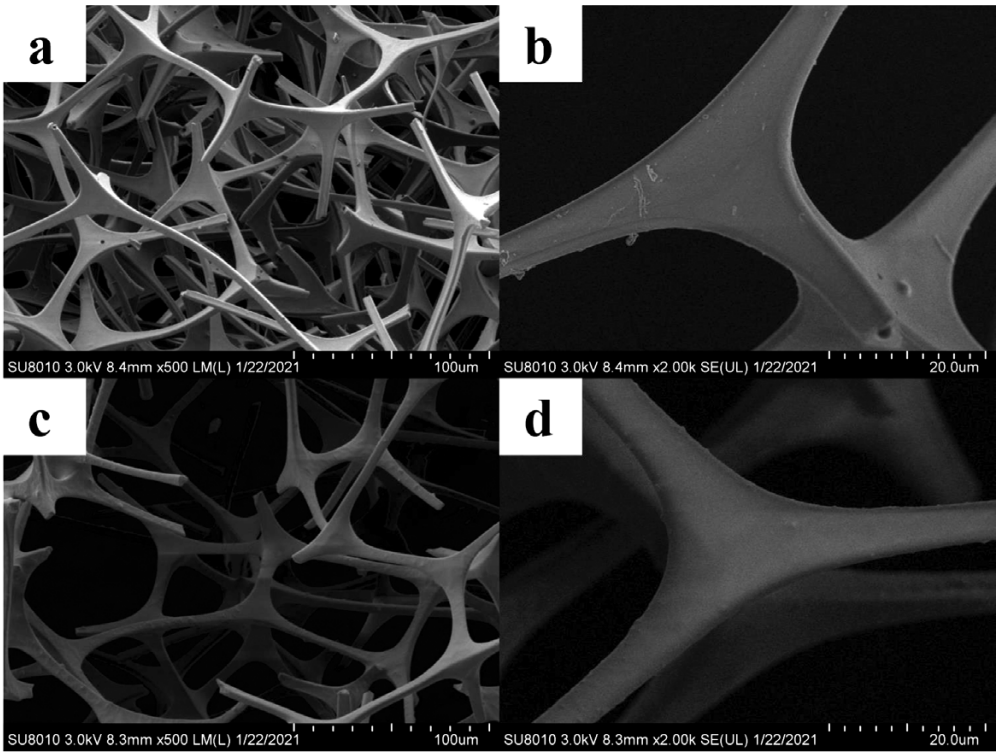

Figure 1: SEM photos of sponge samples: a, b) unmodified sponge and c, d) modified sponge

