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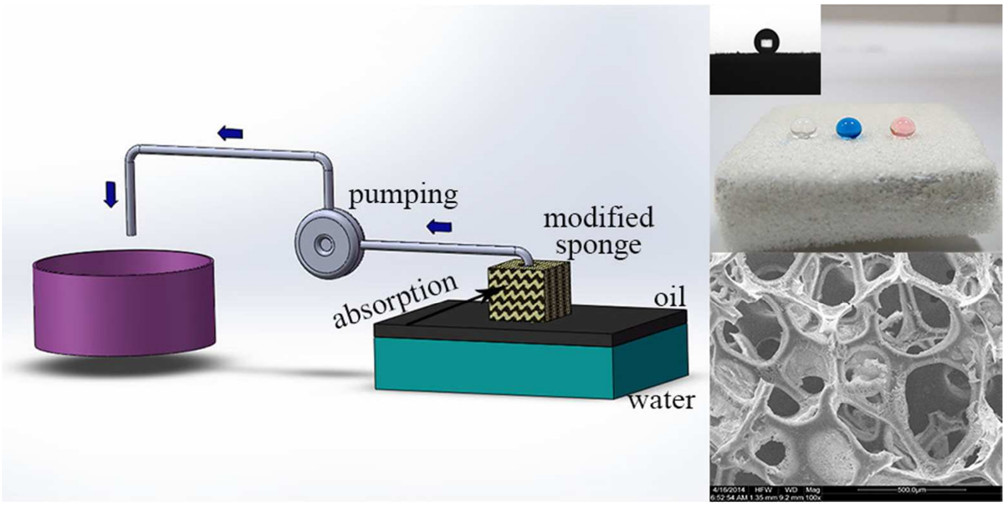

Graphical Abstract

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A Superhydrophobic 3D Porous Material for Spill Oil Cleanup

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Abstract: The spill oil is one serious threat to environment and marine ecosystems, so it is urgent to find an economic and efficient countermeasure to deal with it. In this work, a kind of superhydrophobic 3D porous material is fabricated for spill oil cleanup. Oil is selectively absorbed in the material at first, and then sucked up by a pump. The superhydrophobicity and influencing factors of oil collection rates are studied. The results show that the water contact-angle is 155° and oil collection rate can reach 2.8g/s under appropriate conditions. A plurality of these materials can be connected to a same pump simultaneously, forming a network for oil cleanup. As this 3D material together with the pumping method can realize a consecutive cleanup with high efficiency, it should be thought as a promising candidate in application for spill oil cleanup.

Keywords: superhydrophobic, 3D material, oil, cleanup

Introduction

Oil, as one of the most important and non-renewable energy sources, is usually reported about spillage during exploitation, transport and storage. This spillage always damages the coastal environment and marine ecosystems, as well leads to a severe waste[1]. Thus, it is essential to solve this issue by cleaning and recovering the spilled oil floating on the sea. Currently, the most commonly cleaning techniques include physical absorption by porous materials, oil skimmers, burning, physical diffusion, and biodegradation[2-6]. And some researches about meshes that coated by hydrophobic substances are reported[7-9].

Among these methods, absorption by porous material is considered as a simple, fast and efficient one, and they have attracted broad attention[10-12]. Recently, various high porosity materials, such as carbon nanotube (CNT) sponges, polymethylsilsesquioxane (PMSQ) aerogels sponges, polyurethane (PU) sponges, polypropylene (PP) fibers and graphene aerogels (GA)[13-17], have been reported with good cleaning results and suitable for a wide range of oils. However, oil-absorptions by these absorbent materials are not as good in practice. The preparations of CNT and GA sponges almost require intricate equipment or complicated multi-step synthesis. PMSQ aerogels are susceptible to fracture under squeeze when the high-viscosity oils are absorbed. Actually, polypropylene (PP) fibers are used widely in the practical treatment for oil cleaning because of their low cost and excellent selectivity of oil[16]. However, they also have several drawbacks, such as low loading capability, large volume of PP fibers and difficulty of reusability. PU sponges are also outstanding for their high porosity, durability and buoyancy, along with the deficiencies of original hydrophily[10, 11, 18-23]. Considering the both advantages of PP fibers and PU sponges, we choose to fabricate a superhydrophobic 3D porous material that combines advantages of the both two. Here, we have fabricated a superhydrophobic PU sponge that modified by PP. On the other hand, the methods related to stripping of oil from porous materials are often reported by squeezing[24] or heating[25] or just burning[4]. Actually, these separation methods are always time-consuming or energy-intensive with questionable secondary pollutions, which limit their extensive applications. So, a pumping method with our as-prepared materials is used, through which we realize a continuous collection of spill oils in site from sea[26]. The apparatus of oil cleanup is quite easy-obtained, only including a pump, as-prepared materials and pipes. This superhydrophobic 3D porous material is PU sponge that modified by PP, determining its low cost and facility to obtain.

