Contents lists available at ScienceDirect





journal homepage: www.elsevier.com/locate/porgcoat

# An efficient use of waste PE for hydrophobic surface coating and its application on cotton fibers for oil-water separator

### Check for updates

ORGANIC COATINGS

#### Arun K. Singh, Jayant K. Singh\*

Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

ARTICLE INFO	ABSTRACT		
Keywords: Recycled PE gloves Silres Cotton fiber Hydrophobic coating Oil absorption Contact angle	In this study, we report the fabrication of hydrophobic cotton fibers via simple and cost-effective one step easy fabrication approach by utilizing waste recycled polyethylene (PE) gloves. Also, we prepared silres-modified cotton fibers with hydrophobic and oleophilic properties via a simple dip coating process. The resultant both coated cotton (PE and silres) fibers exhibited high repellency towards the water with water contact angle < 135° and superoleophilicity with an oil contact angle ~ 0°. Due to such special wettability, the as-prepared cotton fibers exhibited high selective oil absorption capacity when used as absorptive materials for separating various oil/water mixtures under acidic, alkaline, and salt aqueous solutions. It was observed that oil/organic solvents absorption capacity of the PE coated cotton fibers was better (16.8–59.7 %, depending on the type of oil) than that of silres modifications. The fabricated PE fiber shows oils and organic solvents absorption ability in the range of 22–61 times their weight as well as good reusability in oil/water separation even after ten absorption-desorption repeated cycles by simple squeezing method. Thus, the utilization of PE waste materials provides an extremely low cost and better approach in the fabrication of promising surfaces for oil/water separation applications.		

#### 1. Introduction

The contamination of oil and organic solvents in the aquatic system is of serious concern [1–4]. In particular, oil spills decrease the dissolved oxygen in water, consequently, killing the aquatic life [5]. The water contaminated with oil also reduces crop yield due to the prevention of air penetration by the clogs of soil pore [5]. Various strategies for oil-water separation have been developed based on skimmer collection [6], air flotation [7], membrane separation [8], biodegradation [9], electrochemical treatment [10] and burning [11]. However, generally, these strategies have drawbacks such as lengthy process, high cost and low efficiency. Thus, it is of great relevance to develop an eco-friendly, economically and efficient method to separate oil/water mixtures.

In the recent years, materials with special wettability viz., hydrophobic/oleophilic or hydrophilic/underwater superoleophobic, have increasingly been investigated by various researchers for the separation of oil/water mixtures because of their high performance [12,13]. For example, sponge-based materials [14–16], mesh-based material [2,17], foam-based material [18,19], microfiltration membrane [20], orange peel powder [21] and filter paper [22] are reported for the separation of oil and organic solvents from the water. Among them, cotton and sponge are the most studied materials because of its high absorption capacity, low cost and easy commercial availability [23].

Cao et al. fabricated superhydrophobic polyurethane sponge via incorporation of superhydrophobic nano diamond particles through dopamine self-polymerization and subsequent fluorination using 1H,1H,2H,2H-perfluorodecanethiol [14]. The resulting sponge showed superhydrophobic property, oil/water separation behavior, and high organic solvents adsorption capacity. Zhang et al. [24] reported preparation of Al porous fiber (Mg-Al PF)/polyurethane (PU) foam composites (Mg-Al PF) using foaming technology. The modified Mg-Al PF composites show high water repellency, with a water contact angle of 146.6°, and swelling properties. Due to its hydrophobic and swelling properties, the Mg-Al PF composites are able to remove oils and organic solvents from water with high selectivity and absorption capacity. Lee et al. reported preparation of hydrophobic fibers using a dip dip-coating a solution of PDMS-coated SiO<sub>2</sub> and adhesives dissolved in hexane, cotton and kapok surface [25]. The resulting fibers exhibited high absorption capacity for various oils and low water content. Wang et al. [26] also synthesized superhydrophobic and superoleophilic ZnOcoated cotton fibers using hydrothermal route followed by modification with dodecyltrimethoxysilane. Eco-friendly, low cost, good mechanical stability, easy-fabrication approach and non-toxic coatings for special

E-mail address: jayantks@iitk.ac.in (J.K. Singh).

https://doi.org/10.1016/j.porgcoat.2019.02.025

Received 17 December 2018; Received in revised form 4 February 2019; Accepted 12 February 2019 Available online 04 March 2019

0300-9440/ © 2019 Elsevier B.V. All rights reserved.

<sup>\*</sup> Corresponding author.

wettability materials is the pursuit of many researchers and essential for large-scale practical application in oil/water separation process. Moreover, utilising waste materials, which are pollutants, in the fabrication of special wettable surfaces for oil/water separation application is one of the mechanism by which the harmful effect on the environment can be reduced [27].

In our daily life, various polyethylene (PE) products such as gloves, droppers, films, and fibers are widely used for food research, laboratories, and other industries because of its low cost, nontoxicity, good chemical resistance, and odourlessness [28]. However, the large scale use of PE-based products generates a huge amount of plastic waste. which is now a serious environmental problem [28]. Thus the recycling of PE-based waste materials in the form of useful products not only minimizes the environmental pollution but also helpful in the fabrication of extremely low cost special wettable surfaces. In a recent work, PE coating on a copper mesh is found to enhance the surface roughness and contributed to the hydrophobicity/superoleophilicity of the copper mesh. [28]. In this work, we extend the use of waste material, recycled PE gloves, in the fabrication of eco-friendly, nontoxic, hydrophobic/ superoleophilic cotton fiber of extremely low cost using simple and inexpensive dip coating process for separation of various oil/water mixture.

