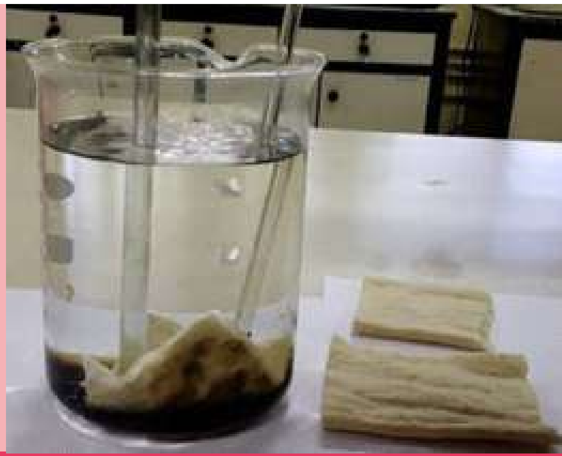
Development of Bio-degradable Cotton Waste Based Super Oleophilic and Super Hydrophobic Sorbent for Oil Spill Clean-up



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Abstract

Cotton waste, which is generated from various processes in a textile mill like carding, blow room, etc. was collected, cleaned, pre-treated, and processed in a carding machine to make the web. The cotton web was converted to a non-woven batt through a needle punching process. The non-woven fabric was chemically modified by treating it with silica nanoparticles synthesized via the Stober process followed by hexadecyltrimethoxysilane (HDTMS) treatment. The chemically functionalized fabric was showing super hydrophobic and super oleophilic property. The oil absorption capacity of the developed sorbent was 25-30 g/g and the water contact angle was more than 150^0. The morphology of the sorbent was characterized by SEM. The sorbent was found to be reusable at least 5-6 times with an oil recovery of more than 60%. Bio-degradability of the chemically modified cotton was also studied and was found to be fully biodegradable. The developed sorbent was found to be useful for cleaning oil spillage on the land surface, oil on surface water, and underwater also and was found to be superior to the commercially available synthetic polypropylene/polyurethane sorbent.

Keywords

Cotton waste, Hydrophobic, Oleophilic, Oil sorbent, Sol-gel, Silica nano particle.

Citation

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1.0 Introduction

Oil is one of the most important sources of energy and is also used as raw material for synthetic polymers and chemicals worldwide [1-3]. Oil has been part of the natural environment for millions of years. Oil spills into land, river, or ocean during production, transportation, tanker disaster, accidents and imposes a severe environmental problem. Oil spills launch unsafe chemical substances along with polycyclic aromatic hydrocarbons which are toxic to each aquatic life and humans and might also additionally require many years to remove [4-7]. Complete removal of crude oil and petroleum product that are spilled at the sea or water bodies is a more difficult task than cleaning on land surface as part of the oil stays in a colloidal form and remains on the water surface. The basic methods for oil spill collection and clean-up are chemical treatment, mechanical treatment, and biological treatment. Chemical treatments are not so popular and effective as it leads to secondary contamination. The mechanical methods involve the transfer of oil from spills to temporary storage using oil sorbents. There are various types of oil sorbents being used for oil spill clean-up. Good oil sorbents are characterized by high sorption capacity, good buoyancy, low density, adequate oil retention and re-usability [8]. The most widely used oil sorbent across the world is polypropylene or polyethylene based mat/boom/pillow as it merits all the prerequisites of a good sorbent except the bio-degradability.

Cotton, a natural and bio-degradable cellulosic material, will be an ideal choice for good oil sorbent but its high density and natural hydrophilic property discourages its usage as an oil sorbent, especially on water bodies. Cotton will be extra benefitted when made hydrophobic through chemical modification. Change of cotton to make it super hydrophobic extends the usage of cotton to various end uses like water repellent self-cleansing of fabric and oil spill clean-up in

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water bodies in which it might repulse water and absorb oil. Good quality cotton has an amazing industrial value in textiles; hence, the use of this value added cotton for oil spill clean-up is not a good option and is commercially no longer viable. Hence, the usage of cotton waste generated from cotton generators of their diverse method like blow room, carding, etc. can be a super choice. In India, high cotton production is accompanied by the generation of tons of waste each year, either from textile mills or cotton fields. These wastes are disposed of through burning, which in flip will increase the carbon dioxide level in the ecosystem which provides worldwide warming and once again it creates pollution. Hence, cotton waste based oil absorbent can have value addition, be economically viable, sustainable product, and biodegradable. Again, the usage of cotton waste as oil sorbent will be a green initiative to control pollution dually. Direct use of cotton fiber as an oil absorbent has many negative aspects as constrained kind of oil absorption, low oil absorption and retention. In addition to this, the inherent water absorption tendency of cotton, which is an undesirable property for oil sorbent, will lessen the oil pickup. To conquer those problems, cotton fibres need to be chemically modified to make them a super- hydrophobic and super oleophilic sorbent. For practical application, loose fibrous sorbents need to be compacted as non-woven mats, or cushions, pads, booms and need to be efficaciously recoverable without prompting secondary contamination so that these sorbents do not disintegrate when applied to oil spill cleanup.

