Underwater superoleophobic palygorskite coated mesh for the efficient oil/water separation

Jian Li *, Long Yan, Haoyu Li, Weijun Li, Fei Zha *, Ziqiang Lei

Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China, Key Laboratory of Gansu Polymer Materials, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China

Abstract

Oil/water separation has recently become a global challenging task due to the frequent oil spill accidents and increasing industrial oily waste water. Here, we first demonstrate underwater superoleophobic palygorskite coated meshes, which were fabricated by spraying palygorskite and polyurethane mixtures on copper mesh substrates. The underwater superoleophobic meshes were then used to study gravity driven oil/water separation for a series of oil/water mixtures, where only the water from the oil/water mixture is allowed to permeate through the mesh. Separation efficiency up to 99.6 % could be achieved through the coated mesh for the kerosene–water mixture. In addition, the palygorskite coated mesh still maintained high separation efficiency over 99.0 % and stable recyclability after 50 separation cycles with the surface morphology of the palygorskite coated mesh nearly unchanged. Furthermore, the palygorskite coated meshes exhibit excellent environmental stability under a series of harsh conditions, which are used for the separation of the mixtures of oil and various corrosive and active aqueous solutions, including strong acidic,

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* Corresponding author. Tel.: +86 931 7971533.
E-mail address:jianli83@126.com (J. Li).
* Corresponding author. Tel.: +86 931 7970237.
E-mail address:zhafei@nwnu.edu.cn (F. Zha).

alkaline, or salt aqueous solutions, even hot water. The fabrication approach presented

here can be applied for coating large surface areas and to develop a large-scale

oil/water separation facility for oil and various corrosive and active aqueous mixtures.

Keywords: Underwater superoleophobic; superoleophilic; palygorskite; oil/water

separation; separation efficiency

1. Introduction

Oil/water separation has become an increasingly important and urgent issue in

modern chemical industrial process and environmental protection because of the

frequent crude oil leakage and increasing industrial oily waste water.[1] Thus, there is

an increasing demand for the development of effective and inexpensive approaches

for the clean-up of the oil and water mixtures. Because oil/water separation is an

interfacial phenomenon, using special wettability to design novel materials is a facile

and effective way.[2–4] And lots of special wettability materials have been fabricated by

many scientists via construction of hierarchal rough surface as well as appropriate

surface energy.[5–13] Recently, materials with superhydrophobic and superoleophilic

properties (termed as "oil-removing" types of materials) have attracted extensive

interest in the field of oil water separation with the water phase repelled while the oil

phase penetrated through the materials easily, exhibiting high oil/water separation

efficiency and selectivity.[14–24] However, these "oil-removing" materials are easily

fouled and plugged by the adhered oil during separation process, thus resulting in

decrease oil/water separation efficiency and limit their practical applications. Inspired

by fish scales, membranes with hydrophilic and underwater superoleophobic

properties have been developed and show promising application as "water-removing" types of materials.[25,26] The water-removal materials avoid the formation of a water barrier between the substrate and the oil phase, which frequently occurs with oil-removal materials due to the fact that water commonly possesses a greater density than that of oils, thus overcoming the aforementioned drawbacks in oil/water separation existed with oil-removal materials. Up to now, various materials such as hydrogel,[26,27] silica,[28,29] TiO_2,[30–32] ZnO,[33,34] $CaCO_3$,[35] silicate,[36] $Cu(OH)_2$,[37-39] zeolite,[40,41] graphene oxide,[42,43] cellulose,[44,45] polymer membrane,[46–49] zwitterionic polymer,[50,51] etc. have been studied in order to achieve underwater superoleophobicity. Among of them, the hydrogen and polymer materials were broadly applied to achieve superhydrophilic and underwater superoleophobic properties to separate oils from oil/water mixtures effectively. However, the main obstacle of these hydrogen and polymeric materials are their weak environmental adaptability, due to their characteristic of swelling in water and/or metamorphosis of the polymeric membrane under long-term scouring by water. In addition, there are few works reported about the separation of the corrosive and hot oil-water mixtures with high separation efficiency. The lifetime of these separation devices would be largely extended if they are durable toward such severe environmental conditions. Therefore, it is of great significance to develop functional materials with stable underwater superoleophobicity for separation the mixtures of oil and harsh corrosive aqueous solutions in a simple, economical and scalable approach.

