"Dissemination of Education for Knowledge, Science and Culture"

-Shikshanmaharshi Dr. Bapuji Salunkhe

Shri Swami Vivekanand Shikshan Sanstha's

Vivekanand College, Kolhapur (Empowered Autonomous)

Department of Physics

M.Sc.-II (2023-24)

Research Project Titles

Roll. No.	Name of Students	Name of Guide	Title of Project
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1602	Shruti Harish Bam	Dr. Sumayya I. Inamdar	Synthesis and Characterization of BiVO4 thin film by spray pyrolysis
1603	Biradar Anand Nagappa	Dr. Sanjay S. Latthe	MTMS-PMMA-based super hydrophobic silica coating on marble for self-cleaning application
1604	-	-	-
1605	Jarkoli Smith Kallappa	Dr. Namrata A. Narewadikar	Synthesis and characterization of metal oxide thin films by chemical method
1606	Kavatagi Shivraj Chandraknat	Mr. Abhijeet V. Shinde	CuO thin film deposited SILAR method for super capacitive applications
1607	Mithari Shweta Sardar	Dr. Sumayya I. Inamdar	Synthesis and characterization of Mnfe2O4 thin film by Spray Pyrolysis
1608	Randive Rajshree Mahesh	Mr. Abhijeet V. Shinde	Electrochemical study of all Solid-State symmetric supercapacitor based of CoFe2O4 thin film
1609	Sagar Shivani Dattatryay	Dr. Sanjay S. Latthe	Photothermal superhydrophobic carbon nanoparticles polymer nanocomposite coated cotton fabric for self- cleaning application
1610	Shirke Pranali Pradip	Dr. Sanjay S. Latthe	The analysis of Aditya-L1 satellite working
1611	-	-	-
1612	Aditi Chauhan Brijesh	Dr. Sumayya I. Inamdar	Birth and Death of stars

VIVEKANAND COLLEGE KOLHAPUR ESTD JUNE 1964 (Empowered Autonomous)

sslatthe

HEAD
DEPARTMENT OF PHYSICS
VIVEKANAND COLLEGE, KOLHAPUR
(EMPOWERED AUTONOMOUS)

Electrochemical study of all solid state symmetric supercapacitor based of $CoFe_2O_4$ thin film

A dissertation Report submitted to

Vivekanand College Kolhapur

(Empowered Autonomous)

For the Partial Fulfillment of

Degree of Master of Science

In

PHYSICS

Under the faculty of Science

By

Miss. Rajshree Mahesh Randive

B.Sc.Physics

Under the Guidance of

Mr. Abhijeet V. Shinde

(M.Sc. SET)

Department of Physics

Vivekanand College Kolhapur,

(Empowered Autonomous)

2023-24

DECLARATION

I hereby declare that the project entitled " **Electrochemical study of all solid state symmetric supercapacitor based of $CoFe_2O_4$ thin film**" completed and written by me has not previously formed the basis for the award of any Degree or Diploma or other similar title of this or any other University or examining body.

Place: Kolhapur

Date: 30 - 04 - 24

R.M.Randive ,

Miss.Rajshree Mahesh Randive

B.Sc. Physics

CERTIFICATE

This is to certify that the project entitled **"Electrochemical study of all solid state symmetric supercapacitor based of $CoFe_2O_4$ thin film"** which is being submitted here with for the award of the Degree of Master Science in Physics of Vivekanand College (Autonomous)Kolhapur is the result of the original project work completed by Miss. Rajshree Mahesh Randive, under our supervision and guidance and to the best of our knowledge and belief the work, embodied in this project has not formed earlier the basis for the award of any Degree or similar title of this or any other University or examining body

Place: Kolhapur

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ACKNOWLEDGEMENT

On the day of completion of this project, I offer sincere gratitude to those who encouraged and helped me a lot at various stages of this work.

I have great pleasure to express my deep sense of indebtedness and heart full gratitude to Prof. Abhijeet Shinde, Assistant Professor, Department of Physics, Vivekanand College (Autonomous), Kolhapur, for his expert and valuable guidance and continuous encouragement given to me during the course of my project work He has already been a source of strength for me I find in him a real researcher who through his own example and devotion for scientific work inspired ne towards a common goal of achieving scientific knowledge and pursuit.

I wish to express my appreciation to Dr. S.S Latthe, and Prof. G.J. Navathe for discussion and co-operation in each and every movement of my project work.

My acknowledgement will be incomplete if I don't express my appreciation towards my family members whose good will & inspiration helped us a lot in completing this project work.

Miss. Rajshree Mahesh Randive

B.Sc. - (Physics)

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Chapter I

Introduction to thin film

A **thin film** is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. The controlled synthesis of materials as thin films (a process referred to as deposition) is a fundamental step in many applications. A familiar example is the household mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface. The process of silvering was once commonly used to produce mirrors, while more recently the metal layer is deposited using techniques such as sputtering. Advances in thin film deposition techniques during the 20th century have enabled a wide range of technological breakthroughs in areas such as magnetic recording media,electronic semiconductor devices,LEDs, optical coatings (such asntireflectivea coatings), hard coatings on cutting tools, and for both energy generation (e.g. thin-film solar cells) and storage (thin-film batteries). It is also being applied to pharmaceuticals, via thin-film drug delivery. A stack of thin films is called a multilayer.

In addition to their applied interest, thin films play an important role in the development and study of materials with new and unique properties. Examples include multiferroic materials, and superlattices that allow the study of quantum.

Thin film deposition involves processing above the substrate surface (typically a silicon wafer with a thickness of 300–700 μm). Material is added to the substrate in the form of thin film layers, which can be either structural layers or act as spacers later to be removed. MEMS deposition techniques fall into two categories, depending on whether the process is primarily chemical or physical (Madou Marc, 1997). In chemical deposition, films are deposited via a chemical reaction between the hot substrate and inert gases in the chamber at low or atmospheric pressure. Depending on the phase of the precursor, chemical deposition is further classified into plating, spin coating, chemical vapour deposition (CVD) (e.g. low pressure CVD, plasma-enhanced CVD, and very low pressure CVD), and atomic layer deposition. In physical deposition, the raw materials (solid, liquid or vapour) are released and physically moved to the substrate surface, e.g. thermal evaporation, sputtering and ion plating. The choice of deposition process is dependent upon several factors, e.g. substrate structure, operating temperature, rate of deposition and source. These film layers are deposited and subsequently patterned using photolithographic techniques.

The development of modern society purely depends on the advancement of technology which in turn is not possible with technological progress in the field of thin film science. Thin films are deposited onto bulk materials so as to achieve required properties .Additional functionality in thin films can be achieved by depositing multiple layers of different material .The multilayer thin films can achieve behave as completely new engineered materials ,unknown,in bulk form.When multiple layer is in combined with lithographic pattern in the plane of the films ,they variety of microstructure can be constructed .The difference between thin film and thick film technologies is that the former involves deposition of individual molecules ,while the later involves deposition of particle .Temperature is a key variable in the process of altering film properties.

Thin film process contains 4 sequential steps viz source material , transport deposition analysis. The sours of film forming material may be a solid , liquid , or vapor. In the transport step , the major issue is uniformity of arrival rate of material over the substrate area. The third step deposition is the actual thin film process formation onto the surface of substrate. Deposition behavior is determined by source and transport factors and also by condition at the deposition surface. The last step in the deposition is the analysis of the films. It is essential to optimize the deposition process parameters during the formation of thin films .

Thin film studies have directly or indirectly advanced and enhanced many new areas of research in solid state physics and chemistry, which are based on the phenomenon exclusively characteristics of the thickness, geometry and structure of the film. Various techniques are available of the deposition of thin films with several materials. Basically thin-film deposition technologies are either purely physical or purely chemical. Physical method covers the deposition technique which depend on the evaporation or ejection of the material from a source i.e. evaporation or sputtering, whereas chemical methods depend on physical properties .Structure property relationships are the key features of such devices and basis of thin film technologies.

Majority of sensor devices based on the material structures are produced by thin film deposition. Earlier in 1897,Fraunhoffer accidently found an optical thin film layer was generated on the surface of glass during the experimentation.It may be considered as the beginning of thin film technology. Thereafter in 1850 Faraday, Grove and Edison developed the deposition techniques such as elecrodeposition , chemical reduction deposition and evaporation of metallic wires by current respectively. Recently, Xie et al reported the fabrication and characterization of a PANI- based gas sensor by ultra-thin film technology.

A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness .Many of the electronic semiconductor devices are the main applications benefiting from thin film construction . The semiconducting material, in thin film form are of particular interest because it has a various number of applications viz transparent electrodes, photovoltaic devices ,solar front panel display, surface acoustic wave devices ,low emmisivity coating for architectural glass, various gas sensors and heat reflector for advanced grazing in solar cells. Due to surface and interface effects, properties of thin film considerably from those of bulk and this will dominates overall behavior of the thin films.

Thin film plays an important rolein the nanotechnology and nanoscience development . Solar cell is an important application of thin film technology from the point in view of global energy crunch. Converts the energy of the solar radiation into useful and constructive electrical energy . Window material is the main condition for thin film solar cells, which allows passing through; the visible region of solar spectrum but reflects the IR radiation . A large number of different deposition techniques are used for the construction of thin films for structural , morphological and optical applications, as outlined in chapter "Thin Film Deposition Techniques ''by H.k.Pulker.The two most important categories are physical vapor deposition (PVD) namely thermal vaporization and sputtering and chemical vapor deposition(CVD).It is clear,that for each deposition technique appropriate coating materials are required. The PVD process normally use of inorganic and organic compounds and gases.Liquid compounds and gases are normally purchased directly from the producer , because it needs no special preparation. Solid materials have to be compact and in the suitable form or shape , free of gas inclusions or even are prepared according to a special recipe . Targets must also fulfill structure requirements i.e. grain size, texture, precipitation .three operations are the tasks of companies specialized in the pro duction of coating materials and targets. This chapter focuses on solid coating. The requirements on these materials are discusse their properties are listed and production is described.