2. Experimental

2.1 Materials, equipment, and methods

2.1.1 Materials

Waste cotton fibers were procured from Tata mills and Techno craft industries, in Mumbai from their various cotton processing sections like carding, combing, blow room, etc. Premium diesel engine oil (API CI-4 15W-40), Diesel oil, and Crude oil (tar) were purchased from a petrol pump, in Mumbai. Ethanol (99.9%, AR grade), Tetraethyl orthosilicate (TEOS, 98%), Ammonia solution (NH_4OH 25%), Methyl triethoxysilane (MTES, 98%), Hexadecyltrimethoxysilane (HDTMS, 85%), were purchased from Sigma Aldrich.

2.1.2 Equipment

Analytical balance (Shimadzu AUX 220), Carding Machine (Dormetx Cormatex Italy), Needle punching machine (DILO – Germany), Scanning electron microscope SEM (JSM IT200 Joel), Easy Drop Analyzer (Stringray & Kruss), Microscope, Mechanical Shaker, were utilized from within BTRA facility.

2.1.3 Preparation of non-woven fabric from cotton waste

Raw cotton waste procured from different textile mills was cleaned in a trash separating machine (Stratex Trash separator) where all dust dirt and non-fibrous contamination are removed. The cleaned fibre was fed into a mini carding machine which individualizes the fibers and aligns them in one direction to develop a cotton web. The purpose of carding was to disentangle and mix fibers to form a homogeneous web of uniform weight per unit area. This was carried out in a series of fiber opening and layering actions accomplished by the interaction of tooth rollers situated throughout the carding machine. The cylinder is the heart of the carding machine and is the central distributor of the fibers during the process. The doffer rollers condense and remove fibers from the cylinder in the form of a continuous web. Carding of cotton fibres was done in Cormatex Prato mini carding machine, wherein the fibre tufts were converted into a carding web. The carding web was passed through a cross lapper to a needle punching machine to form a batt of 200 GSM. Needle punching process is based on subjecting a web in the needle punching machine to the effect of the needles oscillating vertically, slanting, or both directions of the surface of the web. As the needle penetrates the web, there barbs or grooves catch the fibers and draw them in a vertical or slanting direction through the thickness of the web.

We have prepared non -woven fabric by using vertical needle punching, where it was done from one or both sides. Needle punching on both sides was arranged in such ways that the needle heads are located on both sides of the needle web. The modern variations of this type of needle board arrangement in most cases make possible needle punching both with in-stroke and off- stroke movement of needle boards. During the counter movement of the needle boards, the needles enter the material from both sides at the same time. To make this possible, each needle board carries a number of needles equal to half of the matching holes in the stripper and bed plates. The holes for both needle boards are spaced uniformly, in most cases, following the pattern of the plain weave. In this case, the needles on the upper board enter the web as the needles on the lower board leave it, and vice versa. The parameter of needle punching machine was fixed to get 300-600 strokes per minute with a draw of 1.1 m/min.

Fig.1 and Fig.2 are photographs of cotton waste and cotton waste based non-woven fabric respectively.

Fig-1 photograph of cotton waste

Fig-2 photograph of nonwoven fabric

2.1.4 Chemical modification of non-woven cotton fabric

Silica nanoparticles were synthesised in the laboratory via the Stober process (sol-gel). The synthesized nanoparticles were sprayed on both sides of the non–woven fabric by using a spray gun and the fabric was dried at 80^0 C for 10 minutes. The dried fabric was further treated with HDTMS (3 % in ethanol) by using a spray gun. The treated fabric was dried at 80^0 C and cured at 150^0 C for 10 minutes. The entire chemical reaction on cotton takes place in two stages.

