



# Recyclable and biodegradable superhydrophobic and superoleophilic chitosan sponge for the effective removal of oily pollutants from water



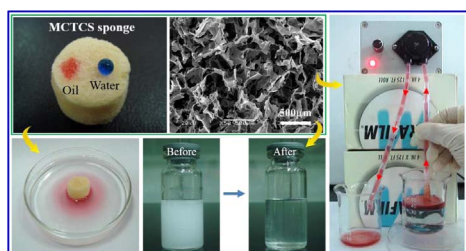
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## GRAPHICAL ABSTRACT

The superhydrophobic/superoleophilic chitosan sponge (MCTCS) was prepared via a facile approach and exhibited good biodegradability, excellent absorption ability and recyclability, efficient emulsified oil/water separation capacity and good continuously selective oil adsorption performance from water.



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## ABSTRACT

Superhydrophobic and superoleophilic chitosan sponge (MCTCS) was successfully prepared via a facile freeze-drying method with the assistance of TPP/citral crosslinking and octadecanethiol modification. The three-dimensional porous structure endowed the MCTCS sponges with large pore volume and good compressive property. Moreover, the MCTCS sponge could effectively absorb oil with an absorptive capacity up to 60 times of its own weight. More importantly, the MCTCS sponge could selectively absorb the emulsified oils in water effectively, and achieve continuous oil–water separation with the assistance of peristaltic pump. The oil and water separation efficiency was up to 99%. Furthermore, the MCTCS sponge still maintained a highly absorptive capacity after being reused for many cycles and possessed ideal biodegradability. It was believed that the superhydrophobic/superoleophilic chitosan sponge would be a promising absorbent material for the removal of oil from water in environmental remediation.

## 1. Introduction

With the development of industry and economy, increasingly serious environmental and ecological problems caused by oily pollutants has emerged as a critical issue on a global scale [1–3]. The hazard of oil spillage and leakage, as well as industrial organic pollutants have greatly affected the quality of human life. To address these problems,

various techniques have been proposed, such as solidification, skimming, absorption, dispersion and controlled burning [4–6]. Among these attempts, oil absorbents including inorganic mineral products, organic natural products and synthetic polymers have been widely applied due to their particular potential [7–9]. In particular, absorbent materials with special wettability are considered as the most promising candidate for the effective treatment of oily wastewater [10]. The

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distinct opposite affinities towards oil and water are beneficial for removing one phase from the oil/water mixture and simultaneously repel another phase, thus achieving selective oil/water separation. Over the recent years, numerous absorbents, including carbon aerogels [11–14], carbon nanotube (CNT) sponges [15,16], graphene sponges [6,17–19], silicone sponge [20], nanocellulose aerogels [8,21,22], synthetic polymers sponges [23–28] etc. have been developed for the separation and recovery of oil pollutants from water. For examples, Yang et al. fabricated a nitrogen-rich carbon aerogel (NRC aerogel) with fire-resistant property by the pyrolysis of the melamine formaldehyde polymer (PMF) porous aerogel at a high temperature [11]. Dong et al. reported the 3D graphene-CNT hybrid sponge with excellent compressibility by two-step chemical vapor deposition to have good recyclability [16]. Li et al. also prepared magnetic porous silicone sponges by polymerization of organosilanes in the presence of  $\text{Fe}_3\text{O}_4$ @silica nanoparticles [20]. Zheng et al. developed a freeze-drying and chemical vapor deposition method for the preparation of methyltrichlorosilane modified polyvinyl alcohol (PVA)-cellulose nanofibril (CNF) hybrid aerogels [21]. Hu et al. prepared graphite/isobutylene-isoprene rubber (IIR) cryogels with excellent buoyancy and good recyclable property by crosslinking IIR rubber in the presence of graphite in benzene, using sulfur monochloride as the crosslinker [28].

Unfortunately, several challenges have hampered the extensive practical applications of these absorbents, such as expensive reagents and devices, relatively inefficient absorption capacity, complicated preparation process, poor mechanical stability and biodegradable property, unsatisfied regeneration and recycling use, as well as secondary pollution. All these issues pushed us to develop novel multifunctional oil absorbents with excellent performance in selective absorption of oils and organic solvents from water, which could possess as much advantage as possible. Therefore, the exploration of low-cost and recyclable absorbent materials that could separate the oil/water mixture in a selective, efficient and ecofriendly manner is highly desirable.

Chitosan (CS), as a low-cost, natural biodegradable, nontoxic, and biocompatible polysaccharides [29–31], has been reported to be widely used in drug delivery carriers, oil removal, heavy metals absorbents and tissue engineering scaffolds [32,33]. In this work, chitosan was selected as raw materials to prepare chitosan sponge with special wettability via a green method with assistant of TPP and citral molecules, which was successfully applied in selective and continuous oil/water separation. The 3D porous structure and superhydrophobic/superoleophilic wettability endowed chitosan sponge with high absorptive capacity, excellent selectivity and recyclability in the removal of oils and organic pollutants from water. To the best of our knowledge, the cheap absorbent materials with excellent absorption capacity, satisfactory regeneration and recyclability, good mechanical stability and biodegradability are scarce in the reported literatures.

## 2. Experimental

### 2.1. Materials

Chitosan (95% degree of deacetylation, viscosity 100–200 mPa.s), sodium tripolyphosphate (TPP), citral (97%), 1-octadecanethiol (97%), oil-soluble dye, oil red O were purchased from Aladdin (Shanghai, China). Acetic acid was purchased from Tianjin Bo Di Chemical Co. Ltd. Ethanol (99.7%) and organic solvents including chloroform, dichloromethane, cyclohexane, hexadecane, hexane and toluene were purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents were analytical grade and used without further purification. The oil used in this study including lubricant oil, soybean oil, pump oil and silicone oil were obtained from local suppliers.