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Chapter 2

Thin film deposition methods:

The properties of thin films depend on the method of deposition. The required properties and versatility can be obtained by choosing proper method of thin films deposition. Thin film deposition methods can be broadly classified as either physical or chemical. In physical methods the film material is moved from a target source with some form of energy to the substrate. This technique is widely used in one-component films, like metal films. Under physical methods, we have vacuum evaporation and sputtering, where the deposition takes place after the material to be deposited has been transferred to a gaseous state either by evaporation or an impact process. Chemical film fabrication methods involve chemical reactions and the precursors are mostly components undergoing reaction at the substrate surface or in the vicinity of the substrate. Under chemical methods, we have the gas phase chemical processes such as conventional chemical vapor deposition (CVD), laser CVD, photo CVD, metal organo-chemical vapor deposition (MOCVD) and plasma enhanced CVD. Liquid phase chemical methods include sol-gel process, electrodeposition, chemical bathe deposition (CBD), modified chemical bath deposition (M-CBD), successive ionic layer adsorption and reaction (SILAR), electroless deposition, anodization, spray pyrolysis, liquid phase epitaxy, etc. The broad classification of thin film deposition methods is outlined in requirement for obtaining good stoichiometric films. Chemical methods are relatively economical and easier ones as compared to physical methods. Among all the thin film deposition methods, sol gel process offers a wide range of advantages over other methods of thin film deposition as shown below:

1. Low temperature processing
2. Requires considerably less equipment and is potentially less expensive
3. Easy coating of large surface
4. Small thickness
5. High optical quality

Thin film deposition techniques :

Certainly one of the most technologically important aspects of sol-gel processing is that, prior to gelation, the fluid sol or solution is ideal for preparing thin films by such common processes as dipping, spinning, or spraying.

A. Basics of dip coating technique :

Dip coating technique can be described as a process where the substrate to be coated is immersed in a coating sol and then withdrawn with a well-defined withdrawal speed under controlled temperature and atmospheric conditions.

In the dip coating process, the atmosphere controls the evaporationof the solvent and subsequent destabilization of the sols by solvent evaporation leads to a gelation process and the formation of a transparent film due to the small particle size in the sols (nanometer range). The gelation process duringThe coating thickness is defined mainly by the withdrawal speed, the solid content and the viscosity of the liquid. There are six forces acting on the coating during withdrawing :

1. viscous drag upward on the liquid by moving substrates

2. force on gravity

3. resultant force of surface tension in the concavely shaped meniscusinertial force of the boundary layer liquid arriving at deposition region

5. surface tension gradient and

6. the disjoining or conjoining pressure (important for films less than 1 μmBasics of spin coating technique In the spin coating process, the substrate spins around an axis that should be perpendicular to the coating area. The stages of the spin coating process are shown schematically in figure 3.3. The spin coating process is carried out in four stages: deposition of the sol, spin up, spin off and gelation by solvent evaporation. An excess of liquid is dispensed on the surface during the deposition stage. In the spin up stage, the liquid flows radially outward,

driven by centrifugal force. In the spin off stage, excess liquid flows to the perimeter and leaves as droplets. As the film thins, the rate of removal of excess liquid by spin off slows down, because the thinner the film, the greater the resistance to flow, and because the concentration of the nonvolatile components increases raising the viscosity. In the fourth stage, evaporation takes over as the primary mechanism of thinningBasics of spray technique The basic principle involved in spray technique is that, when the droplets of spray solution reach to the hot substrate, owing to the pyrolytic decomposition of solution, well adherent pin–hole free, uniform, film is deposited on the substrates. The other volatile byproducts and excess solvent escape in the form of vapors. The thermal energy for decomposition and subsequent recombination of the species is provided by the hot substrate. It is different for the different materials and for the different solvents used in the spray process.

It mainly consists of spray nozzle, rotor for spray nozzle, liquid level

monitor, hot plate, gas regulator value and air tight fiber chamber.

a) Spray nozzle

It is made up of glass and consists of the solution tube surrounded by the

glass bulb. With the application of pressure to the carrier gas, the vacuum is created at the tip of the nozzle and the solution is automatically sucked in the solution tube and the spray starts.

b) Rotor for spray nozzle

Stepper motor based microprocessor controller is used to control the

length of the hot plate.

c) Liquid level monitor

The spray rate at a fixed air pressure depends upon the height of the solution measured with respect to the tip of the nozzle. The arrangement for the change in height of the solution forms the liquid level monitorChapter 3 Thin Film Deposition Methods and Characterization Techniques

d) Hot plate

The iron disc, with diameter 16 cm and thickness 0.7 cm to which 2000

Watt heating coil is fixed is used as a hot plate. Maximum temperature of 500 ± 50C can be obtained with this arrangement. The chromel-alumel thermocouple is used to measure the temperature of the substrates and is fixed at the center of the front side of the iron plate. The temperature of the hot plate is monitored with the help of temperature controller (Aplab make Model No. 9601).

e) Gas regulator value

The gas regulator value is used to control the pressure of the carrier gas flowing through the gas tube of the spray nozzle. A glass tube of length 25cm and of diameter 1.5 cm is converted into gas flow meter. Since air pressure depends upon the size of the air flow meter, the air flow meter should be calibrated from nozzle to nozzle.

f) Air tight fiber chamber

Since the number of toxic gases is evolved during the thermal decomposition of sprayed solution, it is necessary to fix the spraying system

inside with air tight fiber chamber. An air tight fiber chamber of the size (2' x 2' x 2') was fabricated. The fiber avoids the corrosion of the chamber. The outlet of chamber is fitted to exhaust fan to remove the gases evolved during thermal decomposition. Substrate cleaning

Substrate cleaning is the process of breaking the bonds between substrates and contaminants without damaging the substrates. In thin film deposition process substrate cleaning is an important factor to getreproducible films as it affects the smoothness, uniformity, adherence .

Chemical Bath Deposition Method :

Chemical Bath Deposition technique involves controlled precipitation of a compound from the solution on a suitable substrate. This technique offers many advantages over the more established vapour phase routes to semiconducting thin films, such as CVD, MBE and spray pyrolysis. The first CBD thin films were prepared in 1884 and this method was limited to RuO_2 for a long time. After the deposition of$NiFe_2O_4$, a wide range of chalcogenide and chalcopyrite materials have been prepared by this method. In CBD a wide range of substrates such as ebonite, iron, steel, porcelain and brass were specifically used apart from glass. The films were uniform, adherent and able to withstand considerable friction. Around 1980, the focus of CBD films slowly turned towards solar energy applications. One of the earlier developments towards this method was in solar absorber coatings. Application in the field of solar control coatings was suggested in 1989 . On the other hand, CBD method has significant advantages over the other methods as follows effective method

- It is possible to deposit multi compound chalcogenide thin films
- CBD is the simplest cost over a wide range of stoichiometry with this technique

- Chemicals do not require high vacuum and it can be carried out even at room temperature
- Large area deposition is possible by carefully lying down the substrate on a shallow tray containing the deposition bath
- Produces uniform well adherent and reproducible thin films for photovoltaic applications
- An inexpensive method for large scale industrial applications
- The material consumption is low and minimizes the loss
- The crystallite size of the CBD films is very small.

Principle of CBD Technique :

In this technique it is possible to control the film thickness and chemical composition by varying the deposition parameters such as temperature, precursor concentration, complexing agents used and the pH of the solution. The ability of this method to coat large areas in a reproducible and low cost process is the most attractive advantage. This method depends on the deposition of thin films from aqueous solutions either by passing a current or by chemical reactions under
43appropriate conditions [84]. By the nature of their preparative conditions, these films are generally not of high purity. With appropriate control of the deposition parameters definite composition of thin films can be obtained. In CBD process, thin films are deposited on a solid substrate when it is immersed into a dilute solution of one or more metal salts (MP+)ion and a suitable complexing agent in an aqueous solution via four steps as follows

- Establishment of equilibrium between water and the complexing agent
- Formation of metal- complex species
- Formation of the solid film on the substrate

The deposition of the film occurs on the substrate when the value of ionic product exceeds the solubility product, otherwise it is precipitated out. The metal ions are usually complexed by a suitable complexing agent, which would then gradually release metal ions during the course of reaction. The formation of metal-complex ion controls the rate formation of solid metal hydroxides which leads to the formation of solid film. Thus, the metal ion must be complexed in order to prevent precipitation of metal hydroxide. The strength of the complexing agent should not be too weak or too strong in ordered to prevent bulk precipitation or to deposition of the desired film. The basic principle of CBD is to control the chemical reaction so as to affect the deposition of thin film by precipitation. The process depends on the slow release of chalcogenide ion into an alkaline solution in which the free metal ion is buffered at a low concentration.

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♣**Ion by ion process**

This is the simple one in which the ions condense at the reacting surface to form the film.

♣**Cluster by cluster process**

In this case colloidal particles are formed in the solution as a result of homogeneous reaction. These particles are absorbed at the surface of the substrate to form the thin layers.

♣**Mixed process**

Generally both the above said processes may interact with each other leading to the films in which the colloidal material is included in the growing films. In this process, the predominance of one process over the other is governed by the extent of homogeneous and heterogeneous nucleation. Heterogeneous nucleation is a result of reaction taking place at the surface of the substrate, where as homogeneous nucleation is a result of reaction occurring within the bulk of the solution.

Factors Influencing the Deposition Process :

The formation of thin film by chemical bath deposition is influenced by the factors such as

- ❖ Bath temperature
- ❖ Nature and concentration of the precursors
- ❖ Nature and concentration of complexing agent
- ❖ pH of the solution
- ❖ Deposition time
- ❖ Nature of the substrate

❖ **Bath Temperature -**

An important factor that influences the rate of reaction is the bath temperature. As the temperature increases, dissociation of the complex increases. The kinetic energy of the molecule also increases leading to greater interaction between the ions. This results in more increase or decrease in the film thickness depending on the extent of super saturation of the solution [2].

- **Nature and concentration of the precursors -**

Nature of the precursors influences the composition of the product. The growth kinetics also depends on the nature of the precursors. For example, when metal sulphate is used to deposit the metal Sulphide film, the rate of deposition decreases and the thickness increases. Here the SO_4^{2-} ions obtained from the metal sulphate reduce the concentration of selenide ions. The deposition rate and terminal thickness initially increase with an increase in the ionic concentration of precursors. However, at higher concentrations the precipitation becomes very fast leading to decrease in film thickness.

- **Nature and concentration of complexing agent -**

Nature of the complexing agent has great influence on the final products. For example, when EDTA is used as a complexing agent for FeS_2 thin film preparation, it was found that parasite and other phases were formed rather than pyrite FeS_2, while ammonia and EDTA were used this could be avoided to a great extent.

Generally in a reaction, metal ion concentration decreases with the increase of complexing ion concentration. As a consequence, the rate of reaction and hence the precipitation are reduced leading to a large terminal thickness of the film.