When a sol-gel is applied to cotton fabric, the nano - SiO_2 particles are deposited on the surface of the cotton fabric. The condensation reaction between the –OH group from the surface of cotton fabric and the Si-OH group from the nano-SiO_2 particles bonding takes place during the drying process. As the nano- SiO_2 covalently bonded onto the cotton fabric, silica particles deposited on the surface increases the hydrophobic effect of the textile material by decreasing the surface energy. The $–CH_3$ bunch blesses the SiO_2 particles with hydrophobicity and oleophilicity. The combination of nano- roughness of nano- SiO_2 and the inherent micro-roughness of fabrics created a nano–binary surface roughness on cotton fabric's surface, which would greatly enhance the wetting behaviour of the surface of fabrics. In the second stage, sol-gel treated fabric was further treated with HDTMS, wherein HDTMS is hydrolysed in an aqueous ethanol solution to form alkylsilanol. The self-assembly of HDTMS is formed by the reaction between the alkylsilanol and the surface hydroxyl groups of silica nanoparticles on the cotton fabric surface.

2.1.5 Measurement of oil and water absorption properties of sorbents

There are two standard test methods (ASTM F 726) for the evaluation of the oil and water uptake of sorbents. They are static and dynamic tests. In the static condition, the sorbent (4.0 g) was kept in a tray filled with oil, after 15 minutes, the sorbent was removed from the oil and drained for 30 seconds, and weighed. The oil absorption capacity of the sorbent (g/g) was calculated from the initial weights and the final weight of the sorbents.

In dynamic conditions, Synthetic seawater was prepared by dissolving 35g of NaCl in 1000 ml distilled water. A known weight of sorbent was placed in a tray that contains artificial seawater (500ml) and 50 g of crude oil (Mark diamond 15w-40 Premium diesel engine oil APL Cf4). The density of oil used was 0.87 grams per cubic centimeter. 4.0 g of sorbent was placed in the tray and shaken in a laboratory shaker at a frequency of 150 cycles/minute for 15 minutes. The sorbent was held for 30 seconds to drain out excess oil /water and weighed. The oil absorption capacity of the sorbent (g/g) was calculated from the initial weight and final weight of the sorbent. The water absorption property of the sorbent was also measured in a similar manner but using only water and without oil.

$$\text{Absorption capacity (g/g)} = \frac{(Mf - Mo)}{Mo}$$

Where Mf is the weight of oil soaked material and
Mo is the initial weight of the material.

3. Results and Discussion

3.1 Absorption properties of the sorbent

The oil and water absorption property of the chemically modified cotton sorbent of various cotton wastes was studied with motor oil and diesel engine oil. Table-1&2 shows a comparative study of the oil and water absorption capacity of sorbents prepared from carding waste and blow room waste against commercially available polypropylene and polyurethane sorbent. It was observed that under static conditions carding waste absorbs 30 to 30.3 g/g of motor oil and under dynamic conditions, it was 28.2 to 29.1g/g. Similarly blow room waste sorbent, under static conditions motor oil absorption capacity was 21.3 to 25.9 g/g, and that of dynamic conditions the same was 20.2 to 27.2 g/g. At the same time, commercial polypropylene sorbent, motor oil absorption capacity for static and dynamic conditions was 12.3 g/g and 12.7 g/g respectively. For polyurethane sorbent, motor oil absorption capacity for static and dynamic conditions was 10.9 g/g and 14.2 g/g respectively. This indicates that modified cotton waste-based sorbent has a higher oil absorption capacity than polypropylene and polyurethane sorbent. The water absorption property of polypropylene and polyurethane was 0.1g/g and 1.7 g/g respectively and that of cotton waste sorbent was 0.01 to 0.18 g/g which shows chemically modified cotton sorbent is more hydrophobic than polypropylene and polyurethane. A similar trend was also observed in the case of diesel oil in water (Table 2). This indicates cotton, which is hydrophilic has become hydrophobic after chemical modification and is in line with hydrophobic polypropylene. Since the viscosity of diesel oil is lower than motor oil, oil pick up was also lower. Modified cotton sorbent absorbs 2 to 2.5 times more oil than polypropylene fabric. At the same time, the water absorption capacity of both polypropylene and cotton sorbent was almost the same.

