

# In situ reduced graphene oxide-based polyurethane sponge hollow tube for continuous oil removal from water surface

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**Abstract** Graphene oxide (GO) was prepared by using the natural graphite as raw materials via the modified Hummers' method and ultrasonic stripping method. GO was reduced online after its anchoring on the surface of polyurethane sponges by a dip-coating method, then in situ reduced graphene oxide-based polyurethane (IRGOPU) sponges were fabricated. The characterizations of IRGOPU sponges were investigated using Field emission scanning electron microscope (FESEM), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and contact angle measurement. The IRGOPU sponges had an adsorption capacity for a broad range of oils up to 21.7 ~ 55 g/g. A simulation experiment of large-scale oil spill using a simple IRGOPU sponge hollow tube component was designed. The process of continuous oil removal from water surface was quick and effective, and the oil/water separation efficiency could be up to 99.6%. The results indicated that the IRGOPU sponge hollow tube may be an optimum candidate for the oil/water separation of large-scale oil spill.

**Keywords** Graphene oxide · PU sponge · Oil/water separation · Continuous oil removal

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## Introduction

The process of oil production, refining, storage, and transportation in petroleum industry often results in the release of large volumes of oil into the ocean and rivers (Alfutaisi et al. 2007; Machín-Ramírez et al. 2008). Oil spill not only causes the loss of energy but also destroys the local ecological environment (Crone and Tolstoy 2010). Therefore, the liquid-liquid separation of oils (including petroleum, gasoline, kerosene, toluene, etc.) and water has attracted researchers' great attention. In the field of oil/water separation, materials with special capacity and micro-nanostructures are often used as oil adsorbent, which is one of the most efficient techniques for oil-spill cleanup (Korhonen et al. 2011). The earliest oil adsorbents are mainly natural materials with porous structure, including activated carbon, bentonite (Ahmad et al. 2005), wheat straw, rice straw, and cotton grass fiber (Suni et al. 2004). These materials are low cost but with low adsorption capacity and poor oil/water selectivity. For this, high oil-adsorptive materials have been extensively developed. High oil-adsorptive materials have the following characteristics: fast oil adsorption, high adsorption capacity, good oil/water selectivity, and reusability (Zhao et al. 2013a). Our group has prepared a variety of methacrylate series functional fibers and nonwovens via the semi-interpenetrating polymer network technique (Feng and Xiao 2006), wet spinning (Feng and Xiao 2004), twin-screw gelation spinning (Xu and Xiao 2011), and melt-blown nonwoven technique (Zhao et al. 2013b). Recently, the graphene (GE) and reduced graphene oxide (RGO)-based materials have been employed for oil/water separation due to their exciting hydrophobic and oleophilic properties (Li et al. 2008; Moon et al. 2010; Rafiee et al. 2010; Stankovich et al. 2007; Zhang et al. 2011), such as carbon aerogel (Sun et al. 2013), spongy graphene (Bi et al. 2012; Niu et al. 2012), and graphene-based sponge (Liu et al. 2013b; Nguyen et al. 2012).

Sun et al. (2013) prepared carbon aerogel via reducing the graphene oxide-carbon nanotube mixture, which had high adsorption capacity for the kinds of oils. Bi et al. (2012) prepared spongy graphene via reducing the graphene oxide aerogel thermally and its oil adsorption capacity up to 20 to 86 g/g. Liu et al. (2013b) prepared reduced graphene oxide-coated polyurethane (rGPU) sponges, and its absorption capacity was higher than 160 g/g for chloroform. Although these materials could achieve oil/water separation, the adsorbed oil can be readily released by mechanical squeezing, heating, burning, and distillation (Bi et al. 2012; Nguyen et al. 2012; Niu et al. 2012; Sun et al. 2013; Zhang et al. 2011). It is a discontinuous and inefficient disposal. Therefore, it is necessary to develop new materials and new methods that can continuously and effectively remove oil from water. Membrane separation technology has become a feasible option for the oil/water separation due to the property of high oil removal efficiency, no chemical additives, and low-energy costs (Padaki et al. 2015). Our group have prepared PET-braid-reinforced poly(vinylidene fluoride)/GE hollow fiber membranes (Hao et al. 2016) and nonwoven fabric-reinforced PVDF/GE oil-absorptive composite membrane (Zhang et al. 2016) to continuously separate immiscible oil/water mixtures, showing high separation efficiency and outstanding reusability. Nevertheless, the low oil flux cannot meet the demand of the large-scale wastewater treatment.