In the process of oils cleanup by this apparatus, the oils are absorbed upwards spontaneously to the porous material without water and air because of the superhydrophobicity / superoleophilicity and capillary pressures of the porous material. When the absorbed oils are pumped to a container, the oils that floated on water nearby will immediately fill the space of the pumped oils, and then they are also pumped away. By this way, continuous collections process forms. This superhydrophobic 3D porous material with the pumping method will not only make the cleaning process easier, faster, more economical and environmental friendly, but also can be used in a large scale.

Materials

Polyurethane (PU) sponges were obtained from a local store. Polypropylene (PP) was purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Crude oil was obtained from Sinopec Group (Wuhan, China). Acetone, xylene, n-hexane, alcohol were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All chemicals were analytical-grade and used without any further treatment.

Sample preparation

The PU sponges were cleaned ultrasonically with acetone and distilled water successively to remove possible impurities. After drying, the pretreated sponges were immersed in a xylene solution containing PP (1g/100mL and other concentration). And then the solution was squeezed out with little attached on the skeletons. After dried at 120 °C for 2 h, the modified sponges were obtained with the PP anchoring on the skeletons.

Characterization

Scanning electron microscope (SEM) images were obtained by FEI Quanta 200(FEI, Holland). The contact-angles of sponges were measured by DSA 100 (KRŰSS, Germany) using a droplet (10μL) of water. The cleanup of oil was realized by an appliance that composed by a pump, pipes and modified sponges (Figure 1).

RESULTS AND DISCUSSION

The capacity of superhydrophobicity / superoleophilicity

In material preparation process, the PU sponge with open macropores, is easily modified by PP through a dip-coating method. PP is anchored on the skeletons of PU sponge after modification. The modified sponge exhibits its capacity of superhydrophobicity with different kinds of water droplets (pH=1, 7, 14) standing on the surface with spherical shapes (Fig. 2a). It shows that the superhydrophobicity of sponge is excellent no matter in conditions of acids or bases. Because of the buoyancy and superhydrophobicity, it could also float on water easily, and when pressed into water there are many little air bubbles attaching around the surface, forming a mirror-like surface, showing the high repulsive force to water (Fig. 2b). And when the pressure relieves, the sponge returns to water surface with no water absorbed in the sponge. On the other hand, when immersed into crude oil (Fig. 2c) or organic solvent (for example n-hexane) (Fig. 2d), the modified sponges are saturated quickly through the open pores by capillary force, exhibiting its good lipophilicity.

The mechanism of superhydrophobicity / superoleophilicity

To explain the principle of superhydrophobicity of the modified sponge, scanning electronic microscopy (SEM) and water contact-angle are chosen to demonstrate. As shown in Fig. 3, compared with the skeleton of original PU sponge, the modified one is covered with many PP coatings. In high-magnification SEM images (Fig. 3a_2 and Fig. 3b_2), it can be clearly seen that the modified one exhibits some randomly rough coverage, but the original one smooth and flat. The adhesive force between PP and PU sponge is determined by mutual attraction, wettability and cleanliness of sponge surface. The mutual attraction roots in unoccupied hybrid orbital of nitrogen-atoms of PU and electrons of PP.

The superhydrophobicity is estimated by water contact-angle, which is changed from 56° (Fig. 4a) to 155° (Fig. 4b) after the modification of PP. The increase in contact-angle that cause by PP is similar to the reported one in SiO_2-GO[16]. The superhydrophobicity of the sponge is attributable to two reasons, including the low-free-energy, hydrophobic groups of PP, and the roughness morphology that made by coatings of PP. The chains of PP has many hydrophobic groups (-CH_3 and -CH_2-), which determine the low-free-energy of surface and capacity of repelling water. As PP does not cover the skeletons of sponge regularly, the surface of the sponge is rough (Figure 3b_1), and these roughness on multiple scales are very important to the hydrophobicity of the sponges, just like surface protrusions to the hydrophobicity of lotus leaves.

The concentrations of PP and correlation to the properties of the resulted modified sponge (morphology and hydrophobicity) have been shown in ***S.*** 1. With the increase of PP concentrations, the coatings increase. But the water contact-angles increase to a high value (about 150°) and then stay.

