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RESEARCH PAPER

Hydrophobic Treatment of Cotton Fabrics Using Recycled Silica Nanoparticles from Rice Bran Ash

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ABSTRACT

Rice bran, abundant in rice-producing countries, contains lots of silica. In this study, we recycled silica nanoparticles from rice bran ash. Then we used them to enhance the hydrophobicity of cotton fabrics. According to X-ray fluorescence (XRF) results, the recycled nanosilica had high purity (95%). The obtained results from Field Emission Scanning Electron Microscopy (FESEM) showed the structure and morphology of the powder. The particle size of the extracted nanoparticles was around 48 nm. X-Ray Diffraction (XRD) pattern showed that the extracted nanosilica has an amorphous structure. Images of Thermal Emission Microscopy (TEM) also indicated that the nanosilica has an amorphous structure. Then, the cotton fabric hydrophobicity was enhanced using siloxane compounds and recycled nanosilica. The emersion method was employed to apply the nanosilica and siloxane compounds on the fabric's surface. (Energy Dispersive Spectroscopy) EDS examinations showed that the silica nanoparticles were evenly distributed on the surface of the cotton fabric. The water contact angle was 141, meaning that the extracted nanosilica has enhanced the hydrophobicity of cotton fabric.

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INTRODUCTION

Nowadays, nanostructures have wide applications [1-3] and nano-synthesis has become a significant challenge. It is being performed in various branches of chemistry such as hydrophobic treatment of textiles [4-6], creating antibacterial properties on the surface of textile [7], nano-catalyst modification [8, 9], etc.

Researchers have employed different methods to synthesize nanostructures. In some of the previous works, researchers have investigated the effects of a specific synthesis method on the morphology of the nanostructure [10, 11]. For example, Masjedi-Arani et al. [11] prepared spherical silica nanostructures through the sonochemical method and investigated different parameters such as concentration, ultrasonic eave powder and reaction time on the morphology and

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size of the products.

Silicon dioxide (SiO_2) is the most abundant compound in the earth's crust. Silica is present in nature in free form or combination with other oxides. Silica used in industry is obtained in two ways: mineral and synthetic. In the synthetic method, materials including sedimentary silica, silica fume, nano-silica, etc., are obtained. Silica nano-particles include a set of small silicon dioxide particles that connect through covalent and hydrogen bonds and form larger particles. According to the size of the initial particles and final size of agglomerates, this compound can have different applications as nano silica or micro silica. The most crucial advantage of nanosilica is covering a large area. Its applications include rubber, paint, coating industries, adhesives, concrete and cement, plastics, paper industry, etc.

On the other hand, rice bran considered an agricultural waste, [12] is found in abundance in rice producing countries and its ash is rich in silica [13-15]. It's been reported that rice bran is being produced 80 million tons yearly [14, 15]. According to reports, in1997 and 1998, about 26 million tons of rice was produced in India [13, 16] and 400 thousand tons of rice bran are being produced yearly in Malaysia [17]. Also, in Egypt, 3 million tons of rice bran is being produced annually [12]. The annual increase of this product is a significant problem [18] because most farmers burn the rice bran to release its nutrients for the next planting season and get rid of its large amount. Burning rice bran leads to suffocating smoke and increased air pollution [12]. Rice bran has different applications, and it is important to recycle it.

Researchers have tried to extract nanosilica from rice husk in some previous studies. Carmona et al.[19] burned rice husk in high temperature and pressure and extracted nanosilica through its high solubility. They used sulfuric acid, phosphoric acid, etc., as solvents. Liou et al. [20, 21], in two different studies in 2004 and 2011, also extracted nanosilica from two different types of rice with specific surface areas of 235 m^2/g and 634 m2/g. In another study, Yuvakkumar et al.[22], used different concentrations of sodium hydroxide to purify nanosilica. They could extract nanosilica with a purity of 99.9% and a diameter of 25 *nm* using 2.5 N sodium hydroxide. The specific surface area was measured equal to 274 m^2/g. These results were obtained using FTIR, TEM, BET, X-ray and particle size analyzer instrument.

One of the most important applications of silica-based compounds is their use in the formulating water-repellent compounds and hydrophobic coatings. Hydrophobic coatings are completely transparent nonmetric coatings that can be used on different surfaces, such as glass, wood, stone, etc., and are coated on these surfaces in different ways. Hydrophobic surfaces are also observable in other creatures and parts of nature, such as Lotus leaves [23, 24], wings of some insects such as large yellow mosquitos[25], legs of water striders[26], etc.

