TiO_2 -(3-AMINOPROPYL)TRIETHOXYSILANE COATED ON COTTON FABRICS FOR FREE OIL EXTRACTION FROM OIL-WATER EMULSION SOLUTION

by

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LIST OF SYMBOLS

Symbol	Description	Unit
C_e	Concentration of adsorbate	mg/L
C_o	Initial adsorbate concentration	mg/L
K_f	Freundlich equilibrium constant	-
K_L	Amount of solute adsorbed	mg/g
q_e	Amount of adsorbate	mg/g
b	Net enthalpy of adsorption	-
n	Freundlich constant indicative of affinity of the adsorbate for the surface of adsorbent	mg/g

GREEK LETTER

θ	Angle between solid surface and liquid droplet	-
Υ	Interfacial forces	-

LIST OF ABBREVIATION

Symbol	Description
APTES	(3-Aminopropyl)triethoxysilane
EDS	Dispersive X-ray spectroscopy
FTIR	Fourier transform infrared spectroscopy
SEM	Scanning electron microscopy
TiO_2	Titanium dioxide
TTIP	Ti(IV)-isopropoxide
WCA	Water contact angle

TiO_2-(3- AMINOPROPYL) TRIETHOXYSILANE MENYALUT PADA FABRIK KAPAS UNTUK PENGESKTRAAN MINYAK DARIPADA LARUTAN EMULSI MINYAK-AIR

ABSTRAK

Dalam kajian ini, percubaan telah dibuat untuk mencipta fabrik hidrofobik menggunakan prosedur rendaman yang mudah. Untuk menghasilkan kekasaran permukaan yang mencukupi dengan kimia permukaan hidrofobik, kain kapas disalut dengan nanozarah titania yang diperbuat daripada Ti(IV)-isopropoxide (TTIP). Selepas itu, rawatan aminopropyltriethoxysilane (APTES) digunakan pada tekstil bersalut untuk mengurangkan tenaga permukaan. Kami melihat bagaimana salutan kain yang diubah suai dengan TiO_2 dan APTES mempengaruhi morfologi permukaannya dan betapa hidrofobiknya. Mengimbas mikroskop elektron (SEM), sinar-X penyebaran tenaga (EDS), dan spektroskopi inframerah transformasi Fourier (FTIR) digunakan untuk menilai bentuk fabrik hidrofobik serta komposisinya. Penemuan menunjukkan penghasilan lapisan asimetri TiO_2 NP dan APTES di seluruh permukaan fabrik. Siasatan terhadap hidrofobisiti fabrik menggunakan ukuran sudut sentuhan air mendedahkan bahawa fabrik yang diubah suai itu mempamerkan kalis air yang sangat baik. Di samping itu, tumpuan kerja ini adalah pada penjerapan minyak pada fabrik TiO_2-APTES untuk tujuan penyingkiran minyak daripada larutan minyak-air. Berat bahan penjerap mempunyai korelasi langsung dengan peratusan minyak yang dikeluarkan, manakala kepekatan penjerap mempunyai kesan yang bertentangan. Peratusan penyingkiran minyak, sebaliknya, tidak dipengaruhi oleh masa sentuhan. Mengikut keputusan ujian keseimbangan, isoterma Langmuir adalah model yang paling sesuai untuk menggambarkan penyingkiran minyak oleh fabrik TiO_2-APTES. Penyelidikan juga dilakukan terhadap kebolehgunaan semula bahan penjerap, yang terbukti boleh dikitar semula sehingga lima kali.

TiO_2 -(3-AMINOPROPYL) TRIETHOXYSILANE COATED ON COTTON FABRICS FOR FREE OIL EXTRACTION FROM OIL-WATER EMULSION SOLUTION

ABSTRACT

In this study, an attempt was made to create hydrophobic fabric using a straightforward immersion procedure. In order to generate adequate roughness with hydrophobic surface chemistry, cotton fabric was coated with titania nanoparticles made from Ti(IV)-isopropoxide (TTIP). After that, the aminopropyltriethoxysilane (APTES) treatment was applied to the coated textiles in order to lower the surface energy. We looked at how coating modified cloth with TiO_2 and APTES affected its surface morphology and how hydrophobic it was. Scanning electron microscopy (SEM), energy dispersive X-ray (EDS), and Fourier transform infrared (FTIR) spectroscopy were used to evaluate the shape of hydrophobic fabric as well as its composition. The findings indicated the production of asymmetrical layers of TiO_2 NP and APTES throughout the entirety of the surface of the fabric. An investigation into the hydrophobicity of fabrics using the water contact angle (WCA) measurement revealed that the modified fabric exhibited excellent water repellence. In addition to that, the focus of this work is on the adsorption of oil onto TiO_2-APTES fabric for the purpose of removing oil from an oil-water solution. This finding provided proof that the adsorbent was capable of absorbing oil and that various parameters had an effect on the adsorptive capability of the adsorbent. The weight of the adsorbent has a direct correlation to the percentage of oil that is removed, whereas the concentration of the adsorbate has the opposite effect. The oil removal percentages, on the other hand, are not impacted by the contact time. According to the results of equilibrium tests, the Langmuir isotherm was the most appropriate model to describe oil removal by TiO_2-APTES fabric. Research was also done on the reusability of the adsorbent, which was shown to be recyclable up to five times.

CHAPTER 1 INTRODUCTION

1.1 Background

Organic hazardous waste containing oil and grease (O&G) harms aquatic organisms, plants, and animals, as well as being mutagenic and carcinogenic to humans (Islam et al., 2013). Oil discharge from a variety of sources, forming a coating on the water's surface that reduces dissolved oxygen levels. The presence of an O&G layer lowers the biological activity of the treatment process, which involves the creation of an oil film surrounding bacteria in suspended debris and water. As a result, the water's dissolved oxygen levels dropped. The oxygen molecules are then difficult for microbes to oxidise on hydrocarbon molecules, causing ecological damage to water bodies (Abass O et al., 1970).