Palygorskite is one of the most typical hydrophilic materials, consisting of

hydrated octahedral layered magnesium aluminum silicate with reactive -OH groups on the surface and natural crystals.[52-55] Because of their excellent water-absorbing and water-retaining capacities, palygorskite is considered to be a promising candidate for designing novel water-removing material for oil/water separation. The strategy here employs the highly hydrophilic palygorskite coating to form a layer of bounded water surrounding a submerged mesh, and thus resisting the attachment of oil. Moreover, palygorskite has attracted significant attention owing to its low cost, chemical inertness and environmental stability. Therefore, we propose that underwater superoleophobic palygorskite coated mesh combined with anti-corrosion and environmental stability properties will create unique opportunities for the practical application in separating corrosive as well as active oil-water mixtures.

Herein, underwater superoleophobic palygorskite coated meshes were fabricated by spraying palygorskite powders and waterborne polyurethane (PU) mixtures on copper mesh. To the best of our knowledge, it is the first time to use the underwater superoleophobic palygorskite coated meshes for oil/water separation. The waterborne PU was added in order to increase the binding force between the palygorskite powders and copper mesh. The spray-coating is a simple one-step and low-cost process for the widest applications, which can be easily applied to large surface area, independent of substrate properties such as shape and electrical conductivity.[56,57] The as-prepared palygorskite coated mesh surface shows an excellent water affinity and outstanding underwater superoleophobicity. The separation methodology is solely based on gravity, Thus, the superhydrophilic and underwater superoleophobic

palygorskite coated mesh was used for the gravity-driven oil/water separation experiments and showed 99.6 % water/oil separation efficiency for the kerosene–water mixture, which allows water to permeate through the film quickly, whereas the oil phase is retained above the film, thus proving to be an energy-efficient filter for oil/water separation. In addition, the palygorskite coated mesh still maintained high separation efficiency up to 99.0 % and stable recyclability after 50 separation cycles with the surface morphology of the palygorskite coated mesh nearly unchanged. More importantly, the palygorskite coated meshes exhibit excellent environmental stability under a series of harsh conditions, which are used for the separation of the mixtures of oil and various corrosive and active aqueous solutions, including strong acidic, alkaline, or salt aqueous solutions, even hot water. Our work shows that the palygorskite coated meshes are suitable for future practical applications in oil/water separation.

2. Experimental

Materials

Palygorskite micro-powder supplied from Jiuchuan Clay Technology Co., Jiangsu, China, is composed of CaO (1.29%), Al_2O_3 (10.47%), Na_2O (1.52%), MgO (20.41%), SiO_2 (64.31%), K_2O (0.13%) and Fe_2O_3 (0.87%). The palygorskite powder was firstly activated with 4 M HCl solution before use. Waterborne polyurethane (PU) was purchased from Sinopharm Chemical Reagent Co., Ltd.

Preparation of underwater superoleophobic mesh

In a typical procedure, the amount of 0.05 g waterborne polyurethane (PU) was

dissolved in 20 mL acetone, and then 0.3 g palygorskite powers were dispersed in the solution and stirred magnetically for at least 1 h to gain a homogeneous suspension. The suspension was then sprayed onto the copper mesh substrate with 0.2 MPa compressed air gas using a spray gun. Finally, the palygorskite coating was dried at ambient temperature for 1 h to allow the acetone to evaporate completely.

Oil/water separation

Five kinds of oils and organic solvents including kerosene, toluene, petroleum ether, hexane and rapeseed oil were used in this study. They were colored with oil red O and mixed with water that was colored with methylene blue. The underwater superoloephobic palygorskite coated mesh was fixed between two Teflon fixtures, both of which were attached with glass tubes. Before oil/water separation, the palygorskite coated mesh was completely wetted by water. Mixtures of oil and water (50% v/v) were poured slowly into a test tube through the palygorskite coated mesh. The driving force during the separation process is its own gravity. The separation efficiency was calculated according to $\eta = (m_1/m_0) \times 100$, where m_0 and m_1 were the mass of the oil before and after separation process, respectively.[58]

Separation oil and cool solutions

The palygorskite coated mesh was fixed between two Teflon fixtures, both of which were attached with glass tubes. The palygorskite coated mesh was completely wetted by water before separation. Mixtures of kerosene and cool solutions such as 1 M HCl, 1 M NaOH, 1 M NaCl and hot water (50% v/v) were poured slowly into a test tube through the palygorskite coated mesh. The driving force during the separation process

is its own gravity.