An applicable hydrophobic property can be created by placing silica nanoparticles in a suitable polymer substrate and functionalizing the surface of these particles. Understanding and controlling wettability are essential in both basic research and industrial applications. Modification of surface chemistry is also one of the most effective ways to control the behavior of surfaces. However, this surface chemistry modification can have limitations, such as the choice of chemical species and their biochemical compatibility [27-29]. The smoothness and comfortness of the textiles is an important issue, so when any coatings are being applied on their surface should not have any adverse effect on it. As it has been reported before, using nanoparticles affects none of the mentioned properties [30].

Researchers have used SiO_2 many times to improve surface properties. As an example, Xue *et al.* [5], found out that cotton textiles are highly hydrophilic and can be completely soaked in water. When cotton textile is coated with silica hydrocele, the cotton fibers are completely coated with SiO_2 nanostructure. As abundant hydroxyl groups are present on the structure of SiO_2, a drop of water spreads rapidly on the surface of the coated cotton cloth. As a result, the water contact angle of the cotton cloth covered with only silica hydrocele was assumed to be zero. Hao *et al*.[31] after investigating the results of studies on different surfaces found out that properties of the surface change after applying PSAMS and PSAMS-SiO_2. Results show that cotton fabric has a surface roughness of micrometers, and the structural changes of the surface are enhanced by coating with PSAMS and PSAMS-SiO_2. The contact angle of the drop and the coated surfaces with PSAMS and PSMAS-SiO_2 was reported to be 141.5 and 157, respectively. In another study, Xue et al. [6] applied PDMS and SiO_2 compounds several times on the polyester fabric to check the contact angle. They found that as the number of coatings increased, the contact angle between the droplet and the water decreased (144 to 123 degrees). With increasing the number of layers, the roughness will be greater than nanometers and micrometers, and the contact angle will be lower. The surface will not be superhydrophobic through this coating, and with increasing the number of layers the hydrostatic strength of the textile will be enhanced. In this study, nanosilica was obtained from rice bran ash (obtained from farms in Hashtpar city of Guilan province). Then it was used along with other silicon-based compounds such as Polydimethylsiloxane in preparing a suitable formulation for hydrophobization of cotton textiles.

In most of the previous works, researchers have synthesized nanosilica. However, we have extracted nanosilica from rice bran husk in this work and used to enhance the hydrophobicity of cotton fabric's surface. Only a few researchers have obtained nanosilica through this method, but none of them have utilized recycled nanosilica to improve the hydrophobicity of fabrics.

Mostly, chemical methods such as vapor-phase reaction, sol-gel or thermal decomposition are employed to synthesize nanosilica powder. It is easy to synthesize nanosilica with controlled shape and high purity in chemical methods, but reagents are costly [22]. It is also essential to control these specifications in large-scale industrial applications with low cost. As discussed before, rice husk, which contains more than 95% silica, is one of the most abundant by-products in the agriculture industry. So, rice husk can be a valuable source to produce nanosilica in large-scale industrial applications.

MATERIALS AND METHODS

Materials

Hydrochloridic acid (HCl), Sodium Hydroxide (NaOH), Sulfuric acid (H_2SO_4), Tetrahydrofuran (THF), Cetyltrimethylsiloxane (CTMS), Tetraetoxysiloxane (TEOS) were purchased from Merck. Polydimethylsiloxane (PDMS) was purchased from Sigma-Aldrich, and ethanol was purchased industrially. Then we washed the cotton fabrics to remove any contamination from the surface. Deionized water was employed to measure the contact angle.

Nanosilica Extraction

First, the rice bran was placed in the furnace at 700 ° C for 6 hours. Then the rice bran ash was refluxed with HCl 6 normal solution for 6 hours to remove excess metals and so on. The obtained mixture was filtered after 6 hours, and the powder was stirred with 2.5 normal NaOH. Then it was

