

COTTON – GRAPHENE BASED NANO-COMPOSITES AS A SEMI-  
SUSTAINABLE MATERIAL FOR OIL AND CHEMICAL CLEANUP

A Thesis

by

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Submitted to the Office of Graduate and Professional Studies of  
Texas A&M University  
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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August 2018

Major Subject: Energy

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## ABSTRACT

The world is facing severe ecological and environmental problems due to the oil spills and the discharge of organic solvents into the environment. This problem has led to development of different tools and high performance materials that can both effectively and efficiently absorb these discharges from water bodies. Moreover, greener and economical methods to produce these materials are on high demand. Herein, we demonstrate a novel method of attaching graphene to functionalized cotton cellulose. The hydrophobic graphene coated cellulose with a contact angle of  $144.76^\circ$  (with water) shows great oil absorption with a contact angle less than  $10^\circ$  towards oil and non-polar organic solvents. The absorption experiments performed exhibited an absorption capacity of 28.32, 39.91, 42.32, 40.89, 22.1, 27.67, 34.69 and 39.01 for dodecane, paraffin oil, pump oil, mineral oil, hexane, toluene and crude oil respectively. In addition, the graphene coated cellulose revealed excellent reusability, great selectivity and a high capacity. By the combination of cost effective combination, eco-friendly nature and excellent oil absorption performance, the graphene coated cotton is a promising candidate with a strong potential for large scale removal of oils from water and their environmental remediation.

## ACKNOWLEDGEMENTS

I humbly acknowledge the help, guidance and support of my committee chair, Dr. Mustafa Akbulut. I would like to thank Dr. Valentini Pappa, academic coordinator, Dr. Pistikopoulos, the head of the department for their guidance and support throughout the program of Master's of Science in Energy, Texas A&M University.

A special thanks to my seniors in Dr. Akbulut's group, Jun Kyun Oh, Li Hao, Michael Bae, Shuhao Liu, Nirup Nagabandi, Yagmur Yegin and Cengiz Yegin for the training and all the valuable suggestions.

A big shout-out to my classmates Sajjad Haider, Priscille Etoughe, Geovani Susanto, Caitlin Carter, Ryan Alexander Hallowell, Trisha Garcia and Mary Cordes for making this journey through the Master's program such a memorable one.

To my friends in college station : Abhishek Prakash, Abhishek Majumdar, Aparajita Sudan, Prathyusha Rao, Mahesh K Chandrashekhar, Shariful Islam, Mirza Riyaz and Akashchandra Pandey for always being there and supporting me throughout the thesis.

My friends from India : Soujanya Achar, Karthik Shankar, Amrut Bonageri, Shreyas Katta, Anurag Mylavarapu, Mohammed Obaid, Suramya Mishra, Suram Yashwanth, Aditya Kulal, Naga Sravan Kilaru, Sankeerth Kirthu, Sanjana S Thomas, Bhagya Hedge, Sumedh Hedge, Pratwish Shetty, Nowman Sayeed, Darshan Gowda for all the love and motivation despite the distance between us.

Finally, my parents, Panduranga G S and Yashodha R, for being my pillars of strength all my life and inspiring me to give my best every day.

## CONTRIBUTORS AND FUNDING SOURCES

### **Contributors**

This thesis was constantly monitored by Professor Mustafa Akbulut and Li Hao. This work was also supported by a thesis committee consisting of Professor David E. Bergbreiter from department of Chemistry and Professor M. M. Faruque Hasan of the Artie McFerrin Department of Chemical Engineering.

All other work performed for the thesis was conducted by the student.

### **Funding Sources**

Graduate research was supported by the Texas A&M Energy Institute.

## NOMENCLATURE

DMF	N, N- Dimethylformamide
$\text{SOCl}_2$	Thionyl chloride
HCl	Hydrochloric acid
$\text{SO}_2$	Sulphur dioxide
ATR	Attenuated Total Reflection
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning electron microscope
CA	Contact Angle

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## 1. INTRODUCTION

Oil spill has emerged as one of the major growing concerns in today's world. Deep beneath the surface of the earth, a large reserve of natural gas and oil is trapped. Over the years, cracks get developed on the reserves and some oil seeps out. This is a natural phenomenon that occurs occasionally, which cannot be controlled. We have witnessed how human activities like drilling of oil rigs have led to large quantities of oil being discharged causing a great deal of damage to the environment. There are multiple sources through which the spill can occur. The spill can occur during transportation of oil. Activities like drilling of oil through the rigs, wells and offshore platforms has also lead to oil being dispersed into water bodies. Oil spills that occur at sea are usually more damaging than those on land, as they can easily spread over long distances covering the water with thin coating of oil. As we know that oil is less dense than water, it floats on top preventing the sunlight from passing through it and also hinders the dissolution of oxygen in water. The layer of shiny substance that we observe on top of water is that of oil which makes it very hard for aquatic habitat to survive.

Chemical spills are another major hazard that threatens the environment. Chemical spills can involve the spillage of various chemicals such as benzene, toluene and other organic compounds. Benzene happens to one of the biggest contributor to environmental degradation through chemical spillage. A few examples of benzene spillage are "Benzene spill at ExxonMobil in Baton Rouge" and "Chemical spills in Texas due to Hurricane Harvey in Galena Park Facility of Magellan Mid-stream Partners. In the aftermath of

hurricane Harvey more than 22,000 barrels of crude oil spilled. Apart from crude oil, a large volume of chemicals and other toxic substances also spilled. During and after hurricane Harvey impacted Texas. Out of 22,000 barrels, 11,000 barrels of gasoline spilled from the Galena Park Facility of Magellan Mid-stream Partners. According to the coast guard, who has been responding to clean up efforts at refineries around Houston, around 365 tons of toxic chemicals that include Ammonia, Toluene, and Benzene have escaped into the surrounding areas. A similar incident was reported at the Exxon Mobil Chemical plant at Baton Rouge in the year 2012. 28,700 pounds of benzene was leaked in the form of Naphtha. All these spills will continue to degrade the environment and necessary steps would be needed to stop these spills.

## 1.1 Effects of spills

### 1.1.1 Birds:

Few species of birds escape the oil spills by sensing danger and taking precautionary measures to escape oil spills at sea. But few bird species that migrate are far less unfortunate. These birds tend to survive on primarily on fish caught from the sea during migration. They usually dive into the sea for food and are unaware of potential oil spills in the area. As they resurface, they end up being covered in oil. A small amount of oil can prove to be fatal for these birds as the oil sticks on their feathers and destroys the natural insulation and waterproofing of their bodies. It also makes it impossible for them to fly. When the bird desperately tries to clean its feathers with its beak, they tend to take in and swallow this oil which will adversely affect their health and may also lead to their

death. The oil spill due to an incident at Exxon Valdez killed between 250,000 - 500,000 of sea and migratory birds. It was studied that these spills majorly effected the migratory pattern and population because of the contamination caused in the areas where the birds would usually stop during migration for food.



Figure 1. Picture of a migratory fowl covered with oil. <sup>A</sup>

### 1.1.2 Marine Ecology:

The marine life is the one that is usually most effected by oil spills. At the initial stage, oil floats on the surface of the water preventing sunlight and also reducing the amount of oxygen being dissolved into the water. As time progress, these oil drip down and form more harmful substances, coating the fishes and plants disrupting their basic abilities. Corals that were stressed by oil were proved to be more exposed to epidemic diseases and their reproduction and growth rate also seemed to decrease drastically.

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<sup>A</sup><http://wildbirdsbroadcasting.blogspot.com/2007/12/deaths-of-birds-at-oil-spills-continue.html>

Even if some species of fishes were not affected directly, contamination of other organisms and plants affected their food chain. In some cases it was found that even though the effect may not occur immediately, there has been chronic, indirect and delayed effects on the organisms due to these spills. The Exxon Valdez oil spill in Bligh reef which released almost 42 million liters of crude oil killed over thousands of sea otters, around 3 dozen of whales, and thousands of other fishes in the region [1]. The oysters and shrimp population along the coast of Louisiana were adversely effected by the BP accident in Deepwater horizon. Billions of salmon fishes and their eggs were destroyed by the Valdez spill and the population is still recovering after almost 28 years since the incident occurred.



Figure 2. A dead starfish completely coated in oil floating on top. <sup>B</sup>

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<sup>B</sup>[https://greenliving.lovetoknow.com/Effects\\_of\\_Ocean\\_Pollution\\_on\\_Marine\\_Life](https://greenliving.lovetoknow.com/Effects_of_Ocean_Pollution_on_Marine_Life)

### 1.1.3 Economy:

During oil and chemical spills, valuable material and resources are lost. It is a great tragedy as it affects human beings directly and indirectly. It directly affects us by cutting off our access to resources that are used to power our lives. It also negatively affects the companies that have a huge stake in the processing of these resources (oil/chemicals). There is also loss of property in the form of oil rigs, tankers, ships, coastlines, offices etc. It indirectly affects us as it destroys our food supply and also causes the government to end up using large funds to clear out the damage done by the oil spill. The loss in oil also leads the country to import oil from other countries to make up for the deficit. Worker crews that are involved in the cleanup process tend to face health issues in life and their medical treatment is paid by the company or it becomes the responsibility of the government.



## 1.2 Major Oil Spills

Oil spills occurring from leakage at drilling rig to the spillage during transportation has caused major environmental impacts and has drawn the attention of all the countries to focus on curbing such incidents in the future. Some of the major oil spills that shock the world and drew the political attention worldwide are mentioned below.

### 1.2.1 Deepwater Horizon Oil Spill

The oil spill due to an uncontrolled blowout at Deepwater horizon (also referred as the BP oil spill), a drilling rig 66 km southwest of Louisiana coast along the Mississippi Canyon block 252 on the Gulf of Mexico<sup>[2]</sup> is one of the worst oil spills documented in the human history. The leak began on 20<sup>th</sup> April 2010 at the BP operated Macondo field when the oil rig exploded at around 9:45pm. The reason for the explosion was high pressure natural gas which rose through the drilling rig and expanded into the riser in an uncontrollable manner. During the explosion, there were 126 workers on board of which 11 were killed at the rig and almost 30 workers being injured.

It was estimated by the US government that around 4.9 million<sup>[3]</sup> (210 million gallons or  $7.8 \times 10^5 \text{ m}^3$ ) barrels of oil flowed into the gulf of Mexico over the course of nearly 3 months and spread out over a distance of 68,000 square miles i.e. 18,000 square kilometers. Even though BP initially estimated a leakage flow rate between 2,000- 6,000 barrels per day, it was later found that the actual initial flow rate was around 42,000 barrels per day. Multiple methods were used to curb the flow, but most of them failed as the technologies to prevent such spillages at the time were very limited. On 19<sup>th</sup> September

2012, they finally managed to seal the flow. A month after the spill began, oil started being washed up to the coasts of Louisiana, Alabama and Florida. After 2 years of the incident occurred, oil was found across the Louisiana coastline and the tar balls mixed with dispersants was constantly washed to the surface.

The spill majorly effected the aquatic and the marine life. Fishes like tuna, amberjack and many other aquatic species developed deformities. The tourism and fishery industries were the most effected as they could not access the beaches due to contamination.

Initially, robots were used to close the blowout preventer but was unsuccessful due to the extent of the damage caused and it was hard to gain control at depths of 5000 ft under water. The containment dome (weighing 125 tonnes) was used to trap the seeping oil and pump it to the surface. Even this method failed as the methane being released combined with water to form chunks of methane-hydrate that clogged the flow through the pipes. First, BP applied 1900 gallons of oil dispersant to mitigate the slick that makes the oil break up and sink below the surface. As per the reports a total of 1,840,000 gallons of dispersants was used which lead to massive clouds of bedded oil hovering at mid depths threatening a vital underwater rain forest (Desoto Canyon).



