

# CdO-Nanografted Superhydrophobic Hybrid Polymer Composite-Coated Cotton Fabrics for Self-Cleaning and Oil/Water Separation Applications

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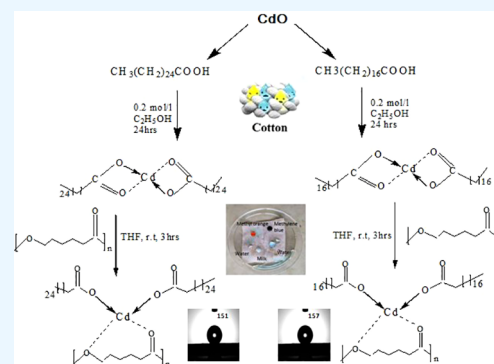
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**ABSTRACT:** The current study presents a simple and cost-competitive method for the development of high-performance superhydrophobic and superoleophilic cotton fabrics coated with cadmium oxide/cerotic acid (CdO/CE)-polycaprolactone (PCL)- and cadmium oxide/stearic acid (CdO/ST)-polycaprolactone-grafted hybrid composites. X-ray powder diffraction, scanning electron microscopy, and Fourier transform infrared spectroscopy are used to characterize the CdO/CE-PCL and CdO/ST-PCL and polycaprolactone-modified cotton fabrics. Using an optical contact angle meter, the wetting behavior of corrosive liquids such as coffee, milk, tea, water dyed with methylene blue, strong acids (HCl), strong alkali (NaOH), and saturated salt solution (NaCl) on the CdO-CE/ST/PCL-modified cotton fabrics is assessed as well as the durability of CdO-CE/ST/PCL-modified cotton fabrics in corrosive liquids. Data obtained from the oil–water separation experiment indicate remarkable separation efficiency with oil purity values of  $\geq 99.97$  wt %, and high permeation flux values of up to  $11,700 \pm 300$  L m<sup>-2</sup> h<sup>-1</sup> are observed for surfactant-stabilized water-in-oil emulsions via a gravity-driven technique. From the data obtained, it is concluded that the nano-CdO-grafted superhydrophobic hybrid polymer composite-coated cotton fabrics (CdO-ST/(CE)/PCL/CFs) can be utilized for self-cleaning and oil/water separation applications.



## 1. INTRODUCTION

It is well known that oil slick/oil spill causes severe environmental damage and affects people's health, including marine living things. As a result, oil/water separation is a global problem that has drawn a lot of interest from both academia and industry.<sup>1</sup> Considerable emphasis has been given in recent years on recovering oil from water using artificial superhydrophobic/superoleophilic materials. The different methods developed so far for oil/water separation include electrocoagulation, biological treatment, adsorption, and gravity separation. Centrifugation, coagulation and flocculation, in situ burning, and chemical dispersion<sup>2</sup> are a few examples of conventional techniques. Self-assembled monolayers, organosilane chemistry, Langmuir–Schaefer deposition, layer-by-layer deposition process, and surface-binding peptides in genetic engineering are some other coating techniques that have been used to modify and tune the surface of a particular material or even to change the properties of inert materials. These surface modification techniques are narrow and often suitable for a specific material.<sup>3,4</sup> In practice, the traditionally used oil–water separation techniques have a number of limitations, including laborious operating procedures, difficult reaction circumstances, specific materials, shape criteria, material damage,

and limited separation efficiency, which incur high costs.<sup>5–7</sup> In addition, the use of dispersants and on-site burning of oil can also cause secondary environmental pollution.<sup>8–14</sup> An efficient, durable, environmentally friendly, and sustainable oil/water separation technology is still needed to address the problems related to oil spills and oily wastewater causing serious damage to aquatic ecosystems and marine life.<sup>15,16</sup>

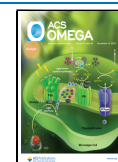
Superhydrophobic surfaces have attracted considerable attention due to their unique properties for widespread applications such as self-cleaning, antiglazing, antifouling, and hydrodynamic drag reduction.<sup>17</sup> However, chemical corrosion, scratches, and wear inevitably affect the superhydrophobic surface properties in practical applications and can lead to the loss of superhydrophobicity.<sup>18</sup> Durability or stability of the waterproof property is one of the most critical and significant

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problems of superhydrophobic materials. This is because the micro- or nanoscale structures of superhydrophobic materials are fragile and easily destroyed.<sup>19</sup> Therefore, it is crucial to develop and produce superhydrophobic materials that are highly effective, durable, and capable of separating oil from water. In particular, it is still extremely difficult to produce degradable and highly hydrophobic materials on a large scale in an efficient and affordable manner.<sup>20</sup>

Recently, advancements in the design and production of superhydrophobic materials with prospective applications have been made. Due to the use of chemicals containing fluorine, labor-intensive, complex operation processes, expensive materials, and challenges in large-scale production, current technologies have some drawbacks and restrict the process of developing superhydrophobic materials. Another significant obstacle to the design and development of superhydrophobic materials is the lack of surface mechanical stability. Therefore, eco-friendly, affordable, stable, and wearable materials with sustainable functions are important factors to take into account when designing and developing superhydrophobic materials.<sup>21,22</sup>

In order to efficiently remove greasy pollutants floating on the water surface, a specific material capable of attracting oily components must be developed.<sup>23</sup> In this regard, a number of conventional approaches have been developed, but they have a number of practical issues that restrict their use in large-scale applications such as difficult production processes, costly equipment, slow response times, and poisonous low-energy materials containing fluorine. In order to develop new types of superhydrophobic materials, the current manufacturing method uses the dip-coating method, which is considered as more easy, straightforward, time-saving, and ecologically safe. Recent research on cotton fabric-based materials received a lot of interest in oil–water separation due to specific characteristics, including ease of handling, low price, flexibility, biodegradability, environmental friendliness, and high efficiency.<sup>24–28</sup> Cotton fabrics can be wetted by both water and oil due to the presence of hydroxyl functional groups and organic moieties in them. Superhydrophobic cotton fabrics are typically made to repel water and act as self-cleaning surfaces. Superhydrophobic fabrics have only been used on a small scale or in laboratory research to separate oil from water; however, they have to be scaled up for industrial uses. Finding a suitable coating technique and coating materials with high mechanical stability and low price is crucial for large-scale and long-term applications because cotton-based materials lose their superhydrophobicity as a result of a weak adhesion between the cotton fibers and surface free energy materials.<sup>29–33</sup>

Different techniques have been adopted to incorporate a nanocomposite into a fiber surface, but still, it is difficult to achieve firm interfacial interaction between nanoparticles and polymer fibers, which acts as indispensable to determine the surface stability and durability. In this regard, Cao et al. reported superhydrophobic cotton fabrics coated with nano-ferric oxide ( $\text{Fe}_2\text{O}_3$ ) and polydimethylsiloxane for oil/water separation using a gravity-driven process.<sup>34</sup> Chen et al. fabricated superhydrophobic grafted cotton fabrics using rosin acid– $\text{SiO}_2$  for separation of oil–water mixtures.<sup>35</sup> Ejeta et al. developed a cotton-based superhydrophobic and superoleophilic material with high flux water-in-oil emulsion separation using a gravity-driven process and external pressure filtration.<sup>36</sup> Cheng et al. fabricated a biobased superhydrophobic durable cotton fabric to separate oil–water mixtures.<sup>37</sup>

Wang et al. developed superhydrophobic and superoleophilic material cotton fibers using a bendable and squeeze-resistant macroporous cellulose aerogel for oil removal from water.<sup>38</sup> Liu et al. prepared a superhydrophobic porous cotton material for the removal of floating oil from the water surface via a magnet-driven method.<sup>39</sup> Wang et al. fabricated a cotton fabric composite with pH-controlled switchable wettability for the separation of both water-in-oil and oil-in-water emulsions.<sup>40</sup> Pan et al. made glass, steel mesh, and cotton surfaces with controllable superwetting for smart oil–water separation.<sup>41</sup> Guo et al. reported a robust material and its flux study for oil–water separation by coating polydimethylsiloxane-based copolymers on cotton textiles via the sol–gel method.<sup>42</sup> Most of the literature is related to modification of raw cotton for oil–water separation, used as an adsorbent or filtering medium. Such reported methods and materials used took more time to complete the separation process and have limited utility. Hence, efficient filtering materials were developed for large-scale separation of oil from water. In this context, the present study adopted a dip-coating method, which is considered an effective, simple, easy, less time-consuming, and cost-competitive method.

In the present work, an attempt has been made to develop superhydrophobic fabrics with sustainable treatments to address the problem of oil–water separation.<sup>29</sup> Cerotic acid (CE), a naturally occurring saturated fatty acid obtained from plants and animals, is nontoxic, biodegradable, and environmentally benign. As such, CE is preferred over fluorinated organic compounds for the hydrophobic treatment of woven cotton fabrics. More intriguingly, CE is a component of the wax layer that is found on the surface of beeswax and carnauba wax, suggesting that CE may be hydrophobic in nature. Stearic acid (ST), another naturally occurring saturated fatty acid obtained from plants or animals that is nontoxic, biodegradable, and environmentally benign, is also preferable to fluorinated chemical compounds. Another more intriguing fact is that ST is a part of the wax layer that covers the surface of lotus leaves,<sup>43,44</sup> which suggests that ST may be hydrophobic in nature.