Traditional procedures use skimming tanks and oil and grease traps in treatment facilities to remove oil and grease, but the fundamental issue of these systems is their low removal efficiency. The leftover oil clogs pipes in treatment units, necessitating pipe cleaning and, in some cases, pipe replacement. As a result, the cost of maintenance and inspection has increased (Mueller et al., 2003). In applications such as the treatment of oily wastewater and the cleanup of oil spills, oil-water separation becomes critical. Many industries, such as textiles, leather, and the food industry, produce a significant amount of oily effluent. For oil-water separation, a variety of techniques are routinely utilised, including gravity settling, centrifugation, gas flotation, electric field, coagulation, membrane filtration, and electrochemical technologies. Traditional oil-water separation systems, on the other hand, have limited selectivity, a long separation time, a high energy input, a huge acreage demand, and the creation of secondary pollutants as negatives (Rasouli et al., 2021).

Surfaces with extreme wetting or non-wetting conditions have been created and employed in a variety of oil-water separation applications. Feng et al. were the first to describe a membrane that was both superhydrophobic and superoleophilic at the same time in 2004 (Feng et al., 2004). Mechanical approaches recovered less than 10% of the water surface oil pollution; this low recovery efficiency rekindled research on superhydrophobic and superoleophilic membranes and sorbents as selective tools for effectively capturing oil by rejecting water (Kostka et al., 2011).

Sorbent materials should be able to evenly distribute and trap oils in their structure, in addition to having an affinity to sorb oils. Furthermore, for better oil-water separation, sorbent materials must meet a number of other important criteria, including the ability to adsorb significant amounts of oil per unit mass, being hydrophobic in nature and having a low water sorption capacity, having a low bulk density, remaining in water for an extended period of time, and having a high oil uptake rate. Oil sorption behaviour of sorbent material, on the other hand, is influenced by oil attributes such as concentration, temperature, specific gravity, and oil kinds (Abdullah et al., 2010). Many natural surfaces, particularly lotus leaves, which are extremely water repellent, have recently drawn a lot of attention (Fürstner et al., 2005).

Strongly hydrophobic and superoleophilic surfaces are now commonly employed in oil-water separation materials, self-cleaning coatings, and wettable functional textiles. Nanostructured fabrics created using nanotechnology increased the hydrophobicity of numerous fabrics (Hsieh et al., 2008). Cotton is a polysaccharide from a chemical standpoint. Acrylic polymers may easily modify the properties of these natural polymers to produce useful materials with a wide range of qualities (Tissera et al., 2015).

Cellulose-based textiles are the most common and widely used garment materials because of their superior comfort, softness, sustainability, tensile strength, and biodegradability. However, cellulose materials are prone to being wet and discoloured by liquids due to the abundance of hydroxyl groups on their surface (Xu & Cai, 2008). The sol-gel approach, chemical vapour deposition method, dip coating method, and layer by layer assembly method are currently new methods for manufacturing extremely hydrophobic cotton fabrics. Despite the preparation of highly hydrophobic and superoleophilic surfaces on the surface of cotton fabrics, there are still numerous issues.

Furthermore, fluorinated chemicals and fluoropolymers have gained a lot of attention because of their low surface free energy, which is owing to the fact that roughening these polymers in a certain way results in highly hydrophobicity (Tissera et al., 2015). Because of their effective and selective removal and separation of oil and water, very hydrophobic and hyper oleophilic materials, which selectively absorb oil-based organic pollution and reject water, have gotten a lot of attention. Although various approaches for replicating extremely hydrophobic surfaces have been very successful, their success is restricted to the production of rigid substrates since displacement of the substrate might remove the hydrophobic qualities. However, flexible hydrophobic and superoleophilic materials must be produced to broaden the application range. As a result, adsorbent technology has continued to evolve in order to build a cost-effective, environmentally friendly, high reusability, and adsorption performance adsorbent.

1.2 Problem Statement

Oil-water separation has gotten a lot of attention across the world because of the rising amount of oil-containing wastewater from our daily lives, as well as oil spills, chemical leaks, and industry discharges, all of which have posed a serious threat to the environment and ecological system. Furthermore, oily wastewater will inevitably be produced in industries and in everyday life. It will have an environmental impact if it is not properly treated before release. Discharging this greasy sewage directly into the environment will further degrade water supplies and even harm the environment. Because of the frequent oil spills and the rising oily wastewater generated by the chemical industry and metal polishing, efficient separation of oil-water mixtures is a global environmental concern. Most sectors, including textiles, foods, petrochemicals, and mining, discharge waste as an oil-water emulsion. It has grown in popularity as a contaminant and a severe environmental hazard. It can also cause damage to machines and be harmful to the environment and animals. Oil spill kits, centrifugation, distillation, industrial filtration, settling tanks, magnetic separation, skimmer flotation technologies, and other processes are used to separate oil from water. These traditional procedures are inefficient, and the leftover oil in the combination can produce blockages in treatment plant pipes, necessitating more regular cleaning or, in some cases, pipe replacement. As a result of the low effectiveness of existing technologies, oil-water separation from effluent has become more expensive. Traditional technologies for oil-water separation require additional development so that they can meet current and future demand, purify huge volumes of mixture, and be cost-effective, ecologically friendly, and reusable (Yu et al., 2016). Recently, superhydrophobic superoleophilic coatings have sparked interest in oil-water separation as a means of overcoming the challenges associated with traditional approaches. These coatings can be applied to a variety of fabrics, which can then be used to separate oil and water mixtures since the hydrophobic nature of the coated material keeps the water upside while the hydrophilic nature allows the oil to flow down from the coated fabric or mesh. In comparison to traditional oil-water separation procedures, this form of oil-water separation approach provides a straightforward and hassle-free operation. Surface roughness and low surface energy are the fundamental elements that determine a surface's superhydrophobicity. Low surface energy can also be accomplished by changing the coating with a low surface energy substance. These materials have a tendency to lower the solid surface's surface free energy. As a result of covering a mixture of nanoparticles with a low surface energy substance, the fabric surface is modified to have superhydrophobic and superoleophilic qualities (Cortese et al., 2014).