Figure 3. The drilling platform of the Deepwater Horizon after the explosion. <sup>C</sup>

A study conducted showed that these dispersants contained hazardous chemicals that were carcinogenic and added to the environmental pollution. In the beginning, there were 47,000 people and 7,000 vessels were deployed to control the situation which was funded by BP. After 3 years of the incident, it was reported that almost 1000 people and some vessels were still working on containing the oil. The oil skimmers or brooms was used to contain the flow and to absorb the oil; spread out covering a distance of 1,300 km. However they were not as efficient as they allowed the oil escape once their absorption capacity was reached. Their efficiency dropped even further in the presence of waves, as they it allowed the oil to escape from above or below.

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<sup>C</sup><https://www.nytimes.com/2017/12/28/us/trump-offshore-drilling.html>

After multiple failed attempts, a replacement blowout preventer was setup and cement was pumped from the surface to seal the leak. Finally on September 19<sup>th</sup>, the well was finally closed and the government confirmed it was taken care of. Even after many years of the incident, minor leaks are still being reported and are adversely affecting the gulf region. BP had to spend over 55 billion dollars for the damage and the clean-up procedures.

Studies show that oil is still scattered in patches across more than 1,200 square miles of seabed. Tar balls still continue to wash ashore. According to the data provided by the shoreline assessment teams, 1,773 km of shoreline was effected<sup>[4]</sup>.

### 1.2.2 Hurricane Harvey

Hurricane Harvey was one of the deadliest hurricanes that hit North America and nearby smaller countries. It was a Category 4 storm that made several landfalls beginning on August 25<sup>th</sup>, 2017. It disrupted the life of over 15 million people across Texas, Tennessee, Mississippi and Louisiana. The total losses it caused is estimated to be around 125 billion US dollars. It killed 88 people overall and injured thousands. In Houston, Texas 1/3<sup>rd</sup> of the city was submerged under water. A total of 200,000 homes were damaged with 13,000 of them completely destroyed. 40,000 people in Texas had to be shifted to the shelter. After 20 days of the landfall of the hurricane Harvey, over 4,000 were without power. More than a million vehicles were damaged and deemed unrepairable. It hit around 850 wastewater facilities in the area that disrupted the water

purification process and reducing the access to clean drinking water for the people. As most of the refiners are generally constructed near the coast, the gasoline prices shot up from \$2.35/gallon to \$2.49/gallon<sup>[5]</sup>. When it came to the rainfall received, it went down as one of the heaviest rainfall ever received in a 1,000 years. The arrival of hurricane Irma, weeks after the landfall of hurricane Harvey added to the losses. Irma was categorized as level 5 storm, which is recorded to be the worst Atlantic storm ever. Luckily Irma did not make a landfall in Miami. As per the insurance companies if Irma would have hit Miami, it would have further increased the losses 175 billion US dollars. According to the US coast guards, over 22,000 barrels of oil and chemicals were spilled across Texas, with millions of tons of other toxic substances<sup>[6]</sup>.

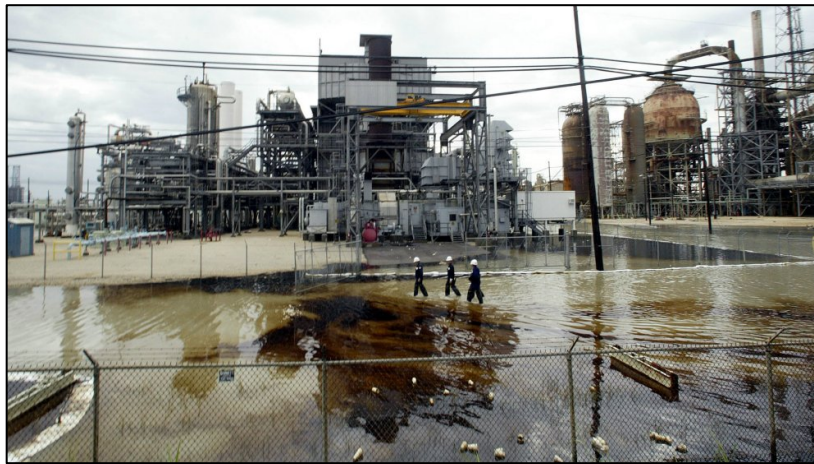


Figure 4. Workers at a Texas refinery inspect an oil spill after it was flooded by Hurricane Harvey.<sup>D</sup>

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<sup>D</sup><https://www.motherjones.com/environment/2017/08/this-should-obvious-but-just-in-case-hurricanes-and-oil-country-are-a-recipe-for-disaster/>

EPA reported one of the major release of carcinogenic chemicals occurred at Valero Energy Partners, Houston. As per the initial emission report submitted by Valero, it estimated a leak of 55,000 pounds of benzene and 212,000 lbs. of 1,3- butadiene which is cancer causing. They also reported over 5.9 million lbs. of emission caused due to the shutdown, startup and gap in the production<sup>6</sup>. Later it was found that these values were underestimated by Valero and actual figures were released later on. Further reports also indicated that a total of over 1 million pounds of 7 toxic compounds (including benzene) escaped into the environment. A month after the landfall of the hurricane, the tests reported a benzene level of 324 parts per billion, double the standard limit which is set at 180 parts per billion<sup>[7]</sup>.

### 1.3 Existing solutions to combat spills

Removal of oil from water bodies is a very important issue due to its effects on the environment. Due to the difference in densities, oil floats on top of water and initially spreads horizontally to form a slippery and a smooth layer called slick. This reduces the area available for the atmospheric oxygen to dissolve in water which adversely effects the aquatic and marine life. Hence, these oils and chemicals needs to be removed on priority before they cause further damage. Some of the commonly used technologies to combat oil spills are listed below.

### 1.3.1 Boomers

Boomers or booms is a barrier that floats on top of the water which is temporarily used to contain oil from spreading. They act as a physical barrier between the oil layer and the unaffected surface water. In oil recovery mood, the booms are carefully moved closer and closer, when a collecting device receives the oil and pumps it into a vessel or oil collector<sup>[15]</sup>. There are different types of boomers available today with special characteristics like fire resistance, flow resistance tendencies and different grade materials. Oil fence is also a kind of boomer which has higher vertical length and is used in places where there are waves. The boomers compliment the skimmers by concentrating the oil in a particular region, thus enhancing the oil recovery<sup>[16]</sup>.



Figure 5. Boomers being employed to prevent the oil from spreading after the incident at Deepwater Horizon in 2010. <sup>E</sup>

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<sup>E</sup><https://sites.google.com/a/udel.edu/cwagner-apec480/project-5-research-proposal>

### 1.3.2 Skimmers

A skimmer is one of the mostly commonly used device to combat oil spills. The mouth of the skimmer collects the oil from the water surface which is taken into the recovery tank. The success of a skimmer depends on the thickness and the type of oil spill. The combination of a skimmer and booms are very effective when the water is calm, i.e., there is no waves generated <sup>[17]</sup>. Thus they are commonly used in industrial setups and large water bodies, where the water below remains stagnant. In presence of any solid waste debris present in oil, there are high chance that it can clog the flow of oil into the skimmers and thus damage them. Lately, oleophilic skimmers are becoming fairly popular that reject the entry of water, enhancing the recovery efficiency <sup>[15]</sup>.



Figure 6. Skimmers along with booms used to contain and collect oil. <sup>F</sup>

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<sup>F</sup><http://blog.nus.edu.sg/lucastange3246/2015/03/22/analysis-alternative-ways-to-clean-oil-spills>



### 1.3.3 Oil Dispersants

Oil dispersants are used to break the complex oil structure into smaller molecules, with an idea that it will be easier for aquatic bacteria's and microbes to break them down. This method does not remove oil from water<sup>[16]</sup>. They are usually made up of emulsifiers that assist in dispersing the oil into smaller droplets. They are generally sprayed into the water bodies through air crafts or by boats. They are mostly used to remove the traces of oil, after other remediation technologies are employed. The most common dispersant is Corexit, which was used during the incident at Deepwater horizon. The trade-off of using this method is it depends on natural degradation of oil whose time frame is still unknown. The dispersants used earlier were very harmful for the environment, but today we have addressed that issue by making the dispersants more environment friendly<sup>[14]</sup>.



Figure 7. C-130 dropping dispersant (Corexit) in the gulf after the Deepwater Horizon incident. <sup>G</sup>

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<sup>G</sup><https://www.popsci.com/science/article/2010-05/how-do-oil-dispersants-work>

#### 1.3.4 Controlled or In situ burning

In situ burning is one of the oldest techniques used to combat oil spills. Development of fire proof brooms has helped in collecting of oil and employment of this technology<sup>[17]</sup>. This method can remove oil from water very effectively, efficiently and in a very short duration. When employed in a are of 10,000m<sup>2</sup>, the oil can be burnt at a rate of 2000m<sup>3</sup>/hr. with efficiency above 90%<sup>[9]</sup>. Once the oil has been burnt, the brooms can be used to collect the remaining tar and other debris reducing their harmful effects. Even though this method seems to successfully remove oil from water, there is a possibility of fire going out of control and harming human life, aquatic animals that live close to the surface and damage property. The burning of oil also produces harmful and carcinogenic gases that will have adverse effect on nature and the surrounding<sup>[16]</sup>.



Figure 8. Black smoke appearing as a result of controlled burning of surface oil during the 2010 Deepwater Horizon oil spill. <sup>H</sup>

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<sup>H</sup><https://www.npr.org/2017/03/21/520861834/researchers-test-hotter-faster-and-cleaner-way-to-fight-oil-spills> : US Coast Guard

### 1.3.5 Bioremediation

This method involves use of microbes to degrade oils and chemicals to remediate their environmental impact. These micro-organisms accelerate the decomposition process exponentially and breaking them into simpler form (to carbon dioxide, water) with generation of heat. There are 2 types of bioremediation: (a) Bio-stimulation where micro-organism are grown by the additions of necessary nutrients; (b) Bio-augmentation where new micro-organism are added to degrade the oil<sup>[15]</sup>. The characteristics of the microbes chosen depend on the properties of oil it will be used to treat. Phosphorus and nitrogen based fertilizers are mostly commonly used to promote the growth of micro-organisms that break the oil down. Comparing the environmental impacts of all the existing technologies, bioremediation is a much safer remediation technique<sup>[17]</sup>.

### 1.3.6 Absorbent materials

Lately, the use of highly hydrophobic and oleophilic materials have taken over all other remediation technologies. It is cleaner, cost effective and the oil (which has economic significance) can be used for various activities. The absorbents can be made from wide range of materials including organic, synthetic and inorganic materials. Even though most of these materials is still in research stage, the commercial available ones absorb oil up to 10 times its weight.

The synthetic absorbents which include plastics, sponges, polyurethane, nylon, etc., can absorb oil up to 50 times its weight, but regeneration is not so effective<sup>[15]</sup>. However, it is emerging as one of the best technologies to combat the issues with a very less effect on the environment at the same time very cost effective.

## 2. PROPOSED IDEA

The proposed idea involves synthesizing graphene based porous structure to adsorb oil/ chemical solvents from water. The material is synthesized using graphene pellets and cotton that are easily available. The cotton used in the process is biodegradable, which is an added benefit with respect to the environment. The proposed methodology has many advantages, one of them being highly cost effective. This is because Graphite pellets are easily available and they less expensive. The proposed methodology also helps in producing a product that has the capability of being reused many times after using it for oil/chemical spill. The final synthesized product is hydrophobic in nature and this allows it to adsorb only oil from water, increasing the efficiency of the material.

The thesis was mainly divided into four parts:

- The first part deals with literature survey to find existing solutions that address oil spills and then, to come up with a novel technique that addresses the problem in a better way when compared to existing solutions.
- The second part of the thesis was to develop that required materials and characterize them.
- The third part of the thesis was to run tests on the synthesized material to estimate effectiveness and efficiency when compared to existing solutions.
- The fourth part was to find long term stability and durability with respect to chemistry and temperature.

### 3. LITERATURE SURVEY

The main idea was to develop cost effective, eco-friendly, reusable material that could be effectively used to remove oil and non-polar solvents from water. The absorption capacity was also considered with respect to already existing technologies.