Cleanup of oil

As the excellent superhydrophobicity / superoleophilicity of modified sponge, the crude oil is absorbed in the modified sponge in seconds (Fig. 2c). This sponge absorbs oil but not water. The reason is related to the Gibbs energy *ΔG*. When the surface of modified sponge contacts the oil-water mixture, the process can be considered as a spreading process. For the spreading process, according to the Gibbs equation $\Delta G = \gamma^{ls} + \gamma^{l} - \gamma^{s}$ and Young's equation $\gamma^{s} = \gamma^{ls} + \gamma^{l}\cos\theta$, $\Delta G = -\gamma^{l}(\cos\theta - 1)$ is derived, where γ refers to the interfacial tension, θ is contact-angle, the superscripts s and l represent the solid, liquid phase, respectively. With the growth of θ, ΔG increases, making the spreading of water harder. As the water contact-angle is as large as 155°, the $\Delta G > 0$, meaning that water cannot spread spontaneously. So, water cannot permeate in sponge. Similarly, the oil can permeate in sponge easily.

Because of the selective absorption of oil, a method that could timely draw the absorbed oil away is used, which would realize a continuous cleanup. This method is that the absorbed oil is drawn away by a pump (Fig. 5). As shown in Fig. 5a, the upstream side of pipe is inserted into the sponge and the export end is connected to the beaker. When put on the water surface, the superhydrophobic sponge absorbs oil selectively without water. And when the pump is turned on, the oil that absorbed in the sponge is pumped away by the suction force, and the oil nearby fill the place immediately. Then they are also pumped away, by which continuous collections process forms. Because of the superhydrophobicity, when the oil is all pumped away, air, but not water, is absorbed in pores of sponge by the suction force until the collection process finishes. Finally, the crude oil is almost completely cleaned and there is no water pumped in the beaker, which shows its excellent cleanup results (Fig. 5b). In addition, the organic solvent (n-hexane as an example) can also be cleaned from water surface by the same pumping method, with good results (***S.*** 2). As shown in ***S.*** 2, n-hexane is dyed red. There is no red liquid on water surface and no water in the beaker after separation. The simulation of crude oil and organic solvent cleanup are shown in Video **V.** 1 and Video **V.** 2. These two videos show the good results of the superhydrophobic 3D porous sponge. As shown in ***S.*** 3, six sponges are connected to a same pump by six pipes. The spilled oil can be cleaned more quickly by this method. In practical use, more sponges and pumps can be used simultaneously to form a network, which will be quicker for oil cleanup.

Actually, there is always wind and waves on the sea. To simulate the wind and waves on the sea, the oil is dispersed in a wide-mouth container and electric blower is used to produce blow and waves when the cleaning. As a result, oil is cleaned in the condition of wind and waves (***S.*** 4). After the suction of pump, most of the oil is collected, with a little oil dispersing on water randomly. This simulation is shown in Video **V.** 3. It shows that the superhydrophobic 3D porous sponge can clean oil in the condition of wind, accommodating the cleaning on sea.

In addition, after usage, the sponges can be washed by n-hexane and stored up for next use (***S.*** 5). The stabilities of sponges are also measured after usage. The PP coatings before and after oil collection are shown in SEM figures (***S.*** 6). As shown in ***S.*** 6, there are also PP coatings anchoring on the skeletons of sponge. The reusability of this 3D porous material is also measured (***S.***7). It shows that the oil collections rates decrease slightly after 5 times, showing the good reusability of this material.

Oil collection rates

Oil collection rate is an important criterion for evaluation of the superhydrophobic 3D porous sponge and the pumping method. In the separation process, oil is absorbed in sponge through the pores which are considered as many small capillaries. The flow state in sponge pores can be considered as laminar flow approximately. The oil collection quantity can be expressed as Hagen-Poisseuille Equation, $Q = \frac{\pi r^4 (P_1 - P_2)}{8\mu l}$. And in practical use, the pump produces a pressure, the oil collection rate $u = \frac{r^2 (\Delta P_1 + \Delta P_2)}{8\mu l}$ is deduced, where Q is the oil collection quantity, r is radius of sponge pores, $P_1 - P_2$ is differential pressure in pores, μ is the viscosity of the oil, and l is the distance from oil surface to pipe nozzle, u is oil collection rate, ΔP_1 is additional pressure of small capillaries, ΔP_2 is pressure that pump produces.