1.3 Research Objective

i. To synthesize TiO_2-APTES coating

ii. To characterize the coating adsorbent of modified fabric using various characterization techniques: SEM, Contact Angle and FTIR.

iii. To evaluate the performance of TiO_2-APTES for oil adsorption at different oil concentration, contact time, and it reusability.

CHAPTER 2 LITERATURE REVIEW

2.1 Adsorption

It is the creation of hydrophobic and superoleophilic surfaces on textiles that serves as the primary separation principle in adsorption for oil-water separation. Purification or bulk separation can be achieved through adsorption, which is determined by how much of a concentration of each component is present in the feed (Seader et al., 2010). One or more components of a mixture may also be defined as selectively concentrated or retained on the surface of another or more components of the mixture (Akkimaradi et al., 2010). The term "adsorbent" refers to the solid that adsorbs a component, and the term "adsorbate" refers to the component that has been adsorbed. In the context of adsorption, surface processes are those that occur as a result of interactions between molecules of the adsorbate and the surface of the adsorbent. It is referred to as adsorption if the sorbed molecules are attracted to the surface of the liquid phase, whereas it is referred to as adsorption if the sorbed molecules are dispersed throughout the fluid phase. The process of desorption is the reversal of the adsorption process. Pressure and temperature are the two most important variables that influence the amount of a solute adsorbed per unit mass of adsorbent at equilibrium, and they are both controlled by the adsorbent. In the case of solid surfaces, adhesion of a component takes place due to an affinity of the surface for the specific component. Adsorbent and adsorbate interact with each other at different strengths depending on the force of interaction that exists between them. Physcial adsorption occurs when the force of interaction between the two substances is weak, such as Van der Waal's force or the electrostatic force, while chemical adsorption occurs when a strong chemical bond is formed between them. Furthermore, physical adsorption is a reversible process, whereas chemisorption is not always the case.

2.2 Cotton fabric as Interfacial Materials

The effective separation of oil-water mixtures at a low cost has emerged as a global challenge in recent years. Traditional oil-water separation materials, on the other hand, were frequently subjected to low separation efficiency as well as poor durability (Wang et al., 2014). As a result, the development of new functional materials for highly efficient oil-water separation is in high demand. Superhydrophobic surfaces, defined as those with a water contact angle greater than 150^{o}, have gotten a lot of attention lately because of their potential applications in practical oil-water separation systems (Wang et al., 2015). Cotton fibre, for example, exhibits integrated characteristics of cellulose recyclability, good mechanical properties, flexibility, and gas permeability, and can be used to fabricate superhydrophobic interfacial materials that can be used as an oil sorbent by manipulating their mechanical properties and flexibility (Deschamps et al., 2003). Having a large number of hydroxyl groups attached to cotton fibre's surface allows for extensive further modification, such as adjusting the surface wettability toward superhydrophobic cotton-based composites, which is extremely important for addressing the resource and environmental issues that are currently being faced. It is widely accepted that the fabrication of superhydrophobic interfacial materials can be accomplished through the manipulation of the surface topography structure in conjunction with the chemical composition of the material (Wang et al., 2017). Various methods for fabricating cotton-based composites for oil-water separation have been developed, with the introduction of surface roughness and the incorporation of low surface energy materials being the most prominent. Nevertheless, when it comes to practical application, the surface roughness of the hydrophobic structured composites is primarily created by modification of traditional inorganic nanoparticle (NP) materials, and as a result, they lack abrasion durability because their bonding with low-surface energy layers is not strong enough. Cheng et al. developed a superhydrophobic cotton fabric using a spray coating-coating method based on a combination of ZnO NPs decoration and stearic acid modification, which demonstrated an oil-water separation efficiency of 97.5 percent when tested in a laboratory setting (Cheng et al., 2018). According to Huang et al., they prepared TiO2-decorated cotton fabric composites by hydrothermal reaction followed by fluoroalkylsilane modification on the cotton fabric surface, which demonstrated efficient oil-water separation (Huang et al., 2015).

2.3 Coating Modification Effect On Fabric Properties

With the growing awareness of the dangers of oil contamination to the environment and public health, several researchers have looked into a variety of decontamination approaches to address the problem. The typical experiments using in situ crosslinking modified cotton fabrics that can be used for efficient oil-water separation are listed in Table 1. The modified substrate created through in situ crosslinking is extremely resistant to abrasion and chemical damage. Nonetheless, the high reaction temperature required for manufacturing consumes a lot of energy.

Table 1 *Modified fabric based for oil-water separation*

Material	Solvent	Drying condition	Contact angle	Shedding angle	Separation cycle	Separation efficiency	Feature	References
SiO_2/PVA/PDMS	THF	65°C ; 1h	156°	1.8	45	90%	1.Superhydrophobic 2. Anti-abrasion 3. Oil-water separation	(Jannatun et al., 2020)
PDMS/FASI15/PVP	Dichloro-methane	50°C; 6h	140°	-	30	96%	1.Superhydrophobic 2. Anti-abrasion 3. Oil-water separation 4. Anti-corrosion	(Guo et al., 2019)

ZnO/OTES/PGMA	Ethanol	$120^{o}C$; 6h	158^{o}	-	-	-	1.Superhydrophobic 2. Anti-abrasion 3. Oil-water separation 4. Anti-corrosion	(Zhang et al., 2019)
PDMS/$CuSA_2$	n-hexane	$80^{o}C$; 3h	158^{o}	-	50	96%	1.Superhydrophobic 2. Anti-fouling 3. Anti-corrosion 4. Anti-abrasion 5. UV-resistance 6. Oil/water separation	(Pan et al., 2019)
PDVB	Ethyl acetate	$80^{o}C$; 1h	158^{o}	-	10	98%	1.Superhydrophobic 2. Anti-abrasion 3. Oil-water separation 4. Anti-corrosion	(Cheng et al., 2019)
ODTMS-HNTs/PDMS	Water/HCl	$120^{o}C$; 2h	164^{o}	-	40	99%	1.Superhydrophobic 2. Oil/water separation	(Song et al., 2020)