Cadmium oxide is a commonly used metal oxide with excellent UV absorption, environmental sustainability, low cost, and good cotton fabric roughening properties. In order to accomplish the desired superhydrophobicity, durability, and biodegradability, CE/ST and cadmium oxide are proposed to be utilized jointly to modify the cotton fabrics. Aliphatic polyesters are a class of polymers that include polycaprolactone (PCL), a polymer made up of repeating hexanoate units. PCL's unusual mechanical qualities, miscibility with a wide range of other polymers, and biodegradability have all been widely explored. PCL's molecular weight and degree of crystallinity also influence its capacity to degrade through the hydrolysis of its ester linkages under physiological conditions, determining its physical, thermal, and mechanical properties. Because PCL is extremely hydrophobic, semicrystalline, highly soluble at room temperature, and simple to process due to its low melting point and great blend compatibility, researchers are encouraged to investigate its possible uses, particularly in the biomedical industry.<sup>45</sup>

In fact, because of its inherent biocompatibility and biodegradability, PCL has undergone substantial research in order to construct regulated drug delivery systems using a variety of formulations of polymers or copolymers. Additionally, the matrix's permeability to a variety of pharmaceuticals

allows for consistent drug distribution throughout and guarantees a lengthy release up to several months by a degradation mechanism. Compared to many of its aliphatic polyester competitors, PCL has superior rheological and viscoelastic qualities, making it simpler to make and manipulate into a wide variety of biodegradable devices. Additionally, the mechanical qualities of PCL make it appropriate for medical applications that complement tissue engineering, including wound dressing, contraception, and dentistry<sup>46</sup> as well as nonmedical ones like environment, packaging, and food.<sup>47,48</sup> From the above review, it was concluded that due to its intriguing biofriendly characteristics, PCL is currently used in conjunction with biopolymers, receiving a lot of attention.

Consequently, the current study presents a unique impregnation technique for producing long-lasting, fluoride-free superhydrophobic cotton fabrics with good acid/base resistance, UV resistance, and oil/water separation qualities. This article reports the facile fabrication of fluoride-free superhydrophobic cotton fabric-based composites via surface roughening by CdO nanoparticles and encapsulation by surface free energy CE/ST coating. To the best of our knowledge, the present approach is the first attempt to prepare a CdO/CEorST/PCL-grafted hybrid composite modified with fluoride-free superhydrophobic cotton fabrics by a simple dip-coating method, which could be conveniently scaled up for the production of superhydrophobic materials for both textile industries and oil–water separation process.

## 2. EXPERIMENTAL PROCEDURE

**2.1. Materials and Chemicals.** Cadmium acetate, ammonia, cerotic acid (CE), stearic acid (ST), chloroform, hexane, methylene blue, sodium hydroxide, ethyl alcohol, tetrahydrofuran (THF), and polycaprolactone were purchased from Lab Chemicals, Chennai. Cotton fabrics, motor oil, and milk were bought from local market. All reagents mentioned above are of analytical grade (AR) except for special annotation, and they are used as received without further purification.

**2.2. Preparation of Cadmium Oxide.** CdO nanoparticles were synthesized at room temperature by a low-cost coprecipitation method using cadmium acetate dihydrate and ammonia solution. For the synthesis of CdO, an appropriate amount of  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  was mixed in 80 mL of deionized water. Then, the solution was continuously stirred for 30 min, and subsequently, ammonia solution was added to the above solution drop by drop until pH reached 9.0. The obtained white precipitate was kept to settle down for 5 h. Then, the solution was filtered and washed several times with deionized water and ethanol. The attained precipitate was dried at 80 °C and then ground to a fine powder with the help of an agate mortar. Then, the final product was calcined at 400 °C for 2 h.

**2.3. Preparation of the Graft Copolymer.** The graft copolymer was fabricated using a three-neck flask equipped with a reflux condenser, a funnel, and a nitrogen line, to which a cross-linked CdO solution (1 mL) at 90 °C was added with 0.25 mol/L cerotic acid or stearic acid for 24 h, which was then dispersed with 30 mL of distilled water while continuous vigorous stirring. The nitrogen was flushed in the system for 30 min, and a polymerization reaction was carried out at atmospheric temperature. A 4 wt % solution of prepared polymer precursors dissolved in 70 mL of THF and the flask

content were continuously stirred for 3 h, and the reaction temperature was maintained at 70 °C to proceed with the polymerization reaction; consequently, a precipitate consisting of a poly( $\epsilon$ -caprolactone) CdO/CE or CdO/ST graft copolymer was formed. Then, the precipitate was filtered, washed several times with cold water, and dried at ambient temperature.

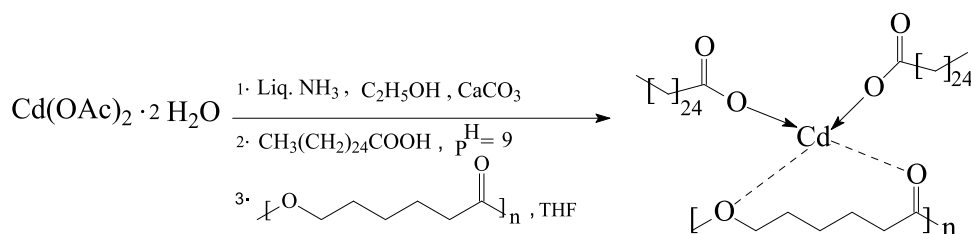
Plain wovens are used as textile fabrics, which are bleached 100% cotton fabrics with  $175 \pm 2 \text{ g/m}^2$  mass density. First, a piece of cotton fabric (4.0 cm  $\times$  4.0 cm) was cut off, and the impurities and paraffin on the surface were removed with NaOH solution (4.0 g/L), EtOH, and distilled water. Then, pretreated cotton fabrics were immersed into a solution, which contained about 20 mL of the poly( $\epsilon$ -caprolactone) CdO/CE or CdO/ST graft copolymer dispersed in THF solvent. The solution was dipped at ambient temperature for 24 h and dried in an oven at 140 °C for 30 min to afford the target products, i.e., graft copolymer hybrid composites coated over the cotton fabrics.

**2.4. Characterization.** The surface morphology of CdO-CE/PCL- and CdO-ST/PCL-grafted polymer-modified cotton fabrics is characterized with a field emission scanning electron microscope (FESEM). An energy-dispersive X-ray spectrometer (EDX) attached to an FESEM was used for elemental analysis. The structural characterization of CdO nanoparticles was carried out using X-ray powder diffraction (XRD), and XRD patterns were collected with an X-ray diffractometer under Cu K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation (operation voltage: 40 kV, current: 40 mA). Thermogravimetric analysis (TGA) under a nitrogen atmosphere at a flow rate of 100 mL/min was conducted with a thermal analyzer Q600 type from room temperature to 800 °C at a heating rate of 20 °C/min, and thus, the thermal stability of the nanoparticles was studied. Fourier transform infrared spectroscopy (FTIR) analysis was conducted in a wavenumber range of 4000–400  $\text{cm}^{-1}$ . Contact angle measurements with water and other liquids at room temperature were conducted with an optical contact angle meter. Moreover, a digital camera was used to observe the wetting behavior of various liquids on CdO/CE/ST/PCL-modified cotton fabrics. UV–vis absorption spectra were recorded with a UV–vis absorption spectrophotometer in a wavelength range of 200–850 nm.

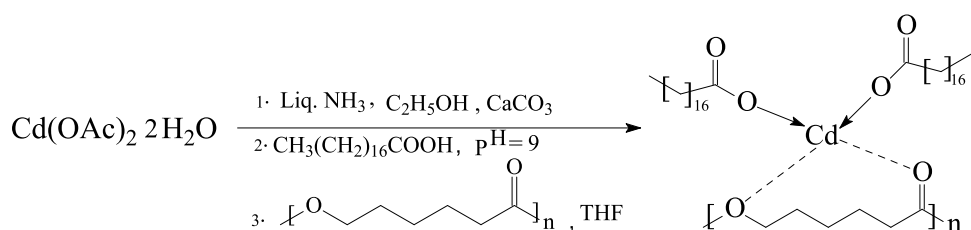
**2.5. Contact Angle Measurements.** In order to study the surface wettability of the fabrics, static water contact angles (WCAs) were measured by using an optical contact angle meter at room temperature ( $\sim 30 \text{ }^\circ\text{C}$ ). As for WCAs, a gastight 500 mL Hamilton precision syringe with a 0.52 mm internal diameter blunt needle was used to deposit Milli-Q water droplets of 5  $\mu\text{L}$ . WCAs were automatically calculated by the software based on the droplet shape. Ten droplets were deposited on each sample in different positions, and then, the averages were calculated.<sup>49</sup> Measurements were repeated five times for each sample, and the average value was taken.

**2.6. Biodegradability Test.** After being submerged in phosphate-buffered saline (PBS) solutions containing lysozyme (pH = 7.4) and cellulase (pH = 4.8) at 37 °C, the biodegradability of the cotton fabrics treated with CdO-CE/ST-PCL was assessed. Two identically sized portions of the as-prepared cotton fabrics were weighed, submerged in PBS–lysozyme solution and PBS–cellulase solution (10,000 U/mL), and then incubated at 37 °C for 15 days. The as-tested cotton fabrics were removed from the incubator at intervals of 5 days, cleaned in distilled water to get rid of contaminants that had adhered to the surface, vacuum-dried at room temperature, and

Scheme 1. Illustration of the Preparation Process of the CdO-CE/PCL Graft Copolymer



Scheme 2. Illustration of the Preparation Process of the CdO-ST/PCL Graft Copolymer



weighed. The degradation rate ( $D$ ) of the as-tested cotton fabrics is calculated according to eq 1.

$$D = \frac{W_t - W_0}{W_0} \times 100\% \quad (1)$$

where  $W_t$  refers to the mass of the as-tested cotton fabrics after drying in vacuum and  $W_0$  is the initial mass before immersion in the buffer solution.

**2.7. Durability Test.** The durability of the CdO-CE (or ST)-PCL-modified grafted superhydrophobic cotton fabrics was tested using the aqueous solutions of HCl ( $\text{pH} = 2$ ), NaOH ( $\text{pH} = 14$ ), and NaCl (saturated solution,  $\text{pH} = 8$ ) independently. Durability tests based on the contact angle measurements were done every 5 min of immersion time in the corrosive aqueous solutions for the prepared cotton fabrics treated with CdO-CE (or ST)/PCL.

