Preparation and performance study of environmentally friendly and durable kaolin/PDMS/cotton fabrics superhydrophobic surface

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In this research work, a fluorine-free, durable, and excellent self-cleaning and oil-water separation performance kaolin/polydimethylsiloxane/cotton fabrics (Kaolin/PDMS/cotton) superhydrophobic surface was successfully prepared. The morphology, wettability, and phase composition of the coating were characterized and tested using scanning electron microscopy (SEM), dynamic contact angle measuring instrument, and X-ray diffraction (XRD). The experimental results showed that the organic composite of hydrophobic modified kaolin particles and cotton fabrics was successfully achieved through the bridging effect of PDMS. A dense superhydrophobic micro-nano structure coating was constructed on the surface of cotton fibers, and the tested performance was excellent. Has good local anti-pollution performance for common coffee, Coca-Cola, dyeing water, and simulated dust; After being worn for a distance of 1200 centimeters under a load of 10KPa, the contact angle with water remained above 150°, indicating excellent durability of the coating; In addition, kaolin/PDMS/cotton also exhibited good oil/water separation performance. After 15 cycles of oil-water separation tests, the separation efficiency for gasoline and dichloromethane both exceeded 96%.

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1. Introduction

In the current industrial field, frequent incidents of oily wastewater and oil spills have serious negative impacts on the global environment and ecosystem[1-3]. Oil water separation is an important process for treating oily wastewater. However, traditional oil removal methods not only face difficulties in recovering adsorbent products, low adsorption rates, high economic costs, but also have limitations such as unfriendly environment[4,5]. Therefore, how to effectively treat oil pollutants in water has become a challenge faced by humans.

In order to solve the above problems, scholars from various countries are actively seeking inspiration from nature and utilizing natural superhydrophobic phenomena (such as the self-cleaning property of lotus leaves, rice leaves, and other surfaces that "ooze without staining") to actively research new superhydrophobic materials[6]. Biomimetic superhydrophobic networks or sponge like materials are a new type of oil-water separation tool with water blocking and oil transportation properties. They can not only effectively separate oil-water mixtures, but also be

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reused multiple times. Therefore, they have great prospects for application in the separation of oil-water mixtures[7]. Jianglei research group [8], the first one to study bionic interface in China, reported for the first time in 2004 that a method of spraying stainless steel mesh with polytetrafl-uoroethylene lotion (PTFE) was used to prepare a superhydrophobic/superlipophilic mesh membrane, and proposed an idea that it could be applied to oil-water separation. In recent years, with the continuous deepening of research on superhydrophobic materials, a series of superhydrophobic oil-water separation membrane materials (mainly copper mesh and stainless steel mesh metal matrix) and superhydrophobic three-dimensional porous adsorption materials (mainly concentrated in polymer based materials such as melamine sponge, polyurethane sponge, and polytetrafluoroethylene) have been prepared [9-11]. Although superhydrophobic materials based on metal mesh and sponge have good oil-water separation efficiency, most of these materials are made from non renewable raw materials and are difficult to clean and degrade after use, ultimately causing secondary environmental pollution and rapid consumption of non renewable resources, which contradicts the concept of sustainable development [12].

Cotton fabric has shown great potential in the design of eco-friendly superhydrophobic oil-water separation materials due to its many advantages such as renewability, biodegradability, good permeability, low cost, high flexibility, and easy to expand manufacturing[13]. Based on the wettability theory model, the two important influencing factors for the preparation of superhydrophobic materials are the surface microstructure and chemical composition. superhydrophobic surfaces can be prepared by impregnation/spraying [14, 15], layer by layer assembly [16], sol-gel method [17] and hydrothermal synthesis [18], but these methods are often limited by some shortcomings in practical application, such as hydrophobic agents are generally expensive and involve environmentally harmful substances, poor mechanical and chemical stability The problem of poor adhesion between the substrate and modified materials [19]. For example, Zhou et al. modified cotton fabrics with tea polyphenols and iron nanoparticles to prepare superhydrophobic cotton fabrics. However, the adhesion between the coating and cotton fabric was weak and easily damaged. After 5 washes, the contact angle of the prepared sample with water decreased from 163 ° to 153 °[20]. Bai et al. used the sol gel method and oxidative coupling polymerization to coat the cotton fabric with SiO_2/polythiophene to prepare the super hydrophobic cotton fabric, although it has a high oil-water separation efficiency, the coating durability is poor, and the contact angle drops from 160 ° to below 150 ° when the wear distance is less than 20 cm [21]. Therefore, solving the problem of cotton fabric superhydrophobicity