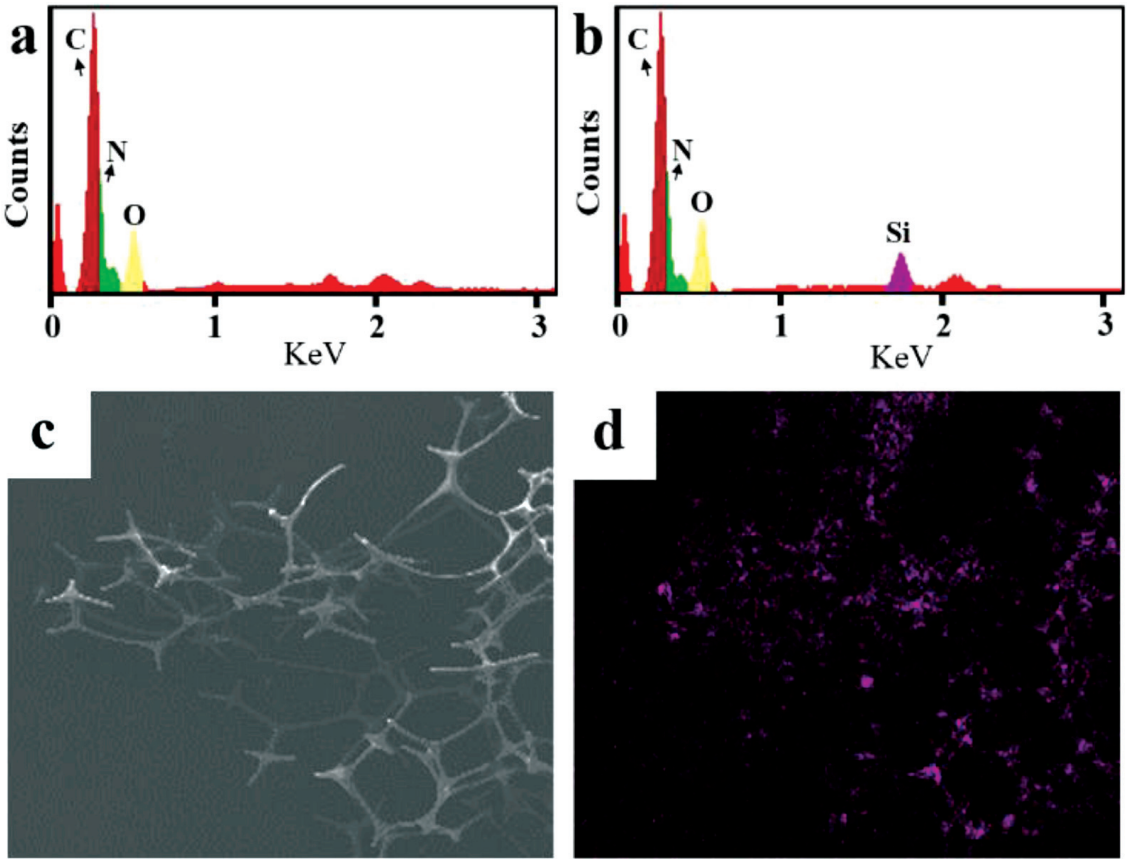

Figure 2: EDS diagrams of: a) unmodified sponge, b) modified sponge and c, d) mapping diagrams of modified sponge

An elemental analysis was done on the unmodified and modified sponges, as shown in **Figure 2**. **Figures 2a** and **2b** show X-ray energy spectra (EDS) before and after the modification. It can be seen that the unmodified melamine sponge is mainly composed of C, N and O. After the modification, the Si element is detected, indicating that siloxane and the melamine sponge had a chemical reaction, which changed the chemical composition of the melamine sponge. It can also be seen from the element-mapping results in **Figures 2c** and **2d** that Si is evenly distributed across the framework of the melamine sponge, which is consistent with the results observed with SEM.

In order to verify the change in the wettability of the sponge before and after the modification, the sponge was placed in water as shown in **Figure 3a**. It can be seen from the experimental phenomena that the unmodified sponge becomes heavier after absorbing water and sinks to the bottom, while the modified sponge does not absorb water and floats on the water surface. When the modified sponge is pressed into the water through external force, the water still cannot infiltrate the sponge, but an air-water interface layer is formed on the surface of the sponge, showing the reflection effect of a silver mirror. As shown in **Figures 3c** and **3d**, water and dyed xylene are dropped onto the unmodified and modified sponges. It can be seen that the unmodified sponge has