Polyurethane (PU) sponge is a porous material with low density, good resiliency, and high adsorption capacity, which can be a good substrate for fabricating oil adsorbents. Not only oil but also water can be adsorbed by PU sponge. Therefore, there is a need to change PU sponge from hydrophilic to hydrophobic or even superhydrophobic (Liu et al. 2013a) to achieve oil/water separation. Nguyen et al. (2012) prepared graphene-based sponge by dip-coating method, and the resulting graphene-based sponge has an excellent oil adsorption capacity of 165 g/g. Wang and Lin (2015) anchored the hydrophobic CNT/PDMS coatings onto PU sponge, and the prepared sponge could remove oil up to 35,000 times of its own weight from water in one step with a vacuum system. Zhou et al. (2016) prepared FGN/PU sponges by a one-pot processing technique, and it could continuously and effectively separate the oil up to 53,000 times of its own mass from water. But the adhesion between coated particles and matrix was weak, and it is difficult to deal with large-scale oil spills via the simple type of separating components.

Herein, we prepared a novel hydrophobic and superoleophilic sponge hollow tube which could be easily assembled into units of different sizes for the continuous oil removal from water surface. The in situ reduced graphene oxide-based polyurethane (IRGOPU) sponge was fabricated via a facile dip coating and in situ chemical reduction method. The morphology, wettability, and oil/water separation performance were discussed in detail. The IRGOPU sponge hollow

**Table 1** Density and porosity of the PU, GOPU, and IRGOPU sponges

S'amples	$\rho$ (g cm <sup>-3</sup> )	$\phi$ (%)
PU sponge	0.032	95.74
GOPU sponge	0.034	94.22
IRGOPU sponge	0.033	94.98

tube may be an optimum candidate for the oil/water separation of large-scale oil spill.

## Experimental

### Materials

Natural graphite was purchased from Qingdao Hongda Nanshu Graphite Products Co., Ltd. The polyurethane sponges (thickness, 3 mm) were supplied by Tianjin Haishen Sponge Products Co., Ltd. Sodium nitrate (AR), concentrated sulfuric acid (AR), hydrochloric acid (AR), potassium permanganate (AR), hydrogen peroxide (AR), DMAc (AR), DMSO (AR), toluene (AR), and ethanol 95% (AR) were all purchased from Tianjin Chemical Reagent Co., Ltd. Hydrazine hydrate 80% (AR) was purchased from Tianjin Yingda Chemical Reagent Co., Ltd. Trichloroethylene (AR) was purchased from Tianjin Guangfu Science and Technology Development Co., Ltd. Kerosene was purchased from Tianjin Kailida Chemical Co., Ltd. Pump oil was purchased from Tianjin Lirunda Co., Ltd. Soybean oil was purchased from Qinhuangdao Jinhai Food Co., Ltd. Olive oil was purchased from Shanghai Pingli Food Co., Ltd. Gasoline was purchased from Tianjin Petrochemical Co., Ltd., Sinopec Group.

### Preparation of GO

GO was prepared by the oxidation and exfoliation of natural graphite powder according to the Hummers' method (Hummers and Offeman 1958). Briefly, 46 mL concentrated sulfuric acid was added into a 250-mL flask filled with 2 g graphite, followed by the addition of 1 g sodium nitrate. Then 12 g potassium permanganate was gradually added with stirring for 2 h while the temperature of the mixture was kept below 20 °C. Then, the temperature was increased to 35 °C lasting for 30 min, and 100 mL distilled water was added into the mixture with continuous stirring at 98 °C for 15 min. 400 mL distilled water and 2 mL hydrogen peroxide were added after the mixture's color turned brilliant yellow. The mixture was washed and filtered several times by 10% hydrochloric acid solution to remove metal ions. The resulting filter cake was repeatedly washed with distilled water until near neutral and diluted to 500 mL, labeled as a graphite oxide aqueous dispersion. After ultrasonic treatment for 30 min to exfoliate it to GO, the GO dispersion was then centrifuged at 10,000 rpm

for 20 min to remove the undefoliated graphite. The resultant GO dispersion was filtered and dried by freeze-drying process.

**Preparation of IRGOPU sponge and IRGOPU sponge hollow tube**

GO was dispersed in distilled water and formed GO solution (2 mg/mL). The PU sponge was cleaned with ethanol and distilled water using an ultrasonic cleaner and dried in a vacuum oven at 80 °C for 24 h to the constant weight. The resulted sponge were immersed in GO dispersion for 30 min and then put in a vacuum oven and dried for 24 h at 40 °C. The treated PU sponges were reduced in hydrazine hydrate vapor at 90 °C for 24 h. Finally, the IRGOPU sponge was obtained after water washing and drying in a vacuum oven at 80 °C for 24 h.

With inspiration from the separation process of hollow fiber membrane, the IRGOPU sponge was made into the IRGOPU sponge hollow tube for the continuous oil removal from water surface, which could be assembled into various testing components. One end of the IRGOPU sponge hollow tube was sealed with epoxy resin, and the other end was connected to a vacuum pump (Fig. 1).

