# Spongy Structures Coated with Carbon Nanomaterials for Efficient Oil/Water Separation

F.R. Sultanov[1,2*], B. Bakbolat[1], Z.A. Mansurov[1,2], Z.M. Azizov[1], S.S. Pei[3], Rabi Ebrahim[3], Ch. Daulbayev[1,2], A.A. Urazgaliyeva[1], M.I. Tulepov[1.2]

[1]Institute of Combustion Problems, Almaty, 172 Bogenbai Batyr st., 050012, Almaty, Kazakhstan
[2]al-Farabi Kazakh National University, al-Farabi ave. 71, 050040 Almaty, Kazakhstan
[3]University of Houston, Center for Advanced Materials, Houston, TX 77204-5004, USA

## Article info

## Abstract

Rapid progress of processing and transportation of oil and petroleum products may cause disaster for environment like oil spill. Oil booms, combustion, and oil skimmer vessels are usually used to clean up the oil spill, but often with poor efficiency and even with undesirable environmental side effects. With obtaining of carbon nanomaterials (CNMs) (graphene, carbon nanotubes) and developing inexpensive technologies for their synthesis it has become perspective to use them for creation of 3D structures which may serve as a hydrophobic sorbents for oil and petroleum products. In this study, sponges coated with carbon nanomaterials were obtained using "dip-coating" method. Walls of commercially available polyurethane (PU) and melamine sponges were coated with reduced graphene oxide (rGO) and multiwalled carbon nanotubes (MWCNTs). The resulting sponges are characterized by excellent mechanical properties, they are superhydprophobic, and they fully repel water and at the same time selectively absorb oil and organic liquids of different densities. We believe that superhydrophobic and superoleophilic sponges, the walls of which are coated with CNMs, are perspective candidates for reusable sorbents for collection of oil and petroleum products from the surface of water and moreover due to its excellent mechanical properties they can serve as a hydrophobic filtering materials for separation of oil from the surface of water.

## 1. Introduction

Aerogels obtained by chemical reduction of GO [1–3], as well as composite aerogels with additives of CNTs [4–6], represent a class of highly porous lightweight materials. Alongside with high porosity and low density, these materials also have good mechanical properties, the ability to repeatedly recover their original shape after mechanical compressions. Aerogels based on CNMs are excellent regenerable and hydrophobic sorbents for organic liquids of different densities [6–9].

However, the high cost of raw materials at the moment and time consuming process of production of aerogels pose a major challenge for creation of new, lower-cost high performance adsorbents based on CNMs. Also an important factor is the possibility of long-term use of sorbents, so applied sorbents must have excellent mechanical properties, ability not to degrade in aggressive environments.

The possibility of using of the existing skeleton with a specific surface morphology and porosity, the walls of which can be coated by CNMs is an interesting and promising direction. Firstly, it can significantly reduce the cost of the final product in view of reduction of consumption of used CNMs, secondly, it significantly reduces complexity of the process of obtaining of these adsorbents, and thirdly, there is a possibility of fast production of these sorbents.

With the growth of oil and petroleum production as well as during transportation, the potential risk of oil spills is becoming stronger. Oil, as well as organic pollutants can be adsorbed by various sorbents, which are used for oil spill recovery, and after sorption, they are usually removed by

mechanical extraction, followed by burning and other specific methods of their processing. They also require high processing time for separation of large quantities of oil and water, while their processing is allocated with a huge amount of evaporated petroleum fractions into the atmosphere, enhancing the greenhouse effect [10–12].

During the research a low-cost method of "dip-coating" was developed for coating the commercially available melamine and PU sponges by carbon nanomaterials in order to create superhydrophobic and thus sorbing organic liquid sponges. These sponges can absorb both water and organic liquids, but after coating their walls with CNMs, particularly with MWCNTs and GO, obtained sponges actively repel water, i.e. become hydrophobic.

## 2. Experimental

GO was obtained from natural graphite using modified Hummer's method [13]. Multiwalled carbon nanotubes (MWCNTs) were purchased in Nanostructured & Amorphous Materials, Inc. (Houston, USA), the purity is 95% and the outer diameter is 20–30 nm. The purchased chemicals were used without further purification.