Based on the above issues, this study uses biodegradable and environmentally friendly material cotton fabric as the substrate, uses cheap and non-toxic calcined kaolin solid particles as the modified material, and uses cheap and non-toxic stearic acid as the modifier. Using a simple and efficient impregnation process, the modified kaolin powder is loaded onto the surface of cotton fibers through the "bridging" effect of polydimethylsiloxane (PDMS), and a dense kaolin/cotton fabric superhydrophobic coating is prepared. The results show that the prepared kaolin/cotton fabrics superhydrophobic material had good oil-water separation, pollution resistance, and wear resistance.

2. Experimental section

2.1. Materials

Anhydrous ethanol, stearic acid, methyl violet, and n-hexane were produced by Tianjin Komio Chemical Reagent Co., Ltd. Acetone and chloroform were produced by Luoyang Chemical Reagent Factory. PDMS prepolymer (Sylgard-184) with the curing agent was obtained from Dow Corning Co. (USA). 400 mesh calcined kaolin was purchased from Shanghai Beimo Industrial Co., Ltd.. 92 # gasoline and 0 # diesel were provided by Sinopec gas stations. Peanut oil (manufactured by JD). Pure sesame oil and cotton fabrics (plain weave, weight: 116.44 $g \cdot m^{-2}$) were purchased from a local market. Sandpaper was produced by Wuxi Gangxia Precision Sandpaper Factory, and deionized water was prepared in the laboratory.

2.2. Preparation of kaolin/PDMS/cotton

Added 0.5 g of stearic acid to 24 mL of anhydrous ethanol and stired magnetically until it was completely dissolved. Next, added 10 g of 400 mesh calcined kaolin to it, sonicated for 30 minutes, transfered to a three necked flask, and distilled at 95 ℃. Finally, dried the obtained suspension in a 60 ℃ oven for 6 hours to obtain modified kaolin powder.

Weighed 3 g of the above modified kaolin powder into 30 mL of n-hexane, then sequentially added 1 mL of PDMS (density 1 $g \cdot mL^{-1}$, 20 ℃) and its curing agent 0.1 mL, sonicated for 30 minutes to fully disperse, then immersed clean cotton fabrics in the solution, shaked at 25 ℃, 140 $r \cdot min^{-1}$ for 30 minutes, and then took it out and cured in a 50 ℃ oven for 2 hours to obtain the final superhydrophobic sample, abbreviated as kaolin/PDMS/cotton.

2.3. Characterization of samples

The phase composition of kaolin/PDMS/cotton was characterized and analyzed using X-ray energy dispersive spectroscopy (EDS, Nova NanoSEM 450) and X-ray powder diffraction (XRD, Bruker D8 ADVANCE). Used field emission scanning electron microscopy (FE-SEM, Nova NanoSEM 450) to characterize the apparent morphology of superhydrophobic samples. Measured the static contact angles (CA) between the sample surface and ion water droplets using a contact angle measuring instrument (C601 solid-liquid interface analyzer, China). Measured at least three different positions on each sample and took the average value of the contact angles.