**Testing and method**

The morphology of the sponge was observed by a field emission scanning electron microscope (S4800, Hitachi, Japan). Fourier transform infrared (FTIR) spectrometer (TENSOR-37 Bruker, Germany) was used for confirming the deposition of RGO on the PU sponge surface. Thermogravimetric analysis (TGA) was carried out in a

NETZSCH STA-449F3 from 30 to 500 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. Contact angle measurements were carried out at room temperature using a Krüss DSA 100 apparatus (Krüss GmbH, Hamburg, Germany).

To evaluate the oil adsorption capacity of the IRGOPU, 1 g IRGOPU sponge was put into a glass bottle with 250 mL toluene, DMAc, DMSO, trichloroethylene, kerosene, pump oil, soybean oil, and olive oil. The bottles were placed on a thermo-static shaker agitating at 100 rpm for 10 min. The wetted IRGOPU sponge was weighed after draining for 1 min on a strainer. Oil adsorption capacity of IRGOPU sponge was calculated by following Eq. (1):

$$Q = \frac{W_2 - W_1}{W_1} \tag{1}$$

where *Q* is oil adsorption capacity of the IRGOPU sponge (g/g), *W*<sub>2</sub> is the weight of the wet adsorbent (g), and *W*<sub>1</sub> is the initial weight of the adsorbent (g).

The single IRGOPU sponge hollow tube was partly immersed in the oil/water mixture and connected to a vacuum pump (Fig. 2). The volume ratio of the oil/water mixture was 1:1. The liquid was driven into the IRGOPU sponge hollow tube under negative pressure and was pumped into a suction flask along the rubber tube. The entire process was recorded by a digital video camera. The distillation technique as described in ASTM D95-05 was used to measure the amount of water in the collected oil. A mixture of xylene and toluene (80/20, v/v) was used as a carrier solvent for distillation (Zhao et al. 2013b).

Oil/water separation efficiency of the IRGOPU sponge hollow tube was quantified according to Eq. (2); the water content of collected oil was calculated according to Eq. (3):

$$\varepsilon = \frac{W_B - W_A}{W_0} \tag{2}$$

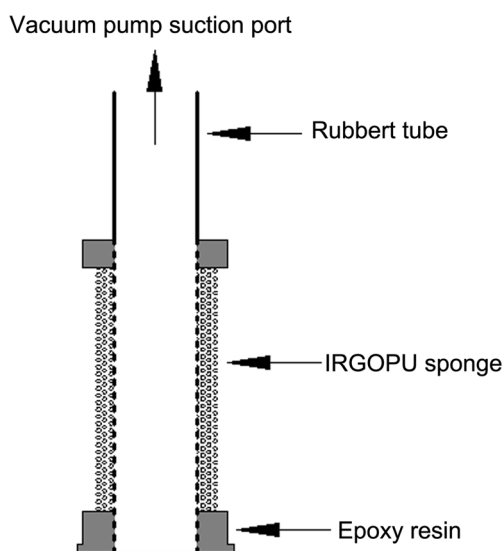
$$\eta = \frac{W_A}{W_B} \tag{3}$$

where *ε* is the IRGOPU sponge hollow tube separation efficiency, *W*<sub>B</sub> is the weight of the collected oil (g), *W*<sub>A</sub> is the weight of water in the collected oil (g), *W*<sub>0</sub> is the initial weight of oil (g), and *η* is the water content of the collected oil.

Flow rate of the collected oil change was recorded at different time intervals (time span, 0 to 540 s; step, 60 s). The flow rate of the collected oil was calculated by following Eq. (4):

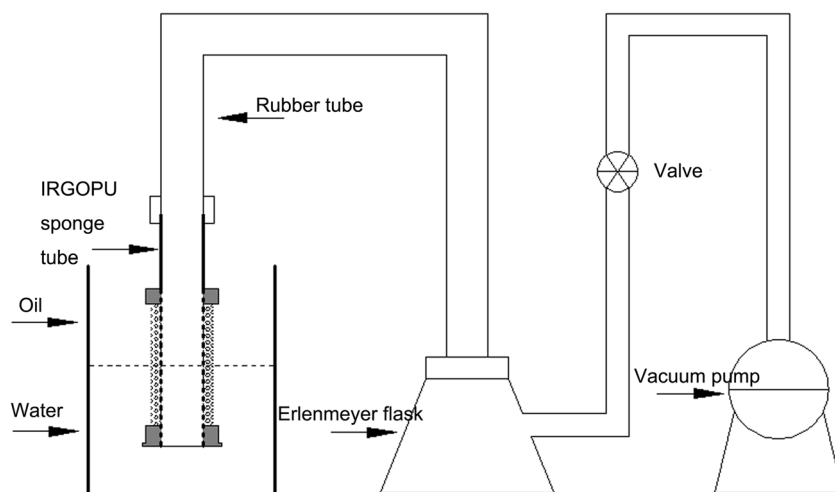
$$s = \frac{V}{t} \tag{4}$$

where *s* is the flow rate of the collected oil, *V* is the volume of the collected oil (mL), and *t* is the collected time (s).