### 2.2. Preparation

0.6 g chitosan was dissolved in 60 mL acetic acid (HAc) aqueous

solution (1%, v/v) under stirring to form homogenous chitosan/HAc solution. Then the chitosan/HAc solution was frozen at  $-20^\circ\text{C}$  for 12 h and treated via a freeze-drying process in a lyophilizer ( $-50^\circ\text{C}$ ,  $\leq 0.63$  mbar) to obtain the aerogel sponge. The freeze-dried sponges were immersed in ethanol for 3 h and washed with deionized water for three times to remove residual acetic acid. Finally, the neutral sponges were freeze-dried under identical conditions to obtain chitosan-based sponge (CS). The TPP-crosslinked chitosan sponge (TCS) was prepared via same procedure by using TPP solution (3 mL, 5 mg/mL) involved chitosan/HAc solution, instead of chitosan/HAc solution. To obtain TPP and citral crosslinked chitosan sponge (CTCS), the TPP-crosslinked chitosan sponges before the second freeze-drying treatment were immersed in citral/ethanol solution (1%, v/v) and heated in water bath at  $80^\circ\text{C}$  for 10 h. Then the sponges were washed with absolute ethanol for several times to remove unreacted citral and drying in room temperature. The prepared CTCS sponges were immersed in n-octadecylthiol anhydrous ethanol solution (5 mmol/L) for 30 min at room temperature. Then the sponges were dried at  $60^\circ\text{C}$  in a drying oven to obtain the superhydrophobic and superoleophilic sponges (MCTCS). To optimize the amount of n-octadecylthiol, different concentrations of n-octadecylthiol (0.5, 1, 3, 10 and 20 mmol/L) were used for the preparation of MCTCS, as demonstrated in Fig. S1 (Supporting Information). The schematic illustration of the preparation of different chitosan sponges was demonstrated in Scheme 1.

### 2.3. Characterization

The microstructure and elemental analysis of the sponges were characterized by a scanning electron microscope (SEM, JSM-5510LV) equipped with an energy-dispersive X-ray spectroscopy (EDX). The SEM samples were treated by gold sputtering before characterization. The Fourier transform infrared spectroscopy (FTIR) spectra were carried on a Nicolet Impact 420 FT-IR spectrometer (Nicolet, USA) in a range of  $600\text{--}4000\text{ cm}^{-1}$  by using an attenuated total reflectance (ATR) system. The static contact angles (CAs) were measured by Dataphysics OCA 20 (Germany) contact angle measuring instrument, using  $3\text{ }\mu\text{L}$  water or oil droplet at an ambient temperature. Compression test was conducted by using an Instron (Model 3365) fitted with a 500 N load. The compression strain rate was set at  $20\text{ min}^{-1}$  for the test. Cylindrical aerogels (with a diameter of 28.8 mm and a height of 16 mm) were used for the compression test. The concentration of n-hexane in water were analyzed by a gas chromatogram (Fuli 9720) equipped a flame ionization detector (FID) and KB-FFAP capillary column ( $30\text{ m} \times 0.32\text{ mm} \times 1\text{ }\mu\text{m}$ ) using high pure  $\text{N}_2$  as the carrier gas. All the photographs and videos were obtained by a digital camera (Sony, Japan).

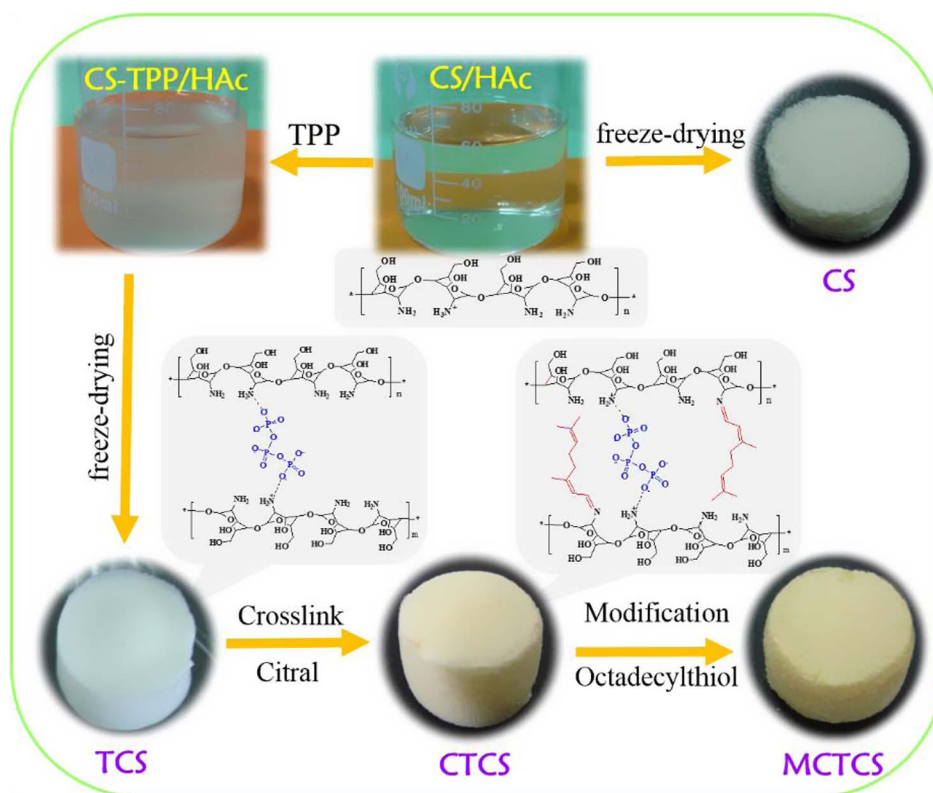
### 2.4. Absorptive capacity measurement

The absorptive capacities of the MCTCS sponge for various oil and organic solvents were determined by the weight variation of the MCTCS sponge before and after absorption. A piece of MCTCS sponge was dipped into the test liquid (oil or organic solvent) at room temperature until the MCTCS sponge was saturated with the liquid. Then it was taken out and drained for several seconds to remove excess oil. The wet MCTCS sponge was weighed for the calculation of absorption capacity. The mass-based absorptive capacity ( $Q_m$ ) and volume-based absorptive capacity ( $Q_v$ ) were calculated according to the following equations:

$$Q_m = (m_s - m_o)/m_o$$

$$Q_v = \rho_o (m_s - m_o)/m_o \rho_s \times 100\%$$

where  $m_o$  and  $m_s$  are the mass of the sponge before and after sorption,  $\rho_o$  and  $\rho_s$  are the apparent densities of the dried sample and the test liquid, respectively.



**Scheme 1.** Schematic illustration of preparation process of different chitosan based sponge.

## 2.5. Selective absorption and oil-in-water emulsion removal test

Soybean oil and chloroform were used to test the selective absorptive property of MCTCS sponge, which was the representative of the oil lighter than water and solvent heavier than water, respectively. To obtain a strong contrast with water, soybean oil and chloroform were dyed with an oil-soluble dye (oil red). Soybean oil and chloroform was dropped into water to form soybean oil/water and water/chloroform mixture, respectively. Then a pair of tweezers was used to force the MCTCS sponge contact soybean oil or chloroform and recorded the selective absorption process with a digital camera.