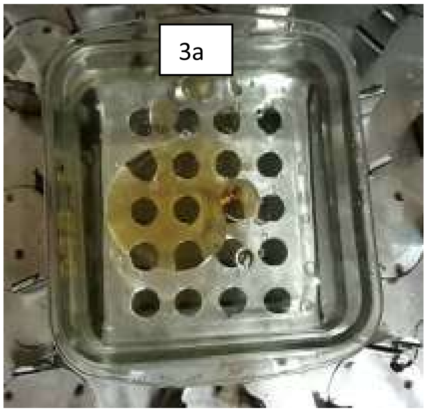

Fig.3a Oil floating on water surface

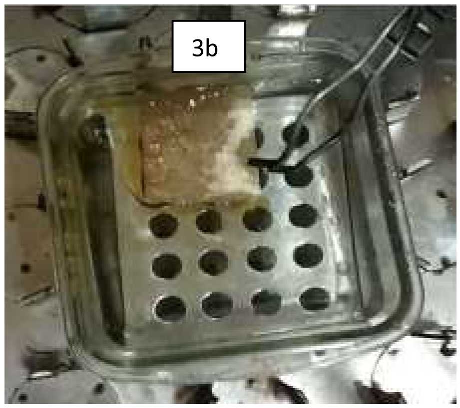

Fig.3b Sorbent absorbs oil from the water surface

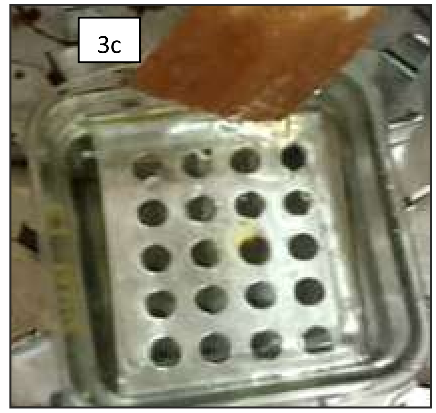

Fig.3c Oil absorbed sorbent

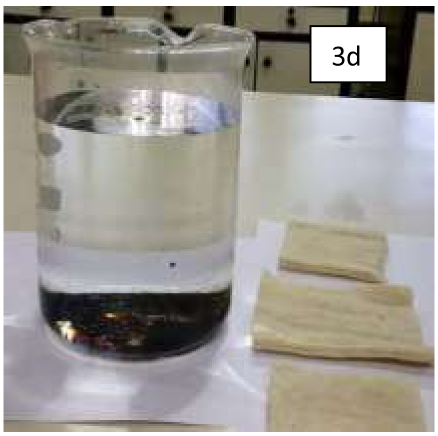

Fig.3d Oil in underwater

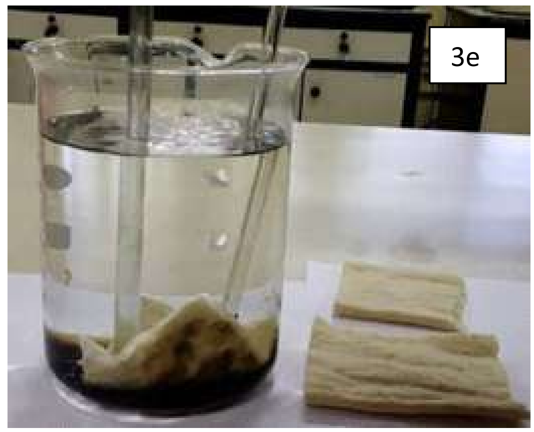

Fig 3e Photograph of underwater oil spill clean-up

Table-1 Absorption properties of sorbent in motor oil and water

Cotton waste-based sorbent	Absorption capacity of Oil (g/g) under static condition	Absorption capacity of oil in Water (g/g) under dynamic condition	Absorption capacity of Water (g/g) under Dynamic conditions
Polypropylene matt	12.3	12.7	0.1
Polyurethane matt	10.9	14.2	1.7
Carding flat stripping	30.3	29.1	0.01
Carding flat stripping lint	30.0	28.2	0.09
Blow room black dropping lint	22.0	20.6	0.18
Blow room super dropping	25.9	27.2	0.15
Blow room super dropping lint	21.3	20.2	0.1

Table-2 Absorption properties of sorbent in diesel oil and water

Cotton waste-based sorbent	Absorption capacity of Oil (g/g) under static condition	Absorption capacity of oil in Water (g/g) under dynamic condition	Absorption capacity of Water (g/g) under Dynamic condition
Polypropylene matt	6.1	8.5	0.1
Polyurethane matt	4.7	7.2	1.3
Carding flat stripping	12.5	13.1	0.1
Carding flat stripping lint	10.2	12.7	0.18
Blow room black dropping lint	9.8	10.2	0.1
Blow room super dropping	11.5	12.1	0.12
Blow room super dropping lint	11.3	11.5	0.07