**2.8. Preparation and Separation of Water-in-Oil Emulsions.** A surfactant-stabilized water-in-oil emulsion was prepared using span 80 (0.5 g) dissolved in an oil (petroleum ether, *n*-hexane, dichloromethane, *n*-octane, *n*-hexadecane, and toluene) and water mixture (98:2, V/V) through an efficient agitation process for 2 h in accordance with a previous report. For the water-in-oil emulsion separation test, the CdO-CE/PCL- and CdO-ST/PCL-modified CFs were placed in a funnel, and the surfactant-stabilized water-in-oil emulsion was allowed to pass through CdO-CE/PCL- and CdO-ST/PCL-modified CFs by a gravity-driven technique. The surface density or thickness of the CdO-ST/PCL coating on CFs was  $5.07 \text{ mg/cm}^2$  and that of the CdO-CE/PCL coating on CFs was  $5.44 \text{ mg/cm}^2$ , which were calculated following a previous report.<sup>50</sup> The flux was attained by calculating the permeated time for 25 mL of the emulsion on the unit area.

**2.9. Self-Cleaning Ability Test.** To study the wetting behavior, several substances including milk, methylene blue-dyed water, strong acids (HCl), strong alkalis (NaOH), and saturated salt solution (NaCl) were individually placed onto the CdO-CE (or ST)/PCL-grafted modified cotton fabrics. In order to test the effectiveness of the self-cleaning capabilities, soil was applied to the surface of the CdO-CE/ST-PCL-modified cotton fabrics and washed away with blue-dyed water.

**2.10. Mechanical Stability.** The mechanical strength of the superhydrophobic coating plays an important key role in

practical applications. In the present study, a sandpaper abrasion test was carried out to evaluate the mechanical durability of the coating. A weight of 150 g was loaded on the superhydrophobic grafted coated cotton fabrics, and it was dragged for a distance of 10 cm on sandpaper with normal acceleration.<sup>51–53</sup>

### 3. RESULTS AND DISCUSSION

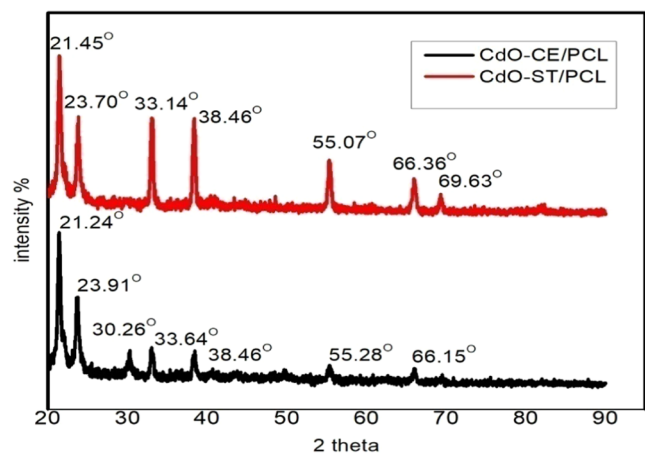
**3.1. Fabrication of Grafting Copolymers in Cotton Fabrics Using CdO-CT/ST-PCL.** As explained before in Section 2, the method for preparing copolymers grafted in cotton fabrics for oil/water separation and self-cleaning is mentioned in Schemes 1 and 2. The pristine cotton fabrics possess obviously hydrophilic and lipophilic properties and could be wetted and easily permeated by both oil and water droplets. After treatment with CdO-CE/ST-PCL graft copolymers in cotton fabrics, the high grafting density of the surface with lipophilic and hydrophobic properties endowed the cotton fabrics with superhydrophobicity, which exhibited oil permeability and repelled the water phase.

As shown in Schemes 1 and 2, cadmium acetate in deionized  $\text{H}_2\text{O}$  was continuously stirred for 30 min. To this solution, ammonia was added in a dropwise manner until pH reached 9. The obtained white precipitate was filtered, and the filtrate was dried, ground to fine powder, and calcinated at  $400 \text{ }^\circ\text{C}$  for 2 h. Then, the calculated quantity of nano-CdO was treated with  $0.25 \text{ mol/L}$  cerotic acid and stearic acid separately for 24 h at  $90 \text{ }^\circ\text{C}$  and then dispersed with 30 mL of ethanol under continuous vigorous stirring. To the above reaction, a 4 wt % solution of prepared polymer precursors dissolved in 70 mL of THF was added, and the reaction temperature was maintained at  $70 \text{ }^\circ\text{C}$  to proceed with the polymerization reaction. Consequently, a precipitate consisting of a poly( $\epsilon$ -caprolactone) CdO/CE or CdO/ST graft copolymer was formed in accordance with Schemes 1 and 2.

**3.2. Structure and Morphology of CdO-CE (or ST)/PCL-Modified Cotton Fabrics.** The XRD pattern shows diffraction peaks at (111), (200), and (220), which are due to polycrystallinity, matching with the characteristic peaks of the cubic structure of CdO (JCPDS 05–0640No), which is in good agreement with previous reports. Some other disenabled planes are (400), (311), and (222), but they have lower

intensities. The CdO cotton fabrics have the (111) plane as the preferred orientation, which was in good agreement with a previous report.<sup>54</sup>

The characteristic peak of the cotton fabric and the polymeric peak could be seen at 21.2° as in the case of CdO-grafted CE/PCL-modified cotton surfaces. The sharp diffraction peaks of CdO particles appeared at  $2\theta$  values of 23.9, 30.2, 33.64, 38.46, 55.28, and 66.1° for the (111), (200), (220), (222), (311), and (400) planes of crystalline CdO particles, respectively. The characteristic peak of the cotton fabric and the polymeric peak could be seen at 21.4° for CdO-ST/PCL-modified cotton surfaces. The sharp diffraction peaks of CdO particles also appeared at  $2\theta$  values of 23.7, 33.1, 38.4, 55.0, 66.3, and 69.3° for the (111), (200), (220), (222), (311), and (400) planes of crystalline CdO particles, respectively (Figure 1). While no XRD signals of CE or ST emerged for



**Figure 1.** XRD patterns of CdO-CE/PCL- and CdO-ST/PCL-coated cotton fabrics.

CdO-CE (or ST)/PCL-modified cotton fabrics, which is possibly because CE and ST are wax-like phases without a crystal structure.<sup>55</sup> The results clearly showed that after hydrophobic modification, the crystalline nature of Cd particles was disturbed, which also confirmed the successful deposition of cerotic acid–PCL and stearic acid–PCL materials.

According to the previous report,<sup>3</sup> the pristine cotton fabrics showed a convoluted and wrinkle-like structure due to the longitudinal fibril structure. After dip-coating with CdO-grafted ST (or CE)/PCL composites, the cotton fabrics were somewhat roughened as a result of the assimilation of CdO-ST (or CE)/PCL after immersion in the coating hybrid solution. The surface roughness of cotton fabrics primarily increased noticeably, and SEM images were used to confirm the surface morphology of the as-prepared CdO-ST (or CE)/PCL cotton surfaces. High-magnification SEM images of cotton fabrics indicated a smooth and longitudinal fibril structure on the fabric's surface.<sup>56</sup> After being treated with CdO-grafted ST (or CE)/PCL polymer hybrid composites, the cotton surface becomes significantly rougher and irregular in character, as can be observed from the change in the morphology of the coated surface shown in (Figure 2). The coating of CdO-ST (or CE)/PCL hybrid composites on cotton provides a rougher surface, which is required for producing superhydrophobicity, as shown by the SEM analysis. It is interesting to note that the surface roughness of the CdO-grafted CE and ST-PCL cotton fabrics

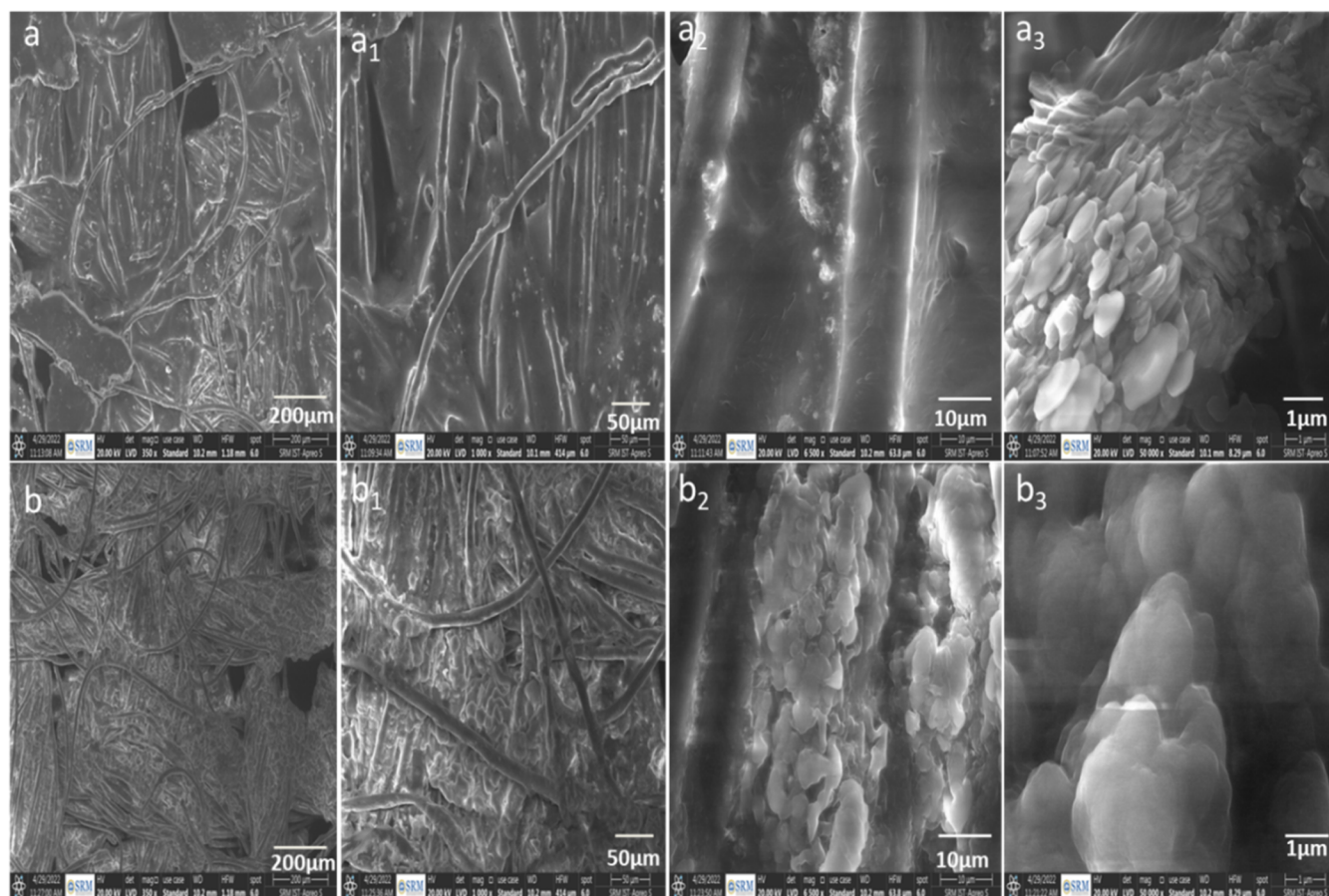
is higher than that of pristine cotton fabrics, which may be due to the fact that CE, ST, and CdO are firmly coated on cotton, and the coated hybrid materials act like waxy surfaces.