- **pH of the solution -**

When the pH of the reaction bath increases, the metal complex usually becomes more stable reducing the availability of free metal ions. This will decrease the reaction rate resulting in higher thickness of the film.

- **Deposition time -**

In general, the growth of good quality thin films proceeds at a slower rate. The CBD method is suitable for producing uniform thickness films in the range of 0.05 - 0.3 nm. The dependence of thickness of the film on the duration of deposition has been studied in detail for different semiconductors [3].

- **Nature of substrates -**

It plays an important role in the reaction kinetics and adhesion of the deposited films. Hence, cleaning of the substrate surface is the first step in the thin film deposition. Higher deposition rates and thicknesses are observed for those substrates whose lattice parameters were well matched with those of the deposited material.

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Techniques, 2nd Ed. Noyes Publications, 2002.

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Chapter 3

Literature Survey ofNiFe$_2$O$_4$

Sr. No	Chemical used	Method	Application	Ref.No
1	Nickel chloride hexahydrate , Nickel nitrate, Nickel sulphate hexahydrate, ferrous chloride tetrahydrate and Ammonia	CBD	Supercapacitor	[1]
2	Ferric Nitrate ,Cobalt Nitrate, Ammonium fluoride, distilled water	CBD	Supercapacitor	[2]
3	Co(C5H7O2)2,Fe(C5H7O2), Si(OC2H5)4)	CBD	Supercapacitor	[3]
4	Ferric Nitrate ,Cobalt Nitrate, Ammonium fluoride,	CBD	Supercapacitor	[4]

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3 P.doresy,p.lubitz,D.chery,novel research lobatory,Washington,DC 20375

4 A.Bagade,V.Ganbavle(submitted January28;in revised form March26,2014)

5 Danyange wang,ji.Zhang,Akimitsu Morisako

Chapter 4

Synthesis and Results

Substrate Cleaning

Substrate cleaning plays an important role in formation of smooth, uniform and well adherent thin film. Extreme cleanliness is required as in order to remove the common contaminates such as dust particles, adsorbed water contents, other depositsetc.because of different processes while manufacturing the substrate. Substrate cleaning is the process of breaking the bonds between substrate and contaminants without damaging the substrate. In thin film deposition process, cleanliness of the substrate is required for the chemical deposition as the contaminated surface provides nucleation sites facilitating growth resulting into non-uniform films with different orientation and impurities. The stainless-steel substrates were used for the deposition of films.

The following process has been adopted for cleaning the stainless-steel substrates.

i) The substrates were mirror polished using zero grade polish paper.

ii) The substrates were washed with detergent (Labo) and double distilled water.

iii) Well cleaned substrates were kept in ultrasonic bath for 15 min

iv) Finally, the substrates were dried, degreased in AR grade acetone and were kept in dust free.

Experimental Procedure

The AR grade cobalt chloride ($CoCl_2 \cdot 6H_2O$) and ferrous chloride ($FeCl_2 \cdot 6H_2O$) received from Loba Chemicals were used for the deposition. Requisite amounts of chemicals were weighed accurately and dissolved in double distilled water to obtain the Fe^{2+} and Co^{2+} concentration ratio as 2:1. The pH of the solution was adjusted using NH_4OH solution which also acted as complexing agent. The pH of the resultant solution was maintained at 9. The chemical deposition of $CoFe_2O_4$ film onto stainless steel from the alkaline bath of Co^{2+} and Fe^{2+} ions involves heterogeneous nucleation, in which there is ion by ion reaction at the substrate surface, followed by subsequent growth of nuclei. The solutions of cobalt chloride ($CoCl_2 \cdot 6H_2O$) and ferrous chloride ($FeCl_2 \cdot 6H_2O$) prepared in double distilled water were mixed together such that the ratio of Co^{2+}:Fe^{2+} ions equal to 1:2. The pH of the solution is adjusted using NH_4OH solution.

Results and discussion :

X-Ray Diffraction :

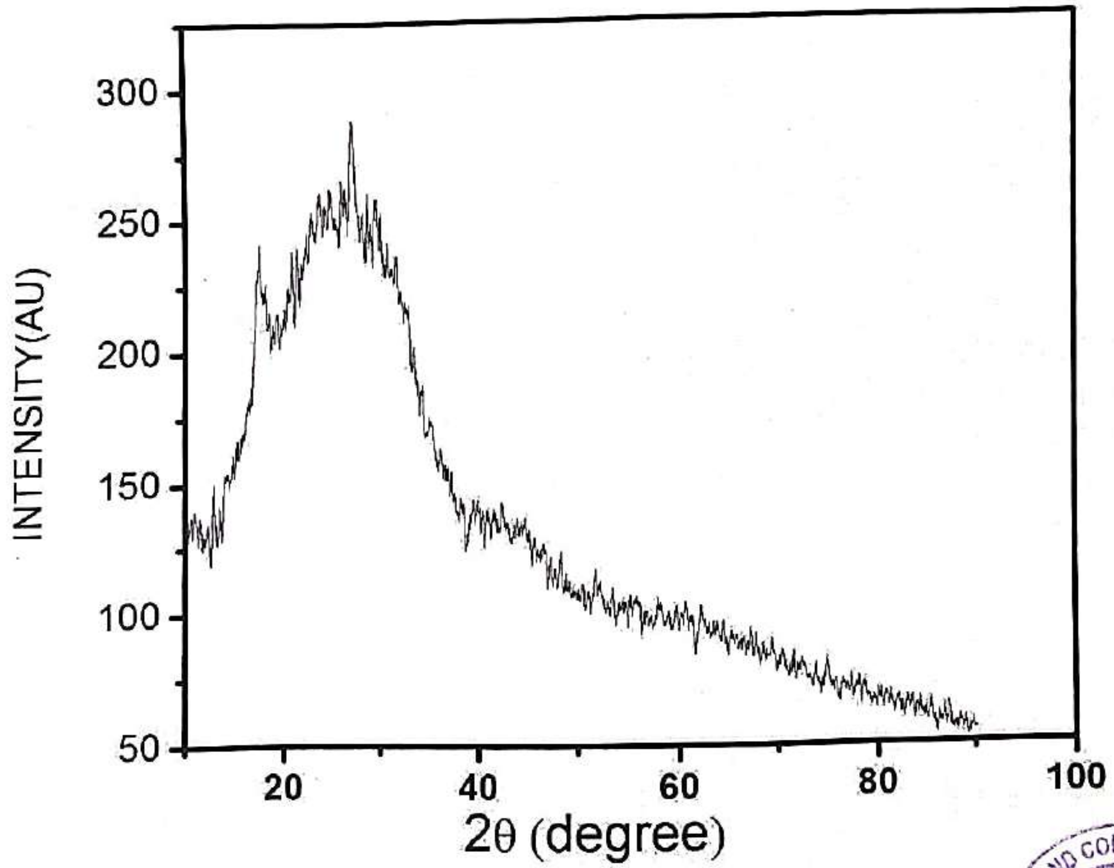

Fig. : X-Ray Diffraction Pattern of $CoFe_2O_4$ thin film

The uniform, well adherent brown coloured thin film of $CoFe_2O_4$ was deposited using CBD technique. Above figure shows X-Ray Diffraction Pattern of $CoFe_2O_4$ thin film. As there are no specific peaks, an amorphous thin film of $CoFe_2O_4$ is formed.

CHAPTER V

Summery and Conclusion

Chapter I

In this chapter, the general introduction of thin film along with their properties, advantages, applications and their different deposition techniques were discussed. This chapter focuses on the coating of solid Thin films can be fabricated with various techniques, in this chapter wide classification of deposition techniques were discussed. These methods involves evaporation, sputtering (CVD), CVD, and plasma enhanced chemical vapour deposition also electrode position, chemical bath deposition. Reflux, spray pyrolysis and SILAR method. Our goal is to enhance understanding of the deposition techniques.

Chapter II

In this chapter, introduction of super capacitor is discussed with their different types, advantages, and applications. Super capacitor is an electrochemical energy storage device with high power density, which is used for a variety of applications such as, hybrid electric vehicles, uninterruptible power supplies, memory protection of computer electronics, and cellular device, as they can be quickly charge, exhibit temperature stability, and have safety properties suitable for such applications. Based on the electric charge storage mechanism, three types of super capacitors-electric double layer (EDLC), Pseudo-capacitors and Hybrid capacitors were discussed.

Chapter III

This chapter gives detailed explanation of various characterization techniques which we have been used for super capacitive applications. It deals with the various structural and electrochemical characterization technique to study the properties of prepare sample. Important thin film parameter that can influence the electrochemical behaviour of $CoFe_2O_4$ based material are summarised.

Chapter IV

In this chapter, the synthesis of $CoFe_2O_4$ thin films by a CBD method were presented. The deposition mechanism of $CoFe_2O_4$thin film is explained using experimental method and detailed properties of prepared sample are studied. A detailed study has been carried out to prepare CuO thin films by the XRD analysis showed the presence of $CoFe_2O_4$ with amorphous nature

Chapter 5

Summary and Conclusion

"PHOTOTHERMAL SUPERHYDROPHOBIC CARBON NANOPARTICLES-POLYMER NANOCOMPOSITE COATED COTTON FABRIC FOR SELF-CLEANING APPLICATION"

A

PROJECT REPORT SUBMITTED TO

VIVEKANAND COLLEGE KOLHAPUR,

(EMPOWERED AUTONOMOUS)

FOR THE DEGREE OF

MASTER OF SCIENCE

IN

PHYSICS

UNDER THE FACULTY OF SCIENCE AND TECHNOLOGY

BY

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UNDER THE GUIDANCE OF

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DEPARTMENT OF PHYSICS,

VIVEKANAND COLLEGE KOLHAPUR

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(2023-2024)

CERTIFICATE

This is to certify that the project entitled **"PHOTOTHERMAL SUPERHYDROPHOBIC COATING ON COTTON FABRIC FOR SELF-STERLIZING AND SELF -CLEANING APPLICATION"** which is being submitted here with for the award of the degree Master of Science in Vivekanand College (Autonomous), Kolhapur, is the result of the original project work completed by **Miss. Shivani Dattatray Sagar** under our supervision and guidance and to the best of our knowledge and belief the work embodied in this project has not formed earlier the basis for the award of any degree or similar title of this pr any other University or examining body.