Fig 3a, 3b, 3c, 3d, and 3e are the photographs of oil spill clean-up by using chemically modified sorbent in surface water and underwater. Fig.3a is the photograph of floating oil on the surface of the water. Fig 3b and 3c are the photographs of oil removal and oil-soaked sorbents respectively. Fig.3d and 3e are the photographs of oil underwater and its clean-up respectively. It was observed that chemically modified cotton absorbs only oil and repels water which is in line with the requirements of a good oil sorbent. In short oil sorbents designed for the oil spill, and clean-up in water bodies should exhibit the property of super oleophilicity and super hydrophobicity. Super hydrophobic fabric cannot be wetted by immersing in water as they always tend to float on the surface of the water. When a hydrophobic fabric was forcibly immersed underwater, a silver colour reflection appeared on the fabric surface due to the reflection of light by the air bubbles trapped on the fabric surface, and this is reported as the plastron layer formation [9]. This further highlights the super hydrophobic effect of oil sorbents. Oil, having high density settles in the bottom of water during oil spillage as shown in figs 3d &3e. If we forcefully push a super oleophilic and super hydrophobic sorbent into the bottom of the water, the sorbent will absorb only oil. The image clearly shows that the entire oil was absorbed by the sorbent, even in water.

3.2 Water repellent property of sorbent

The water repellent property of sorbent was further characterized by contact angle measurement. The contact edge was the edge; routinely estimated through the liquid-vapours interface that meets a strong surface.

For the most part, if the water contact edge is lower than 90^0 the surface is viewed as hydrophilic, and if the water contact edge is higher than 90^0 the surface is considered hydrophobic, whereas, if the water contact angle is greater than 150^0 the solid surface is considered super hydrophobic [10]. This is shown in Fig 4b. Fig 4a and Fig 4b are the images of the contact angle of untreated and chemically modified sorbents. Fig 4c is the photograph of coloured water drops on the surface of the chemically modified sorbent.

The contact angle of the chemically modified cotton and control cotton was measured with an 8 µl deionized water droplet (Easy drop analyzer D-5A 100 of Kruss with Stringray camera) instrument at room temperature. The entire contact angle was determined by averaging the values obtained at 5-6 different points on each sample surface.

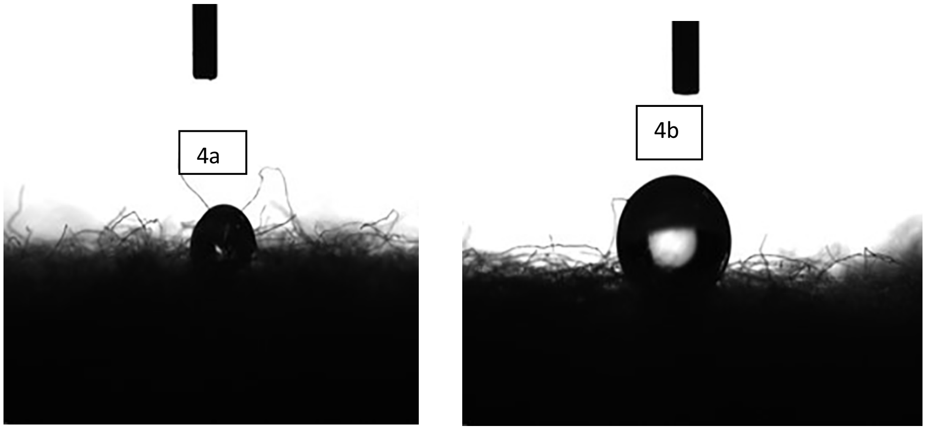

Fig. 4a &4 b Image of contact angle of untreated and chemically modified sorbent.

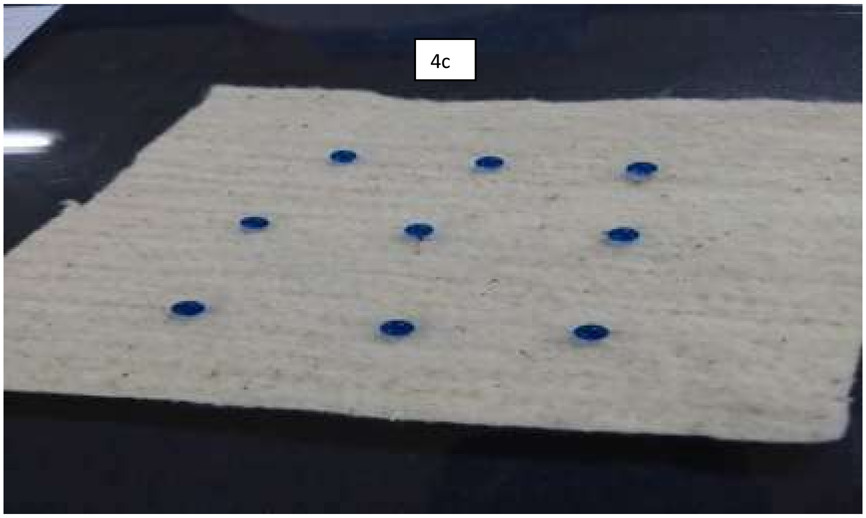

Fig.4c Photograph of coloured water drops on the surface of the chemically modified cotton sorbent.