Figure 3 shows the presence of elements in the developed CdO-CE/PCL- and CdO-ST/PCL-modified cotton fabrics, and it also provides the elemental composition (weight percentage (wt %)) and atomic percentage (atom %) information in the developed CdO-CE/PCL- and CdO-ST/PCL-grafted materials (Table 1). From the SEM images, it can be seen that CdO/CE(or ST)/PCL-modified cotton fabrics have a fibrous surface morphology, and the fibers are of some orientation and consist of C, O, and Cd elements.

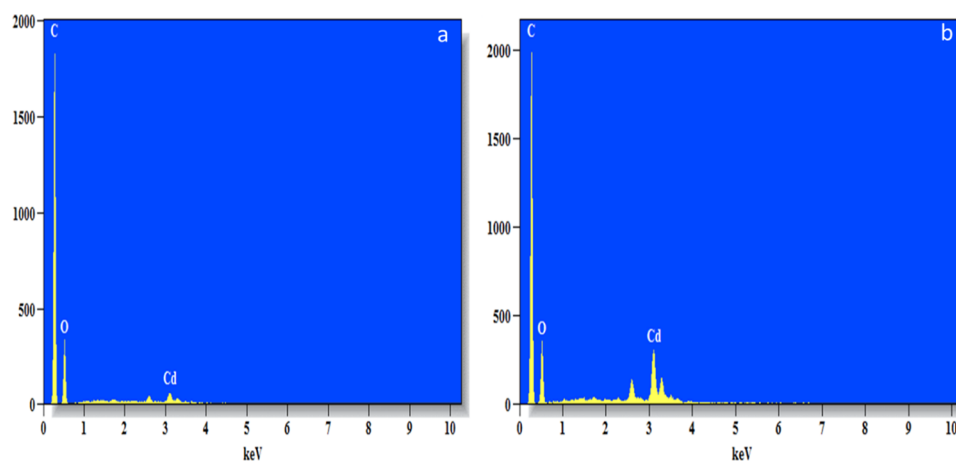
Further, to confirm the stability and firmness of the superhydrophobic materials, an SEM study was again carried out for CdO-CE/PCL- and CdO-ST/PCL-modified CFs after the oil–water separation process (Figure 4). From the results, it was concluded that there was no difference in the structural change seen after oil–water separation. Such results confirm the stability of the superhydrophobic materials.

**3.3. IR Analysis.** The chemical characterization of the samples was carried out by attenuated total reflectance (ATR)-FTIR spectroscopy; Figure 5 illustrates the transmission spectra of pristine cotton fabrics and CdO-CE/PCL and CdO-ST/PCL composite-coated cotton fabrics, which will indicate the chemical bonding states of organic molecules. Pristine cotton fabrics displayed typical cellulose peaks at 3296  $\text{cm}^{-1}$  for OH, 2990  $\text{cm}^{-1}$  for CH, 1640, 1156  $\text{cm}^{-1}$  for asymmetric C–C stretching, 1027  $\text{cm}^{-1}$  for C–O stretching, and 1420  $\text{cm}^{-1}$  for the  $\text{CH}_2$  symmetric bending of cellulose. The peaks appearing at 1356 and 1316  $\text{cm}^{-1}$  are associated with the bending vibrations of C–H and C–O groups, respectively, present in cellulose polysaccharides. The band at 890  $\text{cm}^{-1}$  shows the presence of  $\beta$ -glycosidic linkages between monosaccharides.<sup>57,58</sup> ATR-FTIR can provide us with a means to understand the combination mode of CE (or ST) and CdO with PCL with a frequency range of 500–4000  $\text{cm}^{-1}$ . The characteristic absorption band of PCL appeared at 1721  $\text{cm}^{-1}$ , corresponding to the carbonyl stretching mode, and peaks that appeared at 2917 and 2853  $\text{cm}^{-1}$  were due to symmetric and asymmetric stretching of C–H bonds, respectively. The peak that appeared at 1296  $\text{cm}^{-1}$  was assigned to the backbone C–C and C–O stretching modes in the crystalline phase of PCL, and the peaks that appeared at 1165 and 1168  $\text{cm}^{-1}$  were due to symmetric C–O–C stretching and C–O and C–C stretching in the amorphous phase, respectively. FTIR spectra of PCL showed all characteristic peaks of PCL in Figure 4 along with the ST or CE materials. In the CE (or ST)-CdO-PCL hybrid coatings, the broad absorbance bands appearing at 3441 and 3435  $\text{cm}^{-1}$  are attributed to the carboxyl–hydroxyl stretching vibration, and the absorbance peaks at around 2917, 2853  $\text{cm}^{-1}$  and 2915, 2848  $\text{cm}^{-1}$  in the high-frequency region are assigned to the asymmetric and symmetric tensile vibration of  $-\text{CH}_2-$  groups, respectively. The absorbance bands at 1721, 1548  $\text{cm}^{-1}$  and 1721, 1543  $\text{cm}^{-1}$  arise from the asymmetric and symmetric stretching vibrations of  $-\text{COO}-$ , respectively, and those at 1477 and 1487  $\text{cm}^{-1}$  correspond to the bending vibrations of  $-\text{CH}_2-$  and  $-\text{CH}_3$ , respectively. These ATR-FTIR data for CE (or ST)-CdO-PCL hybrids are almost consistent with previous reports.<sup>59</sup>

It is to be noted that UV light transmittance properties are also important parameters for the cotton fabric to assess the stability aspects of superhydrophobic behavior. The UV–vis spectra of unmodified cotton fabrics (pristine/blank sample of



**Figure 2.** SEM images of (a) CdO-CE/PCL- and (b) CdO-ST/PCL-modified cotton fabrics at various magnifications.



**Figure 3.** EDX spectra of (a) CdO-CE/PCL- and (b) CdO-ST/PCL-coated cotton fabrics.

cotton fabrics) and CE (or ST)-CdO/PCL-modified cotton fibers are shown in Figure 6. In the visible light range, the pristine (blank) cotton fabrics and ST (or CE)-CdO/PCL-modified cotton fabrics display almost the same transmittance, confirming that the ST (or CE)-CdO/PCL coating has a similar transparent nature.<sup>60</sup> In addition, despite having superhydrophilic and superhydrophobic surfaces, the colors of pristine and ST (or CE)-CdO/PCL-modified cotton fabrics are not noticeably different. This might be because the process and reagents used to modify the surface of cotton garments are both gentle.

Figure 7 shows TGA graphs that are obtained from the ST (or CE)-CdO/PCL-modified cotton fabrics. The initial decomposition temperature of CE-CdO/PCL-modified cotton fabrics is around 250 °C, which is due to the decomposition of CE. The CE-CdO/PCL-modified cotton fabric undergoes a total weight loss of about 85.2% at 800 °C, which is due to the presence of nano-CdO particles and their synergic composite effects. Thus, it has a significantly higher thermal stability than organic coatings. Further, in the case of the second sample, the initial decomposition temperature of the ST-CdO/PCL-modified cotton fabric is around 300 °C, which is due to the

**Table 1. Weight and Atomic Percentages of CdO-CE/PCL and CdO-ST/PCL Coating Materials**

element in CdO-CA/PCL	net counts in CdO-CA/PCL	weight % in CdO-CA/PCL	atom % in CdO-CA/PCL
C	10,599	50.97	60.48
O	2062	43.60	38.84
Cd	1006	5.43	0.69
total		100.00	100.00
element in CdO-SA/PCL	net counts in CdO-SA/PCL	weight % in CdO-SA/PCL	atom % in CdO-SA/PCL
C	11,507	40.23	55.93
O	2227	39.31	41.03
Cd	5298	20.47	3.04
total		100.00	100.00

decomposition of ST, and it also possesses significantly higher thermal stability than organic species. The ST-CdO/PCL-modified cotton fabric undergoes a total weight loss of 86.3% at 800 °C. From the results, it was concluded that CE-CdO/PCL and ST-CdO/PCL alteration had a positive effect on enhancing the thermal stability of cotton fabrics. Therefore, the modified coated cotton fabrics contribute to improved thermal stability coupled with superhydrophobic behavior.