3. Results and discussion

3.1. XRD and EDS characterization analysis

The chemical composition of the blank sample and Kaolin/PDMS/cotton were compared and analyzed using XRD and EDS spectra, respectively. Fig.1a shows the XRD patterns of blank cotton fabrics, Kaolin/PDMS/cotton, and modified kaolin. It can be seen that the peaks of the blank cotton fabrics were reflected in the XRD patterns of Kaolin/PDMS/cotton, but the strength was not as strong as before [22]. In addition, there were many other peaks. Comparing the diffraction peaks of modified kaolin in Fig.1c with JCPDS standard cards (1-613) and (1-649), it was found that the main components of calcined kaolin were metakaolin, mullite, and quartz [23], and the diffraction peaks at 2θ values of 16.64 °, 26.09 °, 33.27 °, 35.30 °, 42.87 °, 53.72 °, 57.5 °, 60.65 °, and 67.09 ° correspond to the characteristic diffraction peaks of mullite crystals, and the diffraction peaks at 2θ values of 21.67 °, 26.09 °, 36.76 °, 39.35 °, 40.97 °, 42.87 °, 49.57 °, and 60.65 ° correspond to the characteristic diffraction peaks of quartz crystals [24]. Therefore, it can be inferred that the modified kaolin particles had successfully bridged onto the surface of cotton fabrics.

To confirm the surface composition of Kaolin/PDMS/cotton, EDS analysis was conducted. Figure 1b shows the EDS characterization results of kaolin/PDMS/cotton. It can be seen that the sample surface mainly contains four elements: C, O, Si, and Al, while the main chemical components of calcined kaolin are Al_2O_3 and SiO_2, which further confirms the presence of modified kaolin powder on the surface of Kaolin/PDMS/cotton.

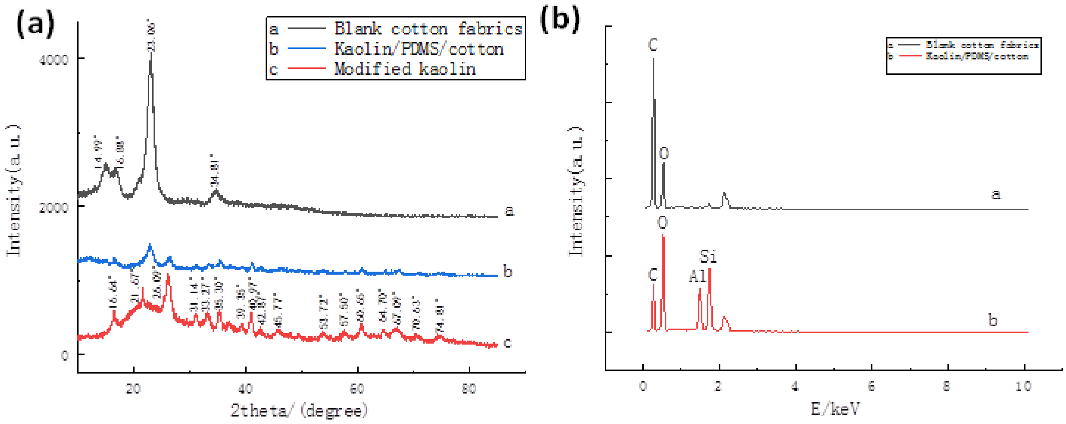

Fig. 1. XRD characterization (a) and EDS characterization (b) results of the prepared samples.

3.2. Morphology and superhydrophobicity analysis

In order to investigate the morphological changes of cotton fabrics before and after modification, scanning electron microscope (SEM) was used to characterize the blank cotton fabrics and Kaolin/PDMS/cotton. The results are shown in Fig.2. It can be seen that the surface of the blank cotton fabrics was relatively smooth without any attached substances(see Fig.2a). On the contrary, the microstructure of Kaolin/PDMS/cotton showed that under the action of PDMS and its curing agent, a large amount of modified kaolin adheres to the surface of the cotton fabrics, forming a uniform and dense micro/nano rough structure coating(see Fig.2b and Fig.2c), increasing the surface roughness of cotton fabrics and laying an excellent morphological foundation for superhydrophobic modification of cotton fabrics.