The main reason for choosing cotton as a base material on which graphene could be attached was that only around 10% of the raw initial weight gets reduced after processing the raw cotton. After all the proteins, wax, twigs and other impurities are removed, we obtain pure cellulose. The purification process of cotton is simple and economical. The cellulose cotton structure has high strength, absorbance capacity and durability. Every cotton fiber is made up of 20 to 30 layers of cellulose bound in a series. These fibers can be separated into flat or twisted or into different shapes<sup>[8]</sup>.

There is abundance of cotton available in the US. The US has emerged as the third largest producer of cotton (after India and China) and fifth largest consumer in 2017/2018.

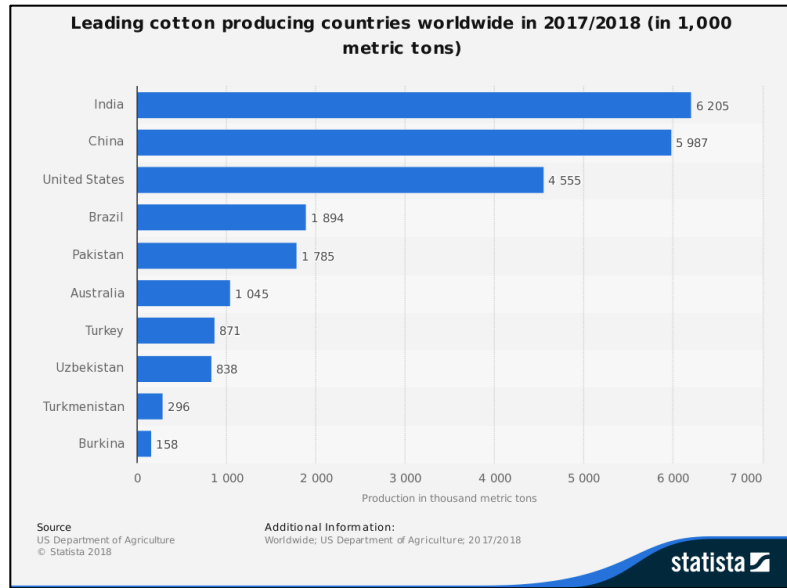


Figure 9. List of leading cost producing countries. <sup>1</sup>“Reprinted from [Statista : Leading cotton importing countries in 2017/2018 (in 1,000 metric tons)]”

Moreover, US is the largest exporter of the cotton in the world. The amount of cotton exported by the US accounts to approximately 40% of the global total. In 2017/2018, US produced 4,555 metric tons of cotton (shown in the figure 9). In terms of production by states, Texas tops the list with production more than 42% of the country’s total cotton production which is followed by Georgia at 18%. In 2017, over USD 1.7 billion worth of cotton was produced in Texas. The reason for cotton mainly being grown in Texas is that it comes under the ‘cotton belt’ where the plantations were established in the 19<sup>th</sup> century. The figure below shows that Texas is the largest producer in the United States with a production of 8,830 thousands bales i.e., 1.923 million metric ton.

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<sup>1</sup><https://www.statista.com/statistics/191896/leading-cotton-importing-countries/>

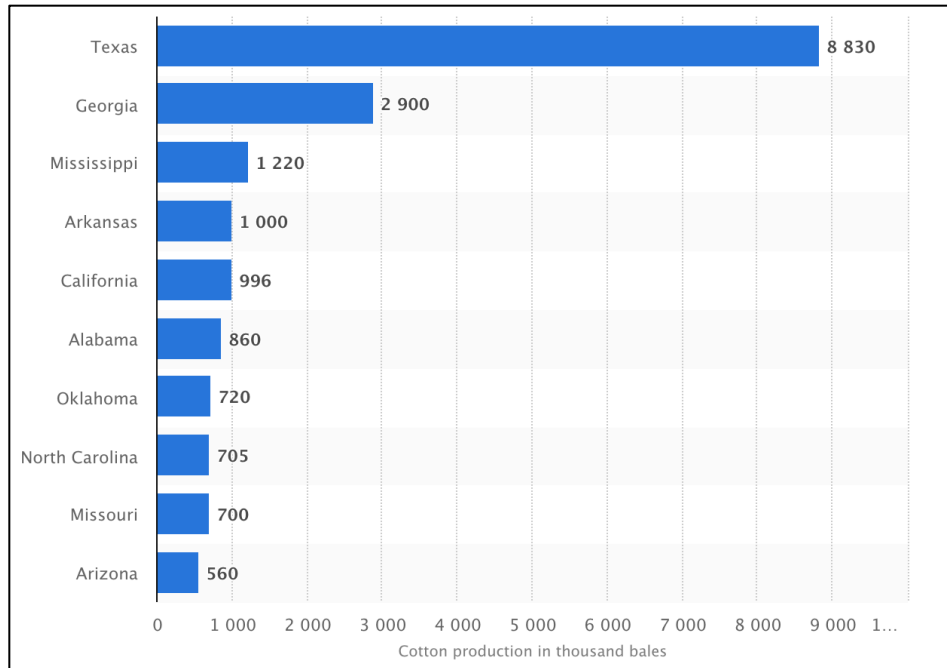


Figure 10. The largest cotton producing states in the US in 2017-2018.<sup>1</sup> “Reprinted from [Statista : Leading cotton importing countries in 2017/2018 (in 1,000 metric tons)]”

Considering it’s the environmental impacts of cotton, it is an excellent material which is eco-friendly fiber through its entire process. It is renewable, biodegradable and sustainable which are the major characteristics we are looking for in the materials for the future.

As per the Annual report by the United States Department of Agriculture, the average price of cotton ranged between 66.24 US cents to 75.75 US cents per pound between August 2016 to July 2017<sup>[10]</sup>. Today the cotton prices are around 0.75<sup>[11]</sup> US dollars per pound making it a very economical raw material.

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<sup>1</sup><https://www.statista.com/statistics/191896/leading-cotton-importing-countries/>



The other major material required was graphene which is prepared by exfoliation of graphite. The basic properties of graphene is that it is flexible, it is single layer thick making it thin and also very light in weight. It is also very strong in nature and used in variety of applications because of its thermal, electrical, optic and mechanical properties.

Graphite is a crystalline allotrope of carbon whose structure consists of hexagonal carbon atoms (graphene) stacked in a horizontal manner. Graphite is a naturally occurring mineral and is obtained in the form of coal. It is greasy and leaves a black mark. Graphite in its natural form is very stable.

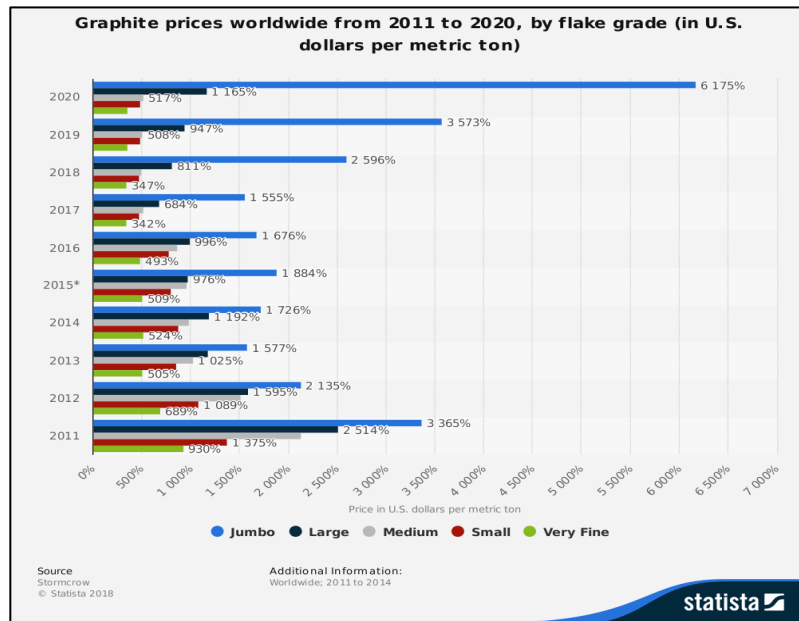


Figure 11. Global graphite flake prices from 2011 to 2020 (USD per metric ton).<sup>K</sup>“Reprinted from [Statista : Graphite prices worldwide from 2011 to 2020, by flake grade (in U.S. dollars per metric ton)]”

<sup>K</sup><https://www.statista.com/statistics/452304/graphite-prices-worldwide-prediction-by-flake-grade/>

Due to the defects developed during the exfoliation of graphite, graphene develops carboxylic and hydroxyl groups making graphene reactive compared to elemental graphite. The purity and the size of the flakes are the major factors on which the graphite prices depend on. Graphite with large flake size<sup>[12]</sup> (above 80 mesh) and higher carbon content (+94%) have the highest price. Today a medium flake graphite (between 50 mesh to 80 mesh) and high carbon purity (+94%), it costs around 500 US dollars per metric ton, i.e., 0.23 US dollars per pound.

The other major component of our material was diamine which was the linking agent to connect graphene to cellulose. Amines naturally occur in nature in the form of amino acids which are found in certain plants. The decay of fishes in the ocean, release amino acid which gets broken down into amines. Through studies it has been found that low molecular weight amines are not toxic to the environment. Since diamine in our procedure is mainly chemically attached to graphene and cellulose, it will not have any impact on the surrounding environment.

## 4. METHODOLOGY

### 4.1 Materials

Cotton balls (100% pure with good middling grade) was obtained from Wal-Mart stores, Inc. Thionyl Chloride (98%, SG = 1.64,  $M_w = 118.96 \text{ g.mol}^{-1}$ ) was procured from TCI chemicals (CAS 7719-09-7, Portland, OR). Since it was moisture sensitive, it was packed thoroughly to avoid contamination and placed under the hood. It was carefully handled under supervision because of its corrosivity and health hazards. N, N-Dimethylformamide (>99.5%, MW= 73.10) was obtained from TCI chemicals (CAS 68-12-2, Portland, OR). N, N- Dimethyl-1,3-propanediamine (99%) used for the amination of cellulose was obtained from Alfa Aesar (CAS 109-55-7). (Tridecafluoro-1-1,2,2-Tetrahydrooctyl) Trichlorosilane was procured from Gelest, Inc (Lot No. 9A-34877). Graphene Oxide Aqueous solution (>99%) with a concentration of 1g/L was obtained from graphene supermarket. Graphite flakes with +100 mesh (150 microns or more in lateral size) with a purity of 99.9% was obtained from graphene supermarket. Isopropyl alcohol (IPA, 99.5%, ACS grade) were purchased from Macron Chemicals (in Center Valley, PA). Hydrazine Monohydrate (98+%, CAS 7803-57-8) was obtained from Alfa Aesar (Ward Hill, MA). Deionized water was used for all the experimental procedures.

## 4.2 Preparation of graphene coated cotton

### 4.2.1 Functionalization of Cellulose

#### 4.2.1.1 Chlorination of Cellulose (COTTON) with Thionyl Chloride in DMF

The chlorination was achieved by allogenic derivative synthesis. Because of its electronegativity, chlorine was preferable for the attack on the hydroxyl group of the cotton cellulose. This chlorine group is more reactive than the original hydroxyl group. For the chlorination of cellulose, DMF was found to be the suitable solvent as it is an acid scavenger and also facilitate reaction. The main function of DMF included (1) It helped in increasing the accessibility of the cotton cellulose by acting as a swelling agent and also increasing the extent of the reaction of the hydroxyl groups with the chlorine ion; (2) It also acts in diffusion of chlorine ion by taking it to the deeper reaction sites of the cellulose fiber and acts as a carrier. The moisture in the cellulose fiber was not extracted by heating as the removal of water from the cellulose by heat would result in the collapse of fiber, making it less accessible to the solvents<sup>[18]</sup>.