A commercially avaible sponges (PU and melamine) – kind of porous and hydrophilic material with absorption capacity of both water and oils or organic solvents, were used as a frame for graphene and MWCNTs coatings. Sponges were cleaned ultrasonically in $C_2H_5OH$ (95%) and distilled water and then dried in an oven at 70 °C for 1 h.

For coating these sponges with graphene, they were dipped to dispersion of GO in $NH_3 \cdot H_2O/C_2H_5OH$, where $NH_3 \cdot H_2O$ is acting as a reducing agent for GO, for 2 h. The taken out sponge was dried at room temperature and the dipping procedure was repeated several times till complete saturation of sponge with GO. Finally, the sponge was washed with distilled water and was dried in a vacuum oven at 30 °C for 24 h.

For coating the sponge with MWCNTs a different methodic was used. PDMS solution in acetaldehyde (300 mg in 200 ml, respectively) with 200 mg of MWCNTs was prepaired by ultrasonication for 40 min. Ultrasonically pre-cleaned and dried sponge was dipped in this suspension, taken out and dried at room temperature. The loading of the MWCNT/PDMS nanocomposites on the sponge was controlled by repeating the dipping and drying process. Finally, the MWCNT/PDMS-coated sponge was cured in an oven (120 °C, 6 h).

## 3. Results and discussion

The "dip-coating" method, schematically shown in Fig. 1, was used to coat the walls of sponges. The pre-cleaned by ultrasonic treatment sponge was placed in a dispersion of MWCNTs in ethyl acetate, kept inside for a certain period of time, then removed and dried to constant weight. Since the sponge by itself is lyophilic, i.e. actively adsorbs both organic liquids and water, while absorbing ethyl acetate dispersion with MWCNTs, MWCNTs are deposited and accumulated in its structure. This action was carried out multiple number of times constantly measuring the weight of the dried sample to determine the degree of loading of CNMs into structure of the sponge.

For multiple reuse of these sponges in separation of organic liquids from the water, a strong binding of MWCNTs on the surface of the sponge's wall is required. For this purpose, as "cementing" agent an insoluble polymer, polydimethylsiloxane, into organic solution of which the hydrophobic sponge was immersed was used. After a thermal heating in the inert medium initializing the polymerization of the polymer on the walls of sponge was carried out – thus fastening of CNMs on the surface of walls of sponge.

Figure 2 presents PU sponge before and after coating its walls with MWCNTs followed by polymerization of the surface using PDMS. Figure 2 shows that after coating the walls of the sponge with MWCNTs, its color changed to black.
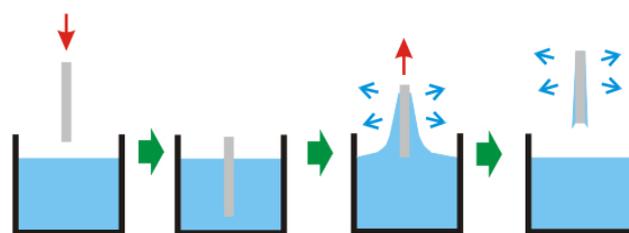


Fig. 1. The schematic illustration of "dip-coating" method.
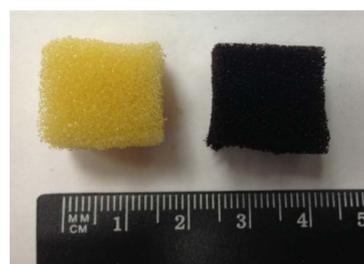


Fig. 2. Photo of PU sponge before treatment (left) and after coating it with MWCNTs (right).
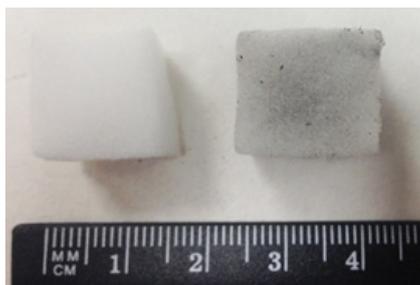
Fig. 3. Photo of melamine sponge before treatment (left) and after coating it with graphene (right).