Place: Kolhapur

Date:

(Dr. Sanjay S. Latthe)
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(EMPOWERED AUTONOMOUS

VIVEKANAND COLLEGE KOLHAPUR
ESTD JUNE 1964
(Empowered Autonomous)

DECLARATION BY STUDENT

I hereby declare that, the project entitled **"PHOTOTHERMAL SUPERHYDROPHOBIC COATING ON COTTON FABRIC FOR SELF-STERLIZING AND SELF -CLEANING APPLICATION"** completed and written by me has not previously formed the basis for the award of any Degree or Diploma or similar title of this or nay other university or examining body.

Place: Kolhapur
Date: 30|04|2024

Miss. Shivani Dattatray Sagar
B.Sc. (Physics)

VIVEKANAND COLLEGE KOLHAPUR (Empowered Autonomous) ESTD JUNE 1964

DECLARATION BY GUIDE

This is to certify that the project entitled **"PHOTOTHERMAL SUPERHYDROPHOBIC COATING ON COTTON FABRIC FOR SELF-STERLIZING AND SELF -CLEANING APPLICATION"** being submitted herewith for the award of the degree of Master of Science in Physics under the Faculty of Science of Shivaji University, Kolhapur is the result of the original research work done by **Miss. Shivani Dattatray Sagar** under my/our supervision and guidance and to the best my/our knowledge and belief the work embodied in this project has not formed earlier the basis for the award of any degree of similar title of this or any other University or Examining body.

Place: Kolhapur

Date: 30/04/2024

(Dr.Sanjay S. Latthe)

Project Guide

Department of Physics,

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ACKNOWLADGEMENT

On the day of completion of this project, I offer sincere gratitude to those who encouraged and helped me at various stages of this work.

I have great pleasure to express my deep sense of indebtedness and heart full gratitude to **Dr.Sanjay S. latthe,** Head Department of Physics, Vivekanand college (Autonomous), Kolhapur, for their expert and valuable guidance and continuous encouragement given to me during the course of my project work.

I wish to express my appreciation to **Miss. Rutuja A. Ekunde** for discussion and co-operation in each and every movement of my project work.

My acknowledgement will be incomplete if I don't express my appreciation towards my family members whose good will & inspiration helped us a lot in completing this project work.

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Chapter 1

Introduction

1.1 Self-Cleaning effect

The self-cleaning effect is inspired from nature. Lotus is one of the most popular example of self-cleaning effect. It is symbol of purity because its property remains clean and does not touches the dirt particle. When water drops fall onto the surface of lotus leaves, they form spherical drops with high contact angles and roll-off from the surface collecting dirt and otherparticles [7]. This property of cleaning on its own is termed as self-cleaning.

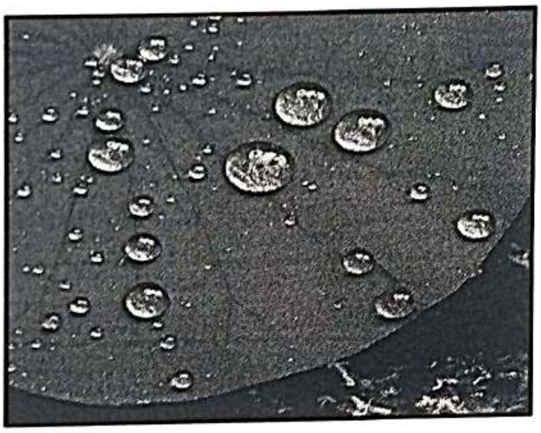


Figure.1 Self Cleaning Effect on lotus leaf

1.2 Wettability and Contact angle

Wetting of the solid surface by liquids is a common interface phenomenon. Wettability is onethe most important properties of the solid surface. The most familiar examples are flashing ofwater droplet on lotus leaf surface in early morning. Wetting phenomenon play important rolein daily lives and industry. It affects the behavior of creature in nature. The ability of the surfaceto hold contact with liquid is known as wettability.

Contact angle is a common way to measure a wettability of solid by a liquid. When an interface exists between liquid and a solid, the angle between the surface of the liquid and the outline ofthe contact surface is described as contact angle.

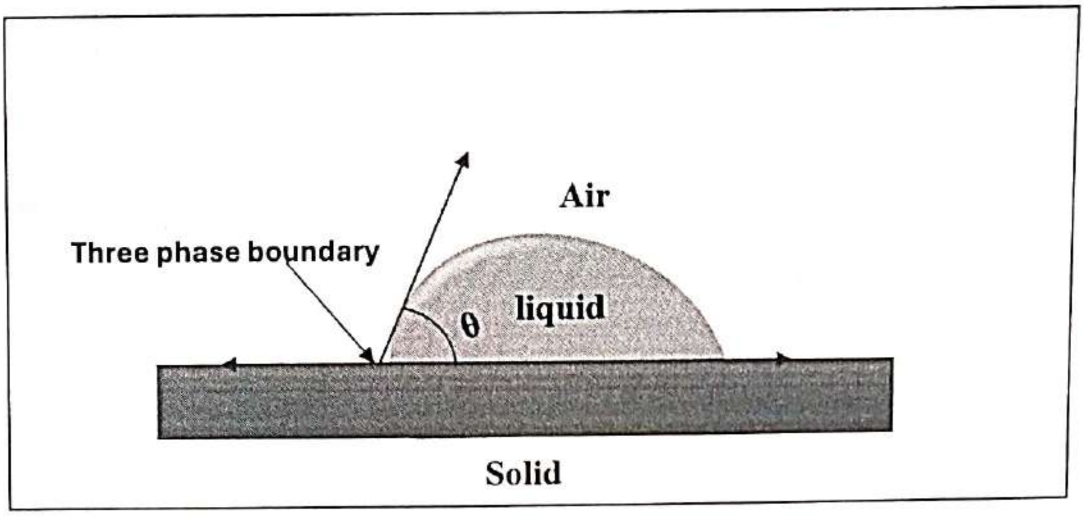


Figure 2: Three phase contact line of liquid on a solid surface.

If the contact angle is less than 90° then these surfaces are known as hydrophilic. It having attraction towards water. If the contact angle is greater than 90° then that surface is said to be hydrophobic. If contact angle is greater than 150° then the surface is known as superhydrophobic. Superhydrophobic surfaces have strong repellence toward water. The best example of superhydrophobic surface is Lotus leaf. If contact angle is less than 10° then that surface is referred as superhydrophilic

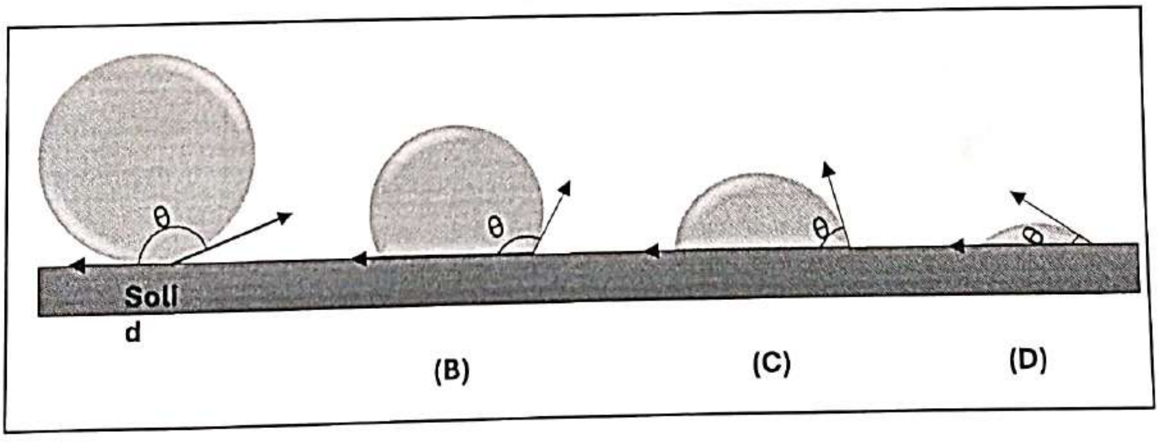


Figure 3: Schematic representing water contact angle on (A) Superhydrophobic, (B) Hydrophobic, (C) Hydrophilic and (D) Superhydrophilic surface.

To understand the correlation between the surface wettability, the famous Wenzel and Cassie-Baxter model proposed [9]. The principle of superhydrophlicity were first discovered by Wenzel in 1936 and in 1944 by Cassie-Baxter.

Wenzel state:

Wenzel developed a model in which state that rough surface is completely wetted by liquid droplet i.e. liquid drop completely pentetrated into rough surface. As roughness goes hand-in-hand with an enlarged surface area, it affects the wettability of solid.

Cassie-Baxter state:

Cassie-Baxter developed a heterogeneous surface, liquid states that liquid drop sit on the top asperities of dual scale surface structure and air can be trapped in the pockets between the liquidand solid substrate which leads to a high water contact angle.

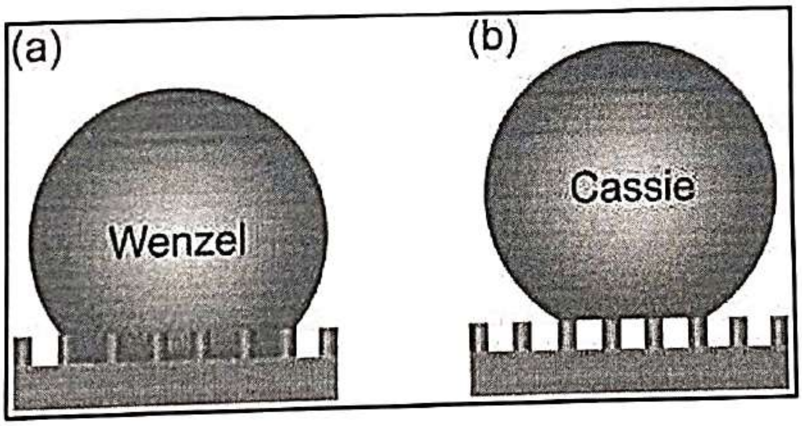


Figure 4: Schematic representation of a water droplet in (a) Wenzel state and (b) Cassie state

CHAPTER 2

METHODOLOGY AND CHARACTERIZATION TECHNIQUES

2.1 Different methods for the preparation of Superhydrophobic coating on Cotton

2.1.1 Layer-by-Layer Method

Layer by Layer method has been used to achieve nano/ microstructure and is used in the fabrication of superhydrophobic surfaces [2]. It is nothing but a process of absorbing others by dipping into the alternating solution. Layer by Layer method tends to reduce the wettability of the surface. Hydrophobicity increases with an increase in the number of layer deposition.

2.1.2 Solution Immersion Method

The solution immersion method is used to prepare superhydrophobic surfaces. A solution immersion method is time-saving procedure and needs cheap reagents. The approach is fairlyfacile to operate, and no special technique or equipment is required.