The oil-in-water emulsion were obtained by mixing the toluene and deionized water (1:9, v/v) under ultrasonic condition. The oil droplets removal test was carried out by forcing the MCTCS sponge into the toluene-in-water emulsions. After oscillation for a certain time, the MCTCS sponge was taken out. Then the remaining toluene in water were determined by using a UV–Vis spectrophotometer (UV2800) based on the calibration curve. The calibration curve was obtained by measuring the absorbance of toluene in ethanol/water (3:1, v/v) solution according to the Lambert-Beer's law (Fig. S2, Supporting Information).

## 2.6. Continuous oil/water separation test

The continuous oil-water separation was carried out through a self-made equipment. The MCTCS sponge was crammed into one end of a pipe, and fixed at the oil-water interface. Another end of the pipe was connected to a peristaltic pump, which was the input of the pump. The output of the pump was collected by a beaker. Turn on the switch of peristaltic pump, the oil/water separation test began.

## 2.7. Regeneration of the MCTCS sponge

The regeneration of the MCTCS sponge after absorption was performed via absorption-distillation for low boiling point oil (toluene, n-hexane and chloroform etc.) and absorption-squeezing for high boiling

point oil (n-hexadecane, pump oil and silicone oil etc.) process. For absorption-distillation treatment, the oil-adsorbed MCTCS sponge was regenerated by heating at the temperature around boiling point of the oil to remove the absorbed oil. Then the dried MCTCS sponge was used in the next cycle. For absorption-squeezing treatment, the oil-adsorbed MCTCS sponge was regenerated by manually squeezing the sponge to extract absorbed oils, and then the squeezed MCTCS sponge was wiped with filter paper and used in the next cycle. In the recycle experiment, the absorptive capacity of MCTCS sponge was determined by the same method described previously after absorption-distillation or absorption-squeezing treatment. The absorbed amount ( $Q_a$ ) and the remnant amount ( $Q_r$ ) was calculated by the following equations:

$$Q_a = (m_a - m_o) / m_o$$

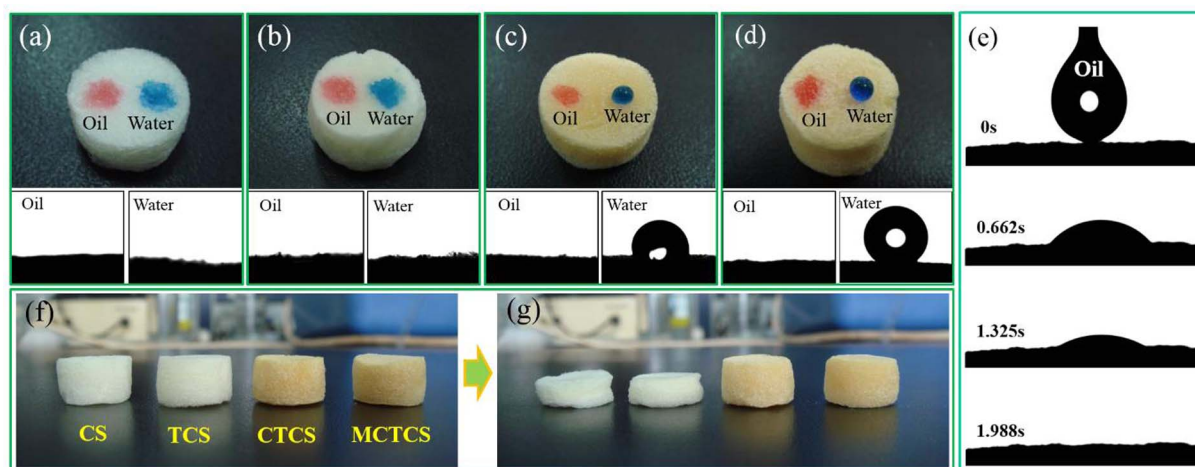
$$Q_r = (m_r - m_o) / m_o$$

where  $m_o$  and  $m_a$  is the mass of the sponge before sorption and after sorption, respectively. And  $m_r$  is the mass of the sponge after distillation or squeezing at  $n$  time. The recovery (%) is calculated by the equation of  $(Q_a - Q_r) / Q_a$ . The adsorptive capacity after multiple cycles is normalized by the initial weight gain.

## 2.8. Biodegradation of the MCTCS sponge

The biodegradation of the MCTCS sponges was studied in a PBS (pH = 7.4) buffer which contained lysozyme and HAc-NaAc (pH = 4.8) buffer solution which contained cellulase at 37 °C. The MCTCS sponges with equal weight were immersed in lysozyme and cellulase solution (10,000 U/mL) and incubated at 37 °C for 15 days, respectively. Then the MCTCS sponges were removed after 5, 10, and 15 days from the enzyme solution and washed with deionized water to remove ions adsorbed on surface and freeze-dried. The degradation rate ( $D$ ) of MCTCS sponge was calculated from the weight after freeze-dried ( $w_t$ ) and initial weight ( $w_o$ ) by using the following equation:

$$D = (w_t - w_o) / w_o \times 100\%$$



**Fig. 1.** Photographs of water (blue) and oil (red) droplets stand on the surface of CS (a), TCS (b), CTCS (c) and MCTCS (d) sponges. The water was labeled with methylene blue and soybean oil was labeled with red oil O for clear observation. Photographs of oil absorption time of the MCTCS sponge (e) and appearance shape of CS, TCS, CTCS and MCTCS sponges before (f) and after (g) manual squeezing. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