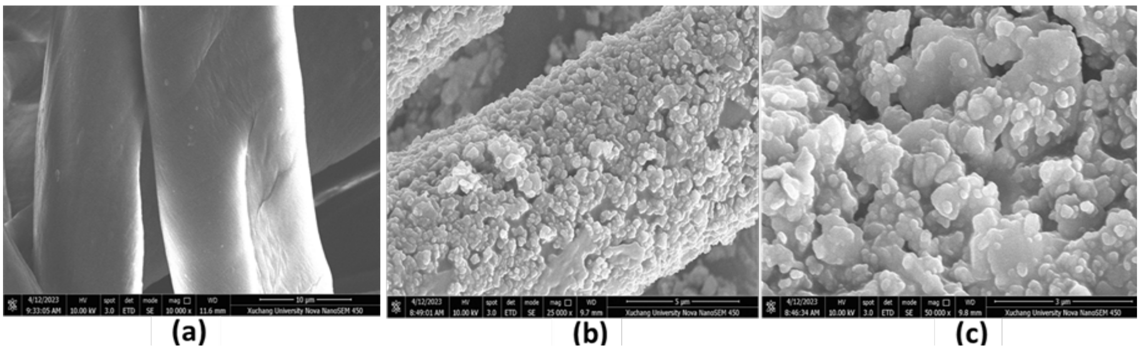

Fig. 2. SEM images of blank cotton fabric and Kaolin/PDMS/cotton at different magnifications. (a) blank cotton fabrics (10000 times); (b) Kaolin/PDMS/cotton (25000 times); (c) Kaolin/PDMS/cotton (50000 times).

A comparative analysis was conducted on the surface hydrophobicity of blank substrate and kaolin/PDMS/cotton, as shown in Fig.3. According to the wettability test of the blank cotton fabrics, the static contact angle between the blank cotton fabric and water was about 91.60 °, and the water droplets appeared hemispherical (see Fig.a and Fig.3b). After inserting them into deionized water stained with red ink, they were clearly dyed red (see Fig.3c), indicating that the blank cotton fabrics had certain hydrophobicity, but didn't have superhydrophobicity. However, the water droplets on the surface of cotton fabrics treated with superhydrophobic modification were perfectly spherical, with a contact angle of approximately 171.07 °(see Fig.3d and Fig.3e). When inserted into deionized water, a beautiful silver mirror surface appeared (see Fig.3f), demonstrating excellent superhydrophobic properties. According to the previous composition and morphology analysis, hydrophobic modified kaolin particles form a uniform micro-nano structure coating on the surface of cotton fabrics through the bridging effect of PDMS. In addition, the synergistic effect of PDMS low surface energy makes cotton fabrics exhibit superhydrophobic properties. When water droplets come into contact with the surface of the sample, the gas-liquid interface will occupy a high proportion of the gas-liquid solid interface, and its area can be calculated using the Cassie Baxter formula[25]:

$$cos\theta_r = (1 - f) \cdot (cos\theta_s + 1) - 1 \quad (1)$$

Here, θ_r and θ_s are the water contact angles of Kaolin/PDMS/cotton and blank substrate surfaces, and f is the area fraction occupied by the gas-liquid interface. Based on the contact angle test results of the samples, the values of θr and θs were 171.07 ° and 91.60 °, respectively. According to formula (1), f=0.9876 could be calculated, indicating that the gas-liquid interface proportion when water droplets came into contact with the Kaolin/PDMS/cotton surface was 98.76%. From this, it could be concluded that the prepared Kaolin/PDMS/cotton surface could store a large amount of air, thereby reducing the contact area between water droplets and the surface, exhibiting superhydrophobic properties.