Coating of walls of sponges by graphene required the methodology that is different from the method of coating with MWCNTs. Ultrasonically pre-cleaned in acetone and distilled water sponge was placed in a GO dispersion in ethanol and ammonium hydroxide, which serves as a reducing agent for GO and was kept there during 2–3 h (Fig. 3).

This procedure was repeated multiple times, after which the sponge was heated at 100 °C in an inert atmosphere of argon for 8 h, followed by thermal reducing of GO, and locking of graphene layers on the walls of the sponge by Van-der-Waals interactions.

The study of mechanical properties of the sponges showed that sponge, coated with MWCNTs is characterized by excellent mechanical properties (the ability to compress and restore its original shape multiple times). These properties are caused by the nature of sponge itself, which can compress and decompress multiple times. It was found that during the mechanical compression of the sponge no CNMs were separated from its surface that indicates complete polymerization of PDMS thus "cementing" of CNMs on the surface.

It was found that after saturation of melamine sponge with CNMs its structure hardened, its mechanical properties (the ability to restore its original shape after compressions) considerably weakened, while PU sponge remained flexible and elastic, restoring its original shape after numerous compressions.

Mechanical properties of resulting spongy materials were studied. Figure 4 shows that after loading of PU sponge coated with MWCNTs by 50 g weight, a complete compression of its structure occurs. However, after compression, the sample of MWCNTs coated sponge is able to easily recover its original shape multiple times, that indicates that coating of the walls of PU sponges with MWCNTs followed by polymerization of its surface using PDMS, does not affect the deterioration of the mechanical properties of the sponge.
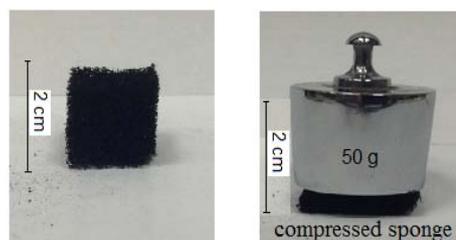


Fig. 4. Illustration of the compression process of PU sponge coated with MWCNTs with loading of 50 g followed by restoring its original shape.
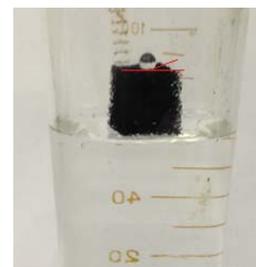


Fig. 5. Study of hydrophobicity of sponges coated with CNMs.

The study of hydrophobicity of the obtained sponges based on CNMs is shown in Fig. 5. PU sponge, coated with MWCNTs easily floats on the surface of water, it does not sink due to high hydrophobicity. Indicated contact angle between a water droplet and the surface of the PU sponge coated with MWCNTs is more than 160º that enables to classify these samples as superhydrophobic.

From SEM images of sponge it is seen that it has a developed pore system with an average pore size ranging from several up to hundreds of microns (Fig. 6a). SEM images of melamine sponges surface show that the morphology of the surface of walls coated with graphene (Fig. 6c) differs from the morphology of the surface of the conventional melamine sponge walls (Fig. 6b). Formation of numerous wrinkles on the walls of the sponge covered with graphene caused by overlapping of thin layers of graphene. The forces of interactions between graphene layers have been converted to $\pi$-$\pi$-interaction from the electrostatic repulsions of functional groups of GO, which lead to binding of graphene layers to the surface of wall of the sponge [14–16].
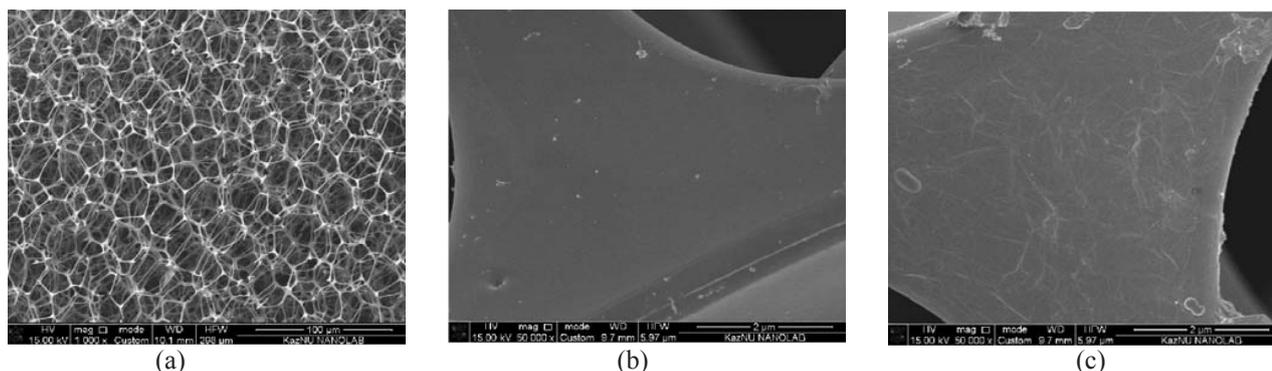
Fig. 6. SEM images of melamine sponge surface coated with graphene: (a) – SEM image of surface of melamine sponge; (b) – SEM image of wall of sponge without coating; (c) – SEM image of wall of sponge coated with graphene.