The images Fig.4a & 4b indicate that the hydrophobicity of cotton increases by treating it with chemicals as the contact angles enhanced from 90^0 to 155^0. There are numerous miniaturized scale convexes circulated on the outside of the film, the smaller scale convexes comprise many sub-micrometer pores and nanoparticles which take after the exemplary geology of a lotus leaf. In this way, the synergistic impact of various leveled unpleasantness from nano – small scale double structure of SiO_2 particles and hydrophobic/oleophilic nature of – CH_3 bunch brings about the super-hydrophobicity and Super oleophilicity of the treated surface [10]. The expansion in water repellence of a regarded texture because of the nearness of the nanoparticles on the textured surface can be credited to the expanded unpleasantness on a superficial level. The wettability of the surfaces with the fluids is controlled by the synthetic structure as well as by the geometry of the surface.

Further, we have tested the chemically modified sorbent as per the AATCC-22, water repellency spray test. The tested specimen was comparable with AATCC standard photographs of rating 100 (No sticking or wetting of upper surface). This further supports the super hydrophobic property of sorbent.

3.3 Morphology of nanoparticle on the sorbent

The morphology of synthesized silica nanoparticles and chemically modified cotton sorbent was studied by JSM IT 200 JOEL Scanning Electron Microscope.

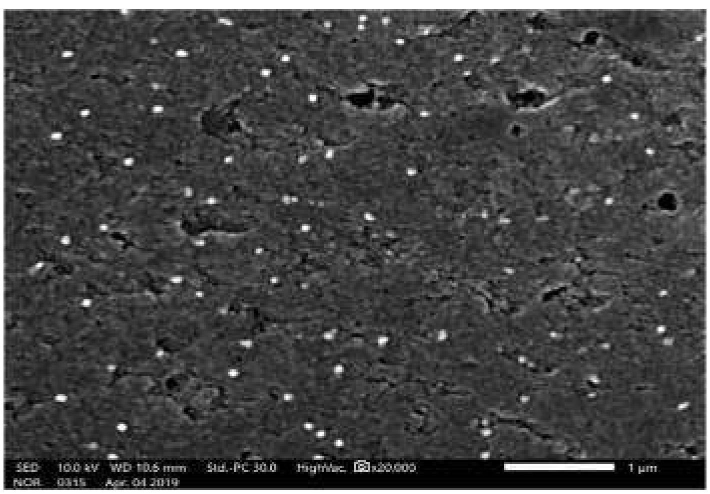

Fig 5 SEM Micrograph of nanoparticle

SEM micrograph of synthesized SiO_2 sol-gel is shown in Fig.5. When measured, the size of silica nano- particles was in the range of 70-100 nm and spherical. The size distribution varies between a diameter of 70 to 130 nm and shows the particles are almost uniformly dispersed.

Fig 6a, 6b, 6c, and 6d are the topographical changes of cotton viewed under the Scanning Electron Microscope. Fig.6a is the SEM micrograph of raw cotton, Fig. 6b is the SEM micrograph of pre-treated cotton, Fig.6c is the SEM micrograph of sol-gel treated cotton, and Fig.6d is the sol-gel and HDTMS treated cotton. Fig 6b image shows that the Pre-treating of cotton with HNO_3 imparts many subtle textures and wrinkles on the fabric surface, which exposed more hydroxyl ions to attach with nanoparticles. Fig 6c image shows the fabric surface covered with nanoparticles. In fig-6d, it can be seen that after chemical modification of cotton with sol-gel and HDTMS, SiO_2 particles attached to the surface evenly. These nanoparticles, impart micro roughness and thus enhance the water repellent property of sorbent.