**Fig. 1** Schematic diagram of IRGOPU sponge hollow tube

**Fig. 2** Schematic diagram of continuous oil/water separation with single IRGOPU sponge hollow tube



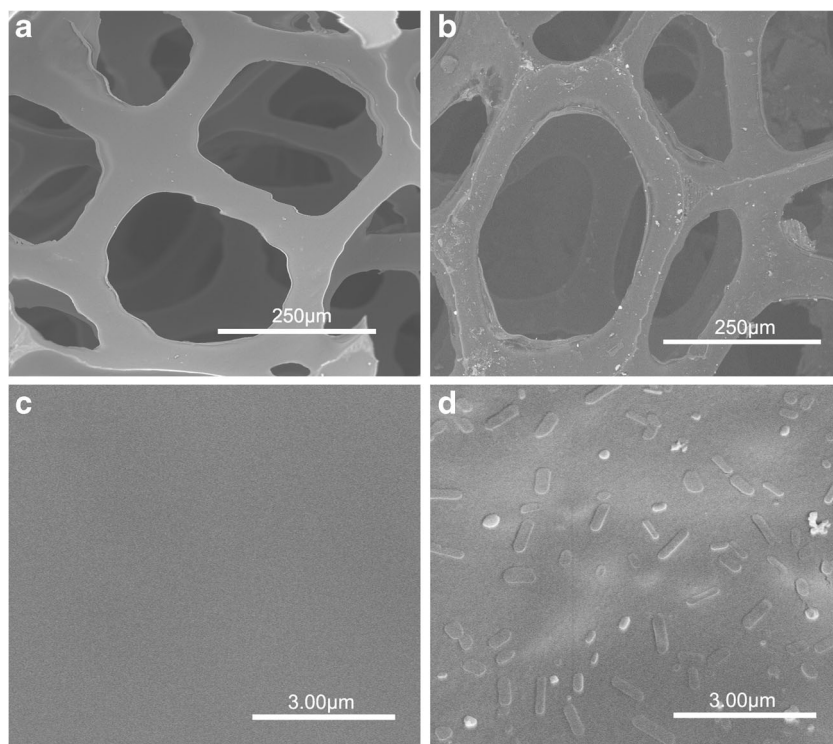
A simulation experiment for continuous oil removal of large-scale oil spill was designed. The IRGOPU sponge hollow tube was assembled into a simple component using for the simulation experiment (Fig. S1 in Supporting information). The separation process was recorded by a digital video camera. To test the reusability, the IRGOPU sponge hollow tube component was tested for ten times in a row according to the previous procedure as mentioned. Then, the IRGOPU sponge hollow tube component was cleaned using ethyl alcohol and dried at room temperature for the next reusability test cycle. Five hundred milliliters of oil was used for testing in once test and the oil/water separation efficiency was recorded.

## Results and discussion

### Sponge structure and surface morphology

The micro-porous structure of the PU and IRGOPU sponge are shown in Fig. 3a, b. They have almost same porous structure, which indicated that the RGO coating procedure did not change the porous structure of PU sponge. The structure of large pore volumes and surface area was useful for trapping oils. From Fig. 3c, d, the surface of PU sponge was smooth, whereas the surface of the IRGOPU sponge was rough, due to the thin coatings of RGO (Liu et al. 2013b; Zhou et al. 2012). These micro/nano-scale protrusions of the hydrophobic RGO

**Fig. 3** FESEM images of PU and IRGOPU sponge



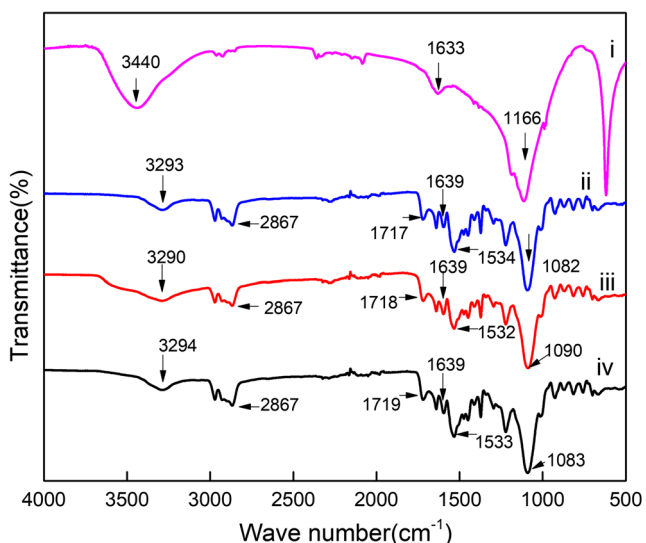
in combination with micro-porous structure of IRGOPU sponge brought out a dually roughened surface, which was close to a lotus leaf structure (Barthlott and Neinhuis 1997).