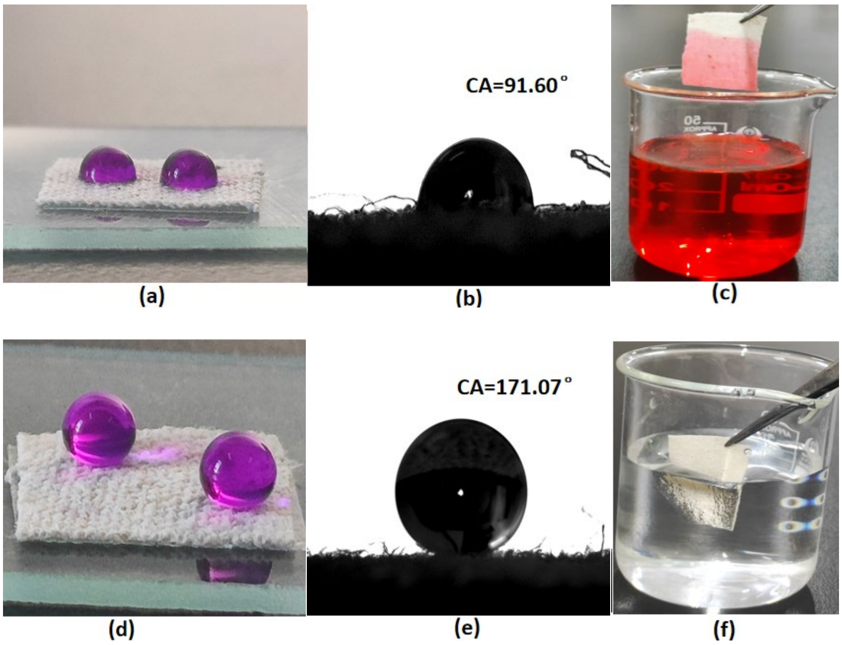

Fig. 3. Stained with methyl violet water droplets on blank cotton fabrics (a) and Kaolin/PDMS/cotton surface (d); Images of water contact angles on the blank cotton fabrics (b) and Kaolin/PDMS/cotton (e) ; Antifouling photograph of blank cotton fabrics (c); Stable silver mirror phenomenon of Kaolin/PDMS/cotton underwater (f).

3.3. Self-cleaning performance of the Kaolin/PDMS/cotton surface

Self-cleaning refers to the process of water droplets falling on the surface of superhydrophobic materials, tilting downwards and rolling to remove dust particles from the surface, thereby achieving anti-pollution. In this work, commonly used chalk powder, coffee, Coca Cola, and dyeing water in daily life were used to simulate pollution sources for testing the self-cleaning performance of kaolin/PDMS/cotton.The testing process is shown in Fig.4a-4d. Placed a glass slide containing kaolin/PDMS/cotton samples diagonally on a glass culture dish, and then sprinkled chalk powder on the surface of the sample. The chalk powder on the surface of the sample was easily carried away by dripping water droplets, and the surface through which the water droplets pass achieved a self-cleaning process (see Fig.4a); Coffee and Coca-Cola rolled off the surface of the sample directly without leaving any traces of contamination (see Fig.4b and Fig.4c); After removing the Kaolin/PDMS/cotton inserted into the staining water, its surface was not contaminated (see Fig.4d). It could be seen that the superhydrophobic surface of kaolin/PDMS/cotton had good self-cleaning function.