In the current study, we also fabricate silres-modified cotton fiber with hydrophobic and oleophilic properties via a simple dip coating process. Silres BS 39 is a mixture of silane/siloxane/polymer content (~25 wt%) in water (~75 wt%). Silres is a water soluble siloxane emulsion and can be used for hydrophobic coatings on various surfaces such as cotton fabric and silk textiles, without the use of any organic solvents [29,30]. Thus, in this work wettability of cotton fiber was modified by two different coating agents: (1) use of recycled PE gloves, and (2) water soluble siloxane emulsion, without the use of any sophisticated equipment. The morphological structures of the as-prepared cotton samples were carried out with a scanning electron microscope (SEM) and an optical profilometer. The wetting behavior (water repellent and oil absorption) of the resulting PE-coated cotton (PE-CC) and silres coated cotton (SCC) fibers were determined by the measurement of the contact angle of liquids. The oil absorption efficiency and selectivity of the modified coated fibers were studied for various oils and organic solvents. Moreover, the recyclability of the as-prepared cotton based absorbents was also demonstrated.

#### 2. Experimental section

#### 2.1. Materials

Cotton fibers were purchased from the local store (Kanpur, India) and ultrasonically washed with distilled water and ethanol. Polyethylene (PE) gloves were recycled from the laboratory as raw materials for the PE coating purpose on cotton fibers. Silres BS39 A from Wacker and sulphuric acid, hydrochloric acid and toluene were purchased from Fisher Scientific. Other solvents and chemicals were used as received without further purification.

#### 2.2. Treatment of cotton fibers

The raw cotton surface was made hydrophobic via a facile strategy using silres and PE gloves as hydrophobic agents according to the procedure illustrated in Fig. 1 (approach-1 and approach-2). The fabrication procedures were based on simple dissolution and immersion approach and did not require the involvement of any sophisticated equipment.

#### 2.2.1. Preparation of Siloxane coated cotton (SCC)

Fabrication of the silres-coated cotton samples was performed using a simple dip coating approach (Fig. 1a). Initially, a water-based homogeneous emulsion of silres (7 wt %, silane, siloxane and organic polymer) was prepared by dilution of Silres BS39 A in distilled water and solution was stirred for 30 min. The clean cotton was dried at 80  $^{\circ}$ C in a drying oven for one hour and immersed into the homogenized emulsion of silres for one h. The resultant cotton was removed and dried at 40  $^{\circ}$ C for overnight and kept at room temperature for 1–2 days.

#### 2.2.2. Preparation of PE coated cotton (PE-CC)

The PE coated cotton was fabricated by simple dissolution and immersion approach using recycled PE gloves as a crude material (Fig. 1b). Initially, the laboratory used PE gloves were washed and cut into small pieces. The specific amount of PE pieces was placed in a beaker which having already 100 ml of toluene solvent. To dissolve PE pieces, the above mixture was stirred for 30 min with heating at 100 °C. Subsequently, a homogeneous solution was obtained after removal of undissolved impurities from the mixture. Finally, cleaned and dried cotton was dipped in the above solution for some seconds, blow-dried at room temperature. Thus, the obtained cotton is considered as PE coated cotton.

#### 2.3. Characterizations

The morphological structure of the prepared cotton fibers was analyzed by field emission scanning electron microscopy (FESEM, Zeiss, Germany, supra-40VP). To prevent charging, before the analysis of surface morphology, a sputtering coater was used to place the thin layer of gold film on the samples. Also, optical profilometer (Bruker GT-KO) was used to examine the changes in the surface roughness of uncoated and coated cotton fibers. Fourier transformed infrared (FTIR) spectra were recorded using FTIR spectrometer (KBR pellet method) in the range of 500 to 4000 cm<sup>-1</sup> to identify the presence of functional groups on the surface of specimens. X-ray photoelectron spectroscopy (XPS) analysis was done using PHI 5000 Versa Prob II, FEI Inc to analyze the surface composition and chemical state of coated fibers. All of the XPS spectra were acquired using Al Ka radiation (1486.6 eV) at the room temperature. The wetting behavior of coated cotton fibers was examined by the measurement of the water contact angle using goniometer (OCA 20, data physics, Germany) instrument by sessile liquid drop method at the room temperature. The injecting volume of water in the measurements of the contact angle was approximately five µL. The values of WCA were as measured in five different spots on the same sample surface, and the mean value of the contact angles was taken, and images were captured. The variations in the measurements are given as error bars.

## 2.4. Selective absorption-based oil/water separation and evaluation of oil absorption capacity

The selective separation of oils from water surface was performed by immersing the PE-CC and SCC samples of specific weight into various oil/water mixtures (1:1, v/v) at room temperature with stirring. After 1 min, oil absorbed cotton samples were removed, drained for 15–20 s to discard excess oil/solvents and then weighed before evaporation of solvents and oils to assess the weight gain of the samples. During this oil sorption process, the weight gain or oil absorption capacity is defined as the ratio between the maximum weight of absorbed oil and the initial weight of the cotton samples (absorbents) [31]. The following equation was used to calculate the oil absorption capacity of the modified cotton fibers:

$$K = \left[\frac{M_1 - M_0}{M_0} x \ 100\right]$$

Where K is the oil sorption capacity of sorbent in terms of g  $g^{-1}$ .  $M_0$  is the initial weight of the dried SCC and PE-CC before immersion in the oil and  $M_1$  is the saturated weight of the SCC and PE-CC. The oil absorption capacity measurements of both modified cotton fibers were



Fig. 1. Schematic illustration of procedure for the fabrication of hydrophobic fibers SCC (approach-1) and PE-CC (approach-2) via dissolution and immersion approach.