The reaction was carried out at room temperature as it was exothermic. The formation of cellulose formate that is favored at higher temperatures were avoided by constantly monitoring and periodic stirring. During the reaction of thionyl chloride and DMF, acids are produced which in a long run might damage the cellulose structure and lead to degradation. This will result in better result and much better tenacity. According to a study it was found that, rate of reaction at 25°C is slower when compared to the reaction at 100°C. For 50% chlorination of the cellulose, the sample at 25°C should be reacted for 28 hours whereas at 100°C the reaction can be achieved in 1.5 hours<sup>[18]</sup>.

However it might lead to the formation of complexes and weaken the cellulose. The reaction was allowed to continue until it turned to pale yellow in color. If the reaction is allowed to continue further, it will lead to reduced chlorination and conversion into dark yellow or brown color indicates the side reaction leading to the formation of dehalogenation and degradation. As the concentration of the chlorine increases, the resistance to flame also gets better. It was found that by reaction at room temperature, the fibrous structure of cellulose is better retained. The final product has white to pale yellow color.

The reaction was carried out in a 200ml conical flask. Initially, the experiment was carried out by taking 1.05g of cellulose in 50 ml of  $\text{SOCl}_2$  and 50ml of DMF. The reaction was carried out at  $60^\circ\text{C}$  or 353K. Nitrogen was constantly purged to remove  $\text{SO}_2$  from interfering and to avoid oxidation. The reaction was very exothermic. Within an hour the cellulose sample was completely dissipated into a slurry form. The reaction was halted and the sample was allowed to cool. The sample then turned into a solid, which was then washed with DMF. On washing, the sample completely dissipated, which was not the desirable product. The procedure was then modified to avoid the formation of cellulose formate which initially looked like a slurry, then became brittle on drying.

According to the modified procedure, 1.04g of cotton was taken in a conical flask. The cellulose cotton yarn was pretreated by soaking it in 21ml of DMF for 5 mins. 2ml of Thionyl chloride ( $\text{SOCl}_2$ ) was added to the flask, under the hood. The concentration of  $\text{SOCl}_2$  to DMF was maintained between 2-20%. There was instant release of a pungent gas, i.e., Sulphur dioxide and the temperature of the flask increased. This showed the

reaction was spontaneous and exothermic. The reaction was allowed to carry out for 24 hours and was constantly stirred. The color of the cotton changed from white to dark yellow during the course of the reaction. The Ph of the sample was 1, indicating that acid formation or generation of hydrochloric acid (HCl).

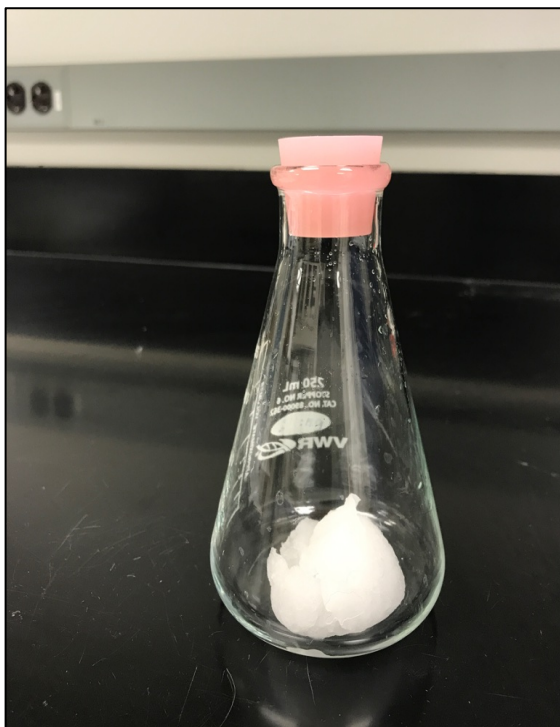


Figure 12. Cotton soaked in DMF.



Figure 13. Cotton treated with  $\text{SOCl}_2$  and DMF.

After the reaction, the sample was initially washed with ice and then rinsed with water for 15 mins unless all the Hydrochloric acid produced was washed away i.e., unless the Ph of the sample increased to 5 or above. The sample was then put in the oven for drying and remove all the moisture.

#### 4.2.1.2 Amination of cellulose

After drying in the oven for 24 hours to remove the moisture. 0.5460g of chlorinated cellulose was taken in a 20 ml glass veil. It was then treated with 10g N,N-Dimethyl-1,3-propanediamine at 90°C for 12 hours. It was made sure there was enough diamine to immerse the cotton. When the diamine reacts with chlorinated cellulose to replace the chlorine with the diamine. The addition of the diamine into the cellulose increases the amount of carbon in the structure. Once the reaction was complete, the sample was rinsed with water to remove HCl produced which was a byproduct of the reaction. The sample was then placed in the oven to remove the water content.

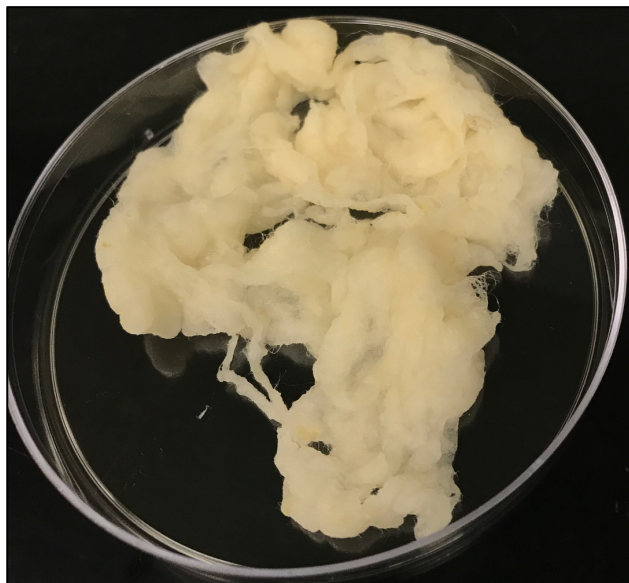


Figure 14. Diamine-cellulose after being rinsed with water.

#### 4.2.2 Preparation of graphene in DMF

10.176g of DMF was taken in 20ml glass veil. Then 0.202g of graphite was added to it. The sample was then exfoliated by ultrasonication by using an ultrasonic probe (SJIA-2000W, Syclon Electronic Instrument Comp., Zhejiang, China) of high intensity. The sonication was carried out for a total of 4hrs, in a cycle of 30 mins each at a power of 400 W. As the sonication process generated a lot of heat, the veil was placed in an ice bath and the process was carried out. Next, the sample was allowed to sit undisturbed for 24 hours to let large graphite particles to settle down. Then the top half of the sample was removed carefully using a syringe and placed separately.

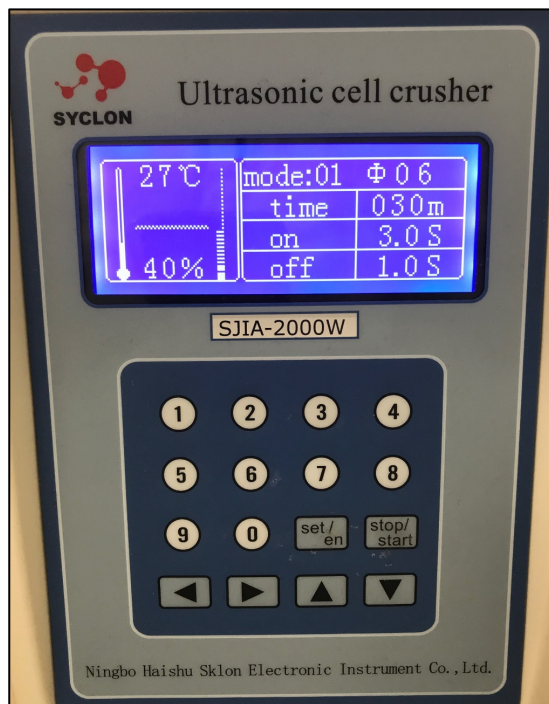


Figure 15. Ultrasonic cell crusher used for probe sonication of graphite to graphene.

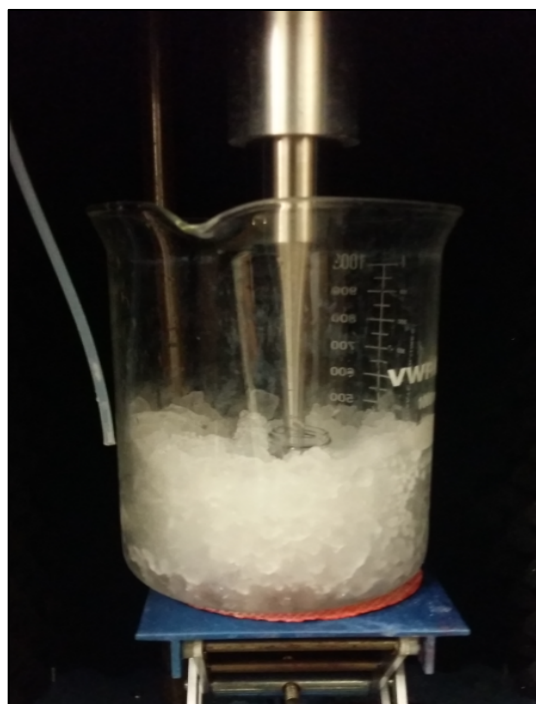


Figure 16. Ice bath setup to control the heat produced during sonication.



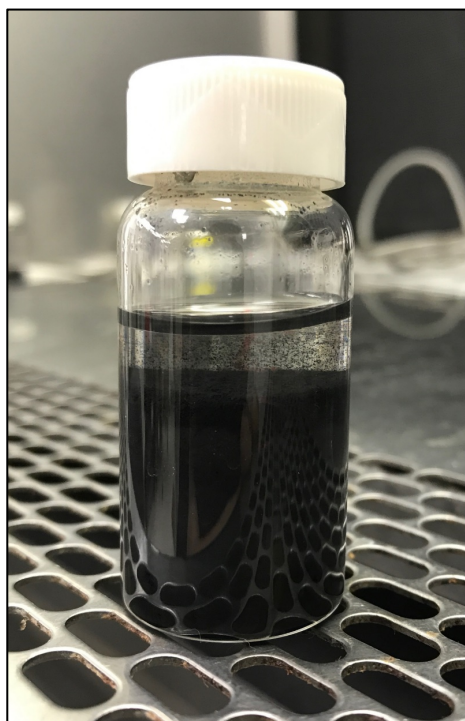


Figure 17. Graphene in DMF after 4 hours of sonication and keeping it undisturbed for 48 hours.

#### 4.2.3 Attachment of Graphene to Cellulose

In this step, 10g of graphene in DMF was taken in a 20 ml glass vial. 0.219g of diamine-cellulose was added to it. The sample was shaken well and heated for 12 hours at 92°C. The purpose of heating the sample was to further increase the hydroxyl group and carboxylic group on the surface of graphene, which will act as an acid group. This will in turn react with amine groups from the cellulose diamine that are basic in nature. In this way we will be able to chemically attach graphene to cellulose. After the completion of

the reaction, the sample was washed with Isopropyl alcohol more than 3 times to completely remove DMF and excess graphene.

Next, the sample was placed in the oven to remove Isopropyl alcohol. The sample was then characterized and the absorption experiments were performed.



Figure 18. Graphene coated cotton after 12 hour reaction of DMF in graphene and diamine cellulose.



Figure 19. Graphene coated cotton after cleaning with Isopropyl Alcohol.