2.1.3 Dip Coating method

Dip coating is a method used to create superhydrophobic surfaces. It involves immersing an object into a solution containing hydrophobic materials, such as fluoroalkylsilane or nanoparticles. When the object is removed from the solution, a thin film of the hydrophobic material coats its surface, creating a water-repellent effect. Multiple dips and drying cycles may be needed to achieve the desired level of hydrophobicity

2.2 Characterization

2.2.1 Scanning Electron Microscopy (SEM)

In 1937, Scanning electron microscopy was initially made by Mafed Von Ardenne. SEMis a type of electron microscope that images a sample by scanning with a high-energy beam of electrons. SEM works on the principle of applying kinetic energy to produce signals on the interaction of electrons. SEM is a powerful tool for the investigation of surface structure. It is used to study the topography of elements used in industries. SEM is the most widely used microscope. IT can be used for large size samples. It is versatile and high resolution as well as depth of field. The SEM has a large depth of field which allows more of the specimen to focus atthtime. It has a large high resolution so closely specimen can magnify at a high level [8]. It has several advantages such as simple, high availability, cost-effective and nontoxic

2.2.2 Contact Angle Measurement:

Contact angle is the angle created by a liquid with solid surface when materials are in contact.The contact angle defined as the angle made by the tangent to the point of contact of the solidand the liquid. It is mostly used for measurement wettability of solid surfaces .The photocatalytic property confirmed by the decrease in water contact angle (WCA) with UV illumination time. The wetting properties of the coating surface before and after UV irradiation was confirmed by WCA measurements.

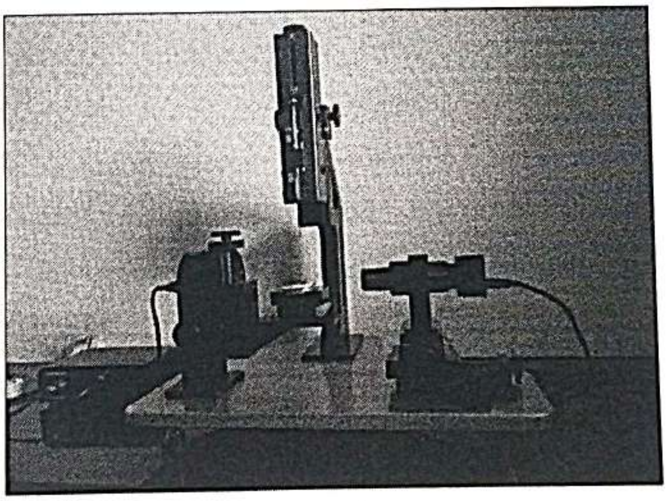


Figure 6. Contact Angle Measurement

CHAPTER 3

EXPERIMENTAL WORK

3.1 Preparation of Superhydrophobic Cotton

Chemicals:

Polydimethylsiloxane (PDMS; viscosity 5cSt) from Sigma-Aldrich, Polylactic acid, Chloroform, Candle soot nanoparticles, cotton fabric from local market

Collection of candle Soot Nanoparticles (CS NPs):

A single candle may be held in place by a silica crucial, which enables the soot from the candle to accumulate in layers on a glass substrate by moving back and forth in the flame. Following their collection, the soot particles will be scraped off the glass substrate and put into a glass bottle. Next, 500g of candle soot will be sonicated for 20 minutes to disperse it in 100 ml of chloroform. A fine-pore stainless steel mesh filter will be used to filter the dispersed soot. To eliminate chloroform, the resultant dispersion of candle soot nanoparticles will be dried at 40 °C on a hot plate. CS NPs that have finally dried will be kept in a glass container.

Preparation of Superhydrophobic Photothermal coating on cotton fabric:

At first, the introduction of 0.024 g of polylactic acid into a chloroform solution containing 25 mL, which was stirred at 450 rpm for 90 minutes, yielding a uniform solution labeled as A. Subsequently, a solution B was prepared by incorporating 350 mg of candle soot nanoparticles (CS NPs) into a mixture of 25 mL chloroform and 2 mL polydimethylsiloxane, followed by 35 min of magnetic stirring. Cotton fabric, previously cleaned, underwent a 5-minute immersion in solution A, followed by air-drying at room temperature for an additional minute. Subsequently, the fabric was immersed for 5 min in solution B and left to air-dry at room temperature for 1 min. This process, involving the application of solution A and dispersion B, constituted one dipping cycle for composite coating. Multiple dipping cycles were performed, and all samples were dried at 120 °C for 30 min.

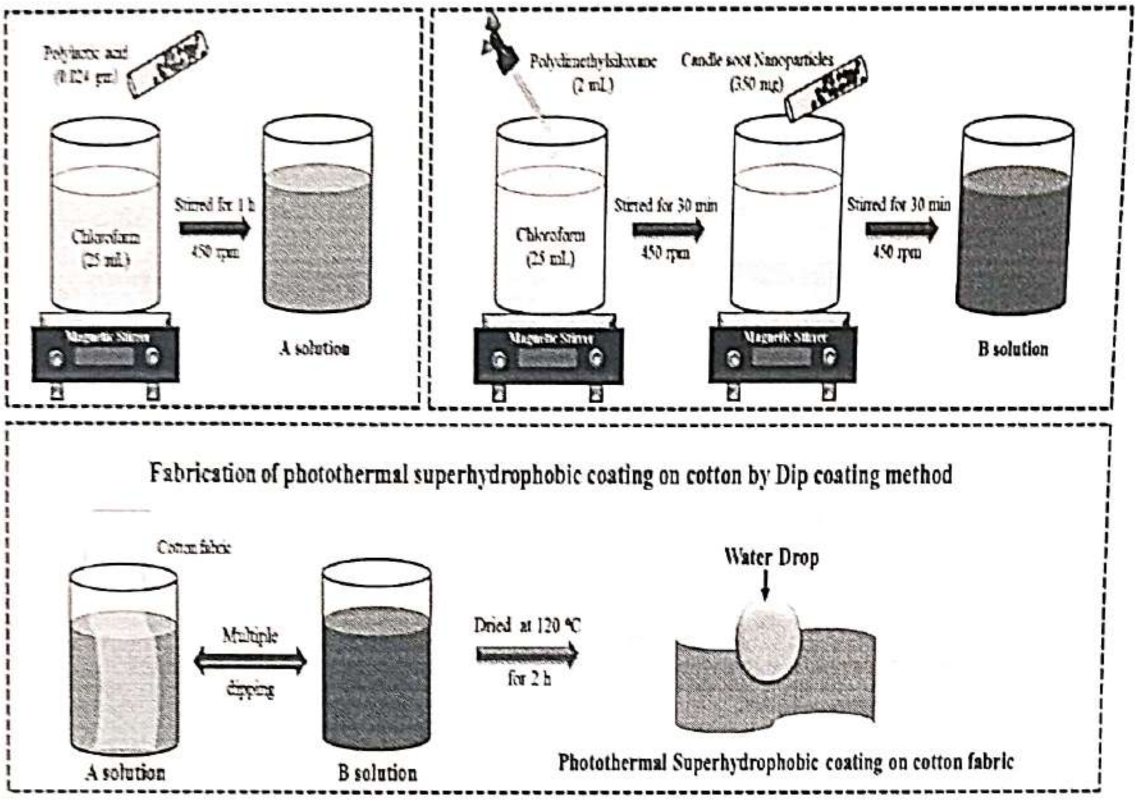


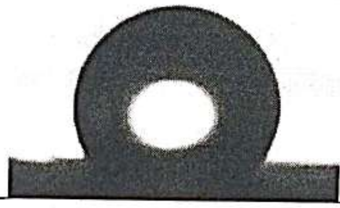
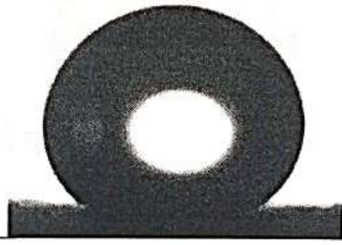
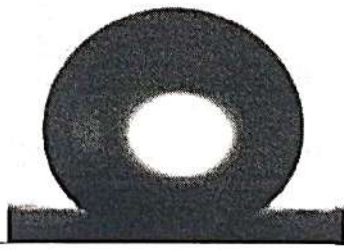
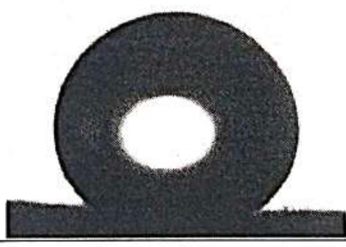
Figure7: Fabrication of photothermal superhydrophobic coating on cotton by Dip coating method

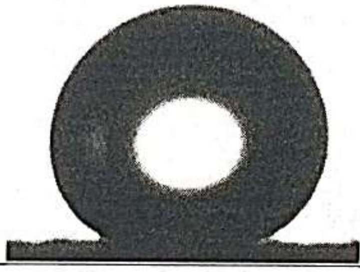
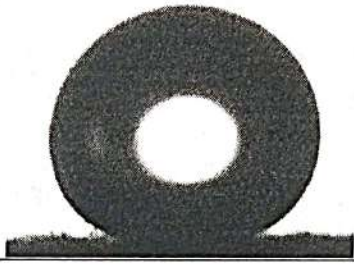
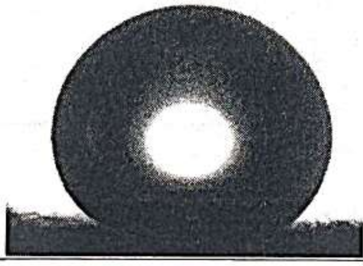
CHAPTER 4