Table	1
-------	---

Characteristics of the studied oils at room temperature.

Type of oil	Viscosity (mPas)	Density (g/ cm <sup>3</sup> )
Chloroform	0.536	1.478
Toluene	0.59	0.867
Dicholoroethane	0.41	1.318
Hexane	0.28	0.659
Diesel Oil	2.0	0.825
Silicone oil	2600	0.970
Sesame oil	47.4	0.918
Olive oil	85	0.918



**PE-coated cotton** 

repeated 3 times for all types of oils and organic solvents to get an average value of K. This process was used for various types of organic solvents and oils such as chloroform, toluene, dichloroethane, hexane, diesel oil, silicone oil, sesame oil, and olive oil. The viscosity and density of the utilized oils and organic solvents are summarized in Table 1 [31].

#### 2.5. Evaluation of recyclability of used absorbents

To evaluate the recyclability of the SCC and PE-CC, several cycles of oil absorption and desorption were performed. Initially, during the absorption process, one piece of each cotton samples of specific weight was immersed in diesel oil for 1 min with stirring and was then taken out and weight of diesel oil absorbed cotton fibers was measured. Subsequently, the desorption process was performed in which cotton fibers (fully wetted with oils) were placed on a stainless-steel mesh inside a centrifuge tube, which was centrifuged at 3000 rpm for 5 min. Next, we get the desorbed coated fibers, and absorbed oils or organic solvents were collected in the centrifuge tube. This absorption and desorption processes were repeated more than ten times, and the recyclability was evaluated by the weight measurement of absorbent in each step of absorption and desorption processes.

#### 3. Results and discussion

#### 3.1. Wetting behavior, surface morphology, and chemical composition

The surface morphologies and wetting properties (by contact angle

**Fig. 2.** Optical Images of water droplets (dyed with phenosafranin) on the bare, silres coated and PE-coated cotton surface with the water contact angle.



Fig. 3. SEM images of raw cotton (a) low and (b) high magnification, SEM images of SCC in (c) low and (d) high magnification and SEM images of PE-CC in (e) low and (f) high magnifications.

measurement) of the resulting SCC and PE-CC were evaluated by using different characterization tools. The wetting behavior of the bare SCC and PE-CC were examined comparatively by the measurement of water contact angle using goniometer (OCA 20, data physics, Germany) and obtained results are shown in Fig. 2.

It was observed that water droplets colored with phenosafranin dye (for clear visibility) were immediately adsorbed on the surface of bare cotton, confirming that bare cotton was hydrophilic. Thus, the water contact angle on such surface is unmeasurable. In contrast, after the treatment of bare cotton with silres and PE the surfaces of the resulting materials viz., SCC and PE-CC, exhibit water repellency with water contact angle of 138  $\pm$  1° and 144  $\pm$  1°, respectively. The significant enhancement of the water contact angle on the surface of SSC and PE-CC strongly indicates that the coating approaches adopted in this work using silres and PE are an effecting strategy to make cotton materials

hydrophobic.

It has been reported that the fabrication of hierarchical structures and chemical structure are the two essential factors in enhancing the surface roughness and subsequently leads to increase in the water contact angle on the surface [28,29]. To understand the changes in surface morphology of cotton fibers before and after the modification with silres and PE, scanning electron microscope (SEM) was used which is shown in Fig. **3a-f** under low and high magnifications. The SEM image of bare cotton fiber is shown in Fig. 3a-b under low and high magnification. After silres modification, a continuous film was deposited on cotton fiber (Fig. 3c-d). It is also observed that compared to bare cotton, the PE-CC showed a rougher surface with a large number of grooves and fibrils (Fig. 3e-f). This is primarily attributed to the deposition of the numerous PE nanoparticles on the surface of bare cotton after dip coating process [28].



**Fig. 4.** Optical profiler images of the surface of (a) raw cotton (b) SCC and (c) PE-CC fibers.

Furthermore, surface morphologies of the cotton fibers before and after modification with silres and PE were also examined by the optical profilometer. Fig. 4a-c displays the optical profilometer images of uncoated, SCC and PE-CC. After the silres and PE coatings (Fig. 4b-c), it is observed that cotton surface become rougher as compared to the uncoated. It is well known that higher surface roughness and lower surface energy are closely related to the hydrophobic property of the surface [29]. It was also reported that silres and PE have low wettabilities because of their reduced surface energy [28,32]. It is therefore concluded that roughness of the coated surface and low surface energy of silres and PE play key roles in enhancing the hydrophobic character of SCC and PE-CC.

Also, it was noticed that the droplets of toluene and diesel (organic solvent and oil) were readily soaked by the coated fibers after being dropped, with a contact angle of 0°. This indicates the superoleophilic nature of the coated fibers. This selective and opposite wetting behavior of water and oil on the surface of coated fibers (SCC and PE-CC) provided a useful base to separate mixtures of oil and water through the selective absorption process.