**Fourier transform infrared spectra**

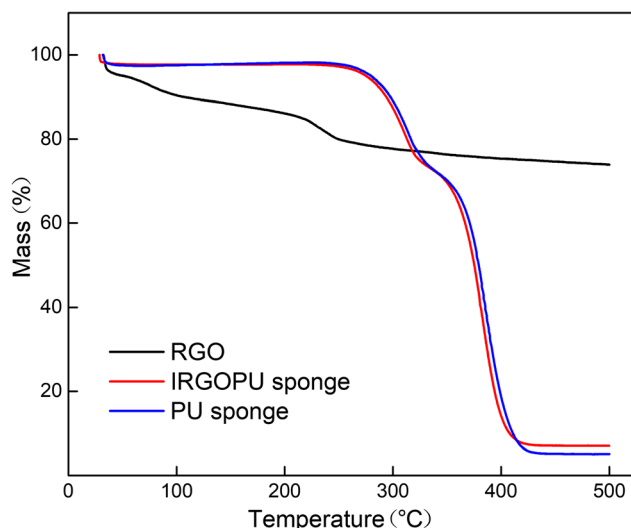
FTIR spectra of GO, PU sponge, GOPU sponge, and IRGOPU sponge are shown in Fig. 4. The peaks at 3440, 1633, and 1166  $\text{cm}^{-1}$  in the GO spectrum were associated with O–H stretching, C=C stretching, and alkoxy C–O stretching, respectively (Zhu et al. 2010). For PU sponge, the peaks at 2867, 1534, and 1082  $\text{cm}^{-1}$  were present and assigned to C–H stretching, amide II band, and C–O–C stretching, respectively. Apparently, most of the typical peaks of PU sponge, GOPU sponge, and IRGOPU sponge between 1000 and 1800  $\text{cm}^{-1}$  were similar. For IRGOPU sponge, the peak at about 3294  $\text{cm}^{-1}$  may be contributed by an overlap of the O–H and N–H stretching, where the intensity of IRGOPU sponge was higher than PU sponge due to the RGO obtained from oxidation-reduction method partially retained a few oxygenated functional groups (Wang et al. 2009). It indicated that the RGO has been successfully coated on the surface of PU sponge.

**Thermogravimetric analysis**

The thermal decomposition behavior of the RGO, PU sponge, and IRGOPU sponge was analyzed by TGA under nitrogen atmosphere ranging from 30 to 500 °C (Fig. 5). The TGA curves of the PU and IRGOPU sponges were similar, and both have a rapid weight loss in the temperature range of 280–500 °C. The DTG curves of the RGO, PU sponge, and IRGOPU sponge are shown in Fig. S2 in the Supporting information.



**Fig. 4** FTIR spectra of GO (i), PU sponge (ii) GOPU sponge (iii), and IRGOPU sponge (iv)



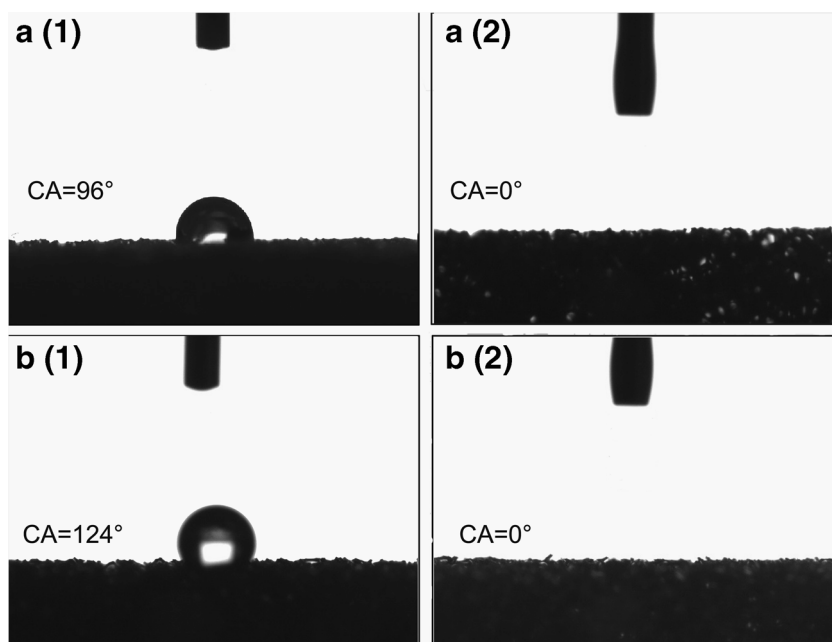
**Fig. 5** TGA curves of the RGO, PU sponge, and IRGOPU sponge

The maximum weight loss rate and the corresponding temperature for the PU sponge and IRGOPU sponge were adjacent. It indicated that the RGO coatings on the IRGOPU sponge did not influence the decomposition behavior of the PU sponge. However, the remaining residues of the IRGOPU sponge were slightly higher than the PU sponge, 73.93, 5.10, and 7.03% for the RGO, PU sponge, and IRGOPU sponge, respectively. Based on these results, the weight percent of RGO coatings in the IRGOPU sponge was about 1.93%.