Characterization

The morphological structures of the as-prepared surfaces were examined by field emission scanning electron microscopy (FE-SEM, JSM-6701F). The phase structure of the as-prepared samples was characterized by an X-ray diffractometer (XRD) (Rigaku Corp., D/max-2400) equipped with graphite monochromatized Cu Kα radiation. The water and oil contact angle and sliding angle were measured with a SL200KB apparatus at ambient temperature. The volume of the individual water and oil droplets in all measurements was 5 μL. The average water, oil contact and oil sliding values were obtained by measuring the same sample at least in five different positions.

3. Results and discussion

In this work, we selected palygorskite powders for the fabrication of superhydrophilic surface, because this material is commercial available and inexpensive with excellent water-absorbing and water-retaining capacities (the schematic structure of palygorskite was shown in Fig. 1a).[53] The waterborne PU was added in order to increase the binding force between the palygorskite powders and copper mesh. The XRD pattern of palygorskite powders is shown in Fig. 1b. The XRD patterns of the palygorskite powders demonstrate a (110) Characteristic diffraction peak at 8.4° of palygorskite, revealing that the structure of palygorskite powders is maintained very well in the preparation process.[54]

The surface morphologies of the original and the coated meshes were characterized

by FE-SEM. As shown in Fig. 2a, the original mesh has an average pore diameter of about 75 μm (200 mesh size), and the magnified view in the inset of Fig. 2a reveals that the original wires have smooth surface. FE-SEM micrograph of palygorskite was also investigated, due to the existence of van der Waals force and hydrogen bonds, the single crystals of palygorskite are inclined to aggregate as crystal bundles and aggregates (Fig. S1, ESI†).[55] After coated with the mixture of palygorskite and PU, it can be seen that the original mesh has been completely covered by densely and randomly distributed palygorskite with the microscale (Fig. 2b). The high magnified FE-SEM image of Fig. 2c shows that the palygorskite is relatively aggregated with the diameter of a single fibril about 100 nm and the length of a single fibril about several hundred of nanometers, resulting to the micro/nanoscale hierarchical rough surface of the as-prepared palygorskite coated meshes. This hierarchical roughness of the palygorskite coated mesh surface combined with the affinity to water is essential to the superhydrophilicity in air and underwater superoleophobicity.

As is well known, the wettability of a solid surface greatly depends on its chemical composition and micro/nanostructure. A hydrophilic palygorskite coating and the special morphology of the coated mesh provide a possibility for the fabrication of underwater superoleophobic mesh films. The wettability of water and oil on palygorskite coated meshes was evaluated by the contact angle measurements. The as-prepared palygorskite coated mesh surfaces are superamphiphilic in a-solid-liquid three phase systems with both the water contact angle and the oil contact angle less than 5° (Fig. S2, ESI†). This ascribes to the cooperative effect of the existence of

massive hydroxyl groups (the palygorskite powders and water PU are both terminated with hydroxyl groups) and the micro/nanoscale binary roughness. The underwater oil wettability was examined by immersing the coated meshes into aqueous solution. As shown in Fig. 3, the palygorskite coated mesh exhibits underwater superoleophobicity to a series of oils with oil contact angles larger than 150°, such as hexane, petroleum ether, kerosene, toluene, rapeseed oil and chloroform. The adhesion between the palygorskite coated mesh surface and the oil (chloroform) droplet is extremely low, thus the chloroform droplet can easily roll for the surface with a sliding angle of 8° (Fig. S3, ESI†). The underwater superoleophobicity on palygorskite coated meshes achieved in oil–water–solid systems originates from the repellency between polar (water) and non-polar (oil) molecules. As a consequence, when the palygorskite coatings contact with the oil droplets, water trapped in the rough nanostructures provides a strong repulsive force, resulting in greater oil contact angles and lower oil sliding angles. Therefore, such underwater superoleophobic property can effectively prevent palygorskite coated meshes to be polluted or blocked up by oils during oil/water separation process.