### 3. Results and discussion

#### 3.1. Surface wettability and structures of chitosan-based sponges

Fig. 1 showed the surface wettability and mechanical property of CS, TCS, CTCS and MCTCS sponges. As shown in Fig. 1a and b, the water and oil droplets could be absorbed into the CS sponge and TCS sponge, and the corresponding contact angle of both water and oil is  $0^\circ$ , indicative of the superhydrophilic/superoleophilic property of non-crosslinked CS sponge and TPP-crosslinked TCS sponge. However, after the citral crosslinking, the water and oil contact angle of the surface of CTCS sponge was  $105^\circ$  and  $0^\circ$ , respectively (Fig. 1c), illustrating that the CTCS sponge possessed superoleophilic and hydrophobic wettability. The change from superhydrophilic to hydrophobic surface could be ascribed to the increase of long chain alkyl when the chemical crosslink reaction took place between citral and chitosan [34]. The hydrophobic wettability of MCTCS sponge was further improved to superhydrophobic after the n-octadecylthiol modification, as demonstrated by the increase of water contact angle to  $150^\circ$ , while the oil contact angle is still  $0^\circ$  (Fig. 1d). Moreover, the oil drop could be fully absorbed by MCTCS sponge within several seconds, indicating that the n-octadecylthiol modification only improved the hydrophobicity, rather than affected the oleophilicity of MCTCS sponge, as shown in Fig. 1e. To evaluate the mechanical properties of the CS, TCS, CTCS and MCTCS sponges, the manual squeezing method was utilized to compare the appearance shape of the sponges when the external force was removed. Fig. 1 f and g showed the photographs of the shapes of different sponges before and after manual squeezing. All the CS, TCS, CTCS and MCTCS sponges could be compressed because of their high porosities. However, after manual squeezing, the deformed CS and TCS sponge could not recover its original shape. Strikingly, the CTCS and MCTCS sponge recovered its original shape without mechanical deformation after squeezing. It indicated that the crosslinking of citral improved the mechanical properties of CS sponges.

The microstructure, pore volume and composition of CS, TCS, CTCS and MCTCS sponges were also characterized. Fig. 2 showed the SEM images of the microstructures of CS, TCS, CTCS and MCTCS sponges. All the sponges including non-crosslinked and crosslinked sponges possessed three dimensional porous structure. The crosslinked TCS and CTCS sponge showed a more regular morphology and porous microstructures than that of non-crosslinked CS sponges. The pore volume of different CS-based sponges was also determined, as illustrated in Fig. 3a. The calculated pore volume of TCS and CTCS sponges was  $42.5 \pm 1.43$  and  $43.8 \pm 1.3$  mL/g, respectively, which was higher

than that of the non-crosslinked CS sponge. It indicated that the addition of TPP could enhance the porosity of sponge. Noticeably, the octadecanethiol-modified MCTCS sponge remained its interconnected three dimensional porous structure (Fig. 2g and h), and the pore volume was up to  $44 \pm 0.78$  mL/g (Fig. 3a). It illustrated that the modification of octadecanethiol did not change the morphology and porosity of MCTCS sponge.

Furthermore, FTIR-ATR spectra was conducted to monitor the change of chemical groups in the chitosan structures before and after crosslinking and modification. Fig. 3b represented the FTIR-ATR spectra of CS, TCS, CTCS and MCTCS sponges. The absorption bands of CS sponge at  $1579\text{ cm}^{-1}$  corresponded to the deformation vibration of N–H groups [35], which disappeared in the FTIR-ATR spectra of CTCS and MCTCS sponges. A new peak at  $1645\text{ cm}^{-1}$  ascribed to the stretching vibration of C=N group [36] emerged, illustrating that the chemical reaction between the amino groups on chitosan and aldehyde of citral took place and generated carbon-nitrogen double bond. The FTIR-ATR spectrum of TCS sponge was similar to that of CS sponges, and the peak centered at  $895\text{ cm}^{-1}$  could be assigned to the stretching vibration of P–O–P groups of TPP. In addition, the absorption peaks at  $2919$  and  $2850\text{ cm}^{-1}$  were found in the FTIR-ATR spectrum of MCTCS sponge, which was corresponding to the stretching vibration of C–H and S–H groups, respectively. The bands observed at  $1462\text{ cm}^{-1}$  could be assigned to the vibrational stretching of C–S groups. The results confirmed that the octadecanethiol had been successfully modified to the surface of the MCTCS sponge. Moreover, the surface element composition of the CTCS and MCTCS sponge was determined by the energy dispersive X-ray (EDX) analysis. As shown in Fig. 3d, the S element was detected in the MCTCS sponge, which also verified the presence of octadecanethiol on the MCTCS sponge.

The superhydrophobic and mechanical property of the MCTCS sponge was further investigated. As shown in Fig. 4a, when CS and MCTCS sponge was put into water, it was observed that the MCTCS sponge floated on the water, while CS sponge submerged in the water. When a piece of MCTCS sponge was immersed in a water via an external force, it was found that water could not soak into the sponge, and the sponge surface was surrounded by large quantities of air bubbles, demonstrating a silver mirror-like surface (Fig. 4b). Upon releasing the external force, the MCTCS sponge floated immediately on the water surface, indicative of its excellent water repellency. Moreover, a water droplet could roll off easily from the surface of MCTCS sponge with a slight tilt (Fig. 4c), also illustrating the good water-repellent property of MCTCS sponge. This phenomenon could be well explained by the non-wetting behavior of Cassie-Baxter [37].



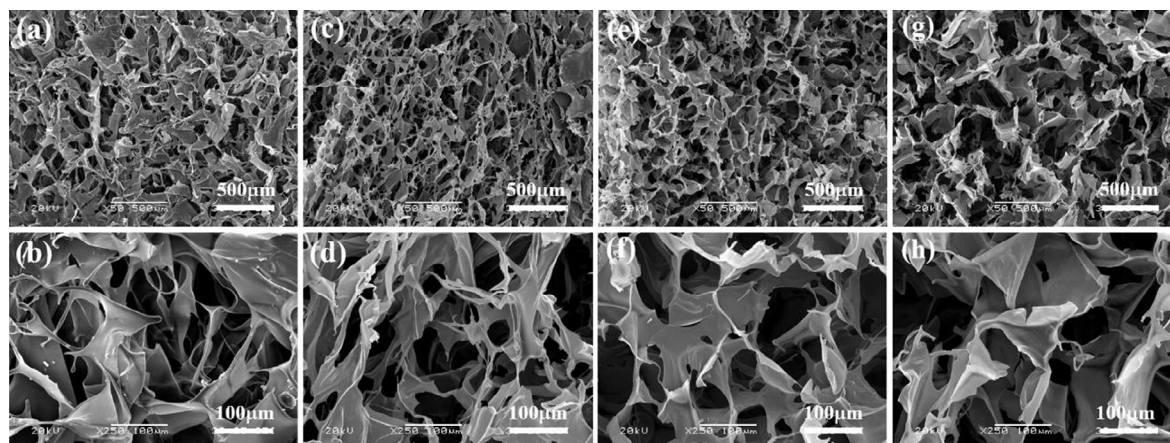


Fig. 2. SEM images of CS (a, b), TCS (c, d), CTCS (e, f) and MCTCS (g, h) sponges.