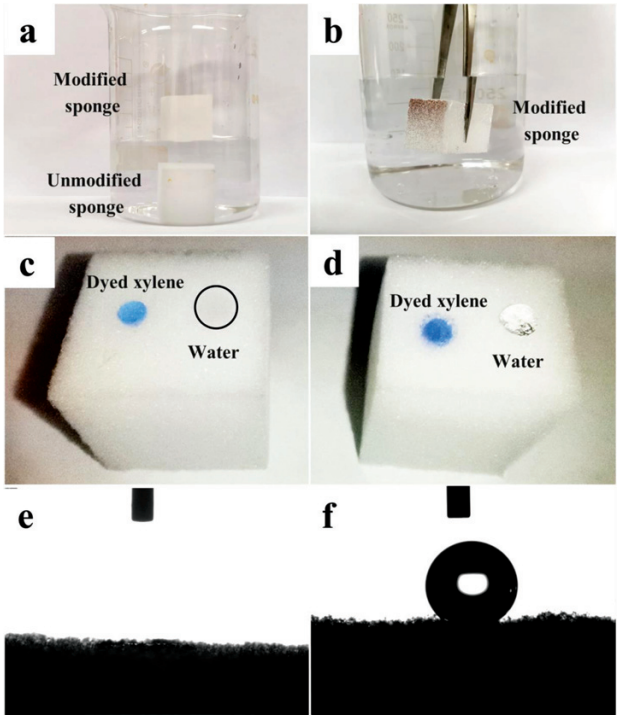

Figure 3: Digital photos of: a) unmodified sponge in water, b) modified sponge in water, c) unmodified sponge with water drops and xylene drops, d) modified sponge with water drops and xylene drops, e) unmodified sponge contact-angle test, f) modified sponge contact-angle test

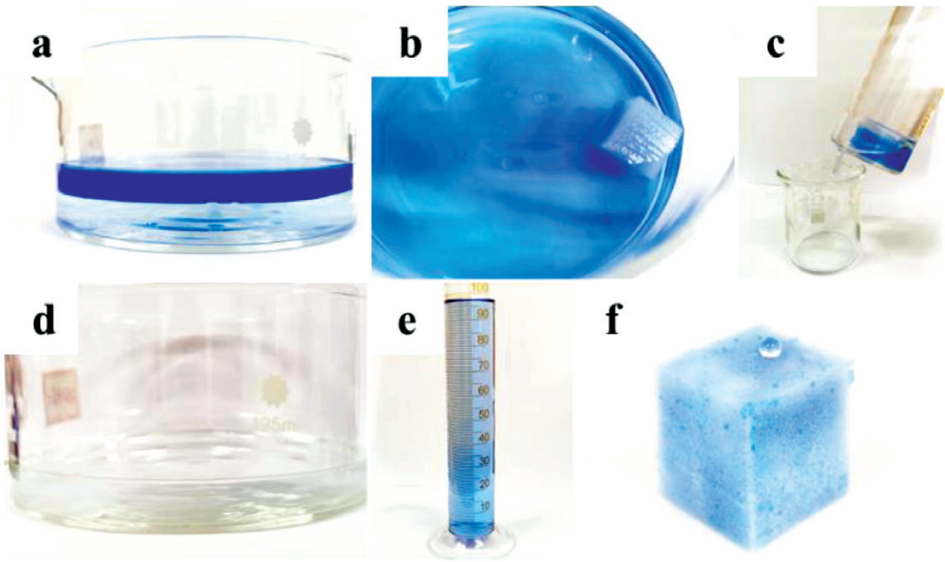

Figure 4: Process of selective adsorption of floating oil on water by modified sponge

good wettability to xylene and water; by contrast, the sponge maintains the wettability to xylene rather than water after modification. In order to evaluate the moistening effect of water precisely, the contact angle was tested. **Figures 3e** and **3f** show the contact-angle test photos of the unmodified and modified sponges. It is obvious that the unmodified sponge is completely hydrophilic, but after modification it is hydrophobic. The contact angle of the modified sponge is 155.7°, reaching a superhydrophobic state.

The modified sponge has superhydrophobic and lipophilic properties, and can selectively adsorb and separate oil from the oil-water mixture. As shown in **Figure 4,** when 100 mL of dyed xylene is added to pure water and the modified sponge is put into it, the dyed xylene is quickly absorbed by the sponge. The absorbed xylene is transferred into a graduated cylinder by squeezing the sponge. The adsorption and extrusion processes are repeated until all the xylene is adsorbed from the water. It can be seen from the experimental phenomena that the recycled xylene in the graduated cylinder is a homogeneous solution without the stratification of an aqueous phase, indicating that the oil-water selectivity of the modified sponge is excellent, while it hardly adsorbs any water. The morphology of the modified sponge after repeated extrusion and adsorption remains stable and still exhibits good hydrophobicity. It shows that the modified sponge can be used for recycling benzene series pollutants while maintaining a stable performance.