The sorption capacity of obtained superhydrophobic sponges was investigated by dipping pre-weighted sponge in organic liquid for 20 sec, after which the sponge was removed, shaken and weighed. The amount of adsorbed organic liquid is determined by the difference in mass.

Table 1 shows the sorption capacity of sponges based on PU and melamine coated with MWCNTs for a number of organic liquids of different densities.

Table 1 shows that the sorption values of PU and melamine sponges coated with MWCNTs in regard to organic liquids of different densities do not differ from each other greatly. It is evident that the sorption capacity of the PU sponge is slightly higher compared with melamine sponge that can be attributed to the different pore sizes of two types of sponges. Superhydrophobic sponge in amount of 1 g is able to adsorb about 115 g of chloroform (density is 1.49 $g/cm^3$) or 65 g of volatile acetone (density 0.786 $g/cm^3$).

Investigation of sorption capacity of sponges coated with graphene was carried out for the same organic liquids with the purpose of comparing the obtained quantitative data.

Table 2 shows that the values of sorption capacities of PU and melamine sponges coated with GO are commensurable with values of sorption capacity of those coated with MWCNTs. The sponge coated with GO in amount of 1 g is able to adsorb about 114 g of chloroform or 63 g of acetone.

The obtained experimental data allow to conclude that sorption capacity of sponges coated with MWCNTs is commensurable with the sorption capacity of sponges coated with GO. However, the degree of hydrophobicity of sponges coated with MWCNTs is higher than that of sponges coated with GO. At the same time PU sponge coated with MWCNTs, unlike melamine sponge, showed excellent mechanical properties, it easily compresses and decompresses, what is important for their recovery and multiple reuse. After analysis and comparison of the experimental data, further investigations were carried out with a PU sponge covered with MWCNTs.

Regeneration of sponges coated by CNMs by ignition is impossible in contrast to aerogels based on CNMs, since the melting temperature of PU is 160º, at temperatures above 220º PU begins to decompose.

**Table 1**
The sorption capacity of PU and melamine sponges coated with MWCNTs for a number of organic liquids (in terms of 1 g of sponge)

| Organic liquid | Type of sponge | |
|---|---|---|
| | PU | Melamine |
| Mass of adsorbed acetone, g | 65.2 | 57.4 |
| Mass of adsorbed gasoline, g | 99.3 | 97.1 |
| Mass of adsorbed kerosene, g | 91.5 | 89.0 |
| Mass of adsorbed engine oil, g | 90.8 | 90.2 |
| Mass of adsorbed chloroform, g | 115.2 | 115.0 |
| Mass of adsorbed oil of "Tengiz" deposit, g | 93.2 | 90.4 |