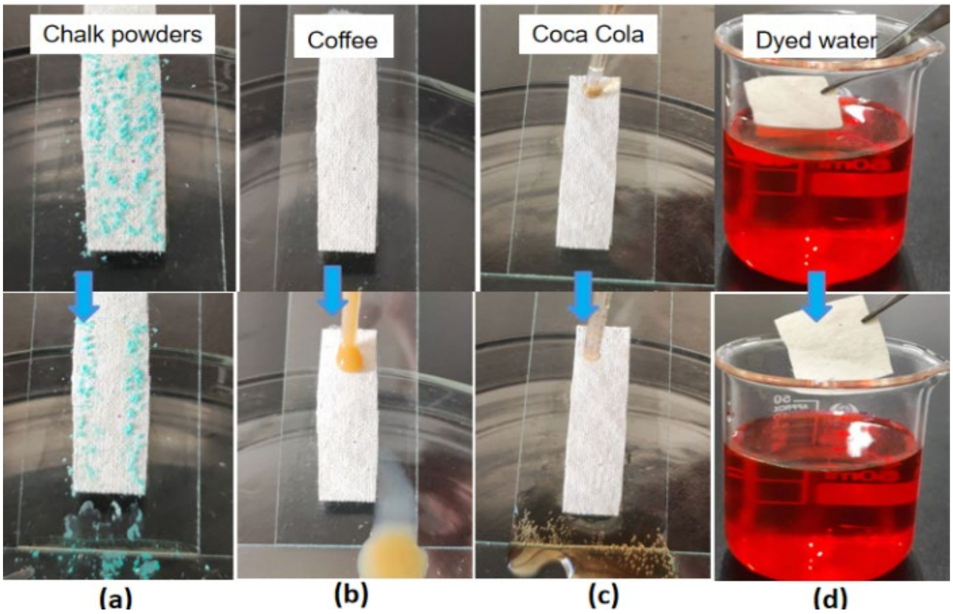

Fig. 4. Self cleaning effect of kaolin/PDMS/cotton superhydrophobic coating on simulated pollutants: (a) Removal of simulated dust process through water droplets; (b-d) Anti-pollution testing process of kaolin/PDMS/cotton superhydrophobic coating surface on coffee, Coca-Cola, and dyeing water.

3.4. Durability of the kaolin/PDMS/cotton surface

In order to study the wear resistance of kaolin/PDMS/cotton surface, a wear resistance test was designed as shown in Figure 5a. Under a load of 10 KPa, pulled the glass slide pressed above the sample at a certain speed, and test the contact angles of the worn surface of Kaolin/PDMS/cotton every 60 cm. Measured the contact angles at three different positions each time and calculated the average value. The wear resistance test results were shown in Fig.5b. As shown in the figure, due to mechanical wear, the superhydrophobic properties of the sample surface gradually weaken. When the wear distance reaches 1200 cm, the contact angle with water remains above 150 °, indicating that the prepared Kaolin/PDMS/cotton superhydrophobic surface has excellent wear resistance.

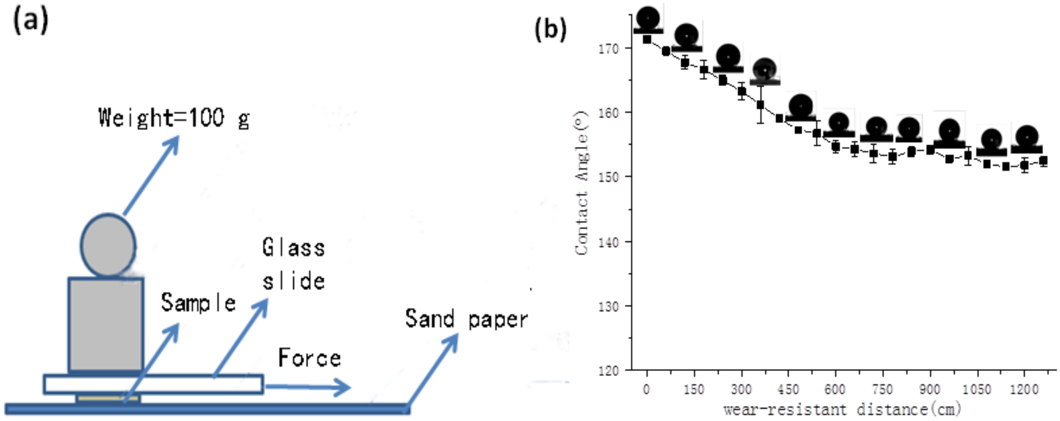

Fig. 5. Schematic diagram of wear-resistance test (a) and variation of water contact angles with wear-resistance distance (b).

3.5. Oil/water separation

Kaolin/PDMS/cotton superhydrophobic samples had the characteristic of blocking water and transporting oil, thus enabling the separation of oil-water mixtures. Here, an equal volume ratio mixture of dichloromethane (stained with methyl violet) and deionized water(stained with red ink) would be used as the separation object for separation experiments. The separation process was as expected, and dichloromethane in the mixture quickly penetrated the superhydrophobic cotton filter membrane under the action of gravity, while water was intercepted, achieving separation. Due to the volatility of dichloromethane, calculating the separation efficiency using the mass of water before and after separation was more accurate. The following formula was used to calculate separation efficiency(η, %)：

$$\eta(\%) = \frac{m_1}{m_0} \times 100\% \tag{2}$$

Here, m_1 and m_0 represent the initial mass of water and the weight after separation, respectively.