The as-prepared palygorskite coated mesh has great potential to separate oil/water mixtures due to the underwater superoleophobic property. A series of studies were carried out to test the oil/water separation capacities of the as-prepared palygorskite coated mesh. A mixture of kerosene (dyed with the Oil Red O) and water (dyed with the methylene blue) was poured onto the water pre-wetted coated mesh that was fixed between two glass tubes and sealed with Teflon flanges (Fig. 4a). Gravity was the

only force for the oil/water separation. Because of the outstanding underwater superoleophobic property of the palygorskite coated mesh, kerosene was retained above the coated mesh, while water with higher density than oil permeated through the coated mesh quickly. And no visible oil was observed in the collected water, indicating a high purity and effectiveness separation of the oil/water mixture (Fig. 4b). The whole separation process was completed within a few min (Movie S1, ESI†). A variety of oil/water mixtures (50 % v/v) also have been successfully separated through the same process including toluene, petroleum ether, hexane and rapeseed oil. The separation efficiency was calculated according to $\eta = (m_1/m_0) \times 100$, where m_0 and m_1 were the mass of the oil before and after separation process, respectively. The separation efficiency of the coated mesh was calculated up to 99.6 % for the kerosene-water mixture and above 96.0 % for other oils, as shown in Fig. 4c. In addition, the coated meshes still retain underwater superoleophobic property after 50 separation cycles with the separation efficiency for the kerosene/water mixture always stayed above 99.0 % (Fig. 4d), which indicated good recyclability of the as-prepared coated meshes. In addition, the surface morphology of the palygorskite coated mesh was nearly unchanged. (Fig. 4e).

Oil (kerosene) intrusion pressure and water flux and were also introduced to testify the separation efficiency of as-prepared palygorskite coated mesh. The intrusion pressure (P) value was measured using eqn (1):

$$P = \rho g h_{max} \quad (1)$$

where ρ is the density of the kerosene, g is acceleration of gravity, and h_{max} is the

maximum height of kerosene the coated mesh can support. As shown in Fig. 4f, the

average maximum bearable height achieved is 19.0 cm, and the intrusion pressure is

about 1.5 kPa and kerosene cannot flow through the mesh under the pressure.

The water flux (F) was measured under a fixed column of water. The values were

calculated using eqn (2):

$$F = V/St \quad (2)$$

where V is the volume of water that permeates through the membrane, here we fixed

V to 1 L, S is the area of the mesh, and t is the required time for the permeation of 1 L

water. Here, the water flux was as high as 15 L m^{-2} s^{-1}.

The as-prepared palygorskite coated mesh also showed stable underwater

superoleophobicity towards many corrosive solutions (1M HCl, 1 M NaOH and 1M

NaCl solutions) and hot water, which was measured by immersing the coated mesh

into corresponding solutions. As shown in Fig. 5a-c, oil contact angles for hexane,

petroleum ether, kerosene, toluene and rapeseed oil are all larger than 150º, when the

palygorskite coated meshes were placed in 1M HCl, 1M NaOH and 1M NaCl aqueous

solutions for 6 h, respectively. In addition, all oil contact angles under hot water are

still as high as 150º (Fig. 5d). The results show that palygorskite coated meshes are

chemical resistant to the extreme environment conditions, such as cool corrosive

solutions and hot water.

The as-prepared palygorskite coated meshes that combined chemical stability and

underwater superoleophobicity will demonstrate efficient separation for corrosive and

active oil/water mixtures. The separation capability of the palygorskite coated mesh

for corrosive oil/water mixtures was performed as shown in Fig. 6. The palygorskite coated mesh was fixed between the two glass tubes, and mixture of kerosene dyed with the Oil Red O and 1M HCl solution was poured onto the pre-wetted palygorskite coated mesh (Fig. 6a and Movie S2, ESI†). The corrosive aqueous solution passed through mesh quickly by the driving force of gravity, while kerosene was kept in the upper glass tube due to the underwater superoleophobicity. Moreover, the other three mixtures, including kerosene/1M NaOH (Fig. 6b and Movie S3, ESI†), kerosene/1M NaCl (Fig. 6c and Movie S4, ESI†) and kerosene/hot water with 85 °C (Fig. 6d and Movie S5, ESI†) are successfully separated by using the same method. As given in Fig. 6b-d, the kerosene was retained above the mesh because of underwater superoleophobicity, while corrosive aqueous solution and hot water permeated through quickly the palygorskite coated mesh and dropped into the breaker below. Nearly no visible oil is presented in the water after separation. The chemical inertness of palygorskite coated mesh is a very vital consideration in harsh environmental applications, which will offer important opportunities in industry and everyday life, such as oil spill cleanup, separation of living waste oil.