**Table 2**
The sorption capacity of PU and melamine sponges coated with graphene oxide for a number of organic liquids (in terms of 1 g of sponge)

| Organic liquid | Type of sponge | |
|---|---|---|
| | PU | Melamine |
| Mass of adsorbed acetone, g | 63.2 | 61.2 |
| Mass of adsorbed gasoline, g | 94.3 | 94.0 |
| Mass of adsorbed kerosene, g | 90.6 | 90.1 |
| Mass of adsorbed engine oil, g | 91.2 | 90.5 |
| Mass of adsorbed chloroform, g | 114.8 | 113.5 |
| Mass of adsorbed oil of "Tengiz" deposit, g | 91.2 | 91.3 |
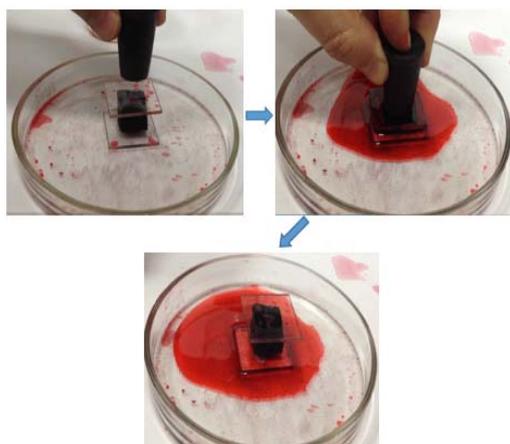
Fig. 7. Illustration of the squeezing process of PU sponge coated with MWCNTs.

The only way, with the exception of heating to 120º in the case of adsorption of volatile organic liquids, is squeezing. With their excellent mechanical properties, the ability to restore the original shape after compression, sponges are perfectly regenerated by squeezing, the process of which is shown in Fig. 7. It is evident that during squeezing most of the adsorbed organic liquid is released, up to 92%. After squeezing, the sponge is able to be used again.

Figure 8 shows the data of recovery of PU sponge coated with MWCNTs that adsorbed kerosene by squeezing. The graph shows that after 10 cycles of adsorption of kerosene, followed by squeezing, the sorption capacity of the sponge is 95.56% of the initial sorption capacity, this suggesting the possibility of their use as water – repelling reusable sorbents.

For development of method for oil spill collection it is more effective to use these materials not as sorbents, but like filtering material, which during the creation of pressure difference are capable to pass organic liquids through their structure, and at the same time repel water.
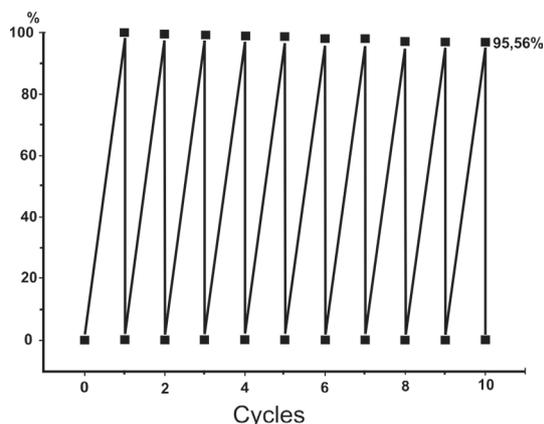


Fig. 8. Regeneration of PU sponge coated with MWCNTs.

## 4. Conclusions

Hydrophobic and oleophilic sponges the wall of which are coated with GO and MWCNTs were obtained by "dip-coating" method. It was found that the coating of walls of sponge by MWCNTs or GO does not affect their mechanical properties, the presence of CNMs on the surface of the sponge significantly increase the hydrophobicity of sponges. It is shown that sorption time of sponges in regard to organic liquids of different densities is fast and they can be easily regenerated by squeezing or heating. Sponges coated with MWCNTs followed by sticking them on the surface using PDMS are more stable to aggressive influences of organic liquids comparing to the GO-coated sponges. After 10 cycles of sorption and desorption of organic liquids the value of sorption capacity of PU sponge coated with MWCNTs is still 95.56% that makes him a promising candidate as a sorbent for oil and water separation. Moreover, strong hydrophobicity and excellent mechanical properties creates the possibility of using them as filtering material, kind of membrane that easily pass organic liquids through its structure and repel water at the same time during the creation of pressure difference (pumping).

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