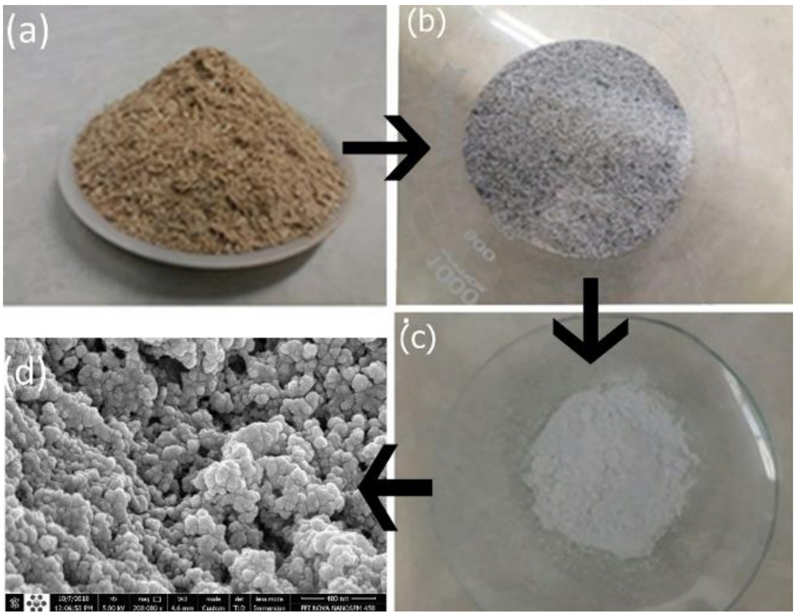

Fig. 1. Nanosilica extraction steps (a) Rice bran before burning (b) Rice bran ash (c) and (d) nano silica powder

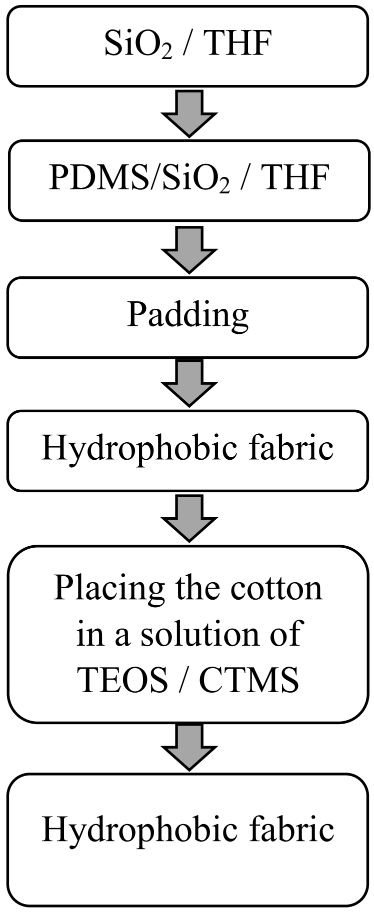

Fig. 2. Cotton fabric hydrophobic treatment steps

Table 1. XRF results of the obtained nanosilica

component	Percentage in Extracted nanosilica
SiO_2	95
Al_2O_3	0.55
Fe_2O_3	0.148
CaO	0.092
Na_2O	0.612
MgO	0.351
K_2O	0.558
TiO_2	0.043
MnO	0.027
P_2O_5	0.01
LOI	N