To evaluate the presence of specific functional groups before and



Fig. 5. FTIR spectra of the bare, silres coated and PE coated cotton fibers.

after modification, the SCC and PE-CC were characterized by FTIR. The FTIR spectra of the bare, SCC and PE-CC fibers over the range of 4000 – 500 cm<sup>-1</sup> are shown in Fig. 5. After PE coating on the cotton fiber, the C–H asymmetrical stretching vibration and C–H symmetrical stretching vibration was observed at 2918 and 2850 cm<sup>-1</sup>, respectively. The sharp peak at 1370 cm<sup>-1</sup> corresponds to the presence of SiOCH (CH<sub>3</sub>)<sub>2</sub> in SCC [28,33]. The results of the FTIR analysis confirmed the silres and PE coating on the surface of the cotton fibers.

XPS analysis was further employed to characterize the chemical composition of coated cotton (CC) with PE and silres for understanding the structure-performance relationship. The surface of raw cotton fiber (untreated) only shows the C 1s and O 1s signal (Fig. 6a). The appearance of Si 2s, and Si 2p peaks were detected at 152.6 and 100.2 along with C1s and O1s signal, indicating the successful coatings of the silres onto the surface of cotton fibers (Fig. 6b). Silres BS 39 is a mixture of silane/siloxane/polymer content (~25 wt%) in water (~75 wt%). Silres has the ability to generate networks of siloxane by polymerization process in room condition under the influence of air humidity. This siloxane network is responsible for the hydrophobicity as well as the stability of coating on the treated surface [34]. The XPS spectra of PE-CC was also recorded. Fig. 6c displays the total survey spectra of PE-CC, which consist of C1s and O1s peaks. The strong and intense peak of C1 s at 283.2 eV, indicating the successful coating of the polyethylene. In addition, high resolution of C1 s peak with binding energy at 283.2 eV are shown in Fig. 6d. which is attributed to the C=C double bond from polyethylene. All these results suggest that the polyethylene and silres were successfully coated onto cotton fibers.

#### 3.2. Oil/water separation and oil absorption capacity

Due to regular oil-contamination [29], the separation and removal of oil contaminants from the water have become increasingly important. The as-prepared SCC and PE-CC exhibit hydrophobic and superoleophilic properties simultaneously, which was characterized by the contact angle measurements with water and oils. Thus, modified cotton fibers (SCC and PE-CC) can be used in the selective removal of oil or water from oil/water mixtures. To evaluate the oil/water separation ability we have used SCC and PE-CC as an "absorbent" as shown in Fig. 7. In this experiment, a mixture of diesel oil and water (1:1 vol ratio) was taken in a beaker, and fabricated cotton fiber was immersed in this mixture. To visualize clearly during the sorption process water was colored by adding phenosafranin dye. It was observed that coated cotton fibers could selectively absorb diesel oil immediately floating on the water surface (Video S1). On the other hand,



Fig. 6. XPS spectra of (a) uncoated cotton fibers (b) SCC and (c) PE-CC fibers (d) high resolution of C 1 s peak in PE-CC.



Fig. 7. Separation of diesel oil from water surface using (a) SCC and (b) PE-CC as absorbent.

water (dyed with dye) was not absorbed by the coated fibers because of their hydrophobic nature. This observation corroborates their ability for oil/water separation.

The absorption efficiency of the coated fibers concerning various oils and organic solvents can be evaluated by weight gain, i.e., the weight of absorbed oil divided by the initial weight of the coated fibers. However, it should be noted that the sorption capacity of the hydrophobic sorbents is significantly affected by the various properties (density, surface tension, and viscosity) of the used oils and organic solvents [26,31,35,36].

The absorption capacities of the bare and fabricated fibers (SCC and PE-CC) were evaluated for a variety of pure oils (diesel oil, silicone oil, sesame oil and olive oil) and organic solvents (chloroform, toluene, dichloroethane, hexane). Fig. 8 displays the summary of weight gains of the bare and coated fibers for absorption of various oils and organic solvents. The absorption capacity of the PE-CC is  $61.2 \text{ g s}^{-1}$ ,  $27.8 \text{ g s}^{-1}$ ,  $37.97 \text{ g s}^{-1}$ ,  $22.79 \text{ g s}^{-1}$ ,  $28.93 \text{ g s}^{-1}$ ,  $52.48 \text{ g s}^{-1}$ ,  $37.14 \text{ g s}^{-1}$ , and  $36.1 \text{ g s}^{-1}$  for chloroform, toluene, dichloroethane, hexane, diesel oil, silicon oil, sesame oil and olive oil, respectively. The fabricated PE-CC fiber shows superior oils and organic solvents absorption ability in



Fig. 8. The absorption capacities (weight gains) of bare, SCC and PE-CC fibers for different oils and organic solvents.

the range of 22–61 g g<sup>-1</sup>. However, the weight gain of SCC fiber was obtained in the range of 15 to 39 times their weight depending on the variety of oils and organic solvents. Hence, it was concluded that the PE-CC have better oil absorption capacity (16.80–59.7 %, depending on the type of oils) compare to the SCC. This could be probably due to the increased capillary effect of the hydrophobic PE-CC which leads to enhanced interactions between the oils/organic solvents, and PE coated strands of the cotton fibers [31,37]. Our results also suggest that the PE-CC exhibits the greater adsorption capacity for the chloroform and dichloroethane than that of the raw cotton. This could be probably due to