From the viewpoint of real applications, the mechanical strength of the palygorskite coated mesh is also an important property. Although the PU was added to increase the binding force between the palygorskite powders and copper mesh, the palygorskite coated mesh is still not strong enough to withstand mechanical scratch. After 40 times adhesive tape scratch, the palygorskite coated mesh lost its underwater superoleophobic property and could not separate oil/water mixtures. However, the

destroyed surfaces can restore under superoleophobicity and be used for oil/water separation once again just by spraying the palygorskite and PU mixtures on the destroyed surface. In addition, the facile spray-process allows the local repair at anytime and almost anywhere with the time of regeneration unlimited.

4. Conclusions

In summary, we have demonstrated that robust superhydrophilic and underwater superoleophobic palygorskite coated meshes for the application of oil/water separation, which can be easily fabricated by spraying palygorskite powders and waterborne PU mixture onto copper meshes. The palygorskite coated meshes can selectively separate water from oil/water mixtures with high separation efficiency up to 99.6 % and resist to oil fouling. In addition, the separation efficiency could still reach up to 99.0 % after 50 separations. Moreover, the palygorskite coated meshes displayed excellent environmental stability for separation mixtures of kerosene and various corrosive and active aqueous solutions, including acid and base, salt, as well as hot water. This study would open up a good future towards rational designing and developing functional materials for oil/water separation.

Acknowledgement

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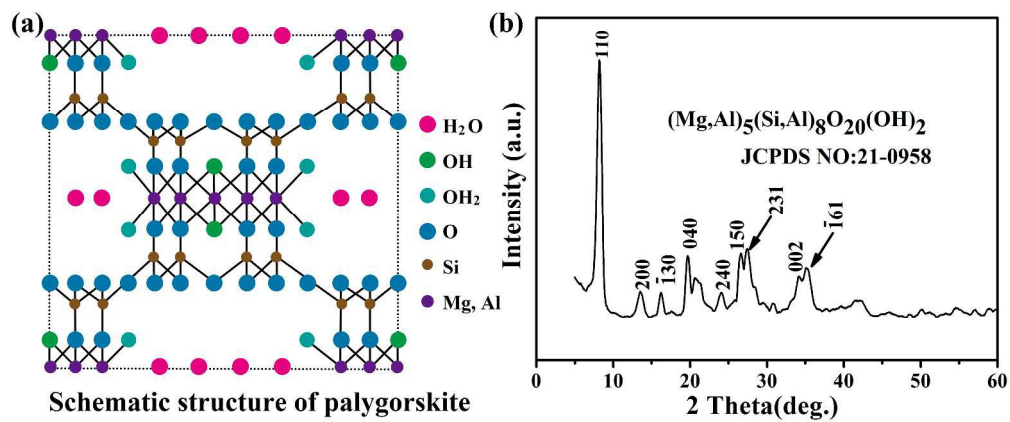
Figure Captions

Figure 1. Schematic structure of palygorskite (a) and (b) XRD pattern of the palygorskite powders.

Figure 2. FE-SEM images of (a) the original copper mesh and (b-c) the as-prepared palygorskite coated mesh surface at low and high magnifications, respectively. The inset (a) is the magnified image of the original mesh.

Figure 3. Photographs of oil droplets on the palygorskite coated mesh underwater with all the oil contact angles larger than of 150°.

Figure 4. Oil/water separation studies of the as-prepared palygorskite coated mesh (water is dyed with methylene blue and oil is dyed with Oil Red O to enhance the visual effect): (a) during separation; (b) after separation; (c) the separation efficiency of the oil/water mixtures; (d) the oil/water separation efficiency versus the recycle numbers by taking kerosene/water mixture as an example; (e) the surface morphology of palygorskite coated mesh has no change after 50 times use; (f) the intrusion pressure of oil taking kerosene as an example.

Figure 5. Various oil contact angles on the palygorskite coated mesh surface under different corrosive and active solutions: (a) 1M HCl solution; (b) 1 M NaOH; and (c) 1M NaCl solution; (d) hot water.