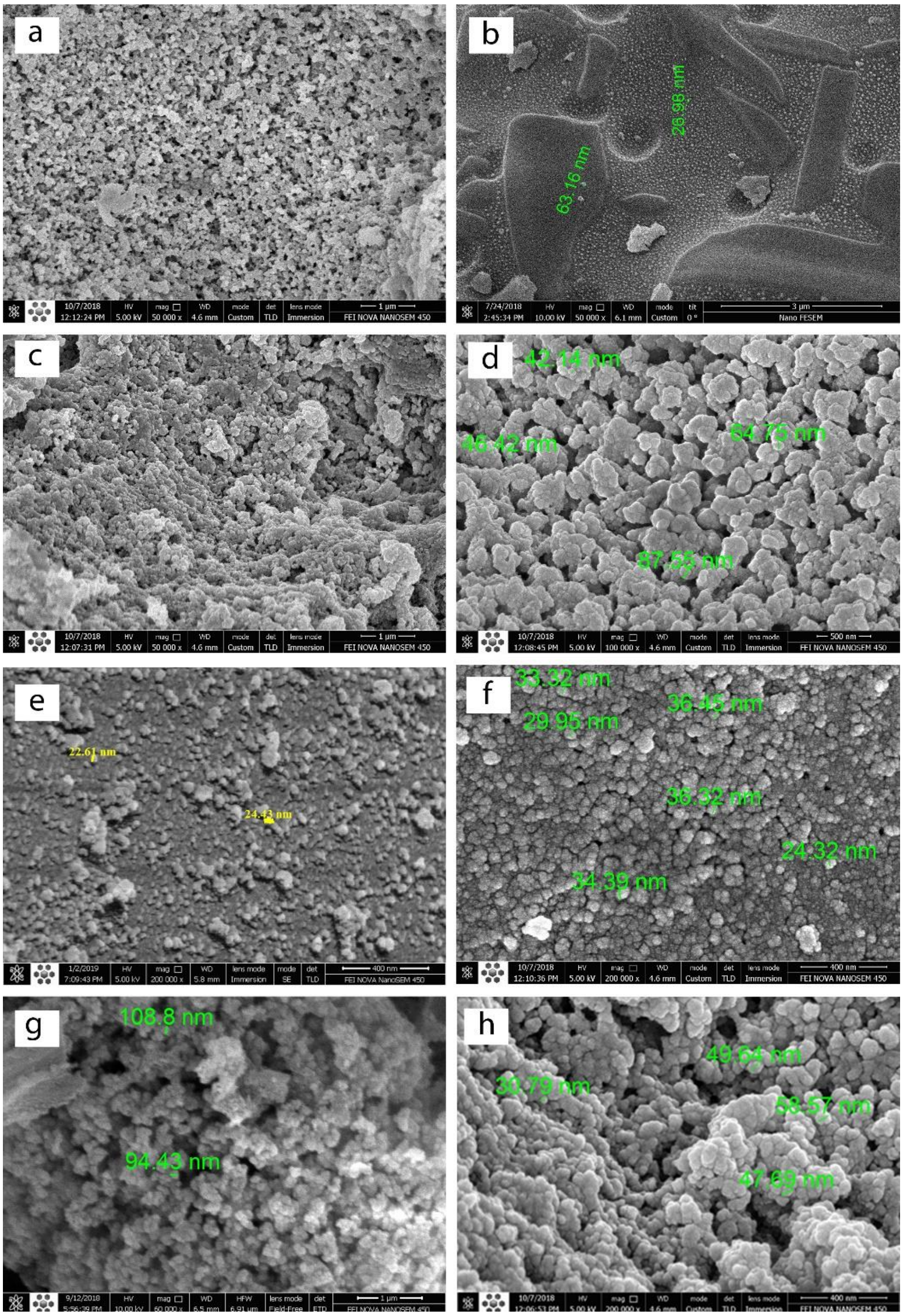

Fig. 3. FESEM photos of the extracted nanosilica

placed in an ultrasonic bath and was filtered at the end. The obtained powder was placed in boiling water, then. The pH of the mixture was adjusted using sulfuric acid (pH=2). After filtering the solution, nanosilica powder was obtained through reactions 1 and 2. Fig. 1 shows the photos of the obtained samples in each step.

$$SiO_2 + NaOH \rightarrow Na_2SiO_3 + H_2O \quad (1)$$

$$Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2 + Na_2SO_4 + H_2O \quad (2)$$

Hydrophobic treatment of the fabrics

We prepared 1 gram of recycled silica. 50 ml of THF, 2.75 grams of PDMS were mixed for half an

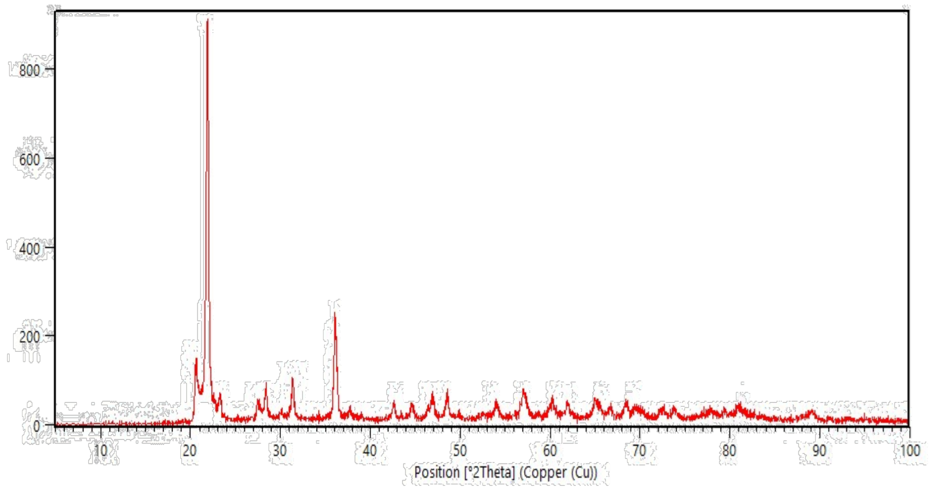

Fig. 4. XRD pattern of the extracted nanosilica from rice bran

hour. The cotton fabric was cut in dimensions of 10 cm x 10 cm, washed and, dehydrated completely. The cotton textile was immersed in the solution for half of an hour. Then it was cured in the oven for 8 hours at a temperature of 135°C. We prepared a solution of 6 ml TEOS, 2 ml MTMS and 100 ml alcohol, and the fabric was immersed in this solution for 30 minutes at a temperature of 80 °C and dehydrated (Fig. 2).

RESULTS AND DISCUSSION

Morphology observation of the extracted nanosilica

To investigate the purity of the recycled nanosilica, Philips PW1410 was utilized to obtain XRF results. As it is observable in table (3.1), the recycled nanosilica has a high purity of 95%.