The hydrophobicity of a surface is determined by the difference in surface energies between the liquid and solid surfaces, which is related to the surface energy of the substrate (Krasowska et al., 2009). If a smooth surface, whether natural or synthetically produced, is exposed to a liquid drop in air, and the solid surface's surface energy is greater than the liquid's, the surface will become wet as the solid tens to draw the liquid molecules to it in order to reduce their overall energy level. If the surface energy of a solid is lower than that of a liquid, the solid will strive to repel the liquid out to keep its energy level from rising. The contact angle between the solid and the liquid is used to calculate the surface energy. Three interfacial forces act on the contact site when a droplet makes contact with a solid surface: interfacial force between solid and vapour (L), interfacial force between solid and vapour (also mean the surface energy of solid) (S), and interfacial force between solid and liquid (SL). The angle between a solid surface and a liquid droplet on the surface is quantified by the contact angle (θ). The Young's equation can be used to represent the interfacial force balance at the three-phase point for a smooth surface:

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL} \qquad (2.1)$$

According to Young's equation, a high angle ($\theta > 90^o$) results in low Υ_S, low Υ_L, and/or high Υ_{SL}. Low Υ_S denotes a surface with few polar and dispersive interactions with the molecules around it. A high contact angle ($\theta > 150^o$) is possible with a superhydrophobic surface.

Jannatun et al. (2020) employed boric acid as a crosslinker to create SiO2/PVA/PDMS modified cotton fabric (Jannatun et al., 2020). Guo et al. (2019) used FAS15 and PDMS crosslinking to create a hydrophobic cotton fabric (Guo et al., 2019). Zhang et al. created a superhydrophobic surface on cotton fabric by immobilising ZnO nanoparticles with octyltriethoxysilane (Zhang et al., 2019). Nanoparticles and polymer monomers can be combined together and crosslinked on the surfaces to generate a superhydrophobic layer in certain circumstances. Fabrication of a CuSA2-modified superhydrophobic cotton fabric capable of separating n-heptane/water mixtures with a 96 percent efficiency (Pan et al., 2019). Cheng et al. (2019) used solvothermal polymerization to create superhydrophobic cotton fabric (Cheng et al., 2019). After 40 cycles of oil/water separation, Song et al. (2020) produced ODTMS-HNTs modified cotton fabric with good separation efficiency (Song et al., 2020). Cotton materials were used for oil spill separation because they are readily available, degradable, and inexpensive. Cotton fabrics are naturally grown as rough and hydrophilic fabrics that must be modified to meet the requirements for oil-water separation. A superhydrophobic and superoeleophilic surface, such as lotus leaves, is sought when using modified cotton fabrics as an oil adsorbent from an oil-water mixture.

Other ways for modifying cotton fabric surfaces for oil-water separation exist. One method for modifying cotton fabrics is to dip coat them. Zhang et al. (2013) used a dip-coating process to make superhydrophobic cotton fabric textiles with modified Zn nanoparticles and polystyrene as a water repellent (Zhang et al., 2013). The affinity of nano particles and the surface of the substrate, which leads to robust particle adhesion, is the key to dip coating. This philosophy is typically straightforward to apply, but it has drawbacks, such as easy particle detachment, which has been reported in several applications and may cause health and environmental concerns (Lee & Lee, 2019). The success of the nanoparticle deposition process for generating superhydrophobic surfaces depends on its lengthy endurance. Apart from that, one of the strategies for changing fabric surfaces is self-affine modification. Dopamine, also known as 3,4-dihydroxyphenethylamine, is a hormone that regulates the human body. Dopamine was used in multifunctional polymer coatings and the production of heparin immobilising membranes, inspired by the composition of sticky proteins in mussels (Jiang et al., 2010). Polydopamine (pDA) can be coated on a range of inorganic and organic material surfaces, and then further modified by a number of functional chemicals by grafting of macromolecules, long-chain molecule deposition, and metal ion reduction. One of the most significant drawbacks of using dopamine as a modifying agent is its high cost and lengthy reaction time. The time it takes to develop a pDA coating, in example, may take days.

2.4 The Langmuir isotherm

The Langmuir equation for solid-liquid system is commonly written as:

$$q_{e=\frac{K_L C_e}{1+bC_e}} \quad (2.2)$$

Where KL is the amount of solute adsorbed/unit weight of an adsorbent in forming a complete monolayer on the surface (mg/g), q_e is the amount of adsorbate per unit weight of adsorbent (mg/g), C_e is the concentration of adsorbate in solution at equilibrium after the adsorption is complete (mg/L), and b is the constant related to the energy or net enthalpy of adsorption The linear form of Langmuir expression is

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{b}{K_L} C_e \quad (2.3)$$

Plotting C_e/q_evs C_e results in a straight line with a slope of b/K_L and an intercept of $1/K_L$. The fundamental properties of the Langmuir isotherm may be described in terms of a separation factor, dimensionless constant, or equilibrium parameter r, which is defined as follows

$$r = \frac{1}{1 + bC_0} \quad (2.4)$$

Where b is the Langmuir constant associated with the energy of adsorption (L/mg) and C_0 is the initial adsorbate concentration (mg/L). If adsorption is unfavourable (r>1), linear (r = 1), or favourable (0 0r 1), the value of r reflects the shape of the adsorption isotherm. else irreversible (r = 0).

2.5 The Freundlich model

The Freundlich isotherm can be applied to nonideal adsorption on heterogenous surfaces as well as multilayer sorption is expressed by the following equations:

$$q_e = K_f C_e^{1/n} \quad (2.5)$$

A linear form of this expression is

$$\log q_e = logK_f + \frac{1}{n} logC_e \quad (2.6)$$

C_e is the concentration of adsorbate in solution at equilibrium after the adsorption is complete (mg/L), where K_f is the Freundlich equilibrium constant that indicates the adsorptive capacity and n is the Freundlich constant indicative of the affinity of the adsorbate for the surface of the adsorbent (mg/g).