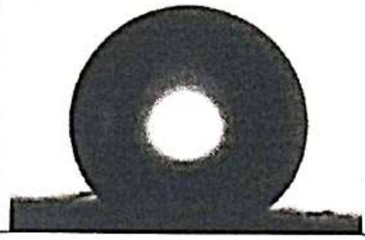
RESULT AND DISCUSSION

4.1 Superhydrophobic Property of Coated Cotton

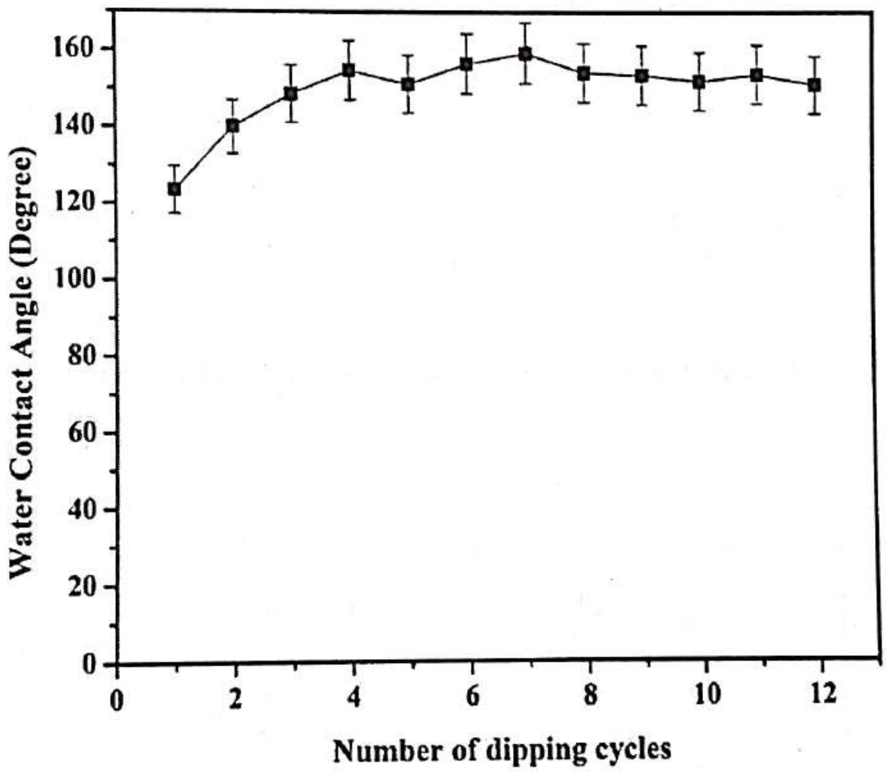
Water Contact Angle

Sr. No	Number of dipping cycles	Water Contact Angle (WCA) in Degree	WCA images
1	1	123.5	
2	2	140	
3	3	148.7	
4	4	154.80	
5	5	151.20	

6	6	156.56	
7	7	159.37	
8	8	154.2	
9	9	153.6	
10	10	151.97	
1ZZZZZZZ1	11	153.77	

12	12		

The relationship between WCA and Number of dipping cycles



4.2 Mechanical Durability

Sandpaper Abrasion test

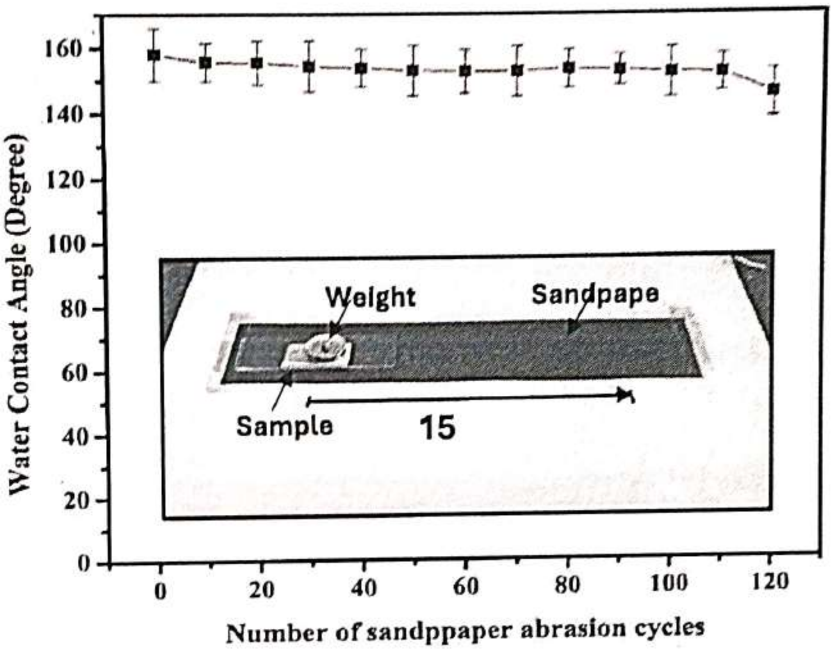


Figure 8: The relationship between (a) WCA and sandpaper abrasion cycles

Adhesive tape peeling test

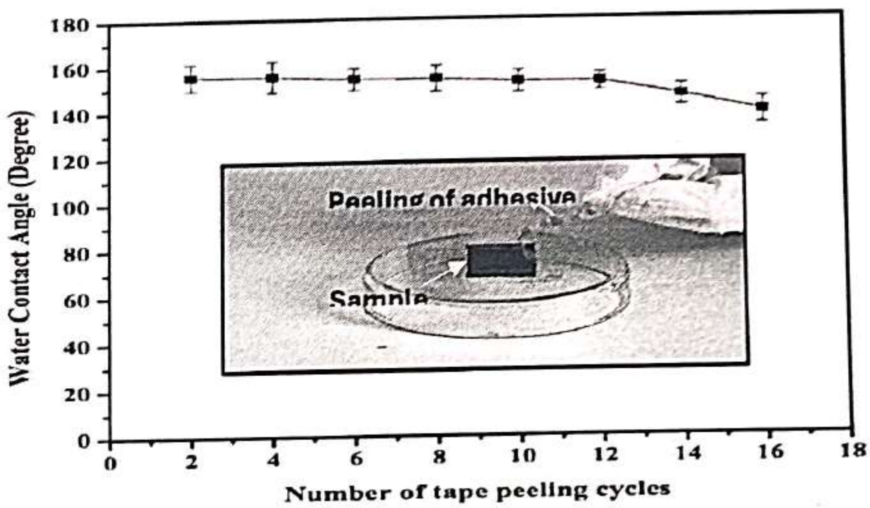


Figure 9: The relationship between (b) WCA and adhesive tape peeling cycles

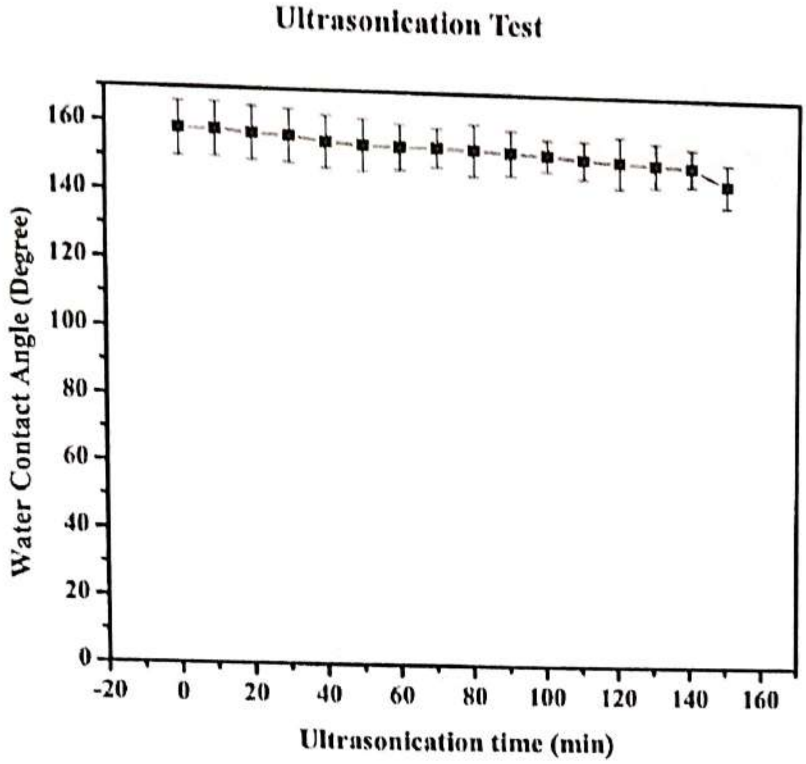


Figure 10: The relationship between WCA and ultrasonication time.

4.3 Self-cleaning property of the prepared superhydrophobic coating

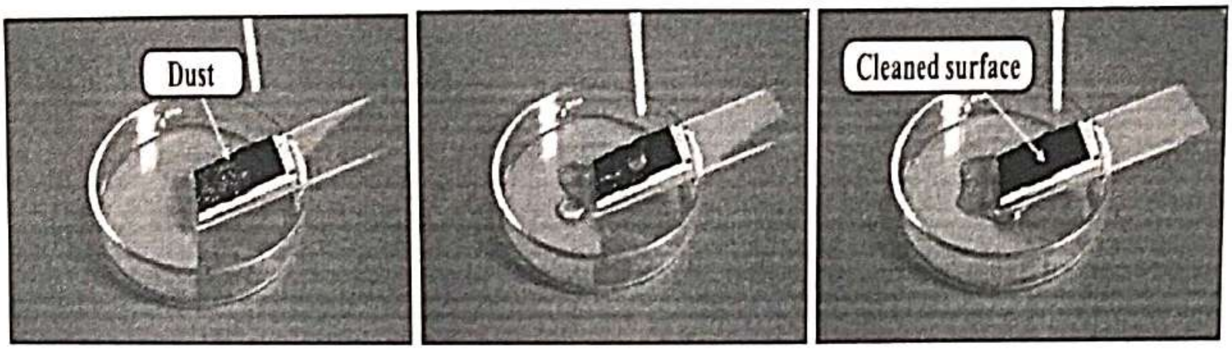


Figure 11: Self-cleaning behavior of prepared superhydrophobic coating

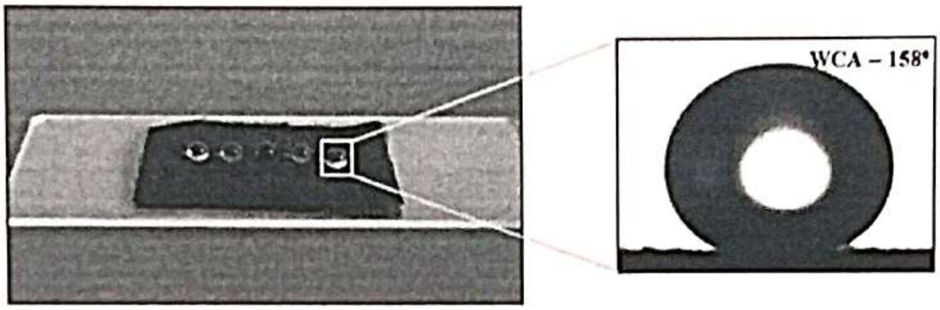


Figure12: Optical photographs of superhydrophobic coating

CHAPTER 5

Conclusion

- The coating showed WCA of 159.37° and rolling angle of 6° was achieved by dipping CS NPs/PDMS composite on cotton fabric.
- The coating exhibited excellent self-cleaning property.
- The mechanical stability of the prepared coating is examined by adhesive tape peeling test, sandpaper abrasion test.
- The coating maintained superhydrophobicity even after 115 sandpaper abrasion cycles and15 adhesive tape peeling cycles.
- The sample underwent ultrasound treatment to assess its laundry stability. The sample was placed in water filled ultrsonication bath. The superhydrophobicity maintained up to 145 min of ultrasound treatment.