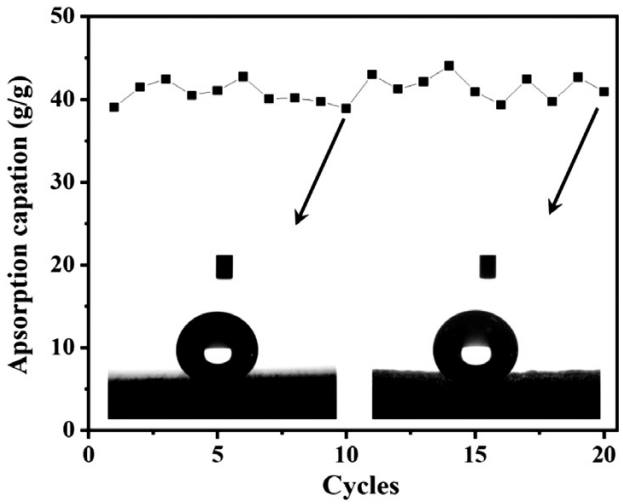

Figure 5: Adsorption-stability test of the modified sponge and xylene, including the contact-angle test of the sponge after the 10th and 20th cycle

After verifying the superhydrophobicity and oil-water selectivity of the modified sponge, the oil absorption rate and stability of the modified sponge were further tested, as shown in **Figure 5**. The modified sponge exhibits excellent oil absorption, reflected in the maximum oil absorption rate that can reach 44 g/g. After 20 cycles, the oil absorption rate remains basically stable, and the fluctuation is due to the loss caused by the sample transfer. The contact angle of the sponge was tested after the tenth and twentieth cycles, as shown in **Figure 5**. After repeated usage, the sponge still maintained superhydrophobic performance without significant degradation. The contact angles were 155.1° and 155.4°, respectively. This experiment shows that the modified sponge exhibits an excellent oil absorption rate and excellent stability.

4 CONCLUSIONS

In this paper, the melamine sponge is modified with a toluene solution of polydimethylsiloxane and silicone rubber. The research results show that hydrophobic siloxane becomes attached to the surface of the modified sponge with superhydrophobic and lipophilic characteristics. Their contact angle reaches 155.7°. Through the adsorption of the oil-water mixture, it is proven that the

modified sponge exhibits excellent oil-water selectivity. At the same time, the oil absorption rate is high, reaching 44 g/g; there is no significant change after 20 cycles, and neither is the contact angle significantly degraded. The method is simple, effective and stable, and the modified sponge can be used for the treatment of oil pollutants.

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5 REFERENCES

[1] S. Sui, H. Quan, Y. Hu, M. Hou, S. Guo, A strategy of heterogeneous polyurethane-based sponge for water purification: Combination of superhydrophobicity and photocatalysis to conduct oil/water separation and dyes degradation, J. Colloid Interface Sci., 589 (**2021**), 275–285, doi:10.1016/j.jcis.2020.12.122

[2] V. H. Pham, J. H. Dickerson, Superhydrophobic silanized melamine sponges as high efficiency oil absorbent materials, ACS Appl. Mater. Interfaces, 6 (**2014**), 14181–14198, doi:10.1021/am503503m

[3] A. Stolz, S. Le Floch, L. Reinert, S. M. M. Ramos, J. Tuaillon-Combes, Y. Soneda, P. Chaudet, D. Baillis, N. Blanchard, L. Duclaux, A. San-Miguel, Melamine-derived carbon sponges for oil-water separation, Carbon, 107 (**2016**), 198–208, doi:10.1016/j.carbon.2016.05.059

[4] C.-H. Chung, W.-C. Liu, J.-L. Hong, Superhydrophobic Melamine Sponge Modified by Cross-Linked Urea Network as Recyclable Oil Absorbent Materials, Ind. Eng. Chem. Res., 57 (**2018**), 8449–8459, doi:10.1021/acs.iecr.8b01595