**Fig. 9.** The water contact angle of hydrophobic SCC and PE-CC after immersion in solutions at different pH (4, 7 and 9) values for 12 h and after mechanical abrasion test (M.A.T.).

the good compatibility between the PE and high-density chloroform and dichloroethane solvents, complex nature of adsorption process that is affected by the density, viscosity of the absorbates and uniform superoleophilic surface nature of the coating materials (PE) [38]. A similar observation has been reported earlier for the absorption of chloroform and dichloromethane using polyethylene coated PU sponge, polystyrene-coated non-woven fabric and octadecyltrichlorosilane modified cotton [38–40].

Table 2 lists the comparison of the oil/organic solvents absorption capacity (weight gains) of our coated fibers with various other hydrophobic materials reported in the literature. As we discussed already that the sorption characteristics largely depend on many factors such as viscosity, density and surface tension of the oils or organic solvents and

#### Table 2

Table 2				
Comparison	of oil sorptio	on capacities of	f different	sorbents

Absorbents	Coating material	Type of oil	Absorption capacity (g $g^{-1}$ )	Ref. No.
Cotton	SiO <sub>2</sub> nanoparticles/ octadecyltrichlorosilane	Diesel oil	~ 21	[40]
Macroporous MWNT nanocomposite	PDMS	Toluene	12.4	[41]
· ·		Chloroform	20.5	
		Hexane	15.05	
Swellable porous PDMS	PDMS	Chloroform	34	[42]
-		Diesel oil	12	
		Toluene	18.7	
PDMS sponge	PDMS	Chloroform	11	[43]
		Toluene	5	
Polyurethane sponge	carbon nanotube/PDMS	Diesel oil	19	[44]
		Hexane	15	
Polyurethane sponge	Nanodiamonds/ polydopamine/ H,1H,2H,2H-perfluorodecanethiol	Chloroform	59.26	[12]
		Diesel oil	31.2	
		Toluene	17.4	
		Hexane	3.75	
Cotton	PDMS	Diesel oil	31.8	[29]
Cotton fibers	ZnO/Dodecyltrimethoxysilane	Chloroform	45.3	[24]
		Diesel oil	41.8	
		Toluene	37.6	
		Hexane	32.3	
Cotton	PDMS	Chloroform	70.80	[21]
		Diesel	35.70	
		Toluene	24.85	
		Silicone oil	61	
Cotton	Silres	Chloroform	39.59	This work
		Diesel	22.24	
		Toluene	18.24	
		Dichloroethane	36.39	
		Silicone oil	28.76	
	PE	Chloroform	61.2	This work
		Diesel	28.93	
		Toluene	27.18	
		Dichloroethane	37.97	
		Silicone oil	52.48	



**Fig. 10.** Oil wetted SCC and PE-CC were placed on the surface of clean water. After 24 h, the oil wetted samples were not dipped in water, showing stability of coatings.



Fig. 11. Effect of UV-irradiation time on water contact angle of the prepared PE-CC and SCC fibers.



**Fig. 12.** The change of oil absorption capacity of the SCC and PE-CC fibers as a function of the number of recycling is plotted. Photographs of SCC and PE-CC fibers after more than 10 recycling process were stably floated on water surface even after 3 days are shown in the inset.

hydrophobicity of the absorbents. According to the above comparison, although the absorbency of the fabricated PE-CC fiber is comparable with the previously reported other adsorbents, the simpler and cheaper fabrication approach and especially the use of waste (recycled PE gloves) materials make the prepared hydrophobic absorbent an attractive alternative to the existing absorbents.

#### 3.3. Hydrophobic stability of the coated cotton fibers

The stability of the hydrophobic coating on the cotton fibers is one of the crucial requirements for their practical applications under the different environmental condition of oil/water mixture. In general, the pH of oily contaminated water exists in the range of 4-9. Thus, we have evaluated the hydrophobic coating stability of the as-prepared PE-CC and SCC fibers with respect to time by immersing them into an aqueous medium with different pH values (4, 7 & 9), ethanol and toluene for 12 h. The pH values (4, 7 & 9) of an aqueous medium were adjusted by the addition of a specific concentration of HCl, NaCl, and NaOH. The water contact angle was measured on the surface of treated cotton fibers before and after immersion. The treated cotton fibers were washed with ethanol and dried at 60° before the measurement of water contact angle.

As shown in Fig. 9, both the coated fibers exhibited the water contact angles higher than 135°, demonstrating the good stability of the hydrophobic coatings of silres and PE coated cotton fibers under complex environmental conditions. Similar to this, water contact angle value also remained over  $135^{\rm o}$  after immersing the PE-CC and SCC in ethanol and toluene for 12 h. The mechanical durability of the hydrophobic coating was also evaluated by the sandpaper abrasion test [45,46]. The test was repeated ten times for each coated sample. After ten times repetition of the abrasion test, the WCA of the both coated cotton fibers were found  $< 135^{\circ}$  (Fig. 9), which further demonstrates the stability of hydrophobic coatings on the surface of cotton fibers. Besides the mechanical durability discussed above, we also evaluated the stability of the hydrophobic coating by the placement of coated cotton fibers (a small piece, fully wetted with oil) on the surface of the clean water. [25] It was observed that cotton fibers were floated on the surface of clean water even after 24 h, demonstrating the stability of the hydrophobic coating (Fig. 10).