### 4.3 Expected Reaction

#### STEP 1 : Chlorination of Cellulose

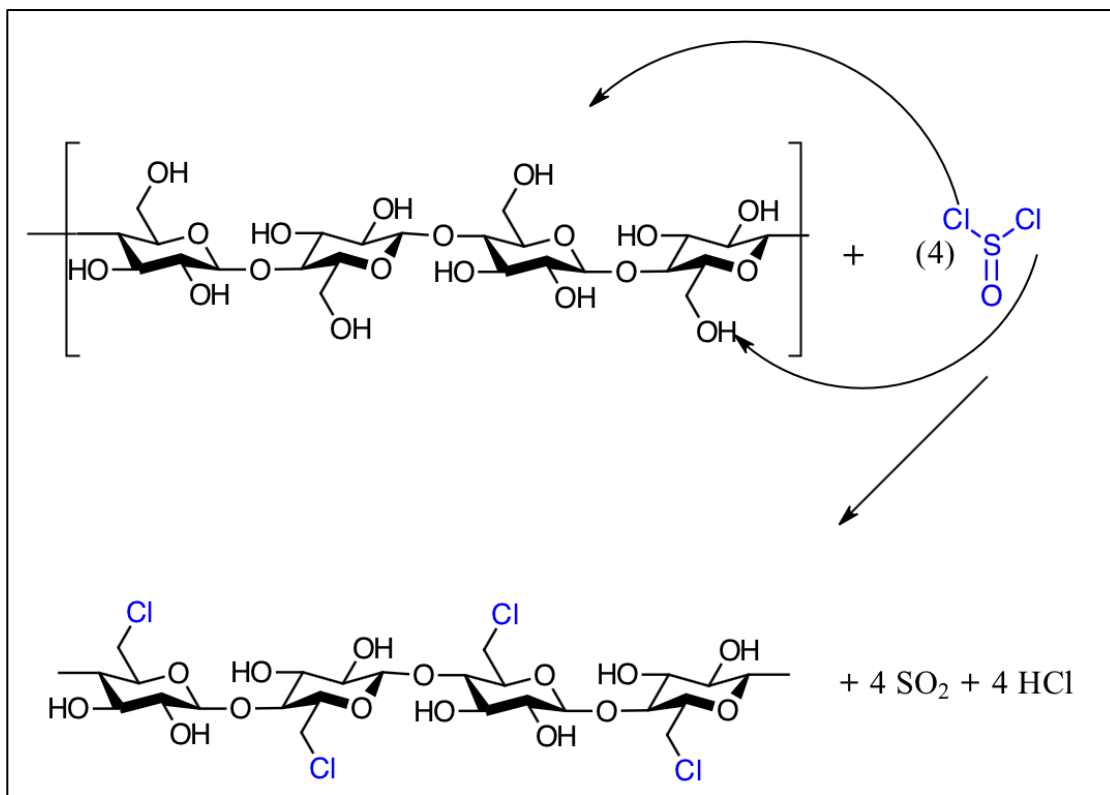


Figure 20. Electrophilic substitution reaction – Chlorination of cellulose.

Sulphur has a partial positive charge as it is bonded to 3 electronegative elements (oxygen and chlorine) which pull the electron towards them. Oxygen from the hydroxyl group, has a partial negative charge. Therefore it is attracted towards Sulphur and the oxygen double bond breaks. This oxygen uses the lone pair, forms a double bond and expels the chlorine atom. Chlorine as we know is a good leaving group, comes in performs a back attack and expels the oxygen atom.

This is an SN 2 mechanism and will give inversion of stereochemistry. Oxygen is much more electronegative than chlorine, so it prefers to form double bond and expel the single bond chlorine atom. Since oxygen is protonated it can form an ion pair. With this oxygen can form double bond and expel chlorine same as before. This will result in the formation of chlorinated cellulose, Sulphur dioxide and hydrogen chloride.

Step 2 : Reaction of Chlorinated Cellulose with Diamine

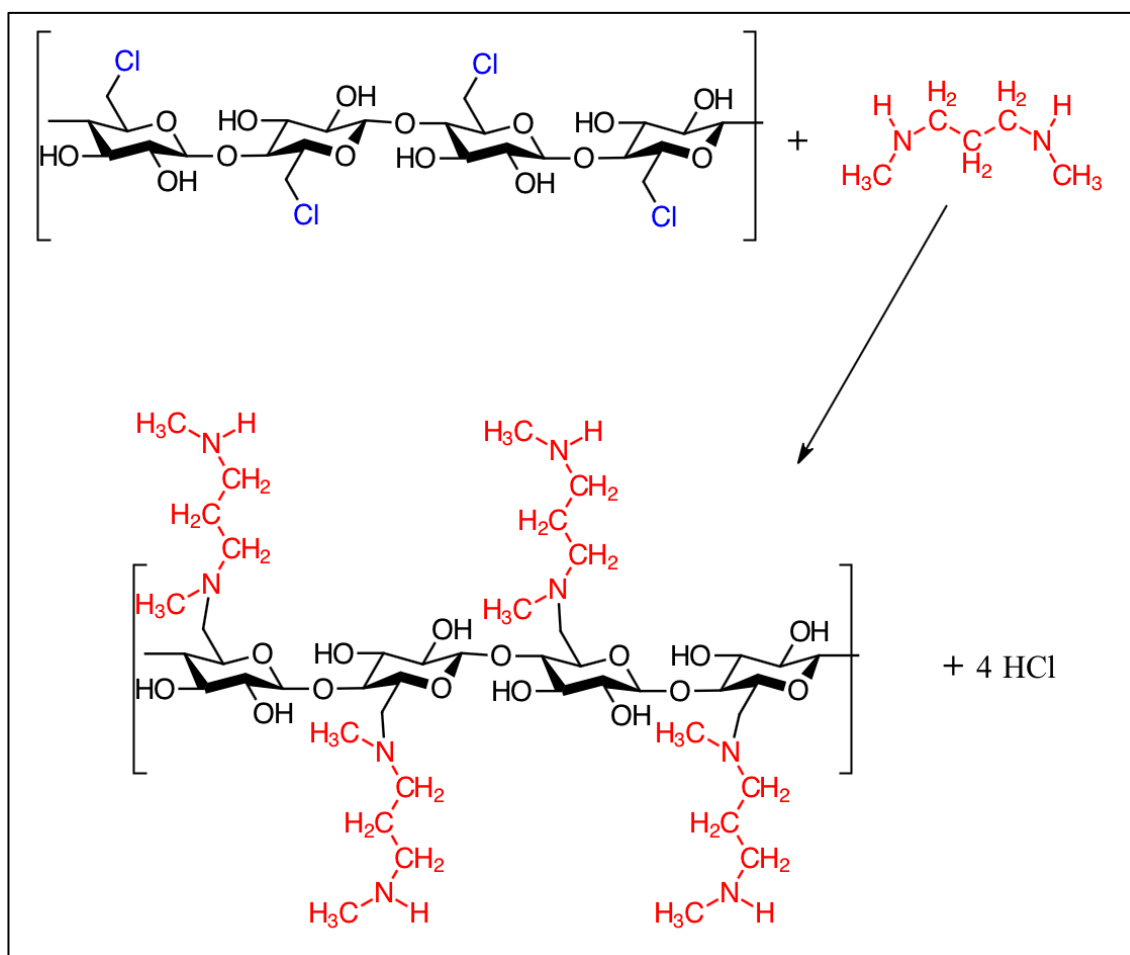


Figure 21. Nucleophilic Substitution Reaction – Chlorinated cellulose with diamine .

An alcohol has a strong basic leaving group and cannot be displaced by a nucleophile, which makes alcohol not undergo a nucleophilic substitution reaction. This makes the chlorination step essential. In the above reaction, the nucleophile (i.e., the amine group) displaces the leaving chlorine group. The chlorine group is more reactive than the original hydroxyl group on C-6 group. The attachment of diamine increases the growth of carbon in the structure. The methyl group present in the diamine chain, also enhances the desired hydrophobic characteristics of the cellulose.

Step 3 : Attaching graphene to cellulose

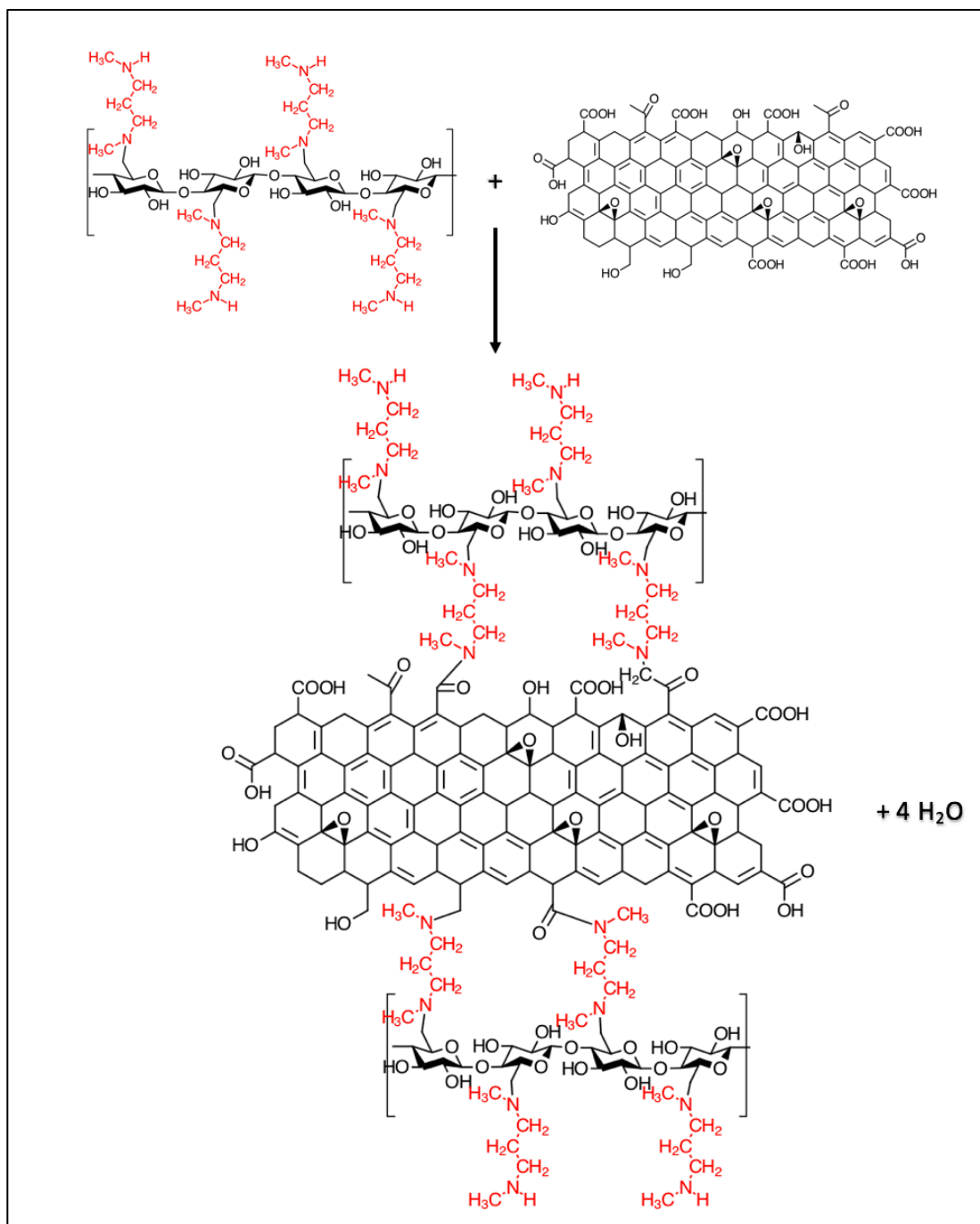


Figure 22. Acid- base condensation reaction.

The hydroxyl and carbonyl group react with the amine groups to attach with graphene and form water molecules.

#### 4.4 Oil and organic solvent removal test

In this experiment, 8 different types of oils and organic solvents which vary in densities. The oils and solvents used to measure the absorption capacity of graphene coated cotton include pump oil, crude oil, paraffin oil, dodecane, mineral oil, hexane and toluene. The absorption test was carried out by submerging the sample in oils and organic solvents for different durations. To ensure the stability and to check the reusability, the absorption experiment was repeated for 10 cycles. The experiment was simultaneously performed with pure cellulosic cotton to compare the absorption and hydrophobicity results. The absorption capacity,  $R$ , was obtained from the measurement of weight of graphene coated cellulose before and after the oil adsorption and by calculating their weight ratios that can be represented by  $R = W_{saturated\_cotton}/W_{dry\_cotton}$  where  $W_{saturated\_cotton}$  = Weight of graphene in cellulose after oil adsorption and  $W_{dry\_cotton}$  = Weight of graphene in cellulose before adsorption. The procedure was carried out carefully minimizing all the possible errors and the weights were noted accurately.