According to Hagen-Poisseuille Equation, to study the factors which influence oil collection rate, the revolving rate of pump, distance from oil surface to pipe nozzle, superficial area of sponge, pumping time, viscosity of oil are taken into account. As shown in Fig. 6a, the slopes of lines increase as revolving rates increase, and then the lines almost overlap after 50 r/ min. It means that the oil collection rates increase with power of pump at first, and when the revolving rates increase to 50 r/ min, power of pump has no influence on collection rates. This trends is in accord with the experimental results shown in porous materials (SiO_2 nanoparticle /PDMS)[26]. This is because the capillary absorption rate increases to a limit, which results in the main factor that influences the collection rates. Actually, when the power increases to a high value, part of air will permeate into sponge to form an air passage and air is pumped away along with oil. In addition, oil collection rates increase when the distances from oil surface to pipe nozzle decrease (Fig. 6b). Oil collection rates increase when the superficial areas of sponges decrease (Fig. 6c). These two factors are in accord with the Equation, $u = \frac{r^2(\Delta P_1 + \Delta P_2)}{8\mu l}$. As superficial areas and distances decrease, they mean l decrease, and u increase. The reasons of these two factors can be considered that the resistances that oil goes through sponge to pipe nozzle decrease when distance and superficial area decrease. Oil can easily reach pipe nozzle and be pumped away by suction force. Viscosity of oil is also a significant factor to collection rates. As shown in Fig. 6d, the slopes of lines decrease as the viscosities increase, which means the increases in viscosities will decrease collection rate. It also shows that this pumping method is suitable for oils with a wide viscosity range that as high as 840 mPa·s.

The oil collection rates that under different salinity of water are also studied (Figure 7). As the salty of sea is 3.5%, the salty 0, 3.5% and 7.0% are chosen. As shown in Figure 7, the oil collection rates do not change obviously under different salt water in 4 hours cleanup, which means the oil collection rates are not sensitive to the salty of water. It also shows good long-time performance of the sponge. So, in practical use, in order to obtain a high collection rate as well as energy conservation, the power of pump should increase to a suitable value, not too small, nor too big; the size of sponge and distance between oil surface and pipe nozzle should also keep an appropriate low value.

CONCLUSION

In this work, a novel superhydrophobic porous PU sponge is fabricated by a dip-coating method with PP coatings anchoring on the skeletons. Using a pumping method, it has been successfully applied in cleaning spilled oil. The superhydrophobicity capacity and some factors of oil collection rate, such as power of pump, distance between oil surface and pipe nozzle, superficial area of sponge, pumping time, salty of water, oil viscosity are discussed. Compared with the traditional clean technology (spread absorbent over the oil spill site; collect the absorbents; recover oil from the absorbents), the pumping method with superhydrophobic sponge can collect oil consecutively, by which it saves absorbents, labor, operation time, as well as largely decreases the cost. We believe that the proposed superhydrophobic porous PU sponge provides a feasible approach in cleaning the spill oil.

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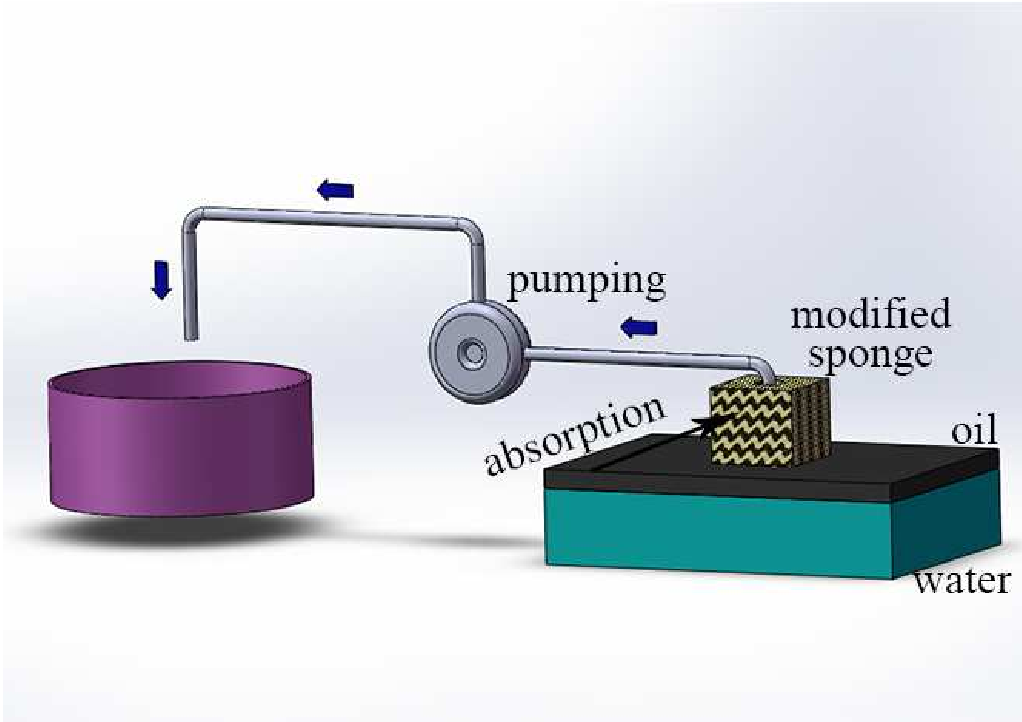