A Field emission scanning electron microscopy (FESEM) model FEI NOVA SEM 450 was employed to investigate the distribution and morphology of the nanosilica particles (Fig. 3). It is observable that the particle size of the obtained nanosilica is around 45 nm. It also indicates the amorphous and spherical structure and uniform morphology of nanosilica. However, a few larger particles with a 90–110 nm diameter are also observable in the image. The formation of these large particles is because of aggregation between adjacent SiO_2

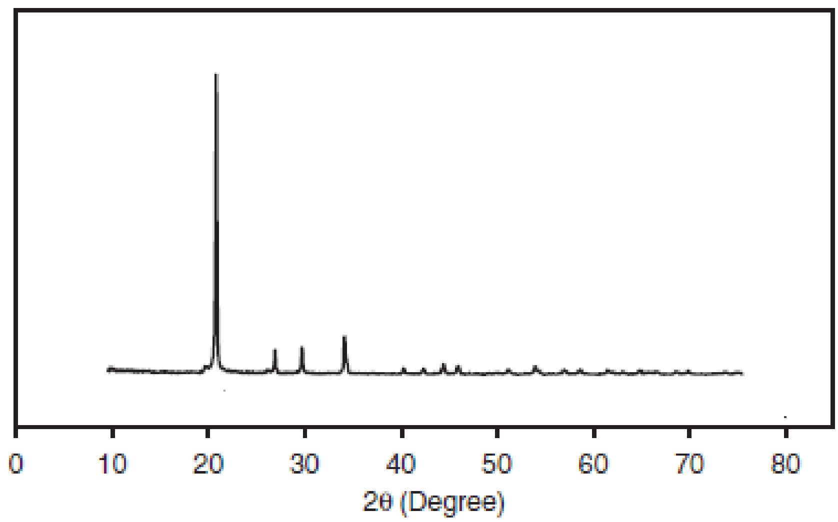

Fig. 5. XRD pattern of the reference nanosilica [22]

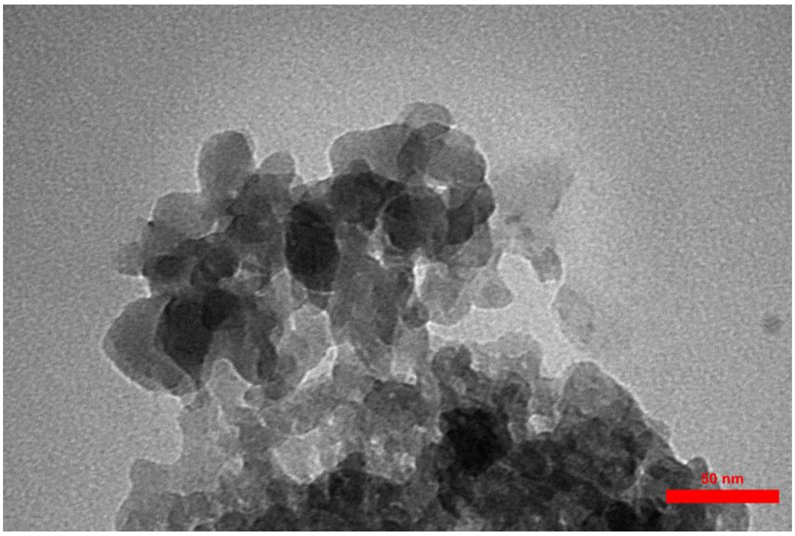

Fig 6. TEM image of the extracted nanosilica

nanoparticles due to their inherent high specific surface area and high surface energy[4].

XRD method was utilized for determining the phase type and amorphous structure of the recycled nanosilica. In Fig. 4, a great peak is observed in 2 θ=22, which is related to the amorphous silica. The absence of sharp peaks at this temperature is due to the absence of crystallinity. The average size of the particles was obtained 48 nanometers through Scherrer formula. The obtained XRD pattern is very similar to the XRD pattern of nanosilica in previous works (Fig. 5) [22].

A TEM image of the extracted nanosilica was also taken utilizing TEM Philips EM 208S (Fig 6.). The amorphous structure of the nanosilica is also