Furthermore, the hydrophobic coating stability of PE-CC and SCC was also investigated by ultraviolet irradiation test with respect to time. During this test, both PE-CC and SCC fibers were placed in a U. V. chamber for 24, equipped with two ultraviolet lamps ( $\lambda = 365$  nm, 8 W). In the U.V. chamber, the distance between the coated surface and U.V. lamp was about 6 cm. The water contact angles on U.V. light exposed surfaces were measured at every 6 h. Fig. 11 shows the values of water contact angle as a function of U.V. irradiation time. It was observed that there is no any significant change in water contact angle with respect to U.V. irradiation up to 24 h. This results further demonstrate excellent U.V. stability of the PE-CC and SCC coatings.

#### 3.4. Recyclability of the coated cotton

The recyclability of the coated fibers was evaluated by the absorption and desorption process in a repeated manner. In this process, we have used diesel oil an absorbate in every absorption step. During this process fabricated fibers of specific weight was immersed initially in diesel oil/water mixture to absorb oils for 1 min with stirring. After the absorption of diesel oil on coated fibers, we have measured the weight gains and performed the desorption of oils using simple squeezing method through centrifuge at 3000 rpm for 5 min. We observed that absorbed diesel oils were desorbed from the surface of the coated fibers. This absorption-desorption process was repeated ten times with both fabricated fibers. As shown in Fig. 12, diesel oil absorption capacity for both PE-CC and SCC and fibers decreased by about 8.2% and 9.9%, respectively after ten repeated cycles. This decrease in absorption capacity with an increase in absorption-desorption cycles may be attributed to the oil residue in the cotton fibers. The results inferred that the as-fabricated fibers have good recyclability in the separation of insoluble oil from oil/water mixtures.

#### 4. Conclusions

In this study, silres and recycled PE gloves were utilized for the modification of cotton surface wettability via simple dissolution and immersion approach without using any expensive and sophisticated equipment. The as-prepared silres and PE modified cotton (SCC and PE-CC) exhibited good hydrophobicity due to the increased roughness onto the surface of the original cotton. After modification, cotton fibers showed good oil absorption efficiencies and recycling abilities. However, the oils and organic solvents absorption capacity of PE-CC (in the range of 22–61 g g<sup>-1</sup>, for various oils and organic solvents) were higher as compared to the SCC, prepared in this study, by 16.80–59.7 %, as well as comparable with other absorbents reported in the literature. Hence, the application of PE waste as a raw material might be a promising substitute in the fabrication of special wettable material for oil/water separation application and thus can decrease the environmental pollution due to PE.

#### Acknowledgments

This work is supported by the Science and Engineering Research Board (SERB) and Department of Science and Technology (DST), Government of India. Arun K. Singh gratefully acknowledges Science and Engineering Research Board (SERB) for awarding the SERB-National Post-Doctoral Fellowship (PDF/2016/002638) to him.

#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.porgcoat.2019.02.025.

#### References

- [1] Y.-Z. Song, X. Kong, X. Yin, Y. Zhang, C.-C. Sun, J.-J. Yuan, B. Zhu, L.-P. Zhu, Tannin-inspired superhydrophilic and underwater superoleophobic polypropylene membrane for effective oil/water emulsions separation, Colloids Surf. A: Physicochem. Eng. Aspects 522 (2017) 585–592.
- [2] H. Zhu, D. Chen, N. Li, Q. Xu, H. Li, J. He, J. Lu, Dual-layer copper mesh for integrated oil-water separation and water purification, Appl. Catal. B Environ 200 (2017) 594–600.
- [3] M. Chen, W. Jiang, F. Wang, P. Shen, P. Maa, J. Gua, J. Mao, F. Li, Synthesis of highly hydrophobic floating magnetic polymer nanocomposites for the removal of oils from water surface, Appl. Surf. Sci. 286 (2013) 249–256.
- [4] A.K. Singh, J.K. Singh, Fabrication of durable superhydrophobic coatings on cotton fabrics with photocatalytic activity by fluorine-free chemical modification for dualfunctional water purification, New J. Chem. 41 (2017) 4618–4628.
- [5] J. Song, S. Li, C. Zhao, Y. Lu, D. Zhao, J. Sun, T. Roy, C.J. Carmalt, X. Deng, I.P. Parkin, A superhydrophilic cement-coated mesh: an acid, alkali, and organic reagent-free material for oil/water separation, Nanoscale 10 (2018) 1920–1929.
- [6] F. Chen, J. Liu, Y. Cui, S. Huang, J. Song, J. Sun, W. Xu, X. Liu, Stability of plasma treated superhydrophobic surfaces under different ambient conditions, J. Colloid Interface Sci. 470 (2016) 221–228.
- [7] A. AAl-Shamrani, A. James, H. Xiao, Separation of oil from water by dissolved air flotation, Colloids and Surfaces A: physicochem, Eng. Aspects 209 (2002) 15–26.
- [8] M. Padaki, R.S. Murali, M.S. Abdullah, N. Misdan, A. Moslehyani, M.A. Kassim, N. Hilal, A.F. Ismail, Membrane technology enhancement in oil-water separation. A review, Desalination 357 (2015) 197–207.
- [9] Georgiana F. dA Cruz, Eugenio V. dOs Santos Neto, A.J. Marsaioli, Petroleum degradation by aerobic microbiota from the Pampo Sul Oil Field, Campos Basin, Brazil, Org. Geochem. 39 (2008) 1204–1209.
- [10] O. Abdelwahab, N.K. Amin, E.S. El-Ashtoukhy, Electrochemical removal of phenol from oil refinery wastewater, J. Hazard. Mater. 163 (2009) 711–716.
- [11] H.-W. Liang, Q.-F. Guan, L.-F. Chen, Z. Zhu, W.-J. Zhang, S.-H. Yu, Macroscopicscale template synthesis of robust carbonaceous nanofiber hydrogels and aerogels and their applications, Angew. Chem. Int. Ed. 51 (2012) 5101–5105.
- [12] J. Li, C. Xu, C. Guo, H. Tian, F. Zhaa, L. Guo, Underoil superhydrophilic desert sand layer for efficient gravity-directed water-in-oil emulsions separation with high flux, J. Mater. Chem. A Mater. Energy Sustain. 6 (2018) 223–230.
- [13] Yifei Long, Yongqian Shen, Haifeng Tian, Yaoxia Yang, Hua Feng, Jian Li, Superwettable Coprinus comatus coated membranes used toward the controllable separation of emulsified oil/water mixtures, J. Membr. Sci. 565 (2018) 85–94.
- [14] N. Cao, B. Yang, A. Barras, S. Szunerits, R. Boukherroub, Polyurethane sponge functionalized with superhydrophobic nano diamond particles for efficient oil/