## 5. RESULT AND DISCUSSION

### 5.1 Characterization of Graphene coated cellulose

The infrared spectra of cellulose and its modifications were obtained by ATR-FTIR analysis spectroscopy. By detecting the functional group present, FTIR helps us in determining the chemical structure of the molecules. All the samples were carefully dried before the ATR-FTIR analysis, to avoid the interaction of the water molecule<sup>[19]</sup>.

The figure 20 compares the ATR-FTIR spectra of pure cotton cellulose, chlorinated cellulose, diamine cellulose and graphene coated cellulose. In the case of bare cotton cellulose, the key characteristic absorption bands were located at 3400 and 3300  $\text{cm}^{-1}$  which is attributed to the vibrations of OH group and the side chains (-CH-OH). Another crucial vibration is spotted in the spectrum of cellulose which appears around the wavelength of 2900  $\text{cm}^{-1}$ <sup>[19]</sup>, which corresponds to the stretching vibration of the methylene group. The stretching vibration peak in the region 3000 to 2800  $\text{cm}^{-1}$ , shows the existence of -CH group<sup>[22]</sup>.

The -OH bending vibration spectrum for the cotton cellulose can be attributed to the peak value at 1639  $\text{cm}^{-1}$ . Several bands appear that shows the deformation of the primary and secondary -OH (hydroxyl) bending that appears between the spectrum 1500 and 1200  $\text{cm}^{-1}$ . The C-O stretching vibration was observed at 1100  $\text{cm}^{-1}$ . The vibration at 1640  $\text{cm}^{-1}$  can be assigned to the C=C stretching bond<sup>[21]</sup>.

The appearance of the C-Cl groups were confirmed by the appearance of two new vibrations at 753 and 709  $\text{cm}^{-1}$ <sup>[22]</sup>. These bands corresponded to the carbon – chlorine



stretch, thus confirming the effectiveness of the chlorination of cellulose [21]. Due to the substitution of the hydroxyl group (-OH) on carbon 6 after the reaction with  $\text{SOCl}_2$ , there was a decrease in the intensity of the peak bands from 1500 to  $1200\text{cm}^{-1}$ . This confirmed that the chlorination process of cellulose was successful (confirmed by the reduction in -OH group and increase in C-Cl group).

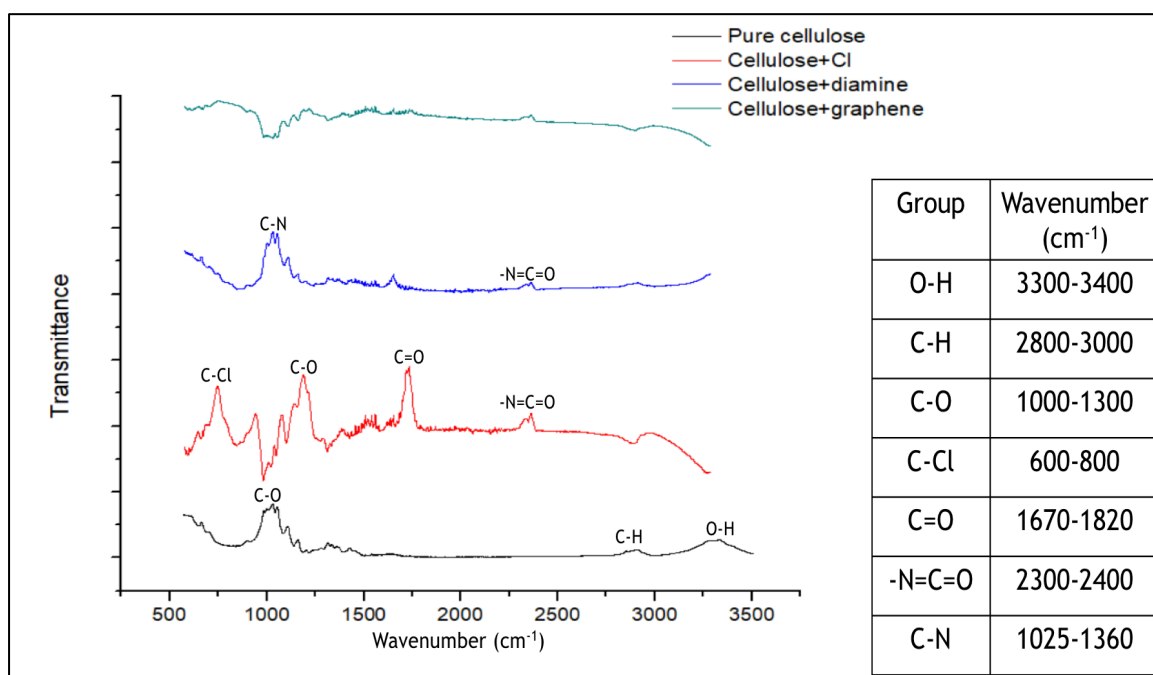


Figure 23. ATR-FTIR analysis spectra of pure cellulose, chlorinated cellulose, diamine treated cellulose and graphene coated cellulose

The spectrum 3 gives the peak value after the reaction with diamine. The peak between 1250 and 1020  $\text{cm}^{-1}$  confirms the presence of C-N stretch (aliphatic amines). The peak at 1655  $\text{cm}^{-1}$  is attributed to N-H bond (primary amine) <sup>[20]</sup>. It is also noted that, the bands present in the spectrum of chlorinated cellulose from 753 and 709  $\text{cm}^{-1}$ , reduces in intensity but does not disappear completely confirming the presence of chlorine even after the reaction with diamine as they were not completely immobilized on reaction with the diamine <sup>[21]</sup>.

## 5.2 Morphological characterization of Graphene coated cellulose

Scanning Electron Microscope (SEM) was successfully employed to study the morphological evolution of cotton before and after reacting with graphene in DMF. The raw cotton is very porous and is made up of a 3D network. As shown in figure 24 (a), the initially untreated cotton has an interconnected network architecture. After coating with graphene, the cotton cellulose still retains the interconnected 3D network and the highly porous structure. The graphene has been only coated on the surface and has not formed any agglomerates clogging the pores. Random but mostly homogeneous distribution of graphene was observed. This open network is very crucial for adsorption, uptake of organic solvents and maximizing the flow.

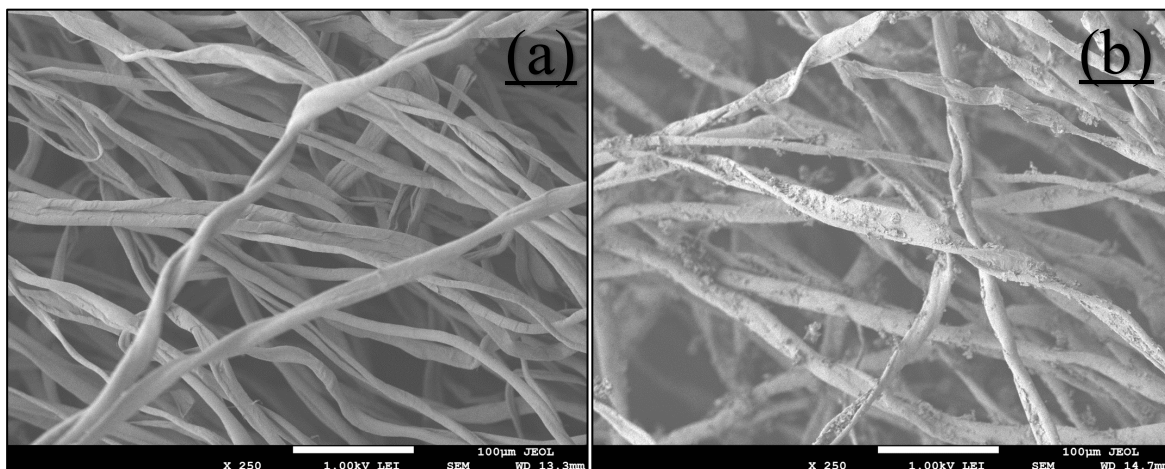


Figure 24. SEM images at 100 microns resolution (x250); (a) pure cotton (b) graphene attached cotton

Figure 25 (a) and (b), reveal that the smooth cellulose skeletons are covered with graphene sheets increasing the surface roughness. It is important to note that increased surface roughness implies a higher surface area will come in contact with oil allowing a higher capacity and loading efficiency.

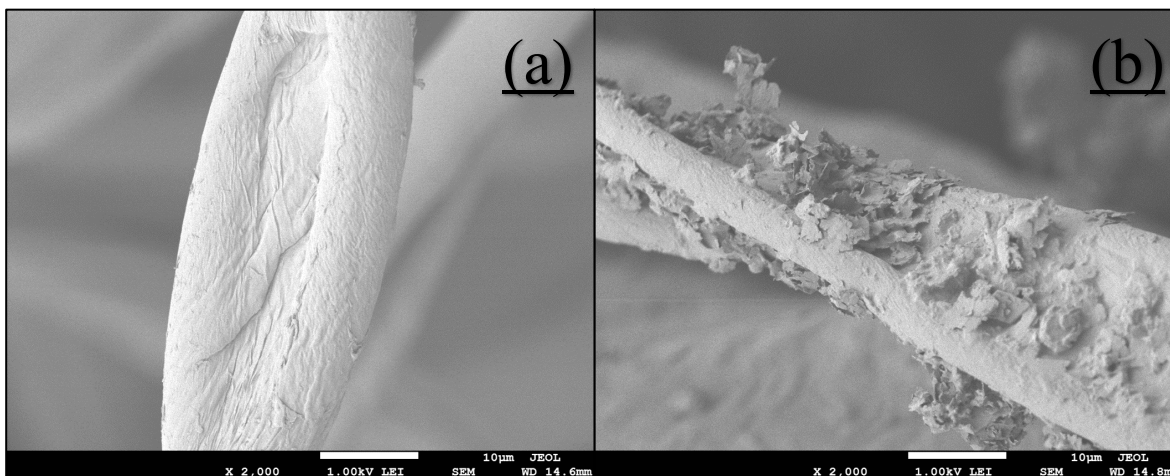


Figure 25. SEM images at 10 microns resolution (x2,000); (a) pure cotton (b) graphene attached cotton.

### 5.3 Wettability of Graphene coated cellulose

The surface wetting property of the graphene coated cotton cellulose and pure cotton cellulose was examined by water contact angle (CA) measurements. The pure cotton cellulose is very hydrophobic in nature and absorbs the droplet of water when placed on it for contact angle measurement. A drop of water spread out completely and was immediately absorbed by the pure sponge. The CA experiment was also carried out on a graphene coated cellulose without the functionalization of cellulose and it showed the same result. This helped in concluding the fact that the functionalization of cellulose was very important before coating it with graphene. In contrast, the functionalized cellulose coated with graphene showed very high contact angle of  $144.756^{\circ}$ . This CA was

close to superhydrophobic CA of  $150^{\circ}$  [23]. The contact angle was measured using ImageJ software and by using droplet analysis packet. When the CA experiment was performed on graphene coated cotton cellulose using crude oil, the sample completely absorbed the oil showing its super-oleophilic nature. This variance in wettability of water and oil for the graphene coated cotton cellulose satisfies a very crucial requirement for its application in oil-water separation.