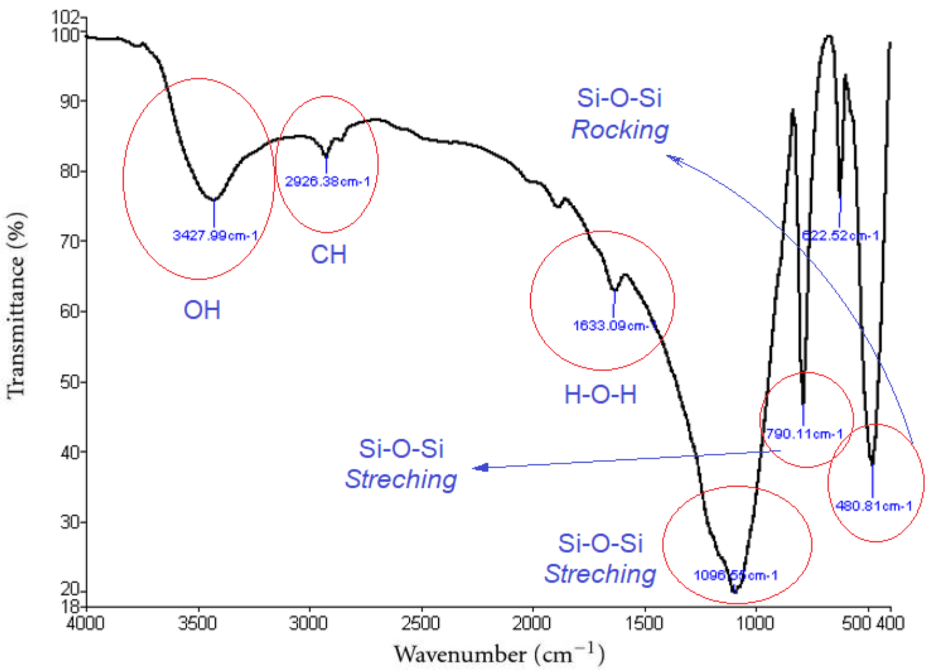

Fig. 7. FTIR spectrum of extracted nanosilica

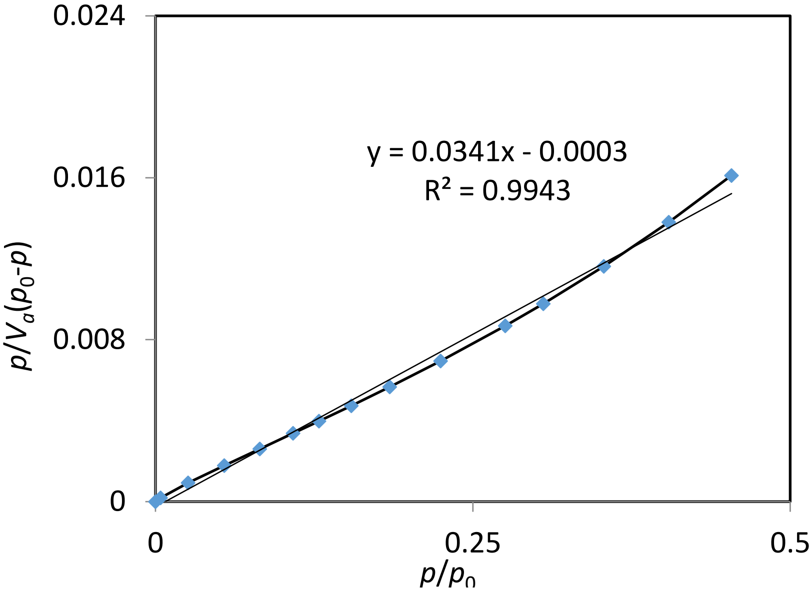

Fig. 8. BET curve of the extracted nanosilica

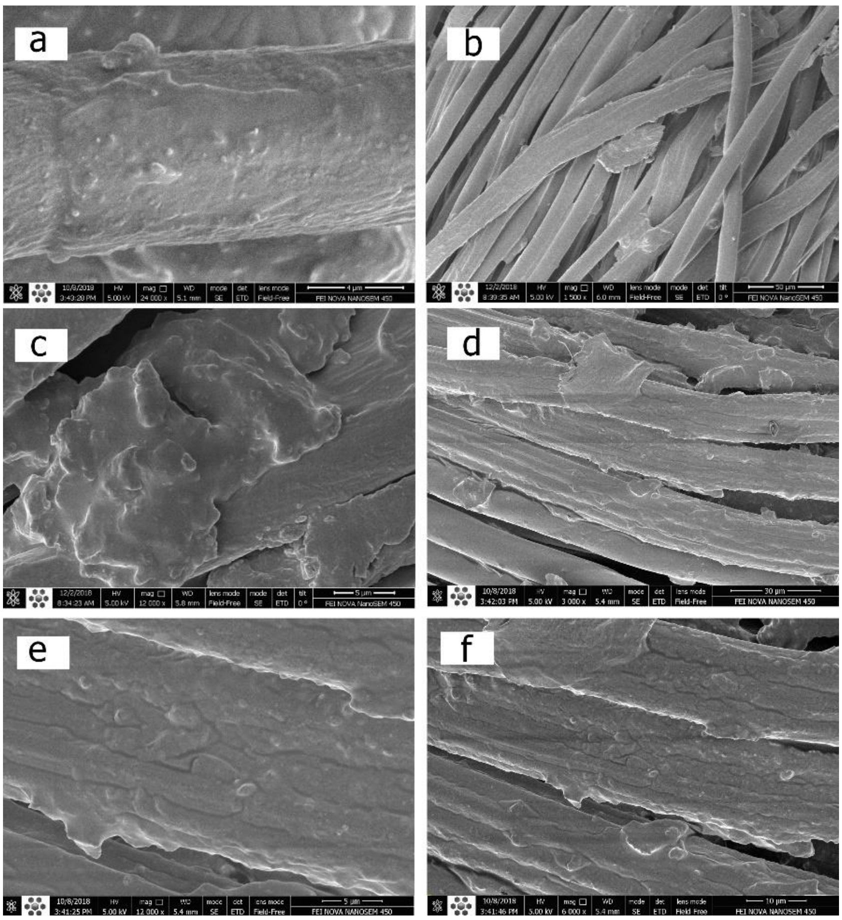

Fig. 9. FESEM photo of the cotton fabrics coated with nanosilica

observable in the TEM image.

Bruker FTIR model Tensor 27 was utilized to investigate the presence of chemical groups. According to FTIR results, the main chemical groups present in extracted silica powder are shown in Fig. 7. The peak of broadband absorption in the range of 400 to 4000 cm^{-1} was observed in the FTIR spectrum. The absorption peak around 3427 cm^{-1} and 1633 cm^{-1} are related to O-H and H-O-H groups, respectively, and it is clear that these peaks are present due to water absorption. O-H groups and H-O-H groups indicate tensile and bending vibrations of water molecules, respectively.

The absorption peak observed in the 480 cm^{-1} is related to the rocking vibrations of the siloxane