Figure 6. Separation experiments of the palygorskite coated mesh for mixtures of kerosene and various corrosive aqueous solutions: (a) 1 M HCl; (b) 1 M NaOH; 1M NaCl; (d) hot water with 85 °C.

The TOC graphic

The palygorskite coated meshes with robust underwater superoleophobicity display excellent environmental stability for separation mixtures of oil and corrosive solutions.

Figure 1. Schematic structure of palygorskite (a) and (b) XRD pattern of the palygorskite powders.
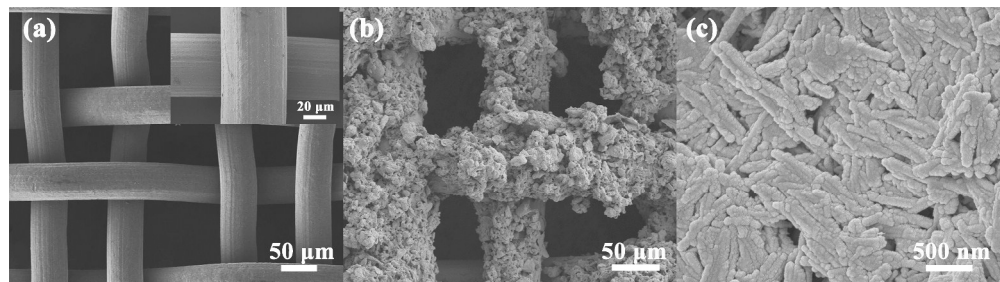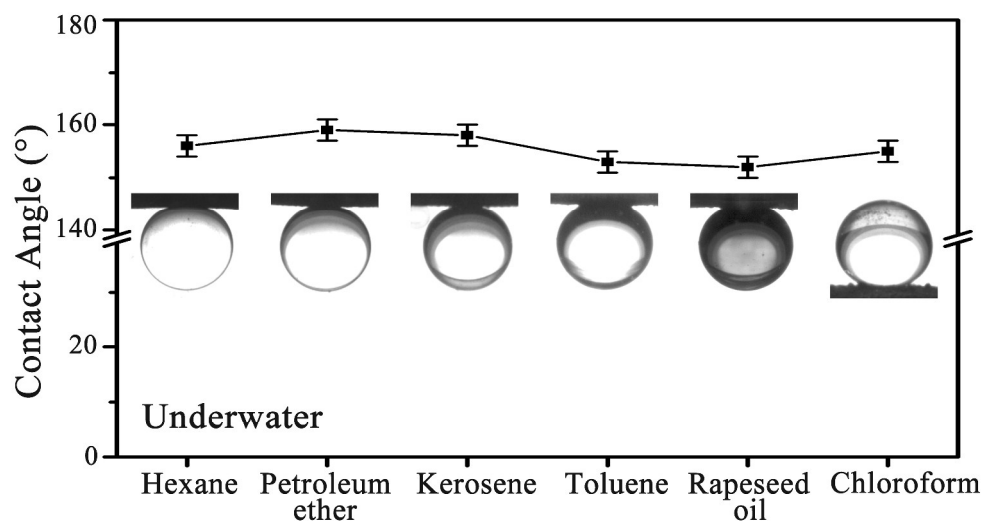
Figure 2. FE-SEM images of (a) the original copper mesh and (b-c) the as-prepared palygorskite coated mesh surface at low and high magnifications, respectively. The inset (a) is the magnified image of the original mesh.