Figure 1: The apparatus for oil collection.

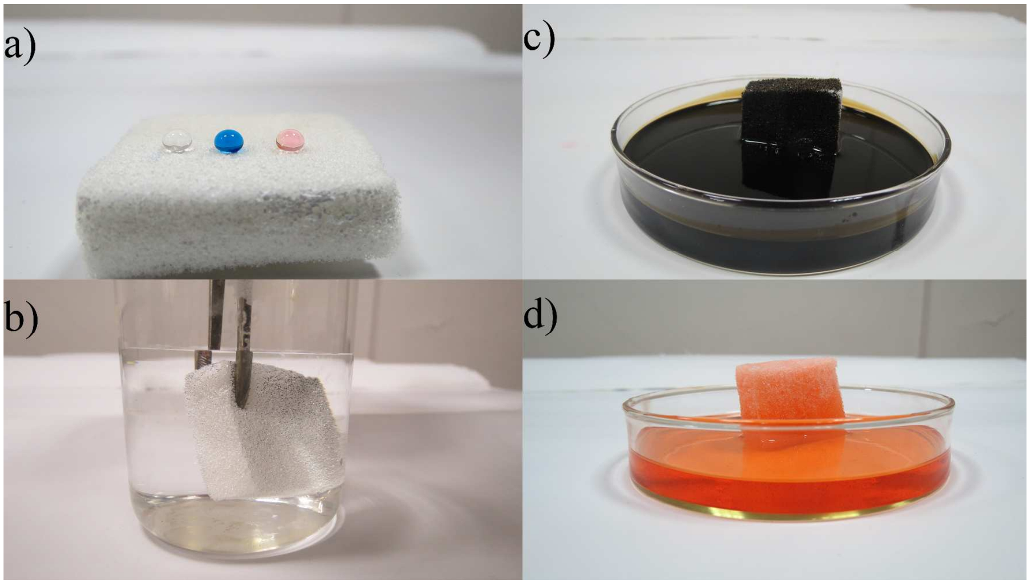

Figure 2: a) Three kinds of water droplets (pH=1, 7, 14) stand on the sponge surface with spherical shapes. b) The modified sponge is pressed into water with small air bubbles attaching around the surface. c) The modified sponge is saturated with crude oil quickly. d) The modified sponge is saturated with organic solvent (n-hexane as an example) quickly.