**3.4. Wettability and Contact Angle.** The wetting behavior of the liquids is attributed to interfacial free energy, which is primarily determined by surface chemical composition and microscopic and macroscopic geometries in accordance with the theory of surface thermodynamics. The property by which the gas on the solid surface cannot be replaced by the liquid is known as the superhydrophobicity of the surface. The property of the wettability of pure water often determines the surface's hydrophilic and hydrophobic characteristics. The wettability is determined by the following Young's equation.

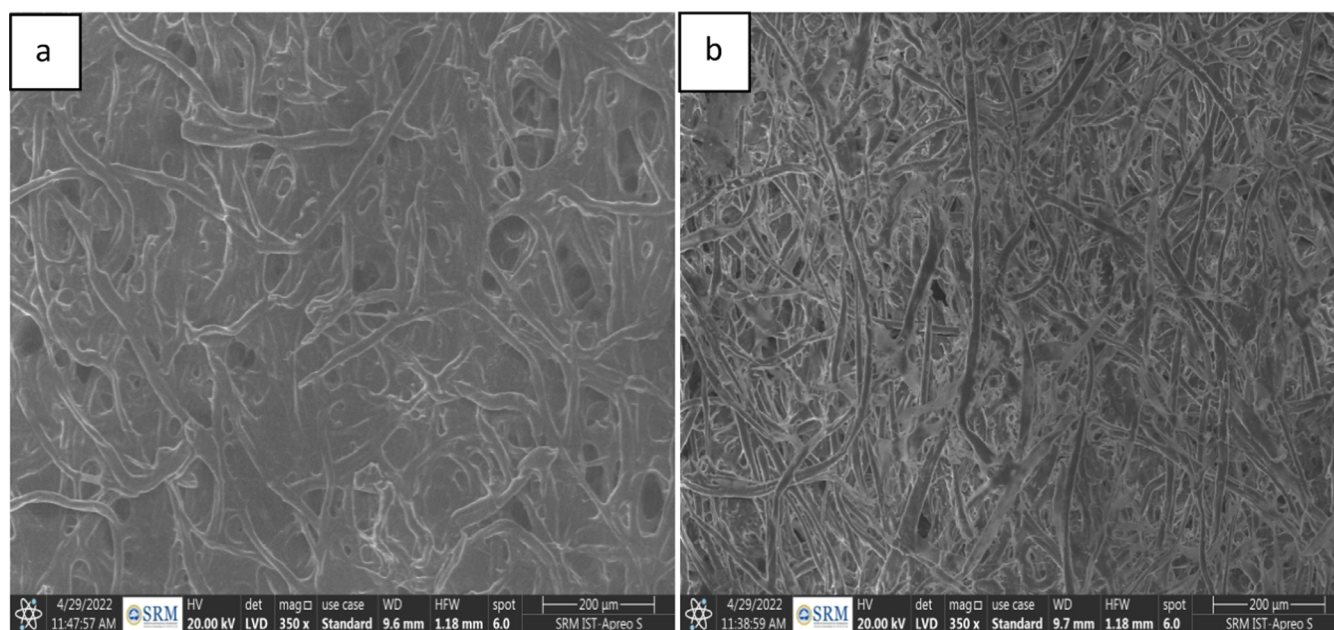
$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos(\theta)$$

Terms  $\gamma_{sl}$  and  $\gamma_{lg}$  are the interfacial tension at the solid/liquid and liquid/gas interfaces, respectively. The resultant contact

angle is known to be the intrinsic contact angle, while the equation is applied to a smooth surface. Solids with perfectly smooth surfaces are rare. It is important to consider how the roughness affects the surface's ability to retain moisture. According to the Wenzel physical model, liquid penetration occurs at surfaces possessing microstructures, and the wettability increases as the number of microstructures increases. According to Cassie's physical model, the liquid cannot easily penetrate the hydrophobic microstructure surface, and the trapped air creates a gas film. The liquid drop appears as a spherical sphere with a slight rolling angle, appearing to "sit" above the surface microstructure.

Figure 8 displays the contact angle images showing the wettability properties of water on the solid surface. Formation of low-surface-energy and micro/nanoscale structures is provided by the CdO-CE/ST and PCL compounds in the present study. Water drops are virtually spherical and effortlessly roll across this surface in accordance with Cassie's physical model. On the other hand, the oil drops are rapidly absorbed upon contact and produce a flat oil sheet in accordance with Wenzel's physical model. Hence, Wenzel's physical model explains the required unique wettability for oil–water separation (superhydrophobic and superoleophilic), and this model's unique wettability was utilized in the present study for oil–water separation investigation.<sup>61</sup>

The wettability of the woven fabric is influenced by the chemical nature of the fiber surface, the geometry of the fiber (particularly the degree of surface roughness), and the structure of the woven fabric. The fiber–liquid contact angles determine a fiber's wettability, and the surface wettability of the prepared cotton fabrics was analyzed by static water contact angle measurements. For this, 5  $\mu$ L water droplets were deposited on the surface of the fabrics for 30 s before it was measured, and three measurements were performed at 10 different WCAs on different locations of each fabric. Pristine cotton fibers are highly hygroscopic in nature and can absorb a significant amount of water on contact.<sup>62</sup> The current measurement setup was unable to measure the water contact

**Figure 4.** SEM images of (a) CdO-CE/PCL/CFs and (b) CdO-ST/PCL/CFs after oil–water separation.

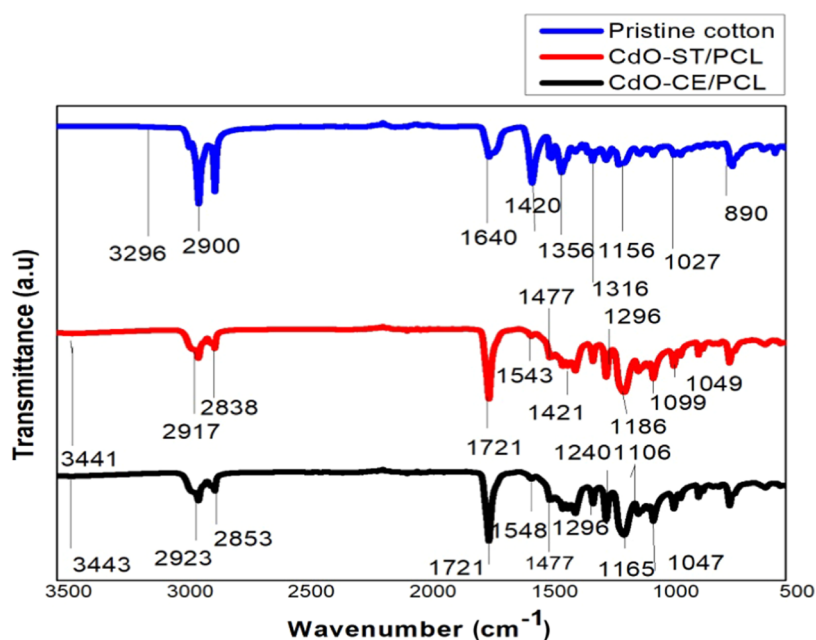


Figure 5. ATR-FTIR spectra of pristine cotton fabrics and CdO-CE/PCL- and CdO-ST/PCL-grafted composite materials.

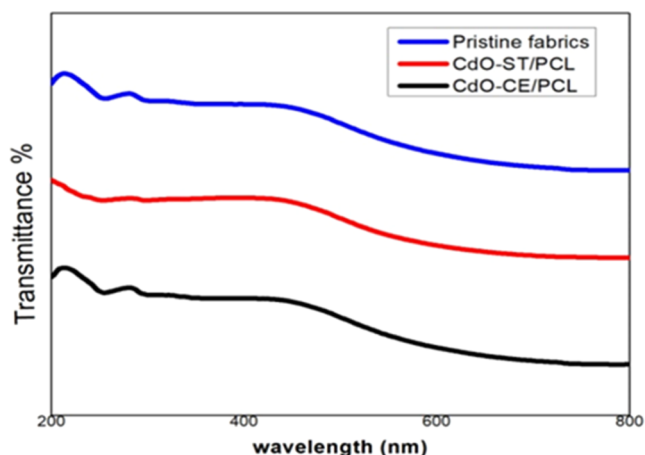


Figure 6. UV-vis transmittance spectra of pristine cotton fabrics and CdO-CE/PCL and CdO-ST/PCL-grafted materials.

angle on the untreated cotton fabric, as the deposited water droplet immediately sank into the fabric. However, the cotton fabrics when treated with CdO-CE (or ST)/PCL maintained water droplets in spherical shapes on their surface, and the average static water contact angles for the treated cotton fabrics are shown in Figure 9. The average static water contact angle (WCA) values are shown in Figure 9 in the form of images.

The pristine cotton fabrics are hydrophilic, and the as-prepared CdO-ST/PCL/CF- and CdO-CE/PCL/CF-modified cotton fabrics have water contact angles of 157 and 151°, respectively. This explains that the incorporation of CdO and CE/ST with PCL endows the cotton fabrics with superhydrophobicity. Figure 9(c) shows the plot of the fluctuation of WCA values as a function of immersion time for both CdO-CE/PCL- and CdO-ST/PCL-coated CF samples. The samples were totally dried after they had undergone dip-coating and annealing processes. The optimum contact angle values achieved in the present study are 157° and 151° for CdO-ST/PCL/CF and CdO-CE/PCL/CF, respectively, for modi-

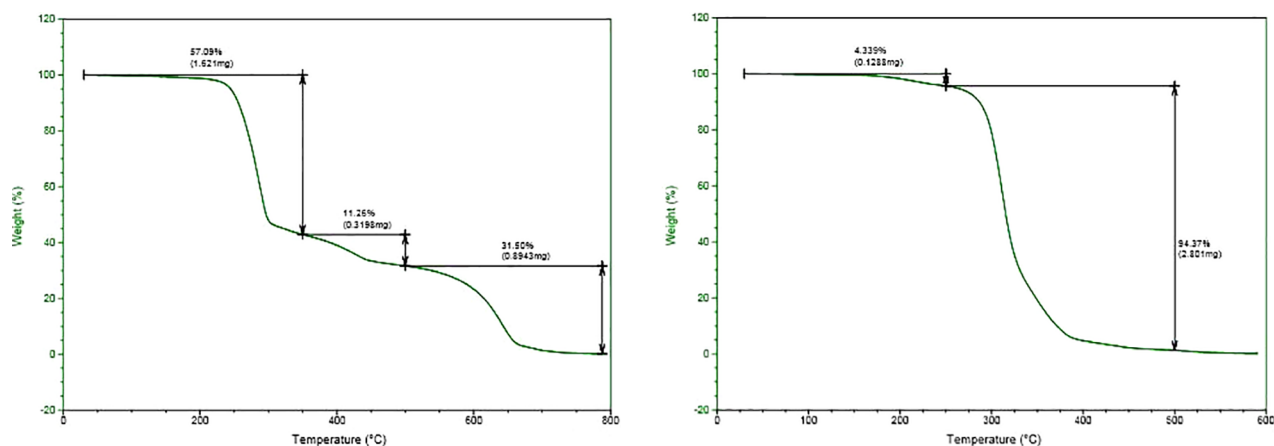


Figure 7. TGA image of CdO-CE/PCL- and CdO-ST/PCL-grafted superhydrophobic composite materials.