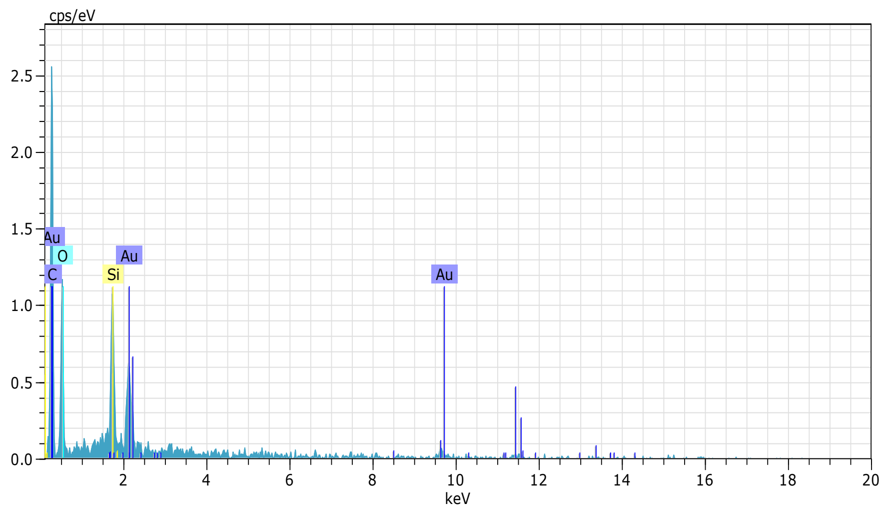

Fig. 10. EDS results of the coated fabrics

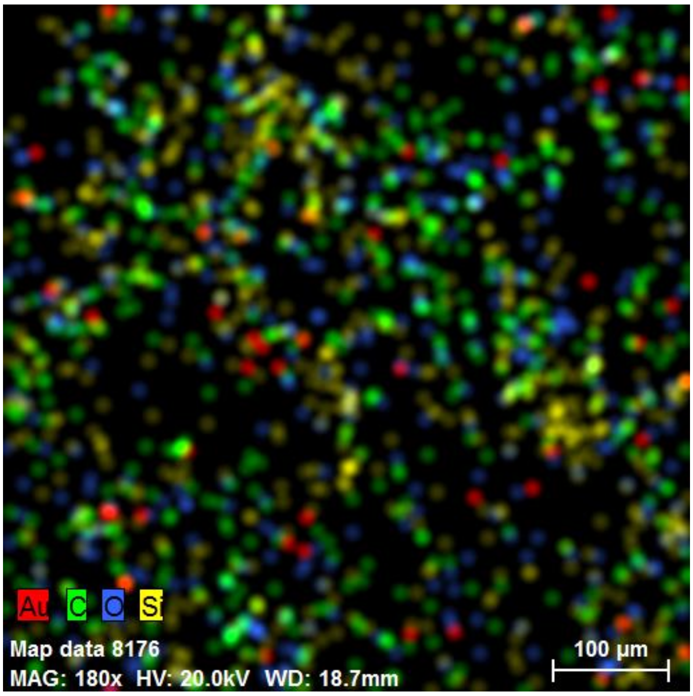

Fig. 11. Map data of the elements distribution on the cotton fabric surface

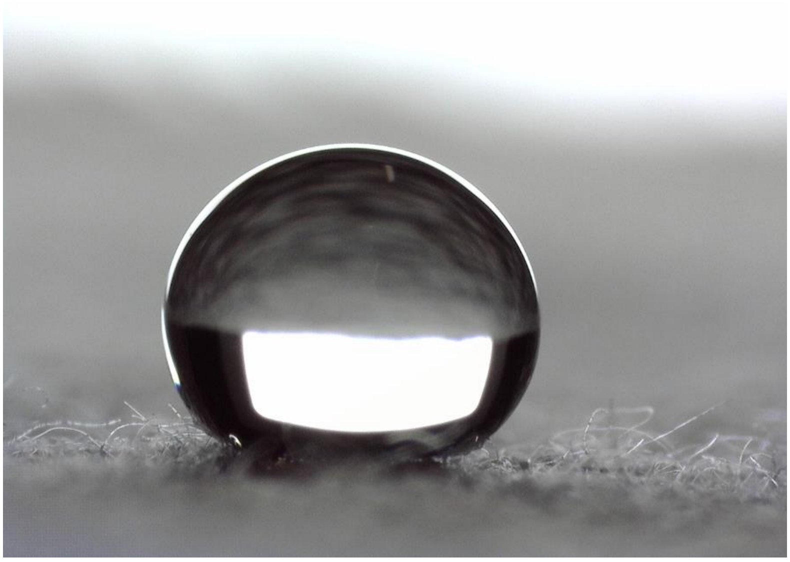

Fig. 12 a water droplet on the surface of the treated cotton fabrics

group (Si-O-Si), and 790 cm^{-1} and 1100 cm^{-1} regions are related to the stretching vibration of the siloxane group (Si-O-Si) [32].

The region with a wavenumber around 2926 cm^{-1} indicates C-H groups. The meager presence of this group can be because of the incomplete transformation of the rice bran, which consists of Hydrocarbon groups.

BET technique was also employed to measure the surface area of the recycled nanosilica. According to BET results specific surface area was 140.34 m^2g^{-1}, the total pure volume was 0.3786 cm^3g^{-1}, and the mean pore volume was 0.3786 cm^3g^{-1}. BET curve is presented in Fig. 8.

Treated fabrics surface observation

According to Fig. 9, FESEM photos of the fabrics coated with recycled silica, nanoparticles are distributed monotonous on the fabric surface. Most parts of the surface are covered with nanoparticles, so water drops do not have direct contact with the cotton fabrics. The air also gets trapped between the layers and avoids water drops penetrating the fabric cotton. As it is observable in Fig. 9 roughness of the fabrics has increased compared to pure cotton fabrics [30].

EDS analysis was also performed to investigate the distribution of elements on the fabric surface (Fig. 10). Map data of the coated compounds is also available (Fig. 11).

The results show that silica nanoparticles have covered the surface, which leads to the high hydrophobicity of the cotton fabric surface.