Figure 3. Photographs of oil droplets on the palygorskite coated mesh underwater with all the oil contact angles larger than of 150°.
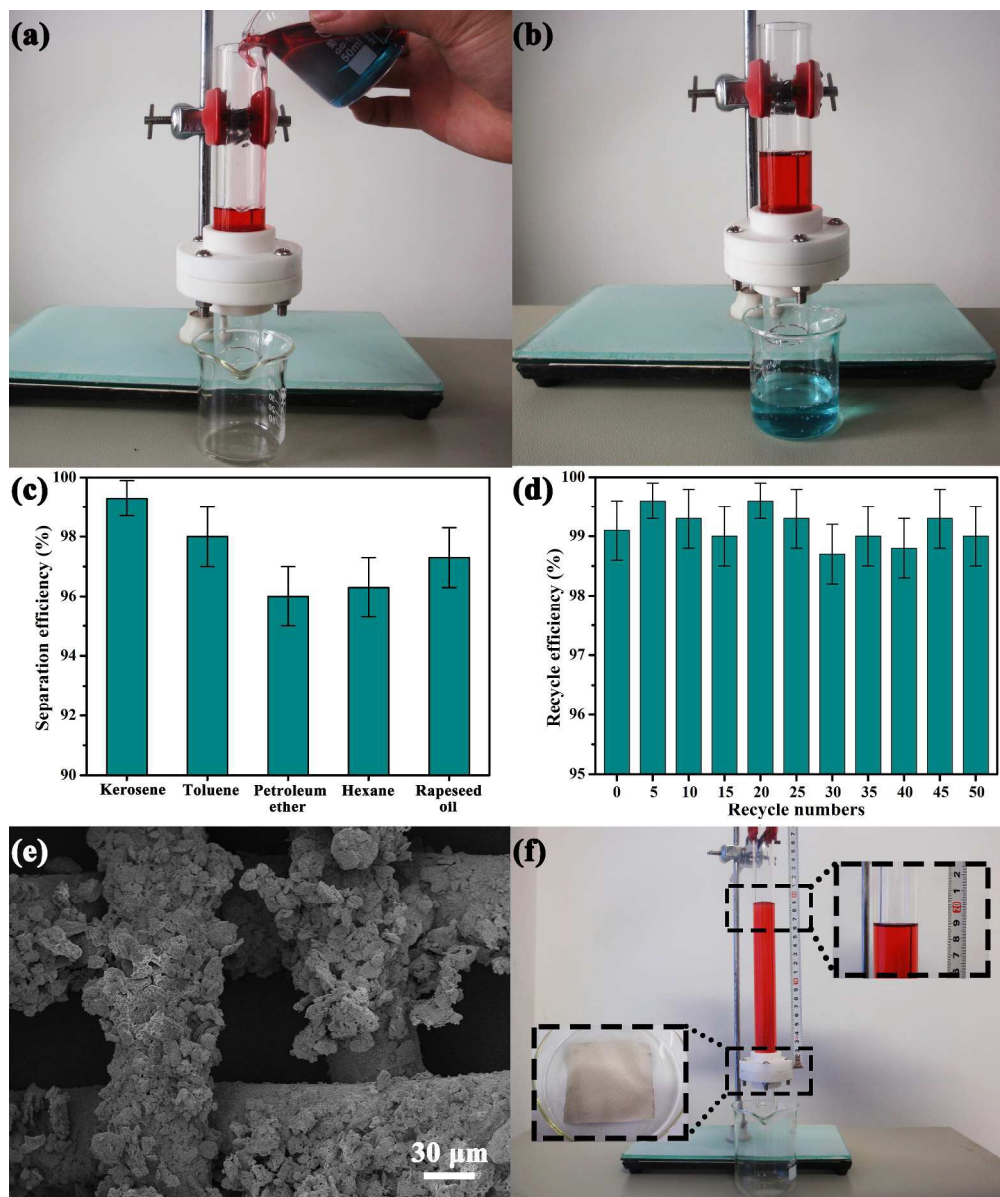
Figure 4. Oil/water separation studies of the as-prepared palygorskite coated mesh (water is dyed with methylene blue and oil is dyed with Oil Red O to enhance the visual effect): (a) during separation; (b) after separation; (c) the separation efficiency of the oil/water mixtures; (d) the oil/water separation efficiency versus the recycle numbers by taking kerosene/water mixture as an example; (e) the surface morphology