The process of oil/water separation testing is shown in Fig.6a-6c. Performed cyclic performance tests on dichloromethane and gasoline using the same operation, and the test datas were shown in Fig.6d. As shown in the figure, after 15 repeated separations, the separation efficiency of the sample from dichloromethane and water changed very little, almost achieving complete separation from water.The separation efficiency of gasoline/water was also above 96%, indicating that the prepared Kaolin/PDMS/cotton superhydrophobic fabrics had excellent recycling performance.

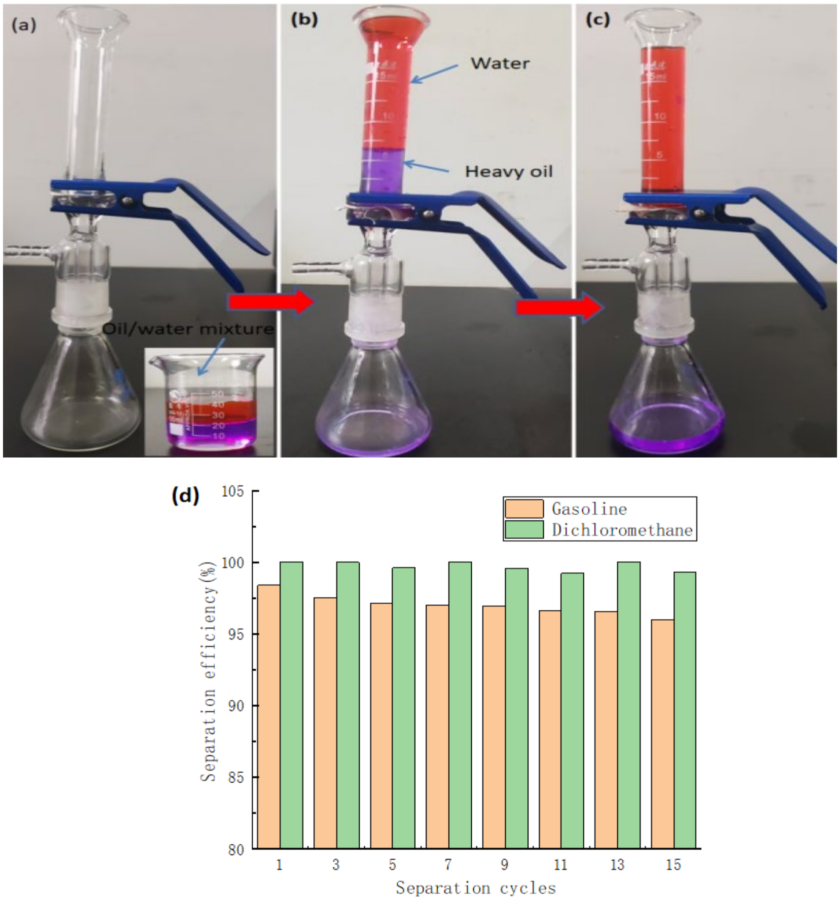

Fig. 6. Photos of oil-water separation testing process (a-c) and Recycling performance test results (d).

4. Conclusions

By utilizing the impregnation method and the "bridging" effect of PDMS, the organic composite of hydrophobic modified kaolin particles and cotton fibers was achieved, resulting in the preparation of kaolin/PDMS/cotton superhydrophobic cotton fabrics. Research on its performance showed that the prepared sample had excellent wear resistance. After a wear distance of 1200 centimeters, the contact angle with water was still above 150 °. Meanwhile, Kaolin/PDMS/cotton also exhibited good anti- pollution performance against common pollutants. In addition, kaolin/PDMS/cotton also showed good oil-water separation performance. After 15 cycles of performance testing, the separation efficiency of gasoline and dichloromethane from water all exceeded 96%. The superhydrophobic modification method of cotton fabrics in this study was simple and environmentally friendly, providing important data support for the modification research of high value-added cotton fabrics.

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