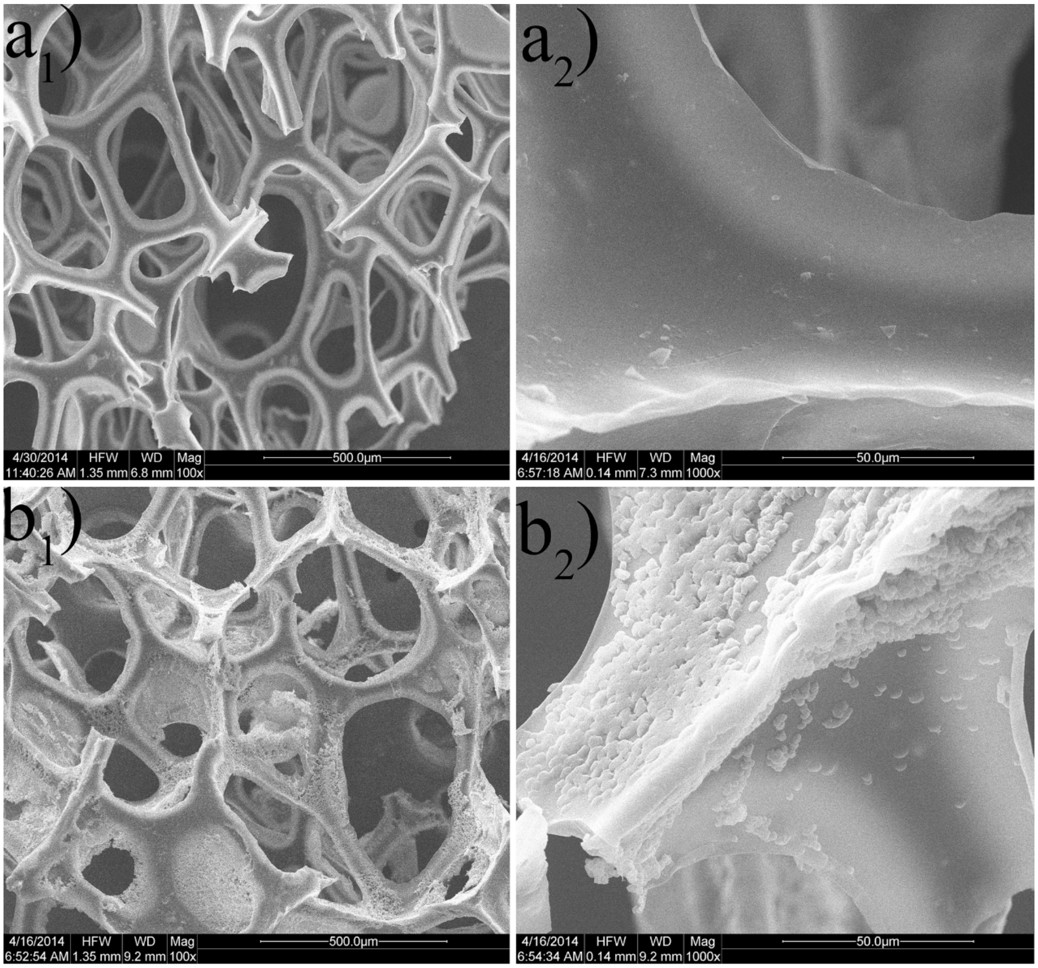

Figure 3: SEM images of PU sponges before (a_1, a_2) and after (b_1, b_2) modification at different magnifications

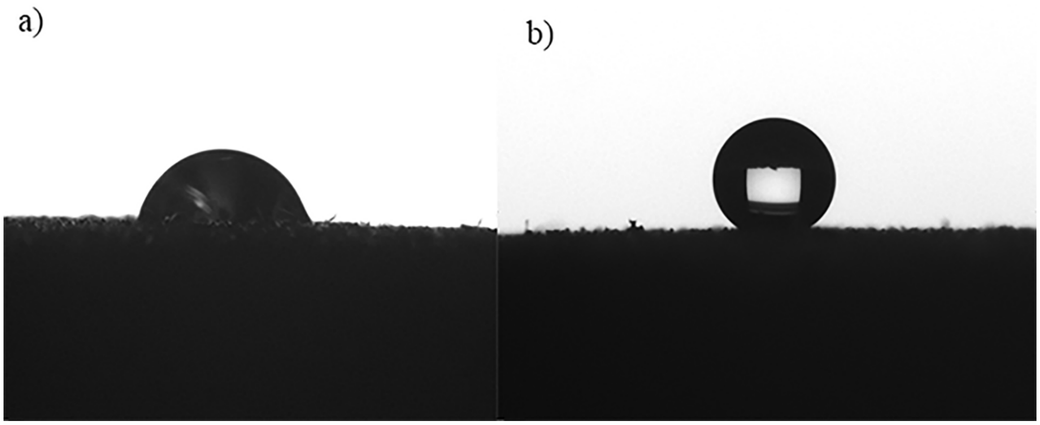

Figure 4: Water contact-angle images of sponges before and after modification.