EDS results in this study were compared to those of previous works. The results had acceptable compliance with the reference sample [33].

Contact angle measurement was also performed using a CCD camera and Digimizer analytical software, which is mostly used to characterize surface wettability. Hydroxyl groups in the structure of untreated cotton fabrics have led to a contact angle of 0 which means they are highly water absorbent [4]. To measure the contact angle on the surface of the treated fabrics a 5 µL droplet of water was placed on its surface (Fig. 12). The contact angle was 140 degrees. The silica particles provide enough roughness to make the textile hydrophobic.

CONCLUSION

This study aimed to investigate the possibility of hydrophobic treatment of textile using rice bran ash and silicone-based compounds such as Polydimethylsiloxane. The obtained results showed that nanosilica was extracted with high purity and coated in the cotton fabric completely. The recycled nanosilica was used for preparing hydrophobic coatings, and the results were satisfying. The hydrophobic chain of PDMS helps PDMS and SiO_2 crosslink with each other. This leads to the increase of clusters with different sizes and micro-nano structure formation. Then the surface becomes more hydrophobic with the increase of roughness. According to the results, nanosilica particles had covered the fabric's surface and were avoiding direct contact of water drops and the fabric surface. The contact angle was 140, which means the surface is entirely hydrophobic. Hydrophobicity price and time can be decreased due to using rice bran, and recycled silica from the rice bran ash can be used with siloxane compounds to increase the hydrophobicity of the cotton fabrics.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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