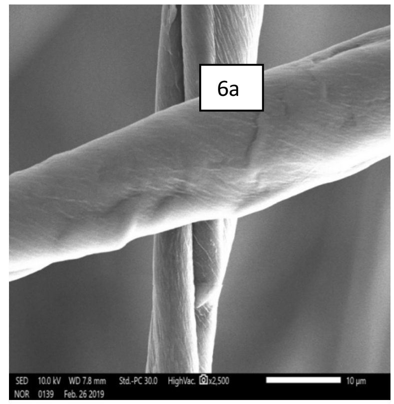

Fig.6a- SEM Micro graph of raw cotton

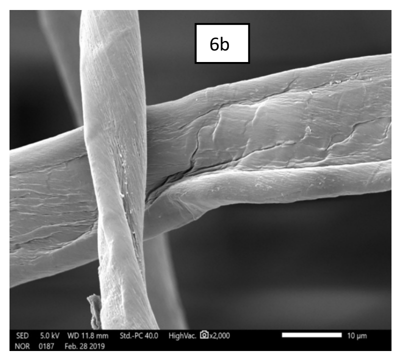

Fig.6b SEM Micro graph of pre-treated cotton

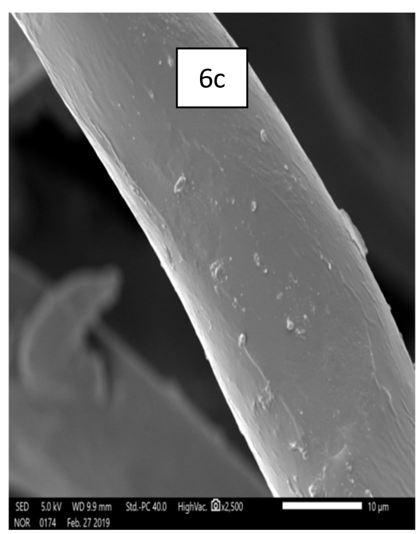

Fig.6c SEM Micro graph of nano Particle-treated cotton.

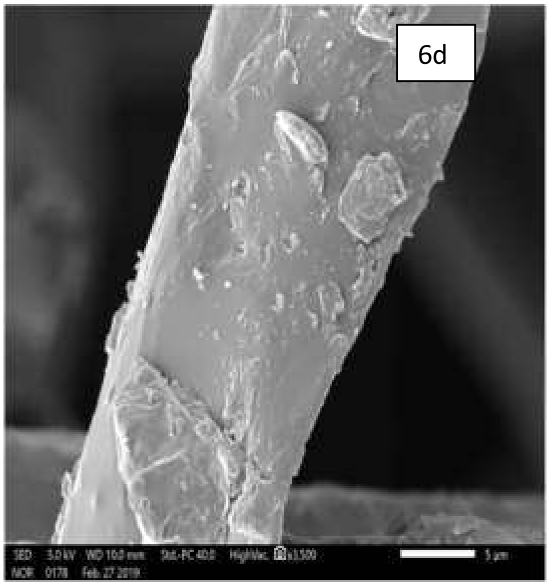

Fig.6d SEM Micro graph of chemically modified cotton

3.4. Bio- degradability of chemically modified sorbent

Soil burial test was carried out on a laboratory scale to examine the bio-degradability of chemically modified cotton sorbent and oil soaked sorbent and the same was compared against polypropylene sorbent. Five test specimens of each sorbent with a dimension of 50 cm^2 in size were buried in the garden soil at a depth of 1-2 feet. The soil was kept moist with water. Specimens were kept under the soil for 90 days. After 90 days period, the specimens were retrieved from under the soil pit. It was found that chemically modified cotton and oil soaked cotton completely degraded and fully disintegrated in the soil whereas polypropylene sorbent was intact without any degradation. It indicates that cotton, even if chemically modified is fully biodegradable as add on nanoparticles are very less which will not affect the biodegradability. Oil soaked cotton sorbent was also found to be fully biodegradable. Fig7-9 is the photographs of oil sorbents under various stages of biodegradation.

Fig.7 Sorbents with a label before soil burial test

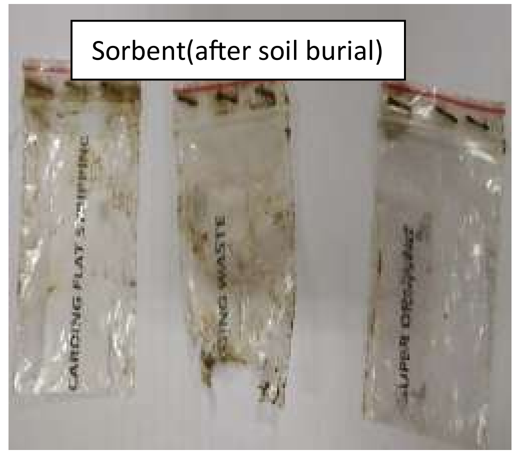

Fig.8 photograph after soil burial test

Fig.9 photograph of polypropylene before and after soil burial test

Fig. 7 is the photographs of sorbents before the soil burial test. Fig. 8 is the photograph after 90 days of the soil burial test, where we can see only labels as the sorbents have completely degraded. Fig.9 is the photograph of polypropylene sorbent before and after the oil burial test. From fig.9 it is clear that after being subjected to 90 days of soil burial test polypropylene sorbent is intact and not degraded.