water separation, Chem. Eng. J. 307 (2017) 319-325.

- [15] S. Zhou, G. Hao, X. Zhou, W. Jiang, T. Wang, N. Zhang, L. Yu, One-pot synthesis of robust superhydrophobic, functionalized graphene/polyurethane sponge for effective continuous oil-water separation, Chem. Eng. J. 302 (2016) 155–162.
- [16] L. Wu, L. Li, B. Li, J. Zhang, A. Wang, Magnetic, durable, and superhydrophobic polyurethane@Fe3O4@SiO2@fluoropolymer sponges for selective oil absorption and oil/water separation, ACS Appl. Mater. Interfaces 7 (2015) 4936–4946.
- [17] J. Zhu, B. Liu, L. Li, Z. Zeng, W. Zhao, G. Wang, X. Guan, Simple and green fabrication of a superhydrophobic surface by one-Step immersion for continuous oil/ water separation, J. Phys. Chem. A 120 (2016) 5617–5623.
- [18] Q. An, Y. Zhang, K. Lv, X. Luan, Q. Zhang, Feng Shi, A facile method to fabricate functionally integrated devices for oil/water separation, Nanoscale 7 (2015) 4553–4558.
- [19] J. Li, D. Li, W. Li, H. She, H. Feng, D. Hu, Facile fabrication of three-dimensional superhydrophobic foam for effective separation of oil and water mixture, Mater. Lett. 171 (2016) 228–231.
- [20] Y. Zhu, W. Xie, F. Zhang, T. Xing, J. Jin, Superhydrophilic in-situ-cross-linked zwitterionic polyelectrolyte/PVDF-blend membrane for highly efficient Oil/Water emulsion separation, ACS Appl. Mater. Interfaces 9 (2017) 9603–9613.
- [21] A, K. Singh, K. Ketan, J.K. Singh, Simple and green fabrication of recyclable magnetic highly hydrophobic sorbents derived from waste orange peels for removal of oil and organic solvents from water surface, J. Environ. Chem. Eng. 5 (2017) 5250–5259.
- [22] K. Rohrbach, Y. Li, H. Zhu, Z. Liu, J. Dai, J. Andreasen, L. Hu, A cellulose based hydrophilic, oleophobic hydrated filter for water/oil separation, Chem. Commun. (Camb.) 50 (2014) 13296–13299.
- [23] Y. Jin, P. Jiang, Q. Ke, F. Cheng, Y. Zhu, Y. Zhang, Superhydrophobic and superoleophilic polydimethylsiloxane-coated cotton for oil–water separation process: an evidence of the relationship between its loading capacity and oil absorption ability, J. Hazard. Mater. 300 (2015) 175–181.
- [24] T. Zhang, L. Kong, M. Zhang, F. Qiu, J. Rong, J. Pan, Synthesis and characterization of porous fibers/polyurethane foam composites for selective removal of oils and organic solvents from water, RSC Adv. 6 (2016) 86510–86519.
- [25] J.H. Lee, D.H. Kim, S.W. Han, B.R. Kim, E.J. Park, M.-G. Jeong, J.H. Kim, Y.D. Kim, Fabrication of superhydrophobic fibre and its application to selective oil spill removal, Chem. Eng. J. 289 (2016) 1–6.
- [26] J. Wang, F. Han, B. Liang, G. Geng, Hydrothermal fabrication of robustly superhydrophobic cotton fibers for efficient separation of oil/water mixtures and oil-inwater emulsions, J. Ind. Eng. Chem. 54 (2017) 174–183.
- [27] J. Li, D. Li, Y. Yang, J. Li, F. Zha, Z. Lei, A prewetting induced underwater superoleophobic or underoil (super) hydrophobic waste potato residue-coated mesh for selective efficient oil/water separation, Green Chem. 18 (2016) 541–549.
- [28] Q. Zhang, Y. Cao, N. Liu, W. Zhang, Y. Chen, X. Lin, Y. Wei, L. Feng, L. Jiang, Recycling of PE glove waste as highly valuable products for efficient separation of oil-based contaminants from water, J. Mater. Chem. A Mater. Energy Sustain. 4 (2016) 18128–18133.
- [29] A.K. Singh, J.K. Singh, Fabrication of durable super-repellent surfaces on cotton fabric with liquids of varying surface tension: low surface energy and high roughness, Appl. Surf. Sci. 416 (2017) 639–648.
- [30] D. Aslanidou, I. Karapanagiotis, C. Panayiotou, Superhydrophobic, superoleophobic coatings for the protection of silk textiles, Prog. Org. Coat. 97 (2016) 44–52.