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SURFACE MODIFICATION TO ACHIVE SUPERHYDROPHBICITY ON PCL-PS MEMBRANE SURFACE FOR OIL WATER SEPARATION

A Research Project Submitted To

VIVEKANAND COLLEGE KOLHAPUR,

(EMPOWERED AUTONOMOUS)

FOR THE DEGREE OF MASTER
OF SCIENCE IN PHYSICS

UNDER THE FACULTY OF SCIENCE

BY

MISS. SNEHAL NITIN AHIWALE

(B.Sc.)

UNDER THE GUIDENCE

OF

DR. SANJAY S. LATTHE

(M.Sc., Ph.D.)

DEPARTMENT OF PHYSICS,

VIVEKANAND COLLEGE KOLHAPUR

(EMPOWRED AUTONOMOUS)

(2023-2024)

CERTIFICATE

This is to certify that the project entitled "**SURFACE MODIFICATION TO ACHIEVE SUPERHYDROPHOBICITY ON PCL-PS MEMBRANE SURFACES FOR OIL-WATER SEPARATION.**" which is being submitted here with for the award of the degree **Master of Science** in **Vivekanand College (Autonomous), Kolhapur,** is the result of the original project work completed by **Miss. Snehal Nitin Ahiwale** under our supervision and guidance and to the best of our knowledge and belief the work embodied in this project has not formed earlier the basis for the award of any degree or similar title of this pr any other University or examining body.

Place:
KolhapurDate:

Project Guide
Dr. Sanjay Latthe
(M.Sc., Ph.D.)

Examiner

Head
Department of Physics
Vivekanand College (Autonomous)

HEAD
DEPARTMENT OF PHYSICS
VIVEKANAND COLLEGE, KOLHAPUR
(EMPOWERED AUTONOMOUS)

VIVEKANAND COLLEGE KOLHAPUR (Empowered Autonomous)
ESTD JUNE 1964

DECLERATION

I hereby declare that, the project entitled "**SURFACE MODIFICATION TO ACHIEVE SUPERHYDROPHOBICITY ON PCL-PS MEMBRANE SURFACES FOR OIL-WATER SEPARATION.**" completed and written by me has not previously formed the basis for the award of any Degree or Diploma or similar title of this or any other university or examining body.

Place:
Kolhapur Date: 30/04/2024

Snehal.
Miss. Snehal Nitin Ahiwale
B.Sc. (Physics)

VIVEKANAND COLLEGE KOLHAPUR (Empowered Autonomous) ESTD JUNE 1964

Acknowledgement

On the day of completion of this project, I offer sincere gratitude to those who encouraged and helped me at various stages of this work.

I have great pleasure to express my deep sense of indebtedness and heart full gratitude to **Dr. Sanjay latthe,** Professor, Department of Physics, Vivekanand college (Autonomous), Kolhapur, for their expert and valuable guidance and continuous encouragement given to me during the course of my project work.

I wish to express my appreciation to **Mr. Pradip Gaikwad** for discussion and co-operation in each movement of my project work.

My acknowledgement will be incomplete if I don't express my appreciation towards my family members whose good will & inspiration helped us a lot in completing this project work.

Miss. Snehal Nitin Ahiwale
B.Sc. (Physics)

VIVEKANAND COLLEGE KOLHAPUR (Empowered Autonomous) ESTD JUNE 1964

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VIVEKANAND COLLEGE KOLHAPUR ESTD JUNE 1964 (Empowered Autonomous)

CHAPTER 1

INTRODUCTION: Nature has provided us with several examples of superhydrophobic surfaces that have inspired researchers to develop similar surfaces with practical applications. Three of the most notable examples are lotus leaves, certain insects, and some plants.The lotus plant is renowned for its ability to repel water, and this property is due to the unique structure of its leaves. The surface of a lotus leaf is covered with tiny bumps, called papillae, which are then covered with even smaller wax crystals. These papillae create an uneven surface, which makes it difficult for water droplets to adhere to the surface. Instead, the water droplets bead up and roll off the surface, taking any dirt or debris with them. The self-cleaning properties of the lotus leaf have inspired researchers to create similar surfaces for use in textiles, coatings, and biomedical devices [1].

Certain insects, such as the water strider, also possess superhydrophobic properties that allow them to move across water surfaces without breaking the surface tension. The water strider's legs are coated with tiny hairs that repel water and prevent the insect from sinking. The ability of water striders to move across the surface of water has inspired the development of superhydrophobic coatings for boats and other watercraft, which can reduce drag and increase speed.

Several plants, such as the pitcher plant, have evolved to use superhydrophobic properties to trap insects. The inside surface of the pitcher plant is coated with a waxy layer that prevents insects from climbing out once they have fallen in. The wax layer also prevents water from getting inside the plant, which could dilute the digestive enzymes that the plant uses to break down insects. Researchers have used this example to develop superhydrophobic surfaces for use in biomedical applications, such as preventing bacteria from adhering to medical devices.

In addition to these examples, there are countless other examples of superhydrophobic surfaces in nature, including the feathers of certain birds, the scales of fish, and the shells of turtles and other reptiles. By studying these natural examples and understanding the underlying physical and chemical principles, researchers have been able to develop synthetic superhydrophobic materials with a wide range of practical applications.

Generally, the study of superhydrophobic surfaces in nature has not only led to a better understanding of the fundamental principles behind these properties but has also inspired researchers to develop new materials and technologies with practical applications in a variety of fields. As we continue to learn more about the natural world around us, expects to find even more examples of superhydrophobic surfaces that can inspire the development of new materials and technologies [2].

- **Superhydrophobic surfaces and their applications**

Superhydrophobic surfaces are characterized by their extremely high-water repellent property. When a water drop is placed on such surfaces, it attains a circular shape, and the contact between the water drop and the superhydrophobic surface is minimized, resulting in a higher contact angle. Moreover, if the surface is tilted, the water drops on the surface rolls or slides off very easily. The sliding angle for superhydrophobic surfaces is typically less than 10°.

The unique property of superhydrophobic surfaces in not allowing water drops to stay on the surface has led to a wide range of applications. Some of these applications include self-cleaning surfaces, anti-icing surfaces, anti-corrosion coatings, and oil-water separation devices. Superhydrophobic surfaces are also used in microfluidic devices for droplet manipulation and in the development of water-repellent fabrics and coatings for various outdoor applications.

1. Self-cleaning

Superhydrophobic surfaces are capable of self-cleaning. When water is sprinkled on a dusty superhydrophobic surface, the water drops form circular shapes and roll off from the surface, collecting dust particles along the way. This makes the surface clean. This property of the superhydrophobic surfaces is known as the self-cleaning property. It can be applied to surfaces such as windows, outer walls of buildings, and many more.

2. Corrosion resistant

Superhydrophobic surfaces have water-repellent properties, preventing water from staying on the surface. This characteristic helps decrease corrosion and increase the corrosion resistance of the surface. Corrosion occurs when metals react with oxygen and corrode.

3. Anti-fogging surfaces

Superhydrophobic surfaces prevent water drops from remaining on the surface. This characteristic makes them anti-fogging surfaces. Water droplets that form on mirrors, windows, etc. due to fog will not remain on superhydrophobic surfaces and roll off instead.

4. Anti-bacterial surfaces

In the medical field, cleanliness is of great importance. All surgical instruments should be sterilized and free from bacteria. Superhydrophobic surfaces are used for this purpose because they prevent bacteria from sticking to the surface. When bacteria cannot stick to a surface, it cannot grow and spread.

e can*5. Anti-icing surfaces*

In snowy areas, snow accumulates on various surfaces such as highways, industries, aircraft, and vehicles. Physical and chemical methods used to remove ice may cause damage and consume much energy. Superhydrophobic surfaces help reduce the chances of damage and conserve energy.

Superhydrophobic surfaces prevent icing by repelling water droplets and minimizing contact with the surface. They feature a rough texture and low surface energy that create a barrier, causing water droplets to bead up and roll off the surface. This prevents the droplets from spreading and freezing, the initial step in ice formation. The roughness and low surface energy also make it difficult for ice to adhere to the surface, allowing any formed ice to be easily removed. Superhydrophobic surfaces have applications in aviation, power transmission, and other fields where preventing ice buildup is essential for safety and efficiency.

6. Oil-water separation

Oil leaks during oil production and transportation through the sea can cause danger to the marine ecosystem. Superhydrophobic porous surfaces are used to separate the oil from seawater.

The need for oil-water separation arises from the widespread use of oil in various industries and the subsequent release of oily wastewater into the environment. This wastewater contains a mixture of oil and water, which can be harmful to the environment if not properly treated. Oil spills in marine environments can have devastating effects on marine life, and untreated oily wastewater can also harm freshwater ecosystems. Therefore, the development of effective oil-water separation technologies is critical to reducing the harmful impacts of oily wastewater on the environment.

Effective oil-water separation technologies are designed to separate oil and water mixtures, removing the oil phase and allowing clean water to be recovered. Several methods are commonly used for this purpose:

1. Gravity Separation:

This technique relies on the difference in densities between oil and water. The mixture is allowed to settle in a tank or vessel, and due to the density difference, the oil floats to the top while water settles at the bottom. The separated oil and water layers can then be collected separately.

2. Coalescence:

Coalescence methods promote the merging of oil droplets to form larger droplets, making their separation easier. Various mechanisms are employed, such as using coalescing media or adding chemical agents that facilitate the aggregation of oil droplets. Once the oil droplets have coalesced into larger sizes, they can be more efficiently separated using gravity or other methods.

3. Dissolved Air Flotation (DAF):

DAF involves the injection of air bubbles into the oil-water mixture. The tiny air bubbles attach themselves to the oil droplets, causing them to rise to the surface, where they can be skimmed off. DAF is particularly effective for treating emulsions and finely dispersed oil.