This study's major goal is to look at how well TiO_2-APTES fabric removes oil from an oil-water mixture. Additionally, variables influencing their adsorptive nature including concentration and stirring duration. For oil removal by TiO_2-APTES fabric, the Freundlich and Langmuir adsorption isotherm models are utilised, and the best suited adsorption isotherm model is determined.

CHAPTER 3 RESEARCH METHODOLOGY

This chapter outlines the overall experimental aspects of the final year project, as well as the specific experimental aspects of the project. A general research flow diagram, fabric preparation, synthesis of TiO_2-APTES, and characterization study using various equipment are all included in this section.

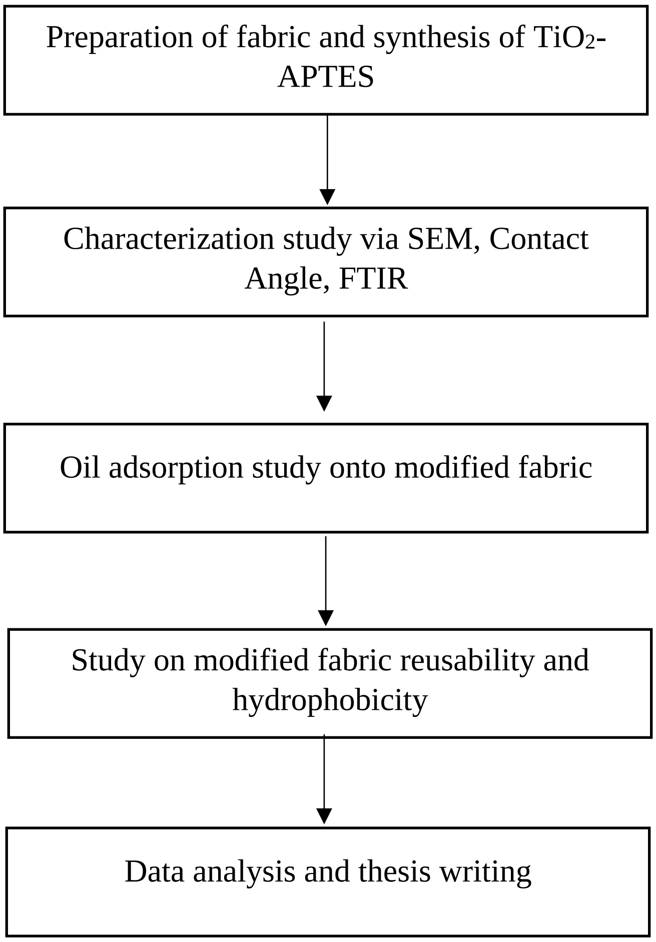

Figure 3. 1 Flow Chart for research

3.1 Material

Ti(IV) isopropoxide (TTIP, 98%), 3-amnipropyltriethoxysilant (APTES, 98 percent), and ethanol (C_2H_6O, 95%) are all readily available in the laboratory. A readily available source nitric acid, (HNO_3, 65%) in the laboratory. The experiment will be conducted with deionized water throughout. All of the chemicals were used immediately, without being treated in any way.

3.2 Pre-treatment of Cotton Fabric

It was necessary to wash and rinse the desired fabric several times with detergent and deionized water to remove the surface impurities before it could be used. After that, the fabric was soaked in acetone for 10 minutes before being gently rinsed with deionized water and dried at 80^{o}C for 20 minutes before being folded.

3.3 Synthesis of TiO_2 particles

Titanium(IV)-iso-propoxide (TTIP) (7.68g) was added to ethanol 95% (21.58g) and the mixture was stirred for 30 min using a magnetically stirrer operating at 500 rpm. After stirring, a mixture of water (300g) and nitric acid (9.06g) was added to the alkoxide solution. The mixture then stirred using magnetic stirrer operating at 500 rpm for 2 hours at 60^{o}C to get TiO_2 solution. The hydrophobic/superoleophilic fabrics were fabricated by a simple dip-coating approach. The treated cotton fabric is cut into 5x5cm size then was dip-coated into colloidal TiO_2 solution (5 wt%) with constant stirring at 200 rpm for 20 mins. Then the cotton fabric was dried at 80^{o}C for 10 min.

3.4 Fabrication of Hydrophobic Cotton Fabric

The cotton fabric 5x5cm treated with TiO_2 NP (5 wt%) then used in this procedure, APTES 98% was diluted to 0.5% using deionized water and stirred using magnetic stirrer operated at 500 rpm for 30 min at room temperature. Finally, the TiO_2 coated fabric were dip-coated in APTES solution for 20 min and cured at 120^{o}C for 60 min to get TiO_2-APTES coated fabric.

3.5 Characterization

The TiO_2-APTES coated fabric prepared will be characterised using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and water contact angle (WCA).

3.5.1 Scanning electron microscopy (SEM)

After the sorbent sample is mounted on aluminium studs, gold plating will be applied. The SEM's acceleration voltage will be 5.0 kV. After that, a SEM analysis of the sorbent sample's microstructure will be performed.

3.5.2 Fourier Transform Infrared Spectroscopy (FTIR)

The functional group of the adsorbent surface changed before and after adsorption, and this was detected using an FTIR spectroscope. With a spectral resolution of 4 cm^{-1}, this study was conducted in the range of wavelengths from 4000 to 400 cm^{-1}.

3.5.3 Water Contact Angle (WCA)

Laboratory equipment was used to perform WCA at room temperature. a microscope that has PCTV vision software and a CCD camera. A 5 µL water droplet was thrown onto the fabric surface five different places, and an average value was recorded.