- [31] J.H. Lee, D.H. Kim, Y.D. Kim, High-performance, recyclable and superhydrophobic oil absorbents consisting of cotton with a polydimethylsiloxane shell, J. Ind. Eng. Chem. 35 (2016) 140–145.
- [32] D. Aslanidou, I. Karapanagiotis, D. Lampakis, Waterborne superhydrophobic and superoleophobic coatings for the protection of marble and sandstone, Materials 11 (2018) 585, https://doi.org/10.3390/ma11040585.
- [33] D. Aslanidou, I. Karapanagiotis, C. Panayiotou, Tuning the wetting properties of siloxane-nanoparticle coatings to induce superhydrophobicity and superoleophobicity for stone protection, Mater. Des. 108 (2016) 736–744.
- [34] I. Karapanagiotis, D. Grosu, D. Aslanidou, K.E. Aifantis, Facile method to prepare superhydrophobic and water repellent cellulosic paper, J. Nanomater. (2015) 9, https://doi.org/10.1155/2015/219013 Article ID 219013.
- [35] X. Liu, L. Ge, W. Li, X. Wang, F. Li, Layered double hydroxide functionalized textile for effective oil/water separation and selective oil adsorption, ACS Appl. Mater. Interfaces 7 (2015) 791–800.
- [36] L. Yu, X. Zhou, W. Jiang, Low-cost and superhydrophobic magnetic foam as an absorbent for oil and organic solvent removal, Ind. Eng. Chem. Res. 55 (2016) 9498–9506.
- [37] L. Zhang, H. Li, X. Lai, X. Su, T. Liang, X. Zeng, Thiolated graphene-based superhydrophobic sponges for oil-water separation, Chem. Eng. J. 316 (2017) 736–743.
- [38] Y. Cheng, B. Wu, X. Ma, S. Lu, W. Xu, S. Szunerits, R. Boukherroub, Facile preparation of high density polyethylene superhydrophobic superoleophilic coatings on glass, copper and polyurethane sponge for self-cleaning, corrosion resistance and efficient oil/water separation, J. Colloid Interface Sci. 525 (2018) 76–85.
- [39] Z. Diao, L. Wang, P. Yu, H. Feng, L. Zhao, W. Zhoua, H. Fu, Super-stable non-woven fabric-based membrane as a high-efficiency oil/water separator in full pH range, RSC Adv. 7 (2017) 19764–19770.
- [40] F. Liu, M.L. Ma, D.L. Zang, Z.X. Gao, C.Y. Wang, Fabrication of superhydrophobic/ superoleophilic cotton for application in the field of water/oil separation, Carbohydr. Polym. 103 (2014) 480.
- [41] A. Turco, C. Malitesta, G. Barillaro, A. Greco, A. Maffezzoli, E. Mazzotta, A magnetic and highly reusable macroporous superhydrophobic/superoleophilic PDMS/MWNT nanocomposite for oil sorption from water, J. Mater. Chem. A Mater. Energy Sustain. 3 (2015) 17685–17696.
- [42] A. Zhang, M. Chen, C. Du, H. Guo, H. Bai, L. Li, Poly(dimethylsiloxane) oil

absorbent with a three-dimensionally interconnected porous structure and swel-

- lable skeleton, ACS Appl. Mater. Interfaces 5 (2013) 10201–10206.[43] S.J. Choi, T.H. Kwon, H. Im, D. Il Moon, D.J. Baek, M.L. Seol, J.P. Duarte, Y.K. Choi, A polydimethylsiloxane (PDMS) sponge for the selective absorption of oil from water, ACS Appl. Mater. Interfaces 3 (2011) 4552-4556.
- [44] C.-F. Wang, S.-J. Lin, Robust Superhydrophobic/Superoleophilic sponge for effective continuous absorption and expulsion of oil pollutants from water, ACS Appl.

Mater. Interfaces 5 (2013) 8861-8864.

- [45] Y. Wu, S. Jia, Y. Qing, S. Luoa, M. Liu, A versatile and efficient method to fabricate durable superhydrophobic surfaces on wood, lignocellulosic fiber, glass, and metal substrates, J. Mater. Chem. A Mater. Energy Sustain. 4 (2016) 14111-14121.
- [46] A.K. Singh, J.K. Singh, Fabrication of zirconia based durable superhydrophobicsuperoleophilic fabrics using non fluorinated materials for oil-water separation and water purification, RSC Adv. 6 (2016) 103632-103640.