### 3.2. Compressive property and biodegradation property of the MCTCS sponge

Fig. 5a showed the photographs of MCTCS sponge before and after being squeezed by an external force. The MCTCS sponge could be easily compressed by exerting an external force, and could recover completely its original shape after releasing the external force (Video S1, Supporting Information). It preliminarily indicated that the MCTCS sponge possessed good elasticity and compressibility. To further study the compressibility of the MCTCS sponge, we measured the compressive stress-strain curves of MCTCS sponge. Fig. 5 b and c showed the cyclic compression stress-strain curves of the MCTCS sponges at maximum strains of 20% and 60%, respectively. The cyclic stress-strain curves showed that the MCTCS sponges could be compressed to large strains (60%) at a relatively low stress (0.023 MPa), owing to the high porosity and elasticity of the sponge. The reproducible cyclic curves in Fig. 5 b

and c demonstrated the good recovery of elasticity in the process of repeated compressions. Moreover, the shape and compressive stress of the MCTCS sponges did not undergo a violent change after 10 loading/unloading cycles, although the MCTCS sponge could not retain its original shape completely. It indicated that the MCTCS sponges possessed ideal elasticity and compressive durability, which was very important for the practical application of the sponges.

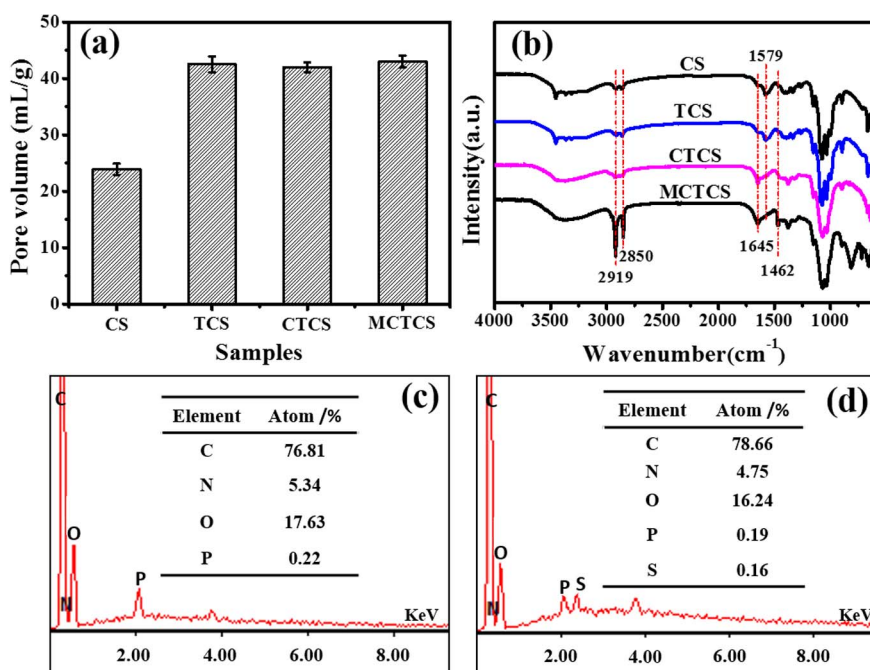


Fig. 3. Pore volume (a) and FTIR-ATR spectra (b) of different CS-based sponges. EDX spectra of CTCS (c) and MCTCS (d) sponges.

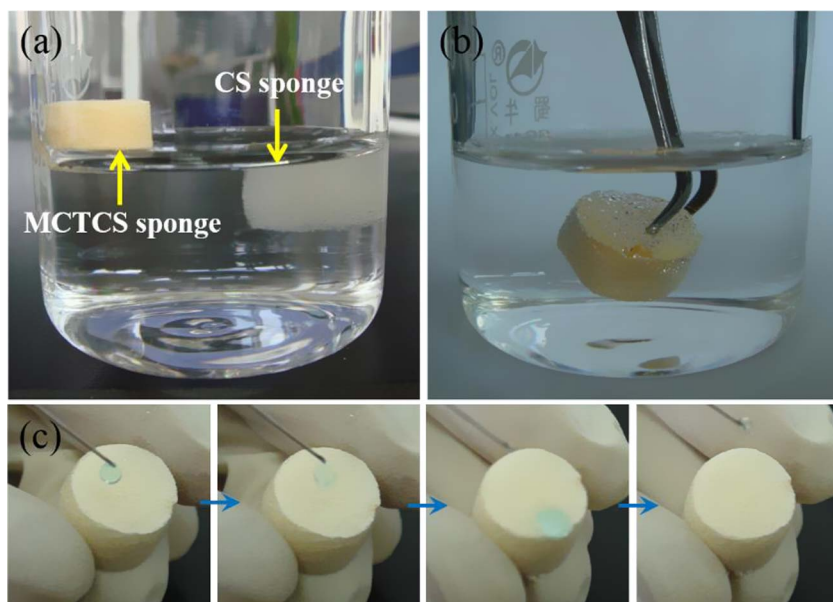


Fig. 4. Photographs of the CS and MCTCS sponges being placed into water (a). MCTCS sponge being immersed into water via an external force (b) and water droplet on the declining surface of MCTCS sponge (c).



Video S1.

Furthermore, the biodegradation property of MCTCS sponge was investigated. As shown in Fig. 6, the MCTCS sponge presented 24% degradation rate in lysozyme solution and 35% degradation rate in cellulase solution after five days. With the extension of time, the MCTCS sponge was degraded gradually in the enzyme solution. After fifteen days, the MCTCS sponge showed 42% degradation rate in lysozyme solution and 48% degradation rate in cellulase solution. It indicated that MCTCS sponge possess good biodegradability, which was considered as an environmental-friendly absorbent material in practice application.

### 3.3. Absorptive capacity of the MCTCS sponge

To investigate the absorptive capacity of the MCTCS sponge, different oils and organic liquids were used to determine its mass-based and volume-based absorptive capacity. As shown in Fig. 7a, the mass-based absorptive capacity of the MCTCS sponge was in the range of 23–60 g/g for different test liquids, which was comparable with that of many reported superhydrophobic/superoleophilic absorbents, such as Ni-doped graphene/carbon cryogels (15–48 g/g)[38], magnetic silicone sponges (7–17 g/g)[20], polyvinyl formaldehyde sponges (19.2–43.1 g/g)[39], carbon soot sponge (22–78 g/g)[40]. Due to the strong effect of

the density of test liquid on the mass-based absorptive capacity, we also calculated the volume-based absorptive capacity to evaluate the absorptive ability of MCTCS sponge. As shown in Fig. 7b, the volume-based absorptive capacity of the MCTCS sponge was about 85–99% for different oils or organic solutions, indicating that almost the whole volume was crammed by the liquid. It was higher than the volumetric absorption capacities of nanocellulose aerogels (70–80%) [22], nitrogen doped graphene aerogel (74–90%) [17]. It illustrated that the MCTCS sponge with high oil absorptive capacity possessed comparability with high-capacity absorptive materials such as carbon-based, graphene and CNT foams [6,12,16], due to its simple preparation method and cheap raw material. Together with its good biodegradation properties, it could be a kind of promising absorption materials for oil spill remediation applications.