**Hydrophobic and oleophilic property of the IRGOPU sponge**

Contact angle measured with the sessile drop method can be used for evaluating the degree of attraction between liquid and IRGOPU sponge. After coating a thin RGO, the water contact angle of PU sponge increased from 96 to 124° (Fig. 6a), showing good hydrophobicity. The wettability of a smooth solid surface would be changed with the increased surface roughness (Peng et al. 2005). The surface of the IRGOPU sponge became rougher after a thin RGO coating on the surface of PU sponge (Fig. 3). A dually roughened surface obtained due to the micro/nano-scale protrusions of the hydrophobic RGO in combination with micro-porous structure of IRGOPU sponge resulted in the increased water contact angle. Once the oil droplet touch the IRGOPU sponge, the droplet spreads out completely and infused into the pores immediately in a very short time (Supplementary video 1; Fig. 5b), showing excellent oleophilic property. It might be a confirmation that the IRGOPU sponge could quickly adsorb oil but repelled water, which was beneficial to oil/water separation.

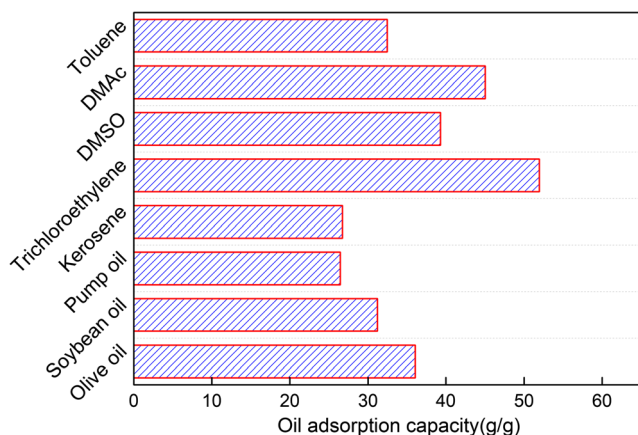
**Fig. 6** Images of contact angles: **a** PU sponge and **b** IRGOPU sponge (1, water droplet; 2, toluene droplet)



### Adsorption behaviors of IRGOPU sponge

According to ASTM F726-81, some typical oils, e.g., toluene, DMAc, DMSO, trichloroethylene, kerosene, pump oil, soybean oil, and olive oil were tested for evaluating the oil adsorption. The data in Fig. 7 which was the adsorption capacity of the IRGOPU sponge was excellent for various oils. The adsorption capacity of the IRGOPU sponge for toluene, DMAc, DMSO, trichloroethylene, kerosene, pump oil, soybean oil, and olive oil was 32.5, 45.0, 39.3, 52.0, 26.8, 26.5, 31.2, and 36.1 g/g, respectively. It showed an excellent absorption capacity due to the huge void volume in the IRGOPU sponge.

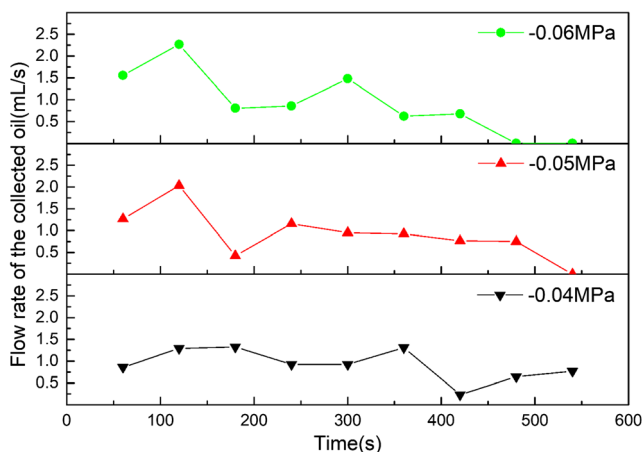
The hydrophobic and superoleophilic IRGOPU sponge could easily remove oils from the water surface (Fig. S3a–d in Supporting information, Supplementary video 2). By dipping



**Fig. 7** Adsorption capacity of IRGOPU sponge for various oils and organic liquid

the IRGOPU sponge (0.05 g) into the kerosene/water mixture (1 mL kerosene was dyed by Solvent Red 24), kerosene was quickly adsorbed and removed in 20 s. As shown in Fig. S3e–g in the Supporting information and Supplementary video 3, the IRGOPU sponge also effectively removed trichloroethylene from water. When a piece of IRGOPU sponge was forced into contact with trichloroethylene (dyed by Solvent Red 24) in water, the trichloroethylene was quickly sucked into the IRGOPU sponge within a few seconds. These results indicated that IRGOPU sponge showed good oil/water selectivity due to its hydrophobic and oleophilic properties as discussed above. It could spontaneously achieved oil/water separation due to the capillary force (Jang et al. 2004) that is generated by the synergy of the porosity and the superoleophilic property of the IRGOPU sponge.