CHAPTER 4 RESULT AND DISCUSSION

4.1 Surface morphology

SEM analysis was used to look at the surface morphology of the coated and uncoated cotton fabrics. Figures 4.1, 4.2, and 4.3 depict the surface morphology and high magnification scanning electron microscopy characteristics of the fabric. The original fabric, the TiO_2 coated fabric, and the TiO_2-APTES coated fabric are shown in Figures 4.1, 4.2, and 4.3, respectively. For TiO_2 fabric and TiO_2-APTES fabric, SEM images at 500 and 3000 times magnification are shown. When magnified 500 times, it is clear that there is no discernible change in their surface morphology, but when magnified 3000 times, it is clear that there is a coating on the surface, which may be TiO_2 and APTES coated in the weave object surface. Based on figure 4.3, the introduction of APTES is not enough to create enough rough geometries, thus the change in this surface topography is not uniform and evident, and portion of the surface is still smooth at changed fabric. When enlarged by 3000 times and then by another 5000 times, the surface of TiO_2 and TiO_2-APTES, however, is no longer flat. It is evident that the surface of the fabric fibres have a significant buildup of micro-nano particles as can be look in figure 4.2. TiO_2 was added, which caused a huge stacking of micro- and nano-geometric structures. After hydrolysis, APTES may be crosslinked or self-crosslinked with TiO_2 before being coated on the surface of TiO_2. To give the fabric a micro-nano rough structure, TiO_2-APTES is coated on the fabric's surface. Modification of surface roughness fiber and low surfaces energy, causing the fabric to not be moistened by water droplets that they have hydrophobic properties.

The stability of the material's qualities will undoubtedly be impacted by the TiO_2-APTES coating's binding to the fabric. EDS is thus used to analyse the TiO_2-APTES fabric's elemental mapping. As shown in table 4.1, the distinctive element Ti is present in the spectrum of the TiO_2 and TiO_2-APTES fabric, demonstrating that the Ti is coated on the fabric's surface.

Table 4. 1 EDS result for TiO_2-APTES fabric

Element	Weight%	Atomic%
C K	43.71	54.69
O K	44.20	41.52
Ti K	12.09	3.79
Totals		100.00

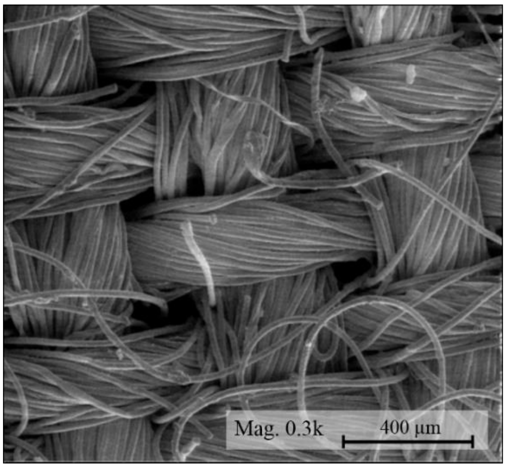

Figure 4. 1 SEM for unmodified fabric at 300 magnification

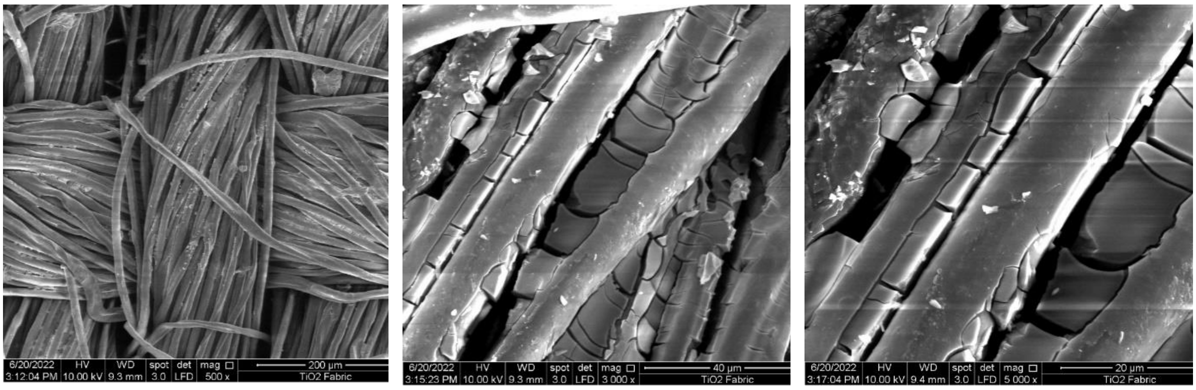

Figure 4. 2 SEM for TiO_2 coated fabric at 500, 1000, and 3000 magnifications

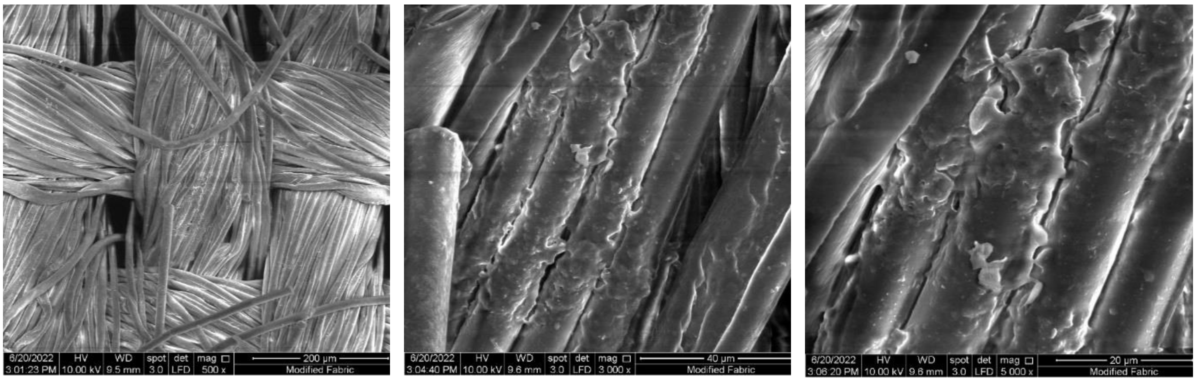

Figure 4. 3 SEM for TiO_2-APTES fabric at 500, 1000, and 3000 magnifications

4.2 Chemical structure analysis

The infrared contrast spectra of the fabric before and after it has been coated with TiO_2 and APTES is shown in Figure 4.4. According to the figure, TiO_2-APTES fabric showed additional absorption peaks at 1095 cm^{-1} when compared to the original fabric. These absorption peaks may be related to the misalignment of Si-O-Si into stretching vibration and symmetrical stretching vibration. The N-H bending vibration corresponds to a new peak that occurred at 1550 cm^{-1} at the same time. The APTES intoduction is responsible for the aforementioned peak shifts, which may demonstrate that APTES was effectively coated on TiO_2 fabric. TiO_2 fabric displays a new adsorption peak at 670 cm^{-1} compared to the original fabric, which represents the stretching vibration between Ti and O, demonstrating the presence of TiO_2. TiO_2-APTES fabric has been successfully made using FTIR analysis.