Considering the highly superhydrophobic surface, high oil absorptive capacity and high porosity of the interconnected porous structure, the selective oil absorption of MCTCS sponge from water was investigated. Fig. 8a showed the absorption process of soybean oil (dyed with oil-red) on water surface over the MCTCS sponge. When the MCTCS sponge was placed on the oil-water interface, it could selectively absorb soybean oil from the oil-water interface. The soybean oil was completely removed from the water by the MCTCS sponge within several minutes. Because of its low density and superhydrophobicity, the MCTCS sponge floated on the water surface after sorption of the soybean oil, indicative of its potential application in the facile removal of oil spillage and chemical leakage. In addition, the MCTCS sponge also could effectively remove chloroform (dyed with oil-red) from the bottom of water, which was heavier organic solvent than water (Fig. 8b). When the MCTCS sponge was forced into the bottom of water to contact with chloroform, it could completely suck the chloroform within a few seconds, which made the MCTCS sponge a promising candidate for absorbing and eliminating heavy organic pollutants under the water surface. For the oil removal of MCTCS sponge, it was proposed that the physisorption played a critical role in this process. When the MCTCS sponge contacted with the oil or organic solvents, the oil or organic solvents could be absorbed into the inner part of the sponge under the action of driving force. The driving force for the oil-sorption mainly arises from hydrophobic interactions between MCTCS sponge and oils (or organic solvents) as well as the capillary effect of the pores [8].

Besides, the removal of oil from emulsified oil/water mixtures is a challenge in oily sewage treatment due to the small drop size and the low interfacial energy [41,42]. Therefore, the micrometer-sized oil droplets removal ability of the MCTCS sponge from oil-in-water mixture

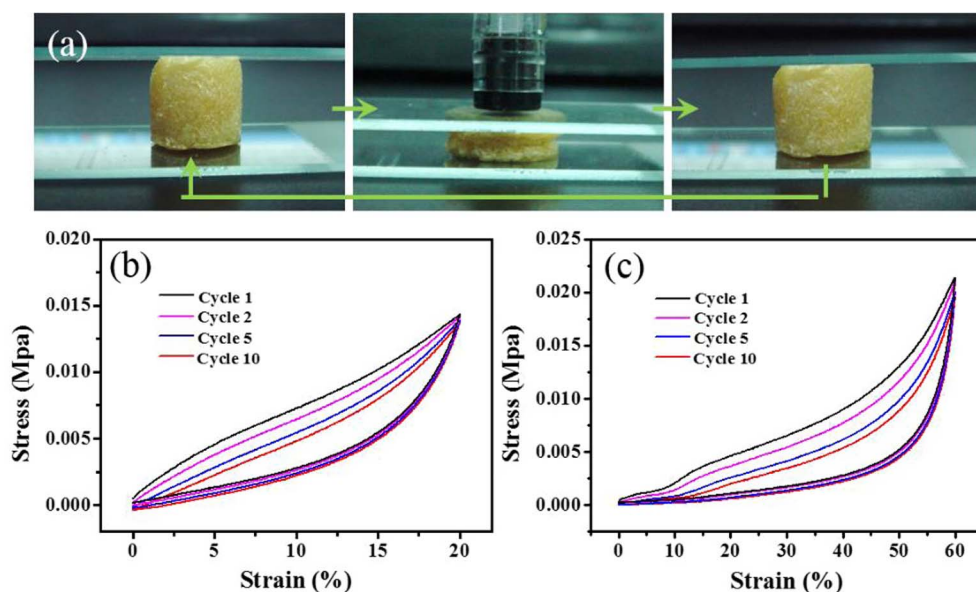


Fig. 5. Photographs of reversible compression of the MCTCS sponge (a). Cyclic stress-strain curves of the MCTCS sponge subjected to a compressive strain of 20% (b) and 60% (c).

was evaluated. A toluene-in-water emulsion (1:9, v/v) with a droplet size at the micrometer scale was prepared. Before separation, the toluene-in-water emulsion was a white milky liquid, as shown in Fig. 9a. When the MCTCS sponge was put into the liquid, the emulsion turned to transparent quickly after oscillation. To clearly observe the effective separation, Fig. 9b and c demonstrated the optical microscopic images of the toluene-in-water emulsion before and after separation. It was observed that there were large quantities of compact droplets in the feeds of emulsions before separation (Fig. 9b). After separation, no oil droplets were observed in the collected water (Fig. 9c). Moreover, the remaining toluene in water was determined, which decreased from 10% to 0.08% after separation, indicating that almost all of toluene in the emulsion was eliminated. It implied that the MCTCS sponge possessed the effective ability for the separation of oil-in-water emulsions.

### 3.4. Regeneration and recycle use of the MCTCS sponge

For practice application, the regeneration and the recovery of the absorbed liquid are key criteria for the absorbent. Hence, the regeneration of MCTCS sponge and recovery of absorbed liquid was evaluated by absorption-distillation and absorption-squeezing method for low boiling point and high boiling point oil, respectively. Hexane

with a boiling point of 68.7 °C and hexadecane with a boiling point of 287 °C was selected as the target liquid in the recycle experiment. As shown in Fig. 10a and b, the MCTCS sponge almost remained its original absorptive capacity after 15 absorption-distillation cycles. The recovery of hexane was still near 100% after 15 cycles. Considering the good compressive property of MCTCS sponge, absorption-squeezing was also used in recycling experiment of hexadecane absorption. The absorptive capacity of the MCTCS sponge has slightly changed after 10 cycles. No apparent deterioration was observed over 10 repetitions, and nearly 80% of the absorbed hexadecane could be mechanically

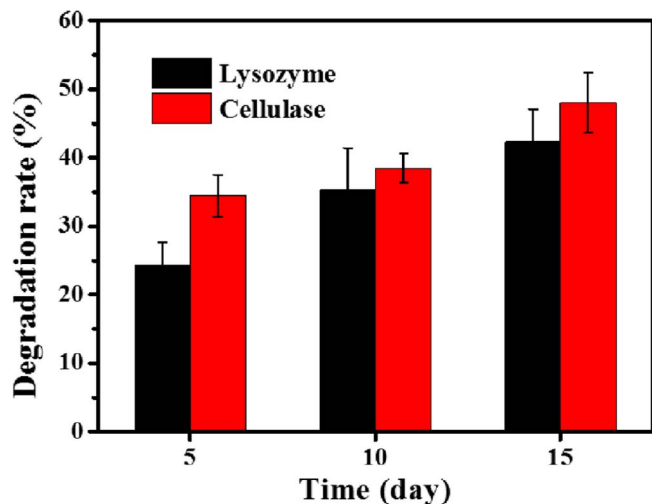


Fig. 6. Biodegradation rate of MCTCS sponge.