3.5. Oil recovery and reusability of sorbents

The most measure for judging the reusability of the oil sorbent is the number of cycles it can endure without getting unusable due to tearing, smashing, pulverizing, or other common deterioration. Other components are the rate of diminishing in its oil absorption capacity and the rate of oil that can be outset with a sensible effort and equipment.

To assess the oil recuperation and reusability of sorbent, counterfeit sea water (500ml) was placed in a 1000 ml tray and 50g of motor oil was added to it. 4g of the sorbent material was then placed in the tray and shaken in a laboratory shaker at a frequency of 110 cycles/min for 15 min. The sorbent with the ingested oil was weighed and then squeezed between the two rollers at a pressure of 2-5N/cm. After evacuating the oil, the sorbent was re-weighed to determine the oil recuperation. The squeezed sorbent was once more utilized in the sorption process as before. The efficiency of sorbent and reusability was determined by oil sorption capacity each time after repeated sorption and desorption cycles.

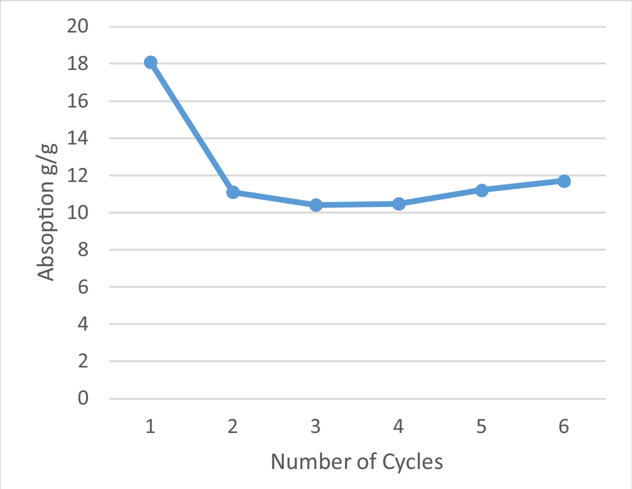

Fig-10 Oil recovery and reusability of sorbent

Fig 10 depicts a graph of absorption of sorbent (g/g) verses the repeated use cycle of sorbent. When a fresh sorbent was put in an oil bath it can absorb 18g/g of oil from an oil water media. After extrusion of the oil, the same sorbent could take up 11g/g oil in the 2nd absorption cycle. Further 3rd 4th and 5th cycles the retention capacity of the sorbent was nearly the same. During the primary six cycles of sorbent recycling, the rate of decline in the sorbent was greatest, with the most significant reduction occurring during the first interaction. This happen because a few oils were still displayed on the sorbent surface amid the extrusion process. In addition, cavities exist inside the cotton and it is not simple to discharge these after oil absorptions. During the repeated cycling utilize, part of the non-woven fabric structure distorts and thereby reduces the interstitial space. Consequently, the rate of absorption of oil reduces. However, after six times reuse, the adsorption rate of cotton was approximately 60%.

4.0 Conclusion

It has been seen that there is an extraordinary potential for oil sorbents produced using characteristic strands to supplant engineered oil sorbents. Thus, in this paper, a novel technique dependent on the synthetic adjustment of waste cotton fibre utilizing nanoparticles has been effectively evolved. Notwithstanding this has given evidence of the warm trustworthiness which could be practiced by the circuit of silica nano molecule onto the cotton the nearness of nanoparticles and nano roughening impact which could be made by nanoparticles statement was seen from SEM pictures. The very hydrophobic property of the sorbent was obvious through the contact angle which was more than 150^0. The created sorbent was seen as too hydrophobic and too oleophilic in nature. The oil absorption limit of the created sorbent was a lot higher than financially accessible polypropylene sorbents. The sorbent can be reused in any event 5-6 times without debasement. The created item can be utilized as oil sorbent to clean oil spillage ashore, water surface, and submerged. The sorbent was seen as completely biodegradable. Using a waste material to a worth included, the biodegradable item was a significant accomplishment in this exploration workout.

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