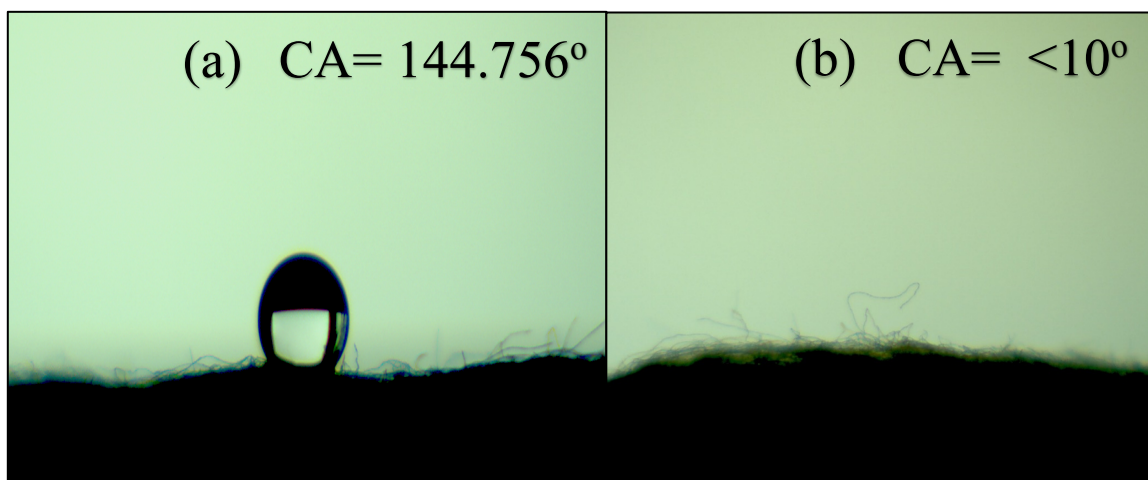


Figure 26. Water contact angle of (a) graphene coated cotton (b) pure cotton cellulose

#### 5.4 Removal of organic solvents and oil from water

The graphene coated cotton cellulose showed strong absorbance towards oil and non-polar organic solvents from water. The figure 24. displays how the graphene coated cotton cellulose absorbs the paraffin oil (with traces of Procion Blue H =5R dye, which was added into the oil for visualization purposes and all the quantitative measurements were conducted in the absence of the dye). In figure24 (a) paraffin oil is seen floating on top of water. In figure24 (c) and (d) shows how the graphene coated cotton cellulose completely absorbs the oil from the surface of the water within 10 seconds. Moreover, no water was absorbed by the graphene coated cotton cellulose after it was taken out and observed. Graphene coated cotton cellulose proved to be a promising absorbent for the removal and cleaning of oils and organic pollutants of varying viscosities and densities [25]. For comparison, when the same experiment was performed with cotton, firstly the cotton completely soak down to the surface as soon as it came in contact with the water (showing its hydrophilicity) and even when the cotton was moved along the surface to pick up the oil, it picked up only some of it (not as much as graphene coated cotton cellulose) [24]. Usually, the wettability if the surface depends on. The surface topography of the microstructure and the surface chemical composition.

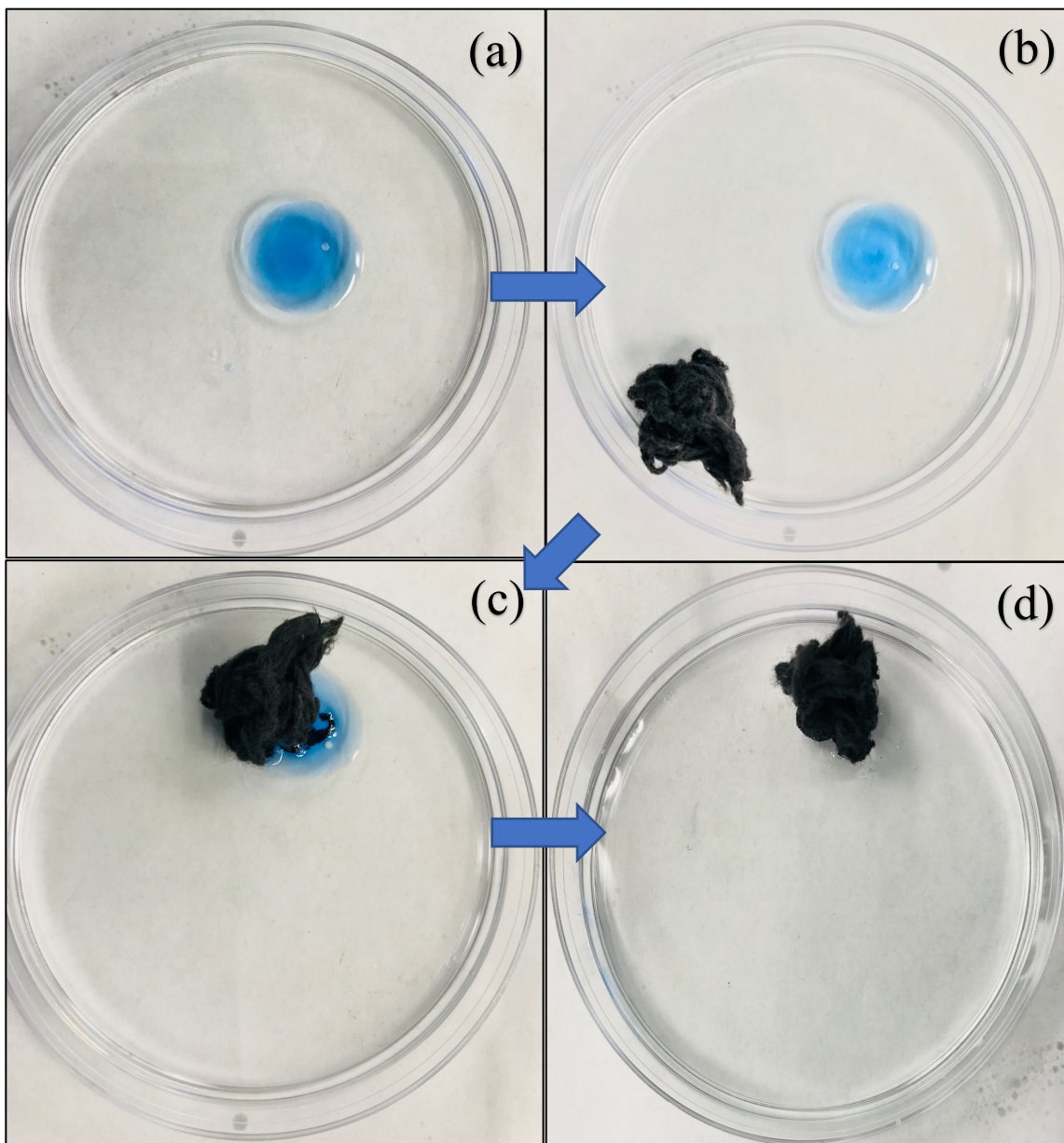


Figure 27. The pictorial representation of the absorption experiment (a) Paraffin oil (blue color) in water (b) graphene coated cotton introduced for oil absorption (c) absorption in progress (d) all the paraffin oil absorbed by the graphene coated cotton.

The absorption experiment was carried out for different oils and organic solvents. The figure 25. shows the oil absorption capacity of the graphene coated cotton cellulose for dodecane, paraffin oil, pump oil, mineral oil, hexane, toluene and crude oil. The sample was immersed in a solution in the mixture of respective oil/ organic solvent for 10 minutes and the absorption capacity was calculated by dividing the final weight after oil absorption by the initial weight. From the figure it was seen that out of all them, the graphene coated cotton cellulose absorbed crude oil almost 26 times its weight in 10 minutes.

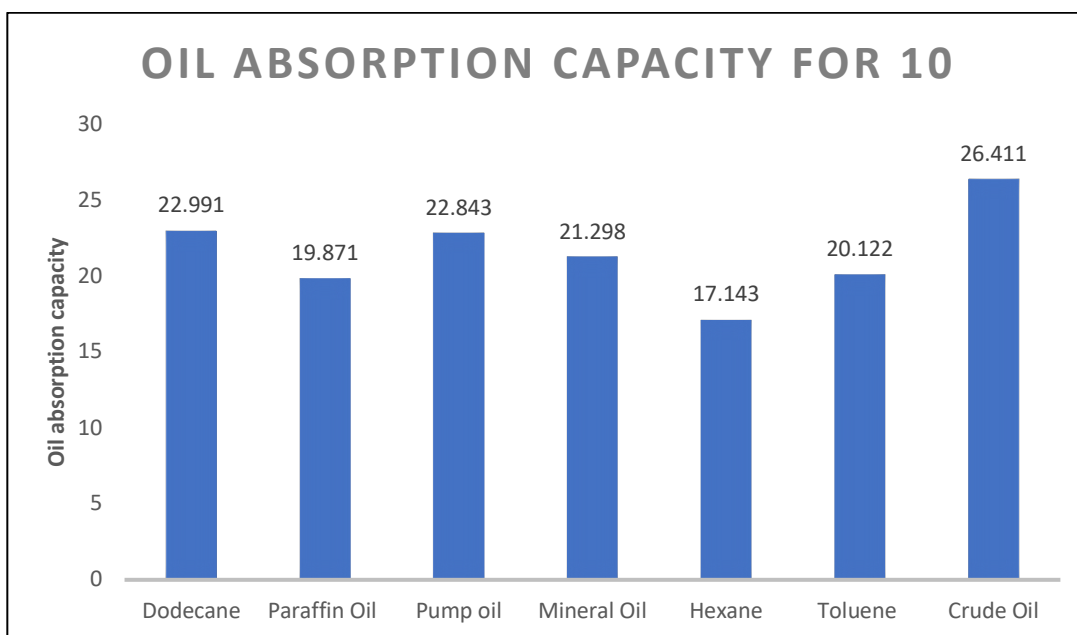


Figure 28. Oil absorption capacity of graphene coated cotton cellulose for different oils and organic solvent when placed in them for 10 minutes.



The absorption experiment was also performed with different oils and organic solvents for a duration of 10 minutes and for 10 cycles. In figure 26, we can observe that as the no. of cycles increases the absorption capacity of the sample decreases gradually. However as per the general trend it can also be noted that, after the 5-6<sup>th</sup> cycle the absorption capacity stops decreasing and starts plateauing.

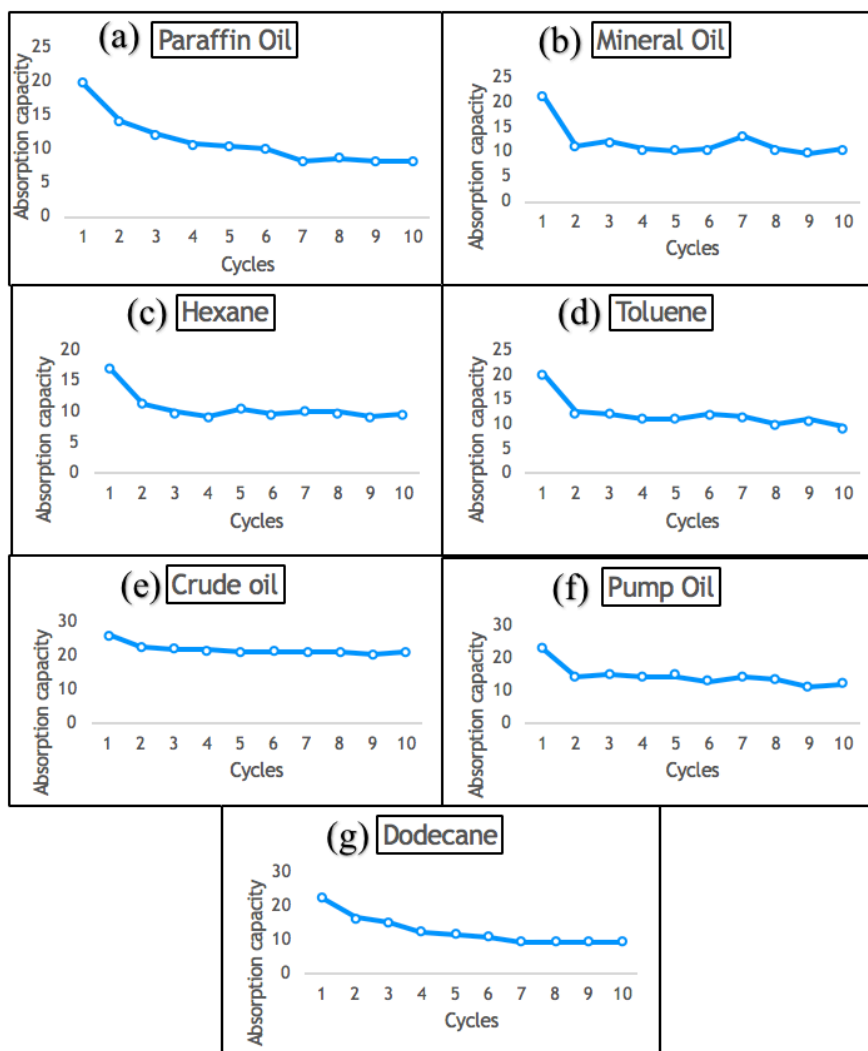


Figure 29. The absorption capacity of different oils and organic solvent for 10 minutes over 10 cycles.