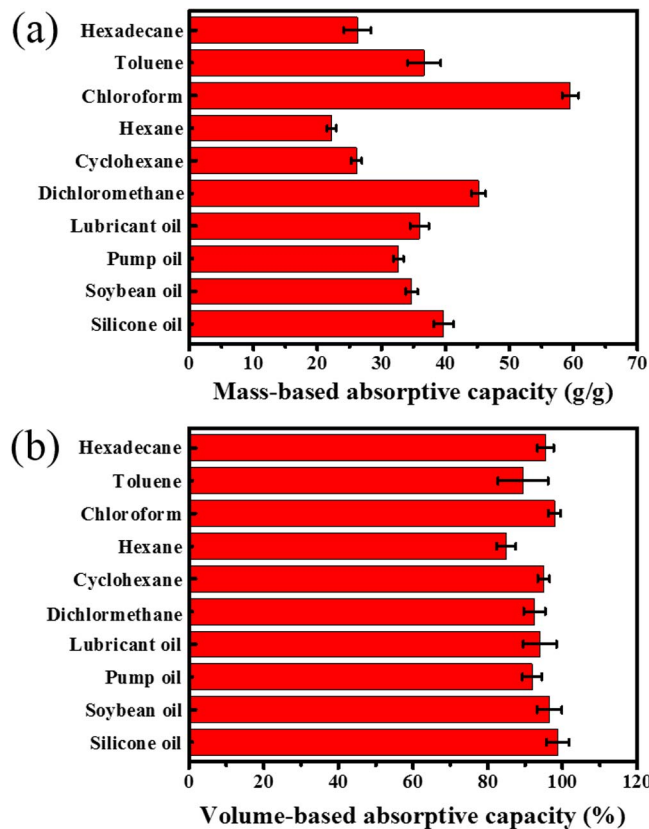
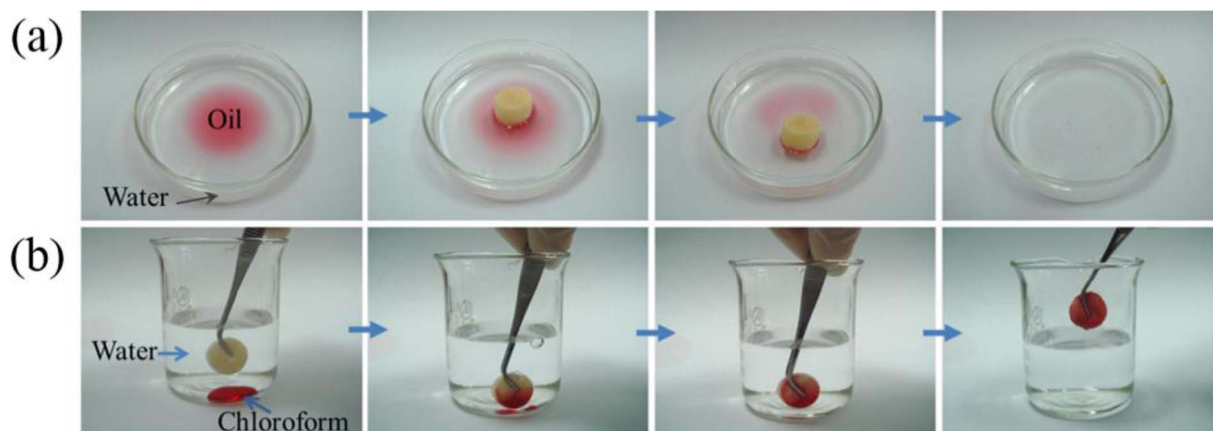


Fig. 7. Mass-based (a) and volume-based (b) absorptive capacity of the MCTCS sponge for different oils and organic solvents.





**Fig. 8.** Photographs of the absorption process of soybean oil absorption from the surface of water (a) and chloroform removal from the bottom of water (b) by the MCTCS sponge. The soybean oil and chloroform was labeled with oil red for clear observation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

squeezed in each cycle, as shown in Fig. 10c and d. The results demonstrated that the MCTCS sponge possessed excellent regeneration and recyclability.

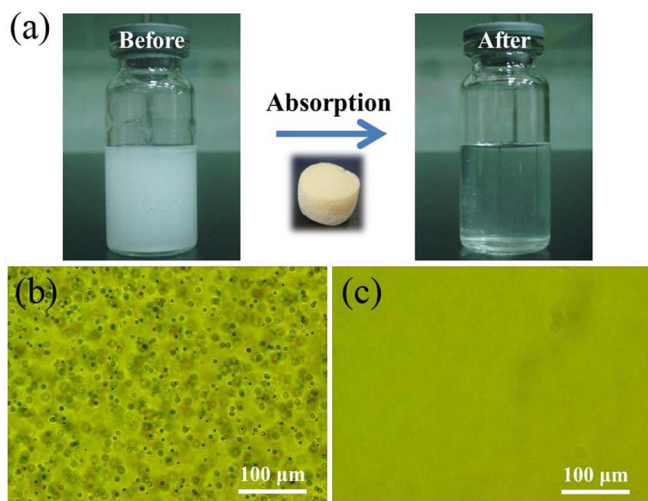
### 3.5. Continuous oil-water separation of the MCTCS sponge

Usually, in order to recycle use, the absorbed oil or organic solvent must be collected or removed from the materials after absorption equilibrium. Therefore, the continuous oil-water separation apparatus combined with a peristaltic pump was set up to investigate the continuous removal of oil from water over the MCTCS sponge, as illustrated in Fig. 11. The results showed that the oil could be continuously separated from the water surface by using this system. In a typical procedure, the MCTCS sponge was placed at the interface of hexane (dyed with oil red) and water. The MCTCS sponge could quickly absorb hexane and repel water completely due to its superhydrophobic and superoleophilic property. Once the peristaltic pump was turned on, the hexane was continuously absorbed and removed from water surface through the MCTCS sponge. Simultaneously, a stream of hexane was formed in the pipe, and the thickness of the hexane layer gradually decreased. Finally, the hexane layer could be successfully removed by using a small piece of the MCTCS sponge with the help of the peristaltic pump (Video S2, Supporting

Information). The collected hexane without water droplets and remaining water without hexane was visible to the naked eye (Fig. 11d and e). Furthermore, the residual content of hexane in the water was tested by gas chromatography. The separation efficiency of hexane and water was up to 99.25%. It implied that the MCTCS sponge with high selective oil-water separation efficiency could be used for continuous oil/water separation, indicative of the potential application in the clean-up of oil spill and industrial organic solvent leakages.