of palygorskite coated mesh has no change after 50 times use; (f) the intrusion pressure of oil taking kerosene as an example.
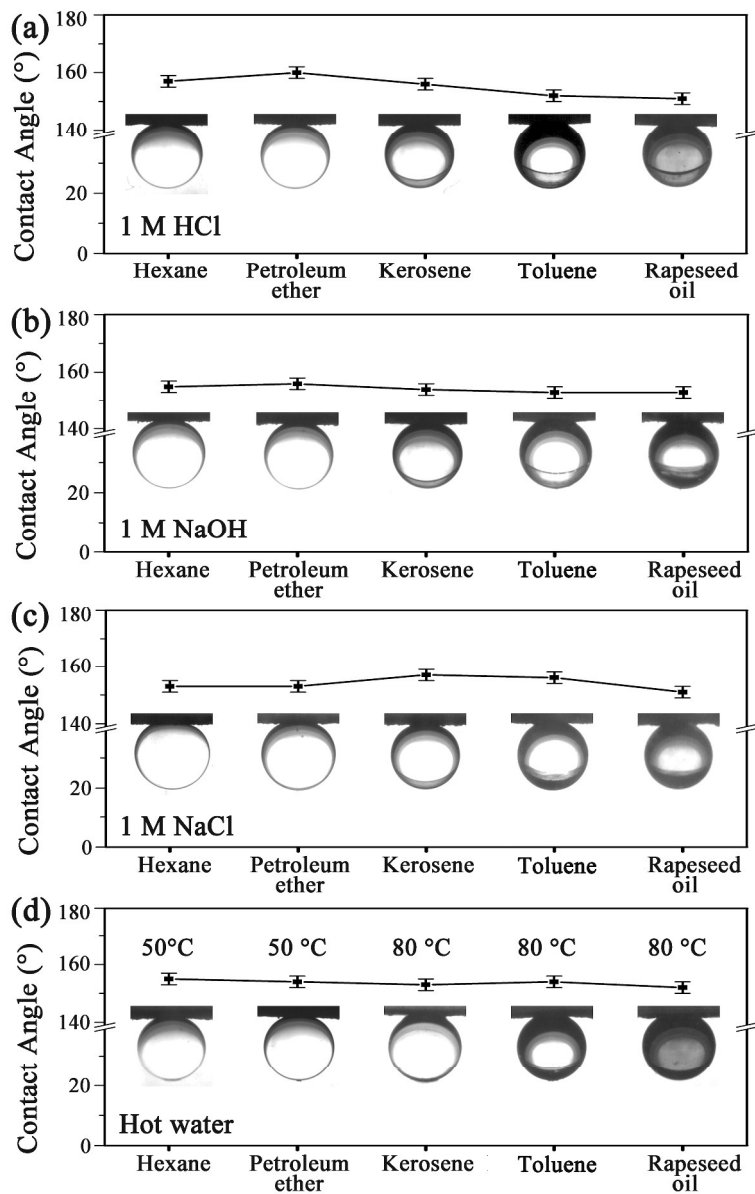
Figure 5. Various oil contact angles on the palygorskite coated mesh surface under different corrosive and active solutions: (a) 1M HCl solution; (b) 1 M NaOH; and (c) 1M NaCl solution; (d) hot water.
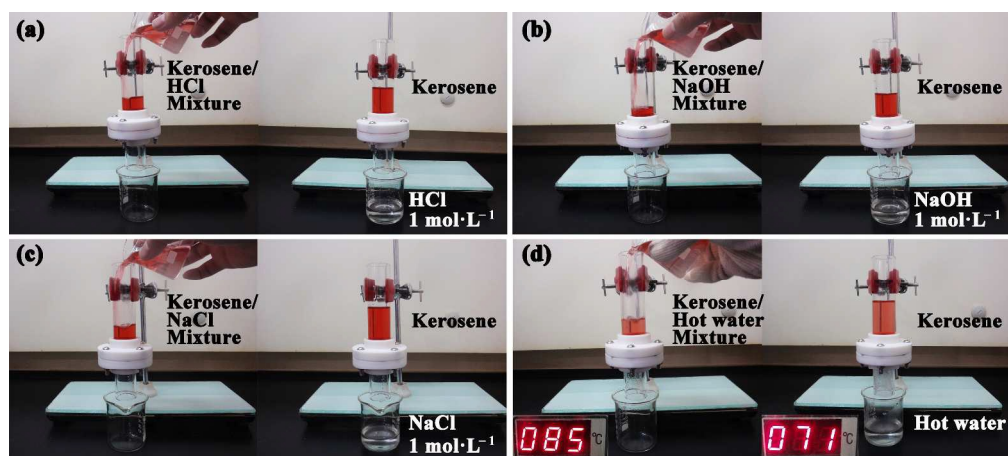
Figure 6. Separation experiments of the palygorskite coated mesh for mixtures of kerosene and various corrosive aqueous solutions: (a) 1 M HCl; (b) 1 M NaOH; 1M NaCl; (d) hot water with 85 °C.