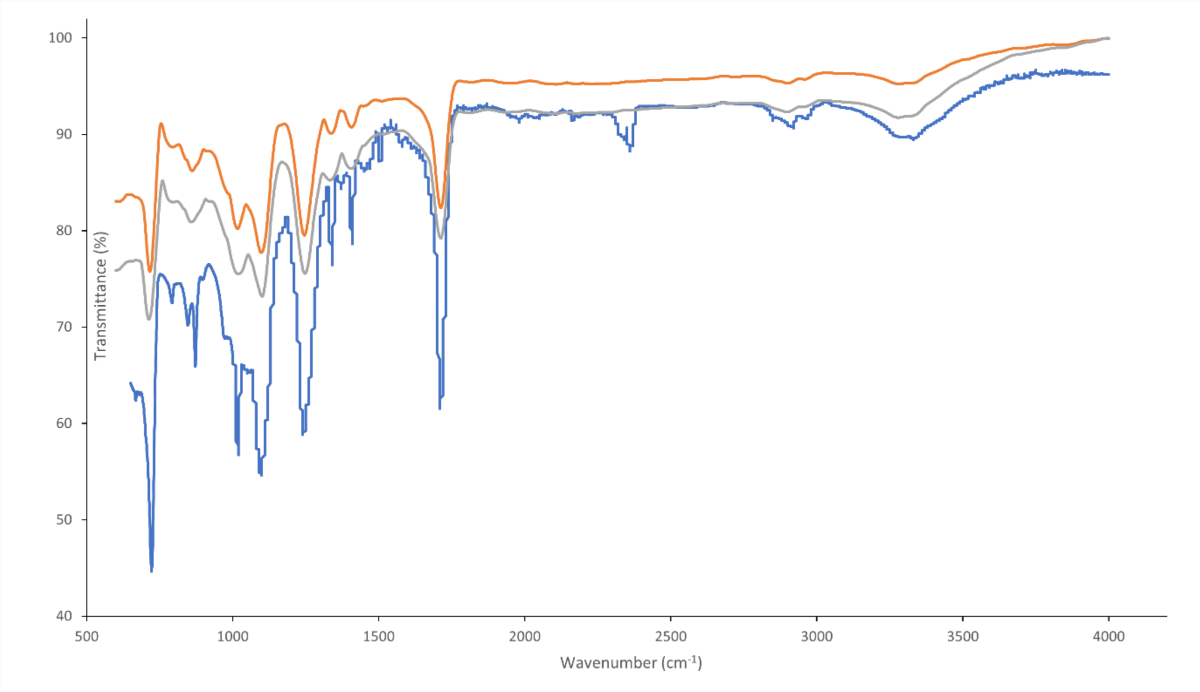

Figure 4. 4 FTIR Spectrum for unmodified, TiO_2, and TiO_2-APTES fabric

4.3 Hydrophobic Property

Utilizing the water contact angle (WCA) measurement, the hydrophobicity of materials was evaluated. Utilizing water contact angle, the wettability of uncoated, TiO_2 coated, and TiO_2-APTES coated fabric were examined. Due to the hydrophilic hydroxyl and carboxyl groups on the clean fabric, a water droplet totally saturated it. The in situ deposition of TiO_2 nanoparticles results in the fabric surface being rough and hydrophobic, as seen in SEM picture figure 4.6. Due to APTES's low surface energy, the hydrophobicity of the TiO_2 coated fabric was enhanced after being modified with the APTES solution in figure 4.7. The pristine fabric WCA is 68.08^o, indicating hydrophilicity and high surface energy; after being coated with TiO2, the WCA is 127.4^o, indicating an increase in surface roughness. The WCA of TiO_2 coated fabric enhanced to 137.4^o by the addition of APTES, which has greater hydrophobic characteristics. Conclusion: The formation of tinatia cluster on the surface increased the surface roughness, whereas APTES coating decreased the surface energy.

The substance in contact with water can be used to determine a material's hydrophilic characteristics. A substance is considered hydrophilic if the water contact angle is less than 90 degrees, and superhydrophilic if the water contact angle is 0^o. The use of surface wetting is crucial for oil-water separation. The contact angle of a liquid on a solid surface while another fluid is present is a popular way to describe the wetting condition. For applications involving oil-water separation, the water contact angle (WCA) and oil contact angle (OCA) on the surface are crucial elements. WCA > 150^o and a modest contact angle hysteresis are frequent indicators of superhydrophobicity. Although the modified fabric in this study could not attain superhydrophobic capabilities, it nevertheless demonstrated good hydrophobic characteristics.