Video S2.



**Fig. 9.** Photographs of toluene-in-water emulsion before and after MCTCS sponge treatment (a). Optical micrographs of the toluene-in-water emulsion before (b) and after (c) MCTCS sponge treatment.

## 4. Conclusions

In summary, we reported a facile approach to prepare an environmental-friendly chitosan sponge (MCTCS) with good mechanical property, biodegradability and excellent superhydrophobic/superoleophilic via TPP/citral crosslinking and octadecanethiol modification method. The MCTCS sponge possessed highly oil absorptive capacity up to 60 times its own weight due to its high porosity and interconnected porous structure. More importantly, the MCTCS sponge could selectively remove the emulsified oils in water effectively and achieve continuous oil-water separation with the assistance of peristaltic pump. Furthermore, the sponge could remain its high absorptive capacity and excellent separation efficiency after repeatedly recycle. And the



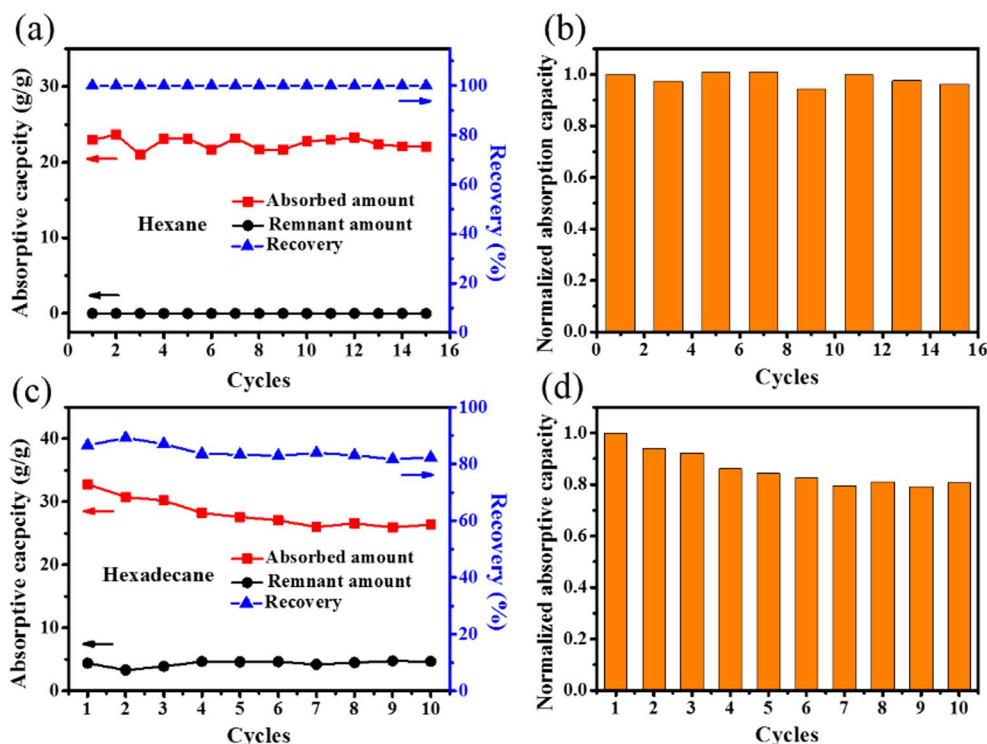


Fig. 10. Recyclability of MCTCS sponge for hexane absorption by distillation method (a and b), and hexadecane absorption by squeezing method (c and d).

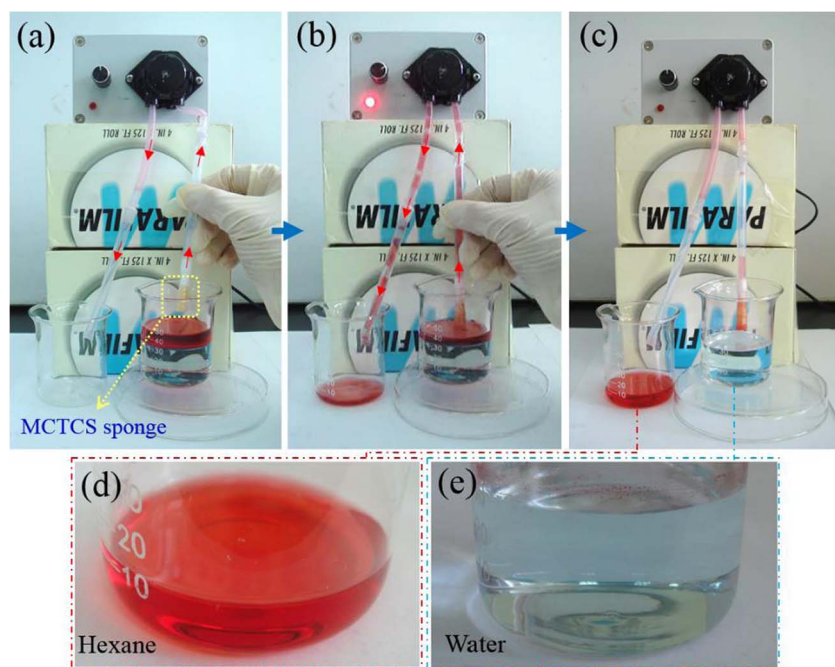


Fig. 11. Pump-assisted continuous oil-water separation process over the MCTCS sponge: original state before oil collection (a), continuous oil collection (b), final state of oil being completely eliminated (c). Enlarge view of hexane (d) and water (e) in the beaker. The hexane was labeled with oil red O and water is colored with methylene blue for clear observation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

absorbed oil was also easily collected by a simple distillation or squeezing process. The results suggested that the MCTCS sponge was a promising absorbent material for the removal of oils from water in environmental remediation.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2017.07.157>.

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