PDMS-GE PU sponge was prepared by dip-coating method (Nguyen et al. 2012), which was used for contrasting the adhesion between GE or RGO and the PU sponge. For PDMS-GE PU sponge, the color of toluene changed from transparent to feculent after the adsorption test (Fig. S4a in Supporting information). After adsorption testing, the PDMS-GE PU sponge was dried in a drying oven and a black mark was observed by naked eyes (Fig. S4c in the Supporting information). However, these phenomena did not appear in the adsorption test of IRGOPU sponge (Fig. S4b in the Supporting information). It indicated that the GE sheets had detached away from the PU sponge. As shown in Fig. S5, the weight of IRGOPU sponge did not deteriorate with the increase in adsorption during testing cycles, while the weight of PDMS-GE PU sponge decreased obviously. These results showed a good adhesion between RGO coatings and PU sponge for IRGOPU sponge.



**Fig. 8** Flow rate of the collected oil under different work pressure

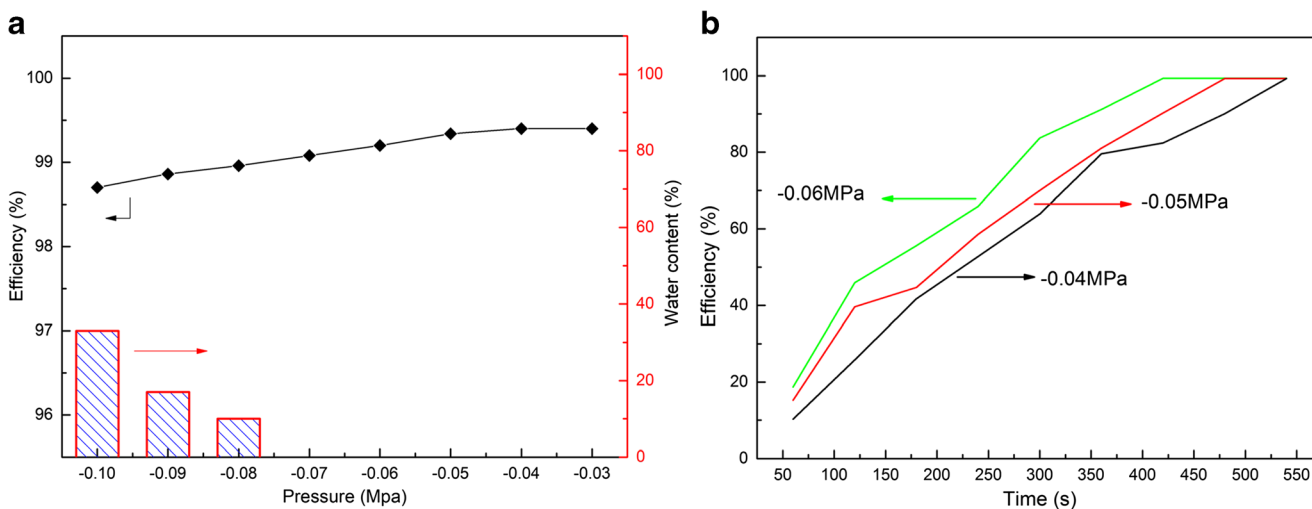
**Continuous oil removal from water surface using the IRGOPU sponge hollow tube**

A single IRGOPU sponge hollow tube was immersed into oil/water mixture and placed at oil/water interface. The oil (dyed by Solvent Red 24) was extracted into the IRGOPU sponge hollow tube under work pressure (− 0.06 MPa), and then pumped into a suction flask. After a few seconds, no red oil could be seen on the water surface and the oil was removed from the mixture completely (Supplementary video 4).