[5] P. Saha, L. Dashairya, Reduced graphene oxide modified melamine formaldehyde (rGOŽMF) superhydrophobic sponge for efficient oil–water separation, J. Porous Mater., 25 (**2018**), 1475–1488, doi:10.1007/s10934-018-0560-0

[6] B. Chen, Z. Dong, M. Zhang, Y. Jia, J. Yang, A Novel Sepiolite-Based Superhydrophilic/Superoleophobic Coating and its Application in Oil-Water Separation, Chem. Lett., 49 (**2020**), 1504–1506, doi:10.1246/cl.200581

[7] Y. Zhang, Q. Zhang, R. Zhang, S. Liu, Y. Zhou, A superhydrophobic and elastic melamine sponge for oil/water separation, New Journal of Chemistry, 43 (**2019**), 6343–6349, doi:10.1039/c9nj00447e

[8] P. Phanthong, P. Reubroycharoen, S. Kongparakul, C. Samart, Z. Wang, X. Hao, A. Abudula, G. Guan, Fabrication and evaluation of nanocellulose sponge for oil/water separation, Carbohydr. Polym., 190 (**2018**), 184–189, doi:10.1016/j.carbpol.2018.02.066

[9] R. M. G. Ahmed, B. Anis, A. S. G. Khalil, Facile surface treatment and decoration of graphene-based 3D polymeric sponges for high performance separation of heavy oil-in-water emulsions, Journal of Environmental Chemical Engineering, 9 (**2021**), 105087, doi:10.1016/j.jece.2021.105087

[10] G. Wang, L. Peng, B. Yu, S. Chen, Z. Ge, H. Uyama, Hierarchically porous sponge for oily water treatment: Facile fabrication by combination of particulate templates and thermally induced phase separation method, Journal of Industrial and Engineering Chemistry, 62 (**2018**), 192–196, doi:10.1016/j.jiec.2017.12.057

[11] H. Niu, Z. Qiang, J. Ren, Durable, magnetic-responsive melamine sponge composite for high efficiency, *in situ* oil-water separation, Nanotechnol., 32 (**2021**), 275705, doi:10.1088/1361-6528/abef2e

[12] G. Birlik Demirel, E. Aygül, Robust and flexible superhydrophobic/superoleophilic melamine sponges for oil-water separation, Colloids Surf. A, 577 (**2019**), 613–621, doi:10.1016/j.colsurfa.2019.05.081

[13] Y. Fang, L. Yan, H. Liu, Facile Preparation of Hydrophobic Melamine Sponges Using Naturally Derived Urushiol for Efficient Oil/Water Separation, ACS Appl. Poly. Mater., 2 (**2020**), 3781–3788, doi:10.1021/acsapm.0c00393

[14] G. W. Wang, J. Y. Niu, T. A. Asoh, H. Uyama, Facile fabrication of an elastics maleic anhydride-grafted polypropylene monolith for oil/water separation, Mater. Today Commun., 21 (**2019**), 100654, doi:10.1016/j.mtcomm.2019.100654

[15] L. Zhang, D. Dong, L. Shao, Y. Xia, T. Zeng, Y. Wang, Cost-effective one-pot surface modified method to engineer a green superhydrophobic sponge for efficient oil/water mixtures as well as emulsions separation, Colloids Surf. A, 576 (**2019**), 43–54, doi:10.1016/j.colsurfa.2019.05.022

[16] Z. Yin, Y. Li, T. Song, M. Bao, Y. Li, J. Lu, Y. Li, An environmentally benign approach to prepare superhydrophobic magnetic melamine sponge for effective oil/water separation, Sep. Purif. Technol., 236 (**2020**), 116308, doi:10.1016/j.seppur.2019.116308

[17] X. Yan, Y. Xie, S. Zhao, X. Sheng, Z. Zhou, Preparation of modified superhydrophobic sponge and its application in xylene leakage recovery, Desalin. Water Treat., 201 (**2020**), 187–194, doi:10.5004/dwt.2020.26066