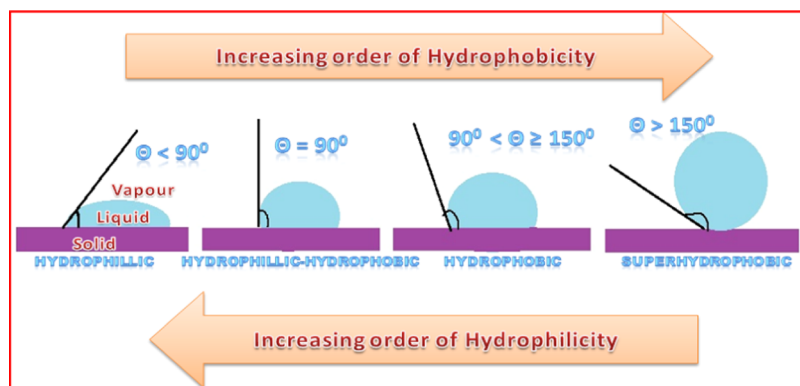


Figure 8. Image of the wettability of water on the solid surface.

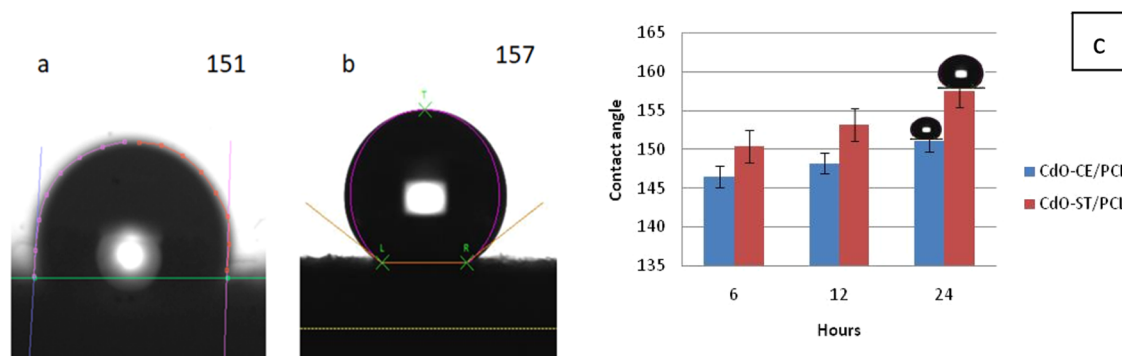


Figure 9. Images of average contact angle values for (a) CdO-CE/PCL-grafted CF and (b) CdO-ST/PCL-coated CF, and (c) variation of static water contact angle with dipping time for both CdO-CE/PCL and CdO-ST/PCL coatings on CF.

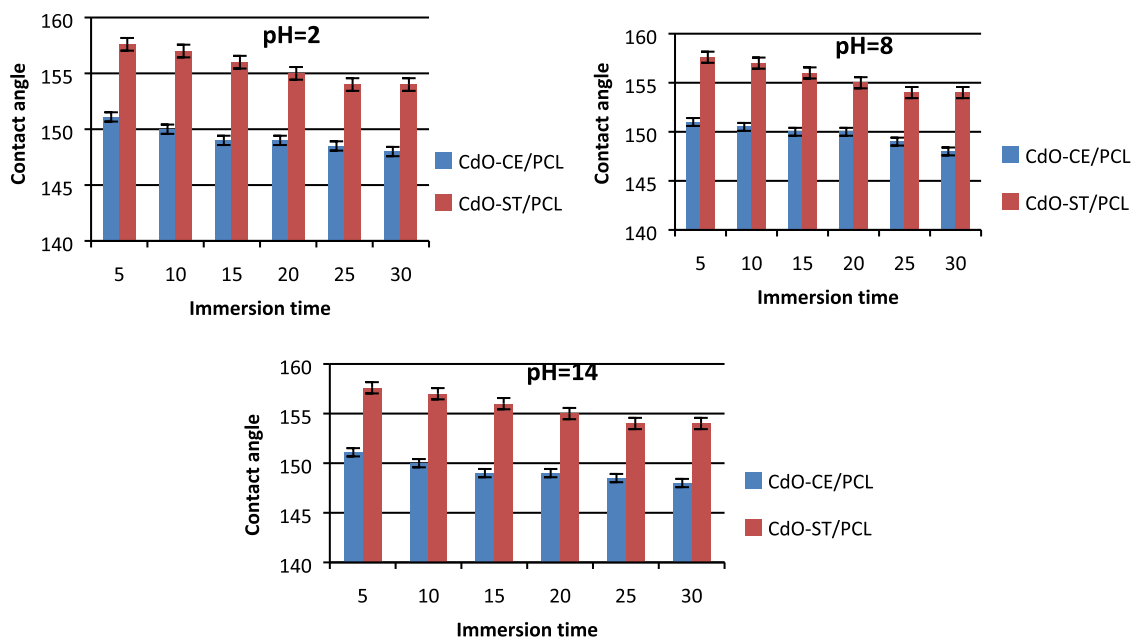
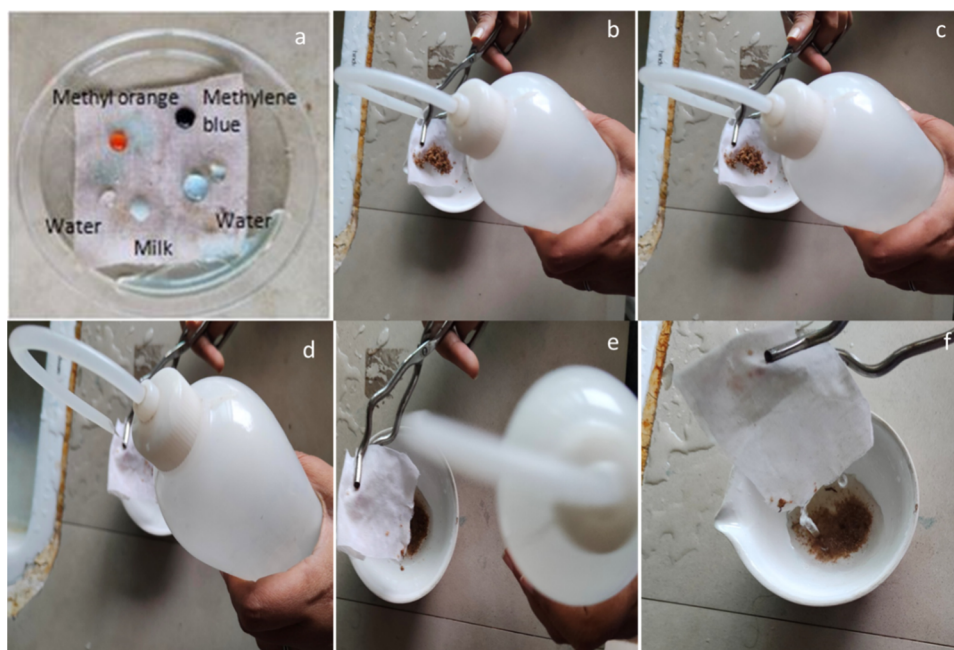


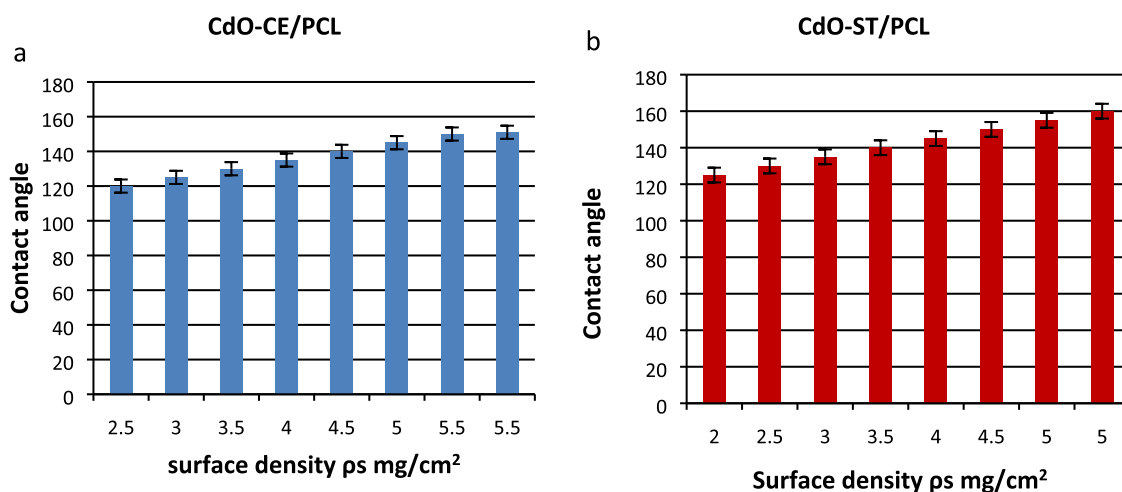
Figure 10. Water contact angles versus immersion time in HCl (pH 2), NaCl (saturated, pH 8), and NaOH (pH 14) for CdO-CE/PCL and CdO-ST/PCL-grafted coated cotton fabrics.

fied cotton fabrics, which are practically achieved after a dipping time of 24 h. Further extending the immersion period has no significant effect on the superhydrophobicity of the coated materials. The contact angle value reports conclude that CdO-ST/PCL/CF exhibits a higher value of WCA than the CdO-CE/PCL/CF sample.