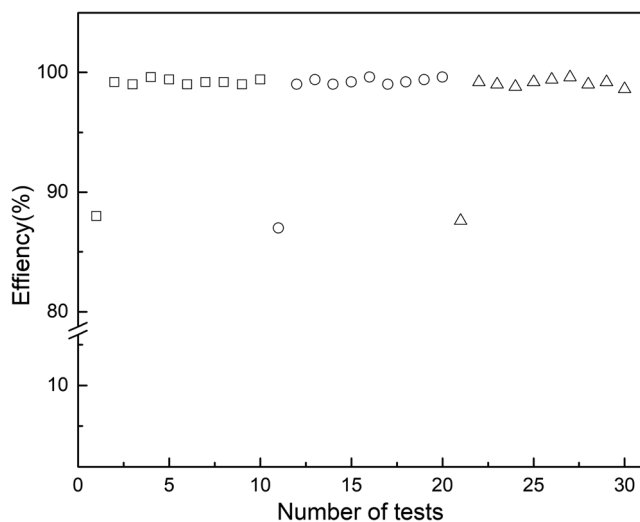
In the process of continuous oil removal from water surface, the IRGOPU sponge hollow tube showed excellent separation velocity and separation efficiency. Figure 8 showed the flow rate of the collected oil under different work pressures. For the work pressure of − 0.06 MPa, the flow rate of the collected oil first increased and then decreased slowly with the increased time. In the initial phase, the air of the suction flask was output, and then the oil was driven into the flask under negative pressure. At this moment, the maximum effective contact area of the IRGOPU sponge hollow tube was performed and the flow rate

of the collected oil reached the highest. Subsequently, the effective contact area of the IRGOPU sponge hollow tube with the oil has declined as the separation process and the flow rate decreased slowly. The change trends of flow rate of different work pressures were similar to each other. In the final, the flow rate of the collected oil became 0 at the work pressure of − 0.06 and − 0.05 MPa. It showed that the oil/water separation efficiency reached the maximum.

The influence of different parameters on the oil/water separation efficiency was discussed in this study. From Fig. 9a, it could be seen that the oil/water separation efficiency gradually increases with the decreasing work pressure, and the maximum efficiency was up to 99.4%. When the absolute value of the work pressure was greater than 0.07 MPa, the water content of the collected liquid is beyond 10%. In other words, the IRGOPU sponge tube could not repel the water completely under high work pressure during the continuous oil/water separation process. Therefore, in order to improve work efficiency, the absolute value of work pressure should be set below 0.07 MPa. Figure 9b shows that the oil/water separation efficiency increased rapidly at the beginning, then a relatively steady value was reached, all above 99%. When the work pressure was − 0.06 MPa, the oil/water separation efficiency achieved the stable value in the shortest time. Hence, the work pressure of − 0.06 MPa was appropriate. As shown in Fig. S6a in the Supporting information, the oil/water separation efficiencies for toluene, gasoline, and kerosene were all above 99% and very close to each other. The relationship between oil/water separation efficiency for toluene and IRGOPU sponge thickness is displayed in Fig. S6b in the Supporting information. It could be seen that the oil/water separation efficiencies for different IRGOPU sponge thickness were close; so it was independent of the sponge thickness. These results can be considered a reference data in the practical application of IRGOPU sponge on oil-spill treatment.



**Fig. 9** Influence of pressure (a) and time (b) on the oil/water separation efficiency



**Fig. 10** Reusability of the IRGOPU sponge hollow tube

For the oil-spill treatment, a single IRGOPU sponge hollow tube was obviously not enough to meet the requirements. Therefore, we designed a simulation experiment for continuous oil removal of large-scale oil spill using a simple IRGOPU sponge hollow tube component as shown in Fig. S1 in the Supporting information. The thickness of oil layer was about 0.03 cm. As shown in Supplementary video 5, the IRGOPU sponge hollow tube component floated on the water surface and parts contact with the oil (dyed by Solvent Red 24). The oil was extracted into the IRGOPU sponge hollow tube under the work pressure, and then pumped into the suction flask. As the components swung back and forth, more and more oil was separated from the water surface, and some places were clear. After a few seconds, the oil completely separated from the mixtures. It might be evidenced that the IRGOPU sponge hollow tube could be used for large-scale oil-spill cleanup.

The reusability of the IRGOPU sponge hollow tube for oil/water separation for 30 times is shown in Fig. 10. In one cycle comprising ten tests, the oil/water separation efficiency of the first test was about 88% and the efficiencies of the last nine tests were all higher than 98%. It might be explained that some oil remained in the pore structure of the IRGOPU sponge hollow tube due to any extra disposal after each test, resulting in the oil/water separation efficiency of the first test being lower than the others. It could be seen that there was no sharp decline of the oil/water separation efficiency observed with the increasing test times, showing a good durability.

## Conclusions

In this study, we prepared a novel oil-adsorptive IRGOPU sponge, and it was made into IRGOPU sponge hollow tube component for the oil/water separation of a large-scale oil

spill. The IRGOPU sponge showed hydrophobicity, oleophilicity, high oil/water selectivity, and excellent oil adsorption capacity of 26.5–52.0 g/g for different oils. When the IRGOPU sponge was used for continuous oil removal from water surface, it could directionally collect and remove oil from the water surface. A separation simulation experiment for continuous oil removal of large-scale oil spill from water surface using a simple IRGOPU sponge hollow tube component was designed. The oil/water separation process was quick and effective, and the oil/water separation efficiency could be up to 99.6%. These results indicated that the IRGOPU sponge hollow tube may be an optimum candidate for the oil/water separation of large-scale oil spill.

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