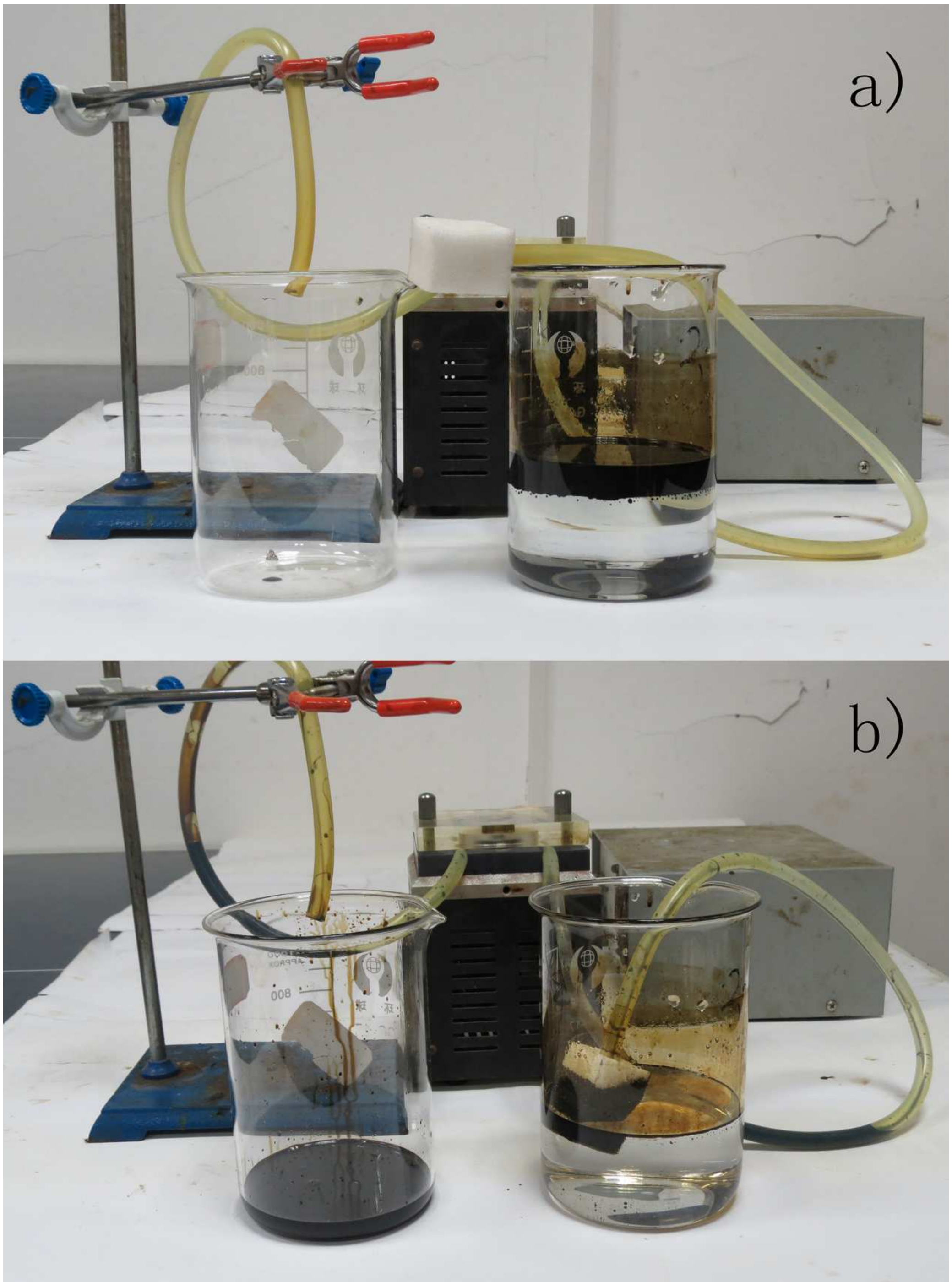

Figure 5: Separation of water and oil by pump.