4. Centrifugation:

Centrifugal separation utilizes high-speed rotation to separate oil and water phases. The mixture is introduced into a centrifuge, and the centrifugal force causes the denser phase (usually water) to move outward, while the lighter phase (usually oil) collects in the center. The separated phases are then discharged through different outlets.

5. Membrane Separation:

Membrane technologies employ porous membranes that selectively allow the passage of either oil or water. The oil-water mixture is passed through the membrane, where the oil or water preferentially permeates, while the other phase is rejected. Membrane separation can be based on various principles, such as microfiltration, ultrafiltration, or reverse osmosis.

These are some of the effective oil-water separation technologies commonly used. Depending on the specific requirements, a combination of these methods may be employed in sequence to achieve a higher degree of separation efficiency and purity in both the oil and water streams.These technologies can be used to treat oily wastewater generated by various industries, including oil and gas, petrochemical, food processing, and textile industries.

Furthermore, the efficient separation of oil from water has significant economic benefits. In the oil and gas industry, the ability to separate oil from produced water can lead to cost savings and increased oil recovery. In addition, the separation of oil from wastewater can help reduce the cost of treating the wastewater before it is discharged into the environment. Oil-water separation is also important in emergency situations such as oil spills. Rapid and efficient oil-water separation can help minimize the impact of oil spills on marine ecosystems and coastal communities.

Oil-water separation using superhydrophobic sponges offers several advantages over other methods of oil-water separation: *1. Efficiency:*

Superhydrophobic sponges have a high affinity for oil while repelling water. When placed in an oil-water mixture, these sponges selectively absorb and retain the oil, allowing clean water to pass through. This selective absorption leads to high separation efficiency, with minimal oil content remaining in the water phase.

2. Reusability:

Superhydrophobic sponges can be easily wrung out or squeezed to recover the absorbed oil. This feature enables their repeated use, making them highly cost-effective and environmentally friendly compared to disposable methods like filters or absorbent materials.

3. Versatility:

Superhydrophobic sponges can be tailored to absorb different types of oils or hydrocarbons, making them versatile for various oil-water separation applications. They can effectively separate a wide range of oils, including crude oil, petroleum, diesel, and lubricants.

4. Scalability:

Superhydrophobic sponges can be manufactured in various sizes and shapes, making them adaptable to different separation systems. They can be used in small-scale applications, such as laboratory experiments, as well as in larger industrial setups.

5. Low energy consumption:

The oil-water separation process using superhydrophobic sponges does not require external energy sources, such as electricity or pumps, for operation. The separation occurs naturally due to the inherent properties of the sponges, resulting in low energy consumption and operating costs.

6. Minimal waste generation:

Since superhydrophobic sponges can be reused multiple times, there is minimal waste generation during the oil-water separation process. This reduces the need for frequent disposal or replacement of separation materials, leading to a more sustainable and environmentally friendly approach.

7. Ease of handling:

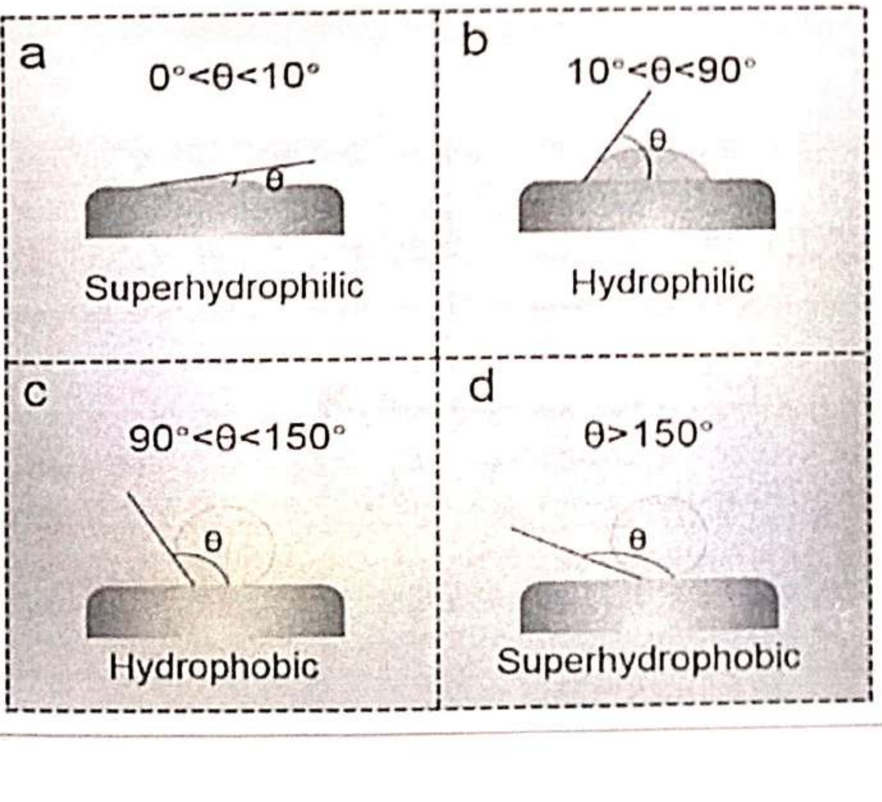
Superhydrophobic sponges are lightweight and easy to handle, making them practical for various applications. They can be easily incorporated into existing separation systems or deployed in remote or challenging environments.

Overall, oil-water separation using superhydrophobic sponges offers advantages such as high efficiency, reusability, versatility, scalability, low energy consumption, minimal waste generation, and ease of handling. These benefits make superhydrophobic sponges an attractive and effective option for oil-water separation in various industries, including wastewater treatment, oil spill clean-up, and industrial processes.

- **Wettability and types of wettability**

Wettability is the property that describes how well a liquid can spread over a solid surface. It can be broadly classified into two categories based on the amount of solid surface that is wetted by the liquid. The contact angle, which is the angle between the solid surface and the tangent line to the liquid drop, is used to determine the amount of liquid in contact with the solid surface. Technically, the contact angle is defined as the angle between the solid-liquid interface and the liquid-vapour interface, and as the contact angle increases, the amount of liquid in contact with the solid surface decreases [3].

For water, wettability is classified based on the contact angle. A solid surface is considered hydrophilic if the contact angle of the water drop is less than 90°, meaning that the surface has an affinity for water. Conversely, a solid surface is considered hydrophobic if the contact angle is



greater than 90°, indicating that the surface lacks an affinity for water, and the water drop tries to minimize contact with the solid surface. There are two additional classifications of wettability that are extremes of the hydrophilic and hydrophobic surfaces. If the water contact angle of the hydrophilic surface decreases below 10°, the surface is known as a superhydrophilic surface, where the water drops spreads evenly over the surface. In contrast, if the water contact angle of the hydrophobic surface exceeds 150°, the surface is known as a superhydrophobic surface, and the water drop forms a circular shape with minimal contact with the solid surface. This classification is explained with the help of following figure.

Fig 1: Classification of the wettability in terms of the contact angle where in (a) the contact angle is less than 10° so the surface is known as superhydrophilic, (b) the contact angle is less than 90° so the surface is known as hydrophilic, (c) the contact angle is greater than 90° so the surface is known as hydrophobic and (d) the contact angle exceeds 150° resulting in superhydrophobic surface [4].

The wetting behavior of a solid surface is not only determined by its chemical properties but also by its surface roughness. This relationship between surface roughness and wettability has been extensively studied by scientists, including Cassie-Baxter and Wenzel. They observed that on rough solid surfaces, two distinct states can be observed.

Surface roughness can be achieved by etching the solid surface, and when a water drop is placed on the surface, it either fills the cavities on the rough surface or lies above them. In the Cassie-Baxter state, the water drop does not wet the entire surface and instead lies above the cavities, resulting in a larger contact angle. In contrast, in the Wenzel state, the water drop wets the entire surface, including the cavities, resulting in a decrease in contact angle. Wenzel also proposed that as the surface roughness increases, the hydrophobicity of hydrophobic surfaces and the hydrophilicity of hydrophilic surfaces increases.

In summary, the wetting behavior of a solid surface is determined by a combination of its chemical properties and surface roughness. Understanding the relationship between surface roughness and wetting behavior is crucial in designing surfaces with specific wettability properties for various applications. The following figure will elaborate both the Cassie-Baxter and Wenzel states.

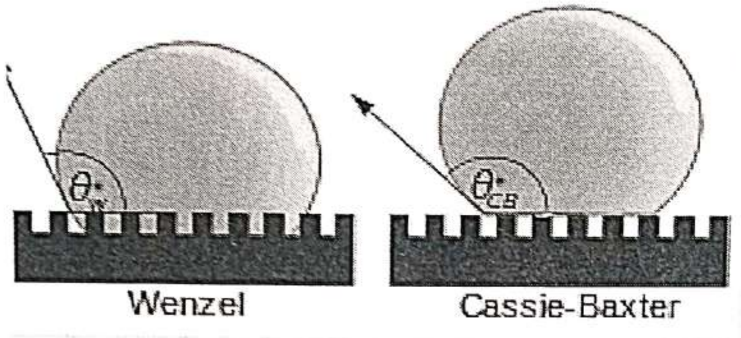


Fig 2: The Cassie-Baxter state and the Wenzel state [5].

1.4 Oil-water separation: Technical concept

The process of oil-water separation involves the creation of a surface that is able to selectively interact with oil and water. This is achieved by designing a surface with specific surface properties that enable the separation of the two liquids. A superhydrophobic surface is one such surface that has been found to be highly effective in separating oil and water.

Superhydrophobic surfaces are characterized by their high water repellency and low surface energy. This means that water droplets do not wet the surface and instead form spherical droplets that easily roll off the surface. These surfaces are created by modifying the surface properties of a material, such as its texture or chemical composition, to produce a surface that is highly water repellent. To separate oil and water using a superhydrophobic surface, the surface is designed to have pores or channels that are smaller than the size of the oil droplets. This allows the oil droplets to pass through the pores while the water droplets are blocked and cannot pass through. The oil droplets are then collected and separated from the water.

There are several techniques that can be used to create superhydrophobic surfaces for oil-water separation. One common technique is to create a surface with micro or nanoscale structures that trap air pockets, which prevent water from wetting the surface. Another technique is to modify the chemical composition of the surface to make it highly hydrophobic. In addition to their use in oil-water separation, superhydrophobic surfaces have many other potential applications. They can be used to create self-cleaning surfaces, anti-fogging surfaces, and anti-icing surfaces. They can also be used in biomedical applications to create anti-bacterial