The oil absorption was further allowed to progress for 6 hours and 24 hours respectively to measure how the oil absorption capacity increases with time. The same procedure was repeated with pure cotton as well to have a reference point. The experiment showed that, as the time increased from 10 minutes to 6 hours, oil absorption also gradually increased and reached a saturation point. We could infer this as the oil absorbed after 24 hours was a little more than the amount of oil absorbed after 6 hours.

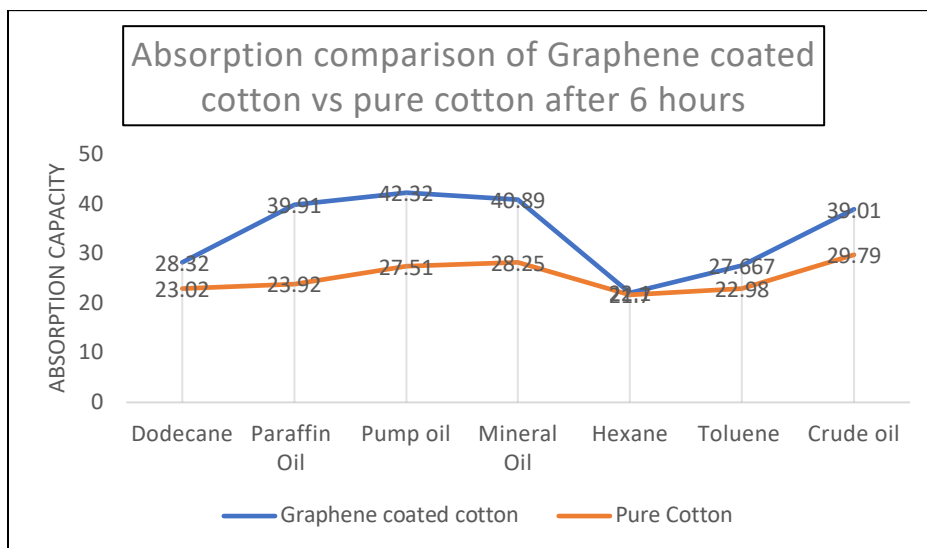


Figure 30. Comparison of absorption capacity of oils and organic solvents for a duration of 6 hours in graphene coated cotton and pure cotton.

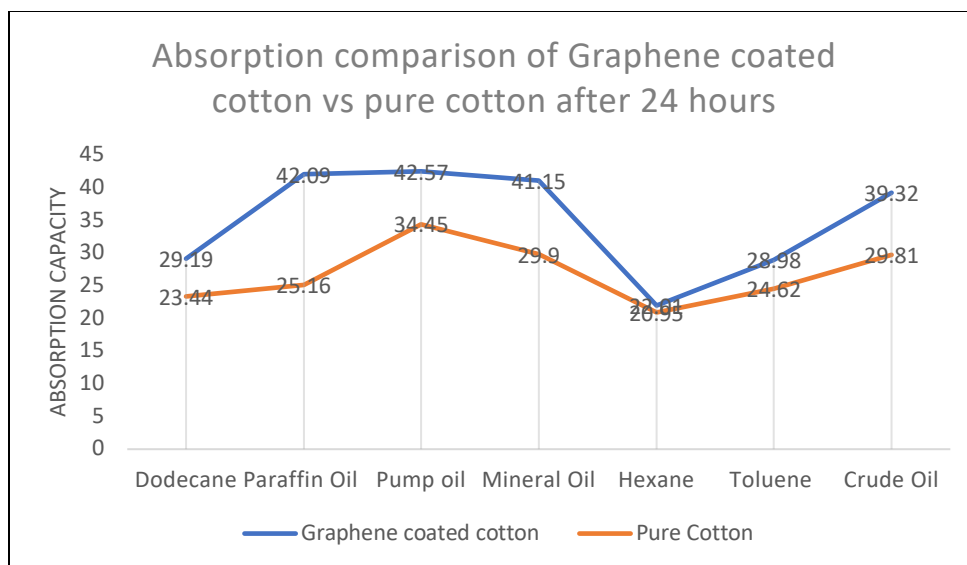


Figure 31. Comparison of absorption capacity of oils and organic solvents for a duration of 24 hours in graphene coated cotton and pure cotton.

In figure 30, the change in the absorption capacity of crude oil by graphene coated cotton with time is shown. We can see that after 6 hours of oil absorption the intake of oil is hardly significant, confirming that the oil has reached its saturation point and using it for oil beyond the saturation point is not so useful.

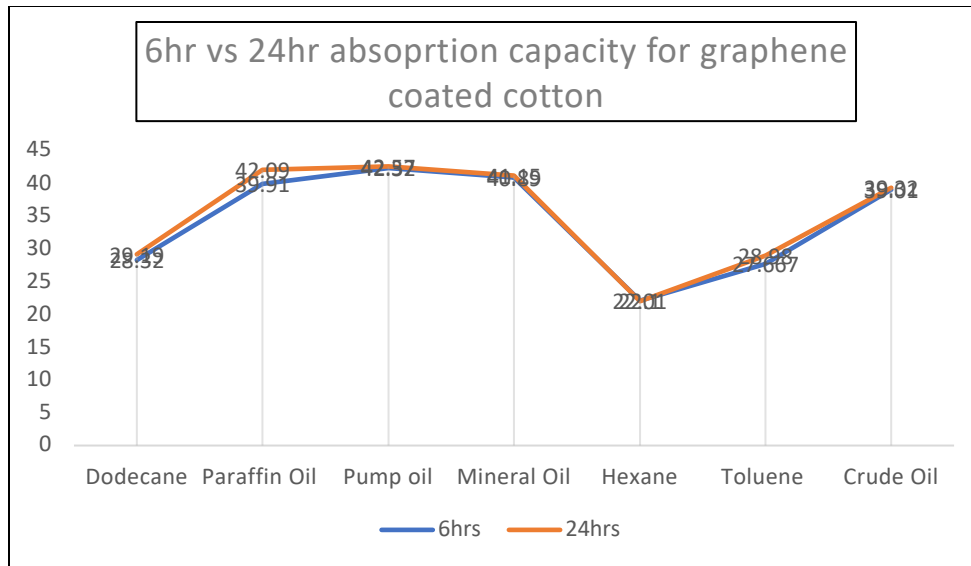


Figure 32. Absorption capacity of oils and organic solvents after 6 hours vs absorption after 24 hours for graphene coated cotton.

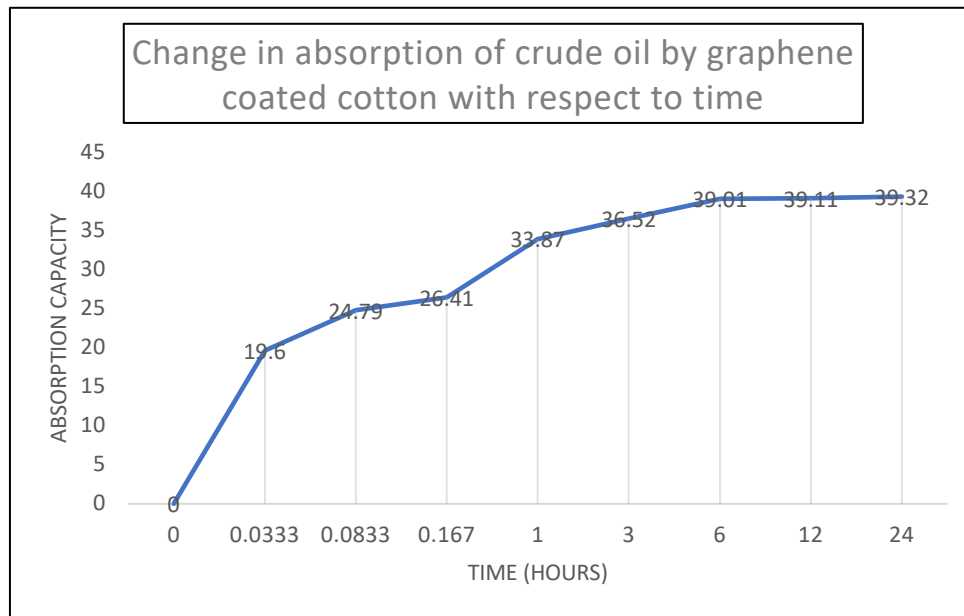


Figure 33. Change in absorption of crude oil by graphene coated cotton as a function of time.

## 5.5 Comparison with existing absorption materials

Sorbent materials	Absorbed substances	Absorption capacity (g/g)	Cost	Method	Ref.
CNT/PDMS coated PU sponge	Oils	15-25	low	Organic solvent, not eco-friendly	26.
Nitrogen-rich carbon aerogel	Oils and organic solvents	5-16	high	High temperature pyrolysis (700 °C), organic solvent	27.
Graphene sponge (glucose)	Oils and organic solvents	18-35	low	Hydrazine hydrate, H <sub>2</sub> SO <sub>4</sub> (Hummers process), 250 °C	28.
boron nitride nanoplatelets and polycaprolactone	Oils and organic solvents	3-7	low	Low absorption capacity	25.
Carbon sponge from Melamine	Oils and organic solvents	90-200	High	High temperature pyrolysis(300-800 °C)	29.
Graphene coated cotton	Oils and organic solvents	23-42	low	Cellulose functionalization and graphene sonication	Present work

Figure 34. Comparison with other existing absorption material.

A lot of research has been performed to develop a material which selectively absorbs oil from water. It has been a challenge to achieve high absorption of oil with a material and process that is economical, clean and sustainable. From the figure above, we can learn that carbon sponge from melamine has a very high absorption rate, but the materials used and the fabrication process is expensive. It is very crucial to consider the overall production cost of the material to economically implement it on a large scale. The graphene coated cotton promises to be a good alternative with low material cost and good absorption capacity.

## 6. CONCLUSION

In summary, a hydrophobic cotton coated with graphene was prepared first by functionalisation of cotton cellulose and then attaching it with graphene. The cotton cellulose was functionalised by first treating it with Thionyl Chloride in DMF and then reacting it with N,N- Dimethyl-1,3-propanediamine. The graphene was prepared by sonication of graphite in DMF. The graphene coated cellulose showed excellent absorption performance for oils and organic solvents, including good selectivity, promising recyclability and a very high absorption capacity. The absorption capacity was 28.32, 39.91, 42.32, 40.89, 22.1, 27.67, 34.69 and 39.01 for dodecane, paraffin oil, pump oil, mineral oil, hexane, toluene and crude oil respectively. These characteristics also helped us to determine that the sample was very effective in the separation of oil from water surfaces. In particular, the fabrication technology employed is ecofriendly, materials can be easily procured and is cost effective, when compared with the existing technologies. It does not require treatment at high temperatures or sophisticated processing units which is an added advantage. As the research progresses, the graphene coated cellulose could be scaled up economically and can be employed in the cleanup and environmental remediation in case of oil/organic solvent spills.

## 7. REFERENCES

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