Table 4. 2 Water contact angle result for unmodified, TiO_2, and TiO_2-APTES fabric

Adsorbent	WCA (^{o})
Unmodified Fabric	68.075
TiO2 Fabric	127.4
TiO2 -APTES fabric	137.225

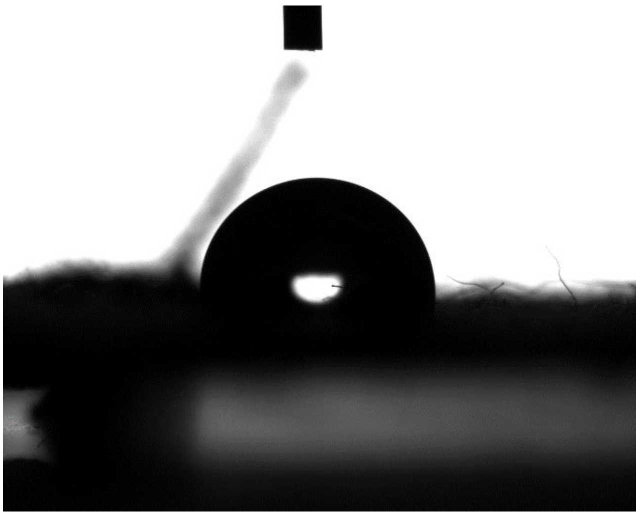

Figure 4. 5 WCA for unmodified fabric

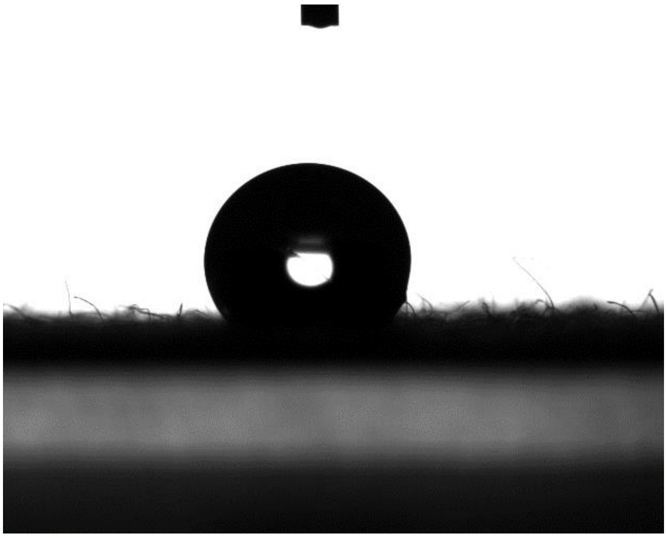

Figure 4. 6 WCA for TiO_2 fabric

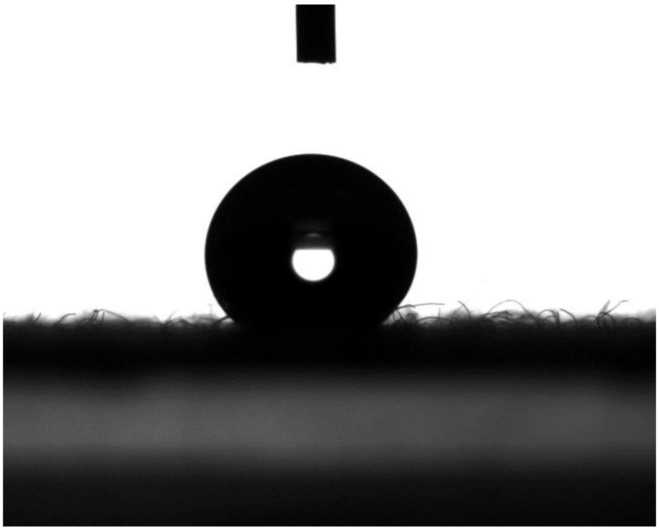

Figure 4. 7 WCA for TiO_2-APTES fabric

4.4 Oil-water separation

It is anticipated that the unique, switchable hydrophobic/oleophilic substance, which resembles the one side of a coin, will have a significant positive influence on both the economy and the environment. The redesigned fabric may be employed for the controlled oil-water separation experiment due to the difference in surface wettability for water and oil. Red dye was added to the oil to give it colour for easier visual examination. The researcher used either a filtering or an adsorption bases separation approach based on the literature study. Adsorption-based oil-water separation was established in this study. The modified fabric can therefore be used to separate oil-water combinations or to remove floating oil. The redesigned fabric demonstrated improved oil adsorption capacity due to its outstanding hydrophobic/oleophilic characteristics. The redesigned fabric captures floating oil from polluted water for microscopic level oil-water separation.

TiO_2-APTES coated fabric or modified fabric absorbed floating oil from the water surface in this adsorption procedure. The coloured oil was successfully absorbed by the modified fabric after a minute, leaving a clean water zone. Similar to this, when small droplets of oil and water were dropped on fabric, the modified fabric selectively absorbed the oil, keeping the water on top of the fabric. As a result, the TiO_2-APTES fabric can effectively and selectively separate an oil-water combination, demonstrating the fabric's superior oil adsorption capacity. TiO_2 sol that had been treated with poly(hexafluorobutyl methacrylate) was another method that other studies used to make superhydrophobic cotton textiles with a high WCA result. (Yang et al., 2018). The manufacture of superhydrophobic cotton with self-cleaning and stain-resistant qualities was described by Chauhan et al. They used the immersion drying process after coating the cotton with hexadecyltrimethoxysilane. It is possible to draw the conclusion that the high hydrophobic qualities were brought about by the hierarchical microstructures as well as the presence of long-chain alkyl groups on the surface of the modified cotton. (Chauhan et al., 2019).

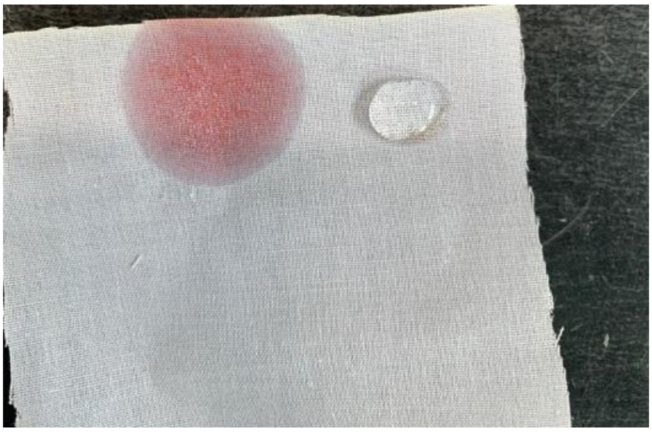

Figure 4. 8 Droplet of water and oil on TiO_2-APTES fabric

Figure 4. 9 Oil-water mixture before immersed of modified fabric

Figure 4. 10 Oil-water mixture after immersed of modified fabric