The pristine cotton fabrics are hydrophilic in nature, and the as-prepared CdO-CE/PCL-grafted CF-modified cotton fabric has a water contact angle of 151°. This indicates that the incorporation of CdO and CE/PCL endows the cotton fabric with superhydrophobic behavior. After immersion in the corrosive aqueous solutions of HCl (pH = 2), NaCl (saturated,



**Figure 11.** Image of the superhydrophobicity of CdO-CE (or ST)/PCL-grafted composite-modified cotton fabrics against various liquids (a) and real-time images for their self-cleaning performance (b–f).



**Figure 12.** Graphical plots of contact angles against different surface densities of (a) CdO-CE/PCL- and (b) CdO-ST/PCL-coated CFs.

pH = 8), and NaOH (pH = 14), the values of water contact angle decline to a marginal extent, namely, 150, 148, and 147° respectively; however, they still retain superhydrophobic behavior (Figure 10). This demonstrates that CdO-CE/PCL-modified cotton fabrics exhibit sustainable superhydrophobicity after immersion in the tested corrosive media, which ascertains that these materials can be utilized under different chemical environments with enhanced longevity. The pristine cotton fabrics are hydrophilic in nature, and the as-prepared CdO-ST/PCL-grafted modified cotton fabrics have a water contact angle value of 157°. This is also due to the incorporation of CdO and ST/PCL, endowing the cotton fabrics with superhydrophobicity. After soaking in the corrosive aqueous solutions of HCl (pH = 2), NaCl (saturated, pH = 8), and NaOH (pH = 14), the value of water contact angles is slightly lowered, i.e., 153, 152, and 151°, respectively; however, they still maintain superhydrophobic behavior (Figure 10). This explains that CdO-ST/PCL-modified cotton fabrics

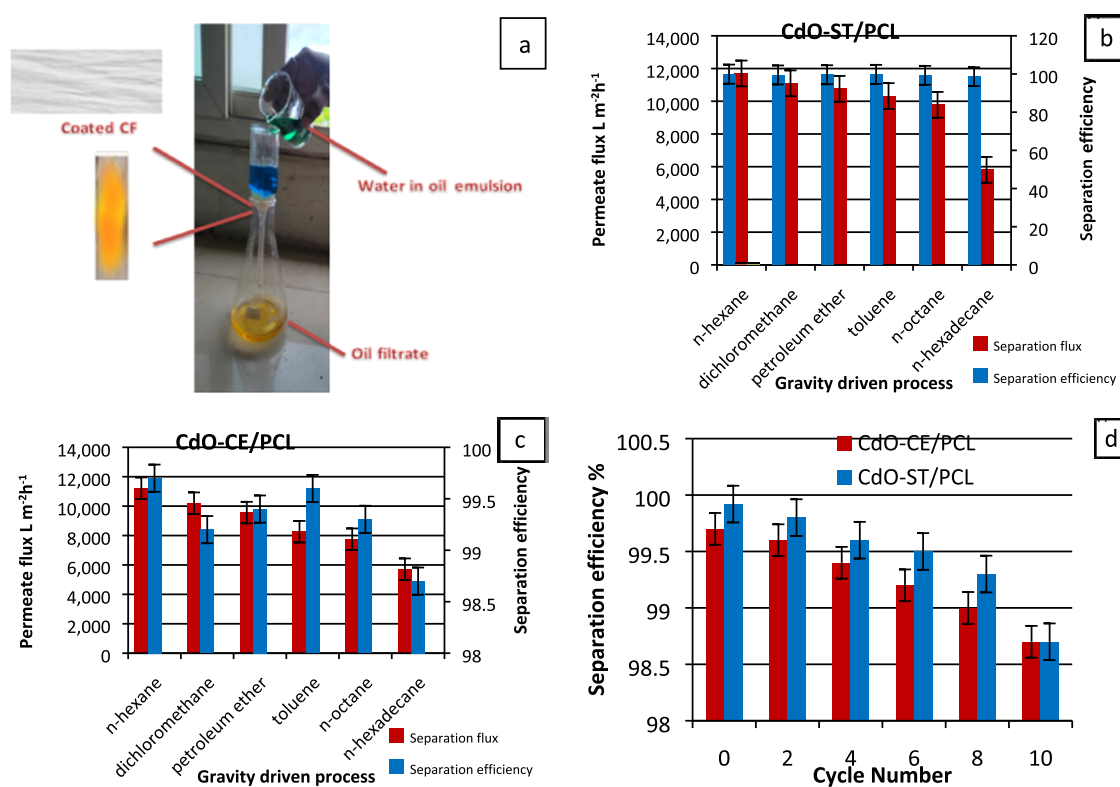
exhibit sustainable superhydrophobicity after immersion in the tested corrosive media, which suggests that these materials can be used under harsh environments with enhanced longevity.

### 3.5. Self-Cleaning Performance of CdO-CE (or ST)/PCL-Modified Cotton Fabrics.

The ability of the lotus leaf surface to clean itself is an intriguing natural occurrence. The surface of a lotus leaf is extremely hydrophobic and allows water droplets to roll off with ease, which helps to remove pollutants like dust and keeps the surface clean.<sup>63</sup> The self-cleaning capabilities of the CdO-CE (or ST)/PCL-grafted modified cotton fabrics are shown in Figure 11. The CdO-CE(or ST)/PCL-grafted modified cotton fabrics, presented in Figure 11(a), showed outstanding superhydrophobicity against coffee and milk as well as methylene blue and methyl orange colored water. In particular, as illustrated in Figure 11(b–f), water may flow across the surface of CdO-CE/ST/PCL-modified cotton fabrics with ease and remove dust from them, indicating that they have the ability to self-clean.



**Figure 13.** Separation process or absorption of oil from water using CdO-CE (or ST)/PCL-grafted composite-modified cotton fabrics.



**Figure 14.** (a) Experimental setup for water-in-oil emulsion separation, (b, c) separation performance of CdO-ST/PCL- and CdO-CE/PCL-modified CFs, respectively, with surfactant-stabilized water-in-oil emulsions using a gravity-driven process, and (d) cyclic separation of the mixed fluids.

**3.6. Surface Density.** In the current study, CdO-CE/ST/PCL and surface micro/nanostructures are two parameters that have an impact on superwettability. Surface density ( $\rho_s$ ) has a significant impact and favors superhydrophobicity, which is the measure of weight per unit area of the CdO-CE/ST/PCL-coated sample. The inadequate surface density of CFs results in contact angles of less than  $100^\circ$ , which are not suitable and cannot be considered for superhydrophobic applications. A considerable rise in the hydrophobicity of CFs was seen when CdO-CE/ST/PCL was coated by the dip-coating method based on the number of cycles of coating layers. This was due to an increase in surface density and in turn contributed to an enhanced value of contact angle. The surface densities of CdO-ST/PCL and CdO-CE/PCL are  $5.07$  and  $5.44$  mg/cm<sup>2</sup> and

these values contribute to obtaining the maximum superhydrophobic behavior (Figure 12a,b). In order to obtain the average static WCA, each surface density measurement is performed five times. Further increase in the surface density ( $\rho_s$ ) could not change the contact angle value, and this result concludes that increasing  $\rho_s$  changes only the thickness of the CdO-CE/ST/PCL without altering the surface morphology.<sup>61</sup>

**3.7. Oil/Water Separation Ability of CdO/CE (or ST)/PCL-Modified Cotton Fabrics.** Cotton fabrics are transformed into superhydrophobic surfaces by the CdO-CE (or ST)/PCL-grafted composite coatings, which is explained in detail in the previous section. On the other hand, CdO-CE (or ST)/PCL-modified cotton fabrics also exhibit superlipophilicity, suggesting that they may find use in oil/water

separation.<sup>64</sup> Figure 13 shows a mixture of oil and water, in which the colorless transparent part is water and the blue part is oil dyed with methylene blue dye. As shown in Figure 13, water floats on the surface of the coated cotton fabric materials and cannot absorb any water drops on the air/water interface, which shows significantly high superhydrophobicity. Once contacted, the floating oil drop is quickly and selectively collected inside the coated cotton fabric material. The oil drops in the treated oil/water mixture were completely removed or disappeared. In the practical application of oil–water separation materials, it is often necessary to separate an oil drop whose density is greater than that of water.