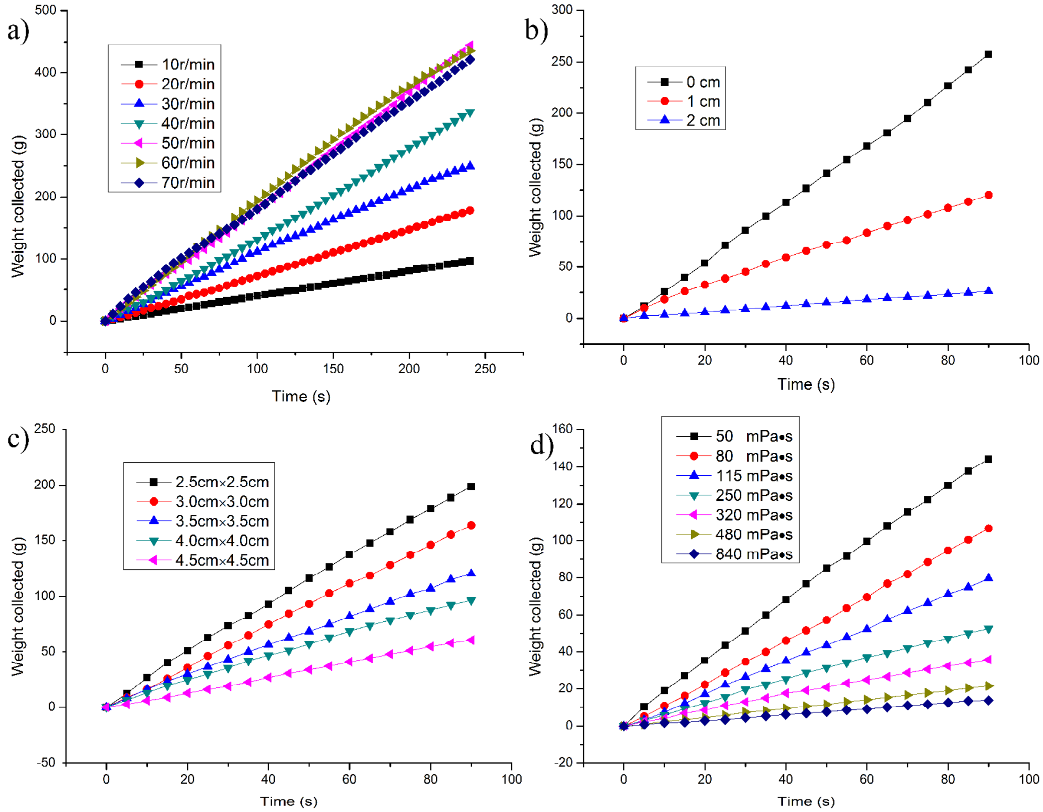

Figure 6: a) Weight collected at different revolving rates of pump. b) Oil collection rates with different distances of oil surface to pipe nozzle. c) Oil collection rates with different superficial area. d) Oil collection rates under different viscosities of oil.

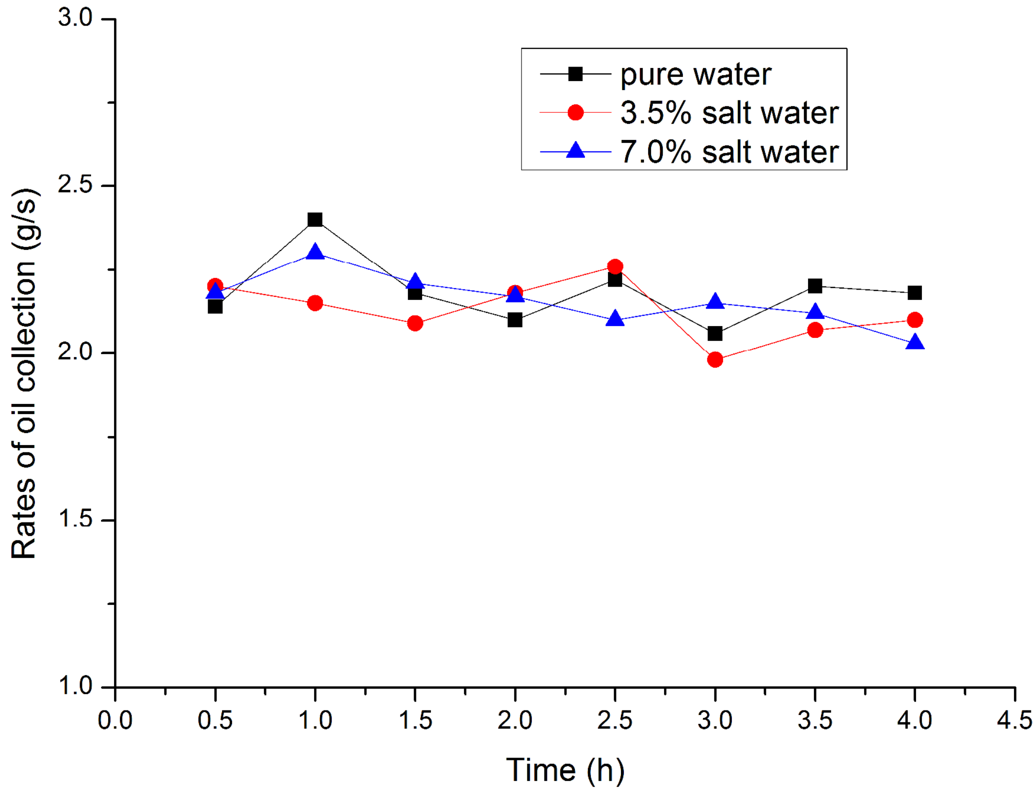

Figure 7: Oil collection rates under different salt water.