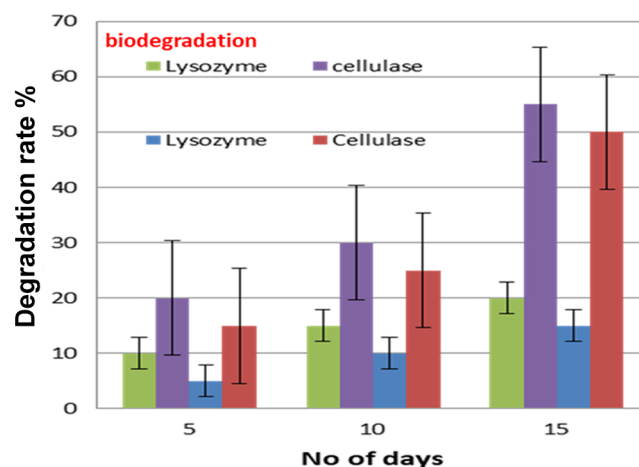
Figure 14a presents a simple setup that separates a surfactant-stabilized water-in-oil emulsion using CdO-CE/PCL- and CdO-ST/PCL-modified CFs fixed in the funnel. With the aid of a gravity-driven technique, the filtrate of an emulsion stabilized by surfactants was obtained. Droplet diameter is seen in the opaque emulsion, and droplets vanish after separation, which produces a filtrate that is identical to that produced by the gravity-driven water/oil separation method. This outcome shows that water has been removed from the water-in-oil emulsion. DLS was used to identify the water particle size in water-in-oil emulsions. The DLS results show that the droplet size changed from  $1045 \pm 35$  to  $7.5 \pm 0.2$  nm under the gravity-driven separation technique.<sup>65,66</sup>

These results showed that CdO-ST/PCL-modified CFs can effectively separate the water-in-oil emulsions with good performance by a gravity-driven process. The permeate fluxes via CdO-CE/PCL-coated CFs for water-in-oil emulsions of *n*-hexane, dichloromethane, petroleum ether, toluene, *n*-octane, and *n*-hexadecane are  $11,220 \pm 120$ ,  $10,200 \pm 100$ ,  $9,560 \pm 150$ ,  $8,260 \pm 160$ ,  $7,750 \pm 130$ , and  $5710 \pm 310$  L m<sup>-2</sup>h<sup>-1</sup>, respectively. Similarly, the permeate fluxes via CdO-ST/PCL-modified CFs for water-in-oil emulsions of *n*-hexane, dichloromethane, petroleum ether, toluene, *n*-octane, and *n*-hexadecane are  $11,700 \pm 300$ ,  $11,100 \pm 200$ ,  $10,760 \pm 160$ ,  $10,320 \pm 110$ ,  $9780 \pm 240$ , and  $5810 \pm 50$  L m<sup>-2</sup> h<sup>-1</sup>, respectively (Figure 14b,c). These flux results indicate that CdO-ST/PCL-coated CFs can effectively separate water-in-oil emulsions with better performance.<sup>67</sup>

The results from the water-in-oil separation test demonstrate that the CdO-CE/PCL/CFs and CdO-ST/PCL/CFs have outstanding capacity for separating liquid mixtures that are mixed with surfactant-stabilized emulsions. Additionally, all of the examined mixed fluids exhibit very high separation efficiency, namely, 99.9% for CdO-ST/PCL-modified CFs and 99.7% for CdO-CE/PCL-modified CFs (Figure 14(d)). Further, the water-in-oil mixture separation test maintains 98.7% separation efficiency even after 10 cycles of the experiment (Figure 14(d)). The cycle test indicates their efficient performance and longevity for oil/water separation applications.<sup>68,69</sup>

**3.8. Biodegradation Rate of CdO-CE(or ST)/PCL-Grafted Cotton Fabrics.** Besides the durable superhydrophobicity, high separation efficiency for oil/water mixed liquids, and good self-cleaning ability, the desired biodegradability and environmental acceptance of CdO-CE(or ST)/PCL-modified cotton fabrics are also favorable for their applications in pollution control engineering, due to the biodegradability, nontoxicity, and low cost of cotton fabrics, CE/ST, and CdO.<sup>70</sup> In fact, CdO would have very little or no harmful effects on the environment, since it can be degraded into Cd<sup>2+</sup>, and ST/CE with an active carbonyl group is also

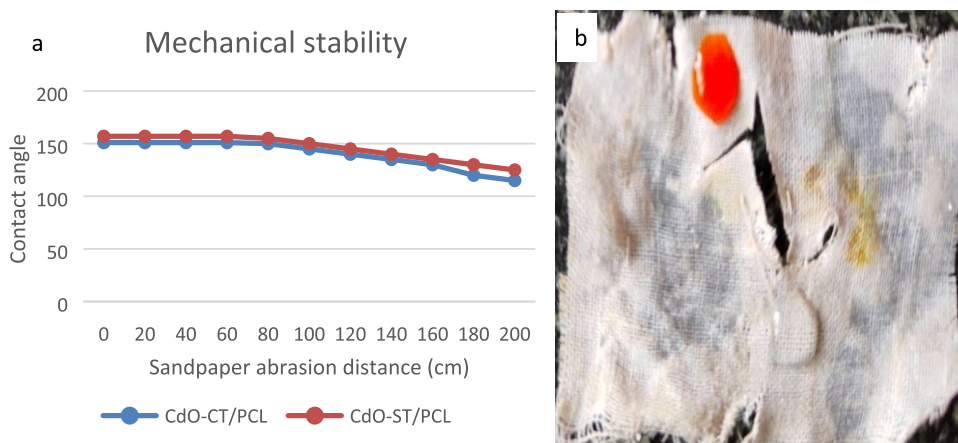
liable to degradation.<sup>71</sup> Figure 15 shows the biodegradation rate of CdO/CE (or ST)/PCL-grafted modified cotton fabrics



**Figure 15.** Biodegradation rate of CdO-CE/PCL- and CdO-ST/PCL-modified cotton fabrics in PBS–lysozyme and PBS–cellulase solutions.

in PBS–lysozyme and PBS–cellulase solutions. It can be seen that the CdO/CE (or ST)/PCL-modified cotton fabrics have degradation rates of 5 and 10% after 5 days of immersion in the PBS–lysozyme and PBS–cellulase solutions, respectively, and their degradation rate tends to increase significantly with extending immersion time. Particularly, their degradation rate reaches 15 and 50.0% after immersion in PBS–cellulase solution for 10 and 15 days, respectively. Moreover, the degradation rate of CdO/CE (or ST)/PCL-modified cotton fabrics in the PBS–cellulase solution is higher than that in the PBS–lysozyme solution, which could be due to the specificity of the enzyme.<sup>72</sup> Namely, cotton fibers predominantly consist of cellulose whose degradation would not be disturbed in the PBA–cellulase solution, but lysozyme with intrinsic specificity could hinder the degradation of cellulose, thereby affording a lowered degradation rate of the CdO/CE (or ST)/PCL-modified cotton fabrics. Therefore, the as-prepared CdO/CE (or ST)/PCL-grafted modified cotton fabrics exhibit excellent degradation performance, especially in the PBS–cellulase solution, which could be of special significance for their application in oil–water separation engineering.

**3.9. Mechanical Stability.** The WCAs of the CdO-CE/PCL- and CdO-ST/PCL-coated cotton superhydrophobic fabrics were measured during the abrasion distance test. It was evaluated that after moving the grafted coated cotton superhydrophobic fabrics on sandpaper for 80 cm, the coated cotton fabrics showed WCA values of 150 and 155°, respectively. These results show that the grafted coated cotton fabrics show good abrasive strength. Thereafter, the WCA value gradually decreased with abrasion distance. After moving 180 cm over the sandpaper, the WCAs of CdO-ST/PCL and CdO-CE/PCL decreased to 130° and 120°, respectively, because of degradation of the coating surface. After 200 cm of dragging, the coating was completely removed, and it became hydrophilic with a WCA value of ≈75°. The variation of the value of WCA of the coated sample after sandpaper abrasion is shown in Figure 16. After the examination of the mechanical durability of superhydrophobic fabric hybrid coated cotton fabrics, the water droplets took on a spherical shape on the damaged area of the cloth, the cotton fabric structure was



**Figure 16.** (a) Mechanical stability of CdO-CE/PCL- and CdO-ST/PCL-modified cotton fabrics and (b) image of coated CdO-ST (CE)/PCL-modified cotton fabrics after the abrasion test.

distorted, and also some of the fibers were torn after a severe scratch. These findings supported the behavior of the superhydrophobic surface's mechanical stability and mechanical resilience of modified cotton fabrics.

#### 4. CONCLUSIONS

In the present work, grafted hybrid material-coated cotton fabrics were developed through a facile, eco-friendly, and cost-competitive method. The superhydrophobic cotton fabrics were prepared using cadmium oxide nanoparticles, cerotic acid/stearic acid, and a polycaprolactone-grafted composite using the dip-coating method with a view to utilize them for oil/water separation and thus extend the applications in environment engineering. The contact angle values for CdO-CE/PCL and CdO-ST/PCL are 151 and 157°, respectively. XRD, SEM, EDX, FTIR, TGA, and UV characterization techniques show that CdO-CE/PCL- and CdO-ST/PCL-grafted composites are robustly fixed on the surface of cotton fabrics. The superhydrophobic coatings not only exhibit durability under harsh chemical environments but also possess the desired self-cleaning ability toward a wide range of liquids. Furthermore, the as-prepared CdO-CE/PCL- and CdO-ST/PCL-coated superhydrophobic cotton fabrics effectively separate water–oil emulsions that had been stabilized using surfactants, which possess excellent permeation fluxes of up to  $11,700 \pm 300 \text{ L m}^{-2} \text{ h}^{-1}$  and high separation efficiency (oil purity of  $\geq 99.97 \text{ wt } \%$ ) with acceptable cyclability. The modified cotton fabrics showed high separation efficiency for a variety of oil/water mixed solutions and retained a separation efficiency of 98.7% even after 10 cycles of the separation test. Another important fact is that the CdO-CE/PCL- and CdO-ST/PCL-modified cotton fabrics exhibit an excellent degradation performance, especially in the PBS–cellulase solution, which is because of the cellulose (major component of cotton fabrics). In the abrasion test, the water droplets took on a spherical shape on the damaged area of the cloth, the cotton fabric structure was distorted, and also some of the fibers were torn after a severe scratch, which confirms superhydrophobic cotton's mechanical resilience in its manufactured form. Among the fabricated cotton fabrics, CdO-ST/PCL shows excellent separation efficiency compared to CdO-CE/PCL. This study not only deals with the separation efficiency for oil/water but also explains the self-cleaning ability and durability of

modified cotton fabrics that can be considered for pollution control applications.

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##### Notes

The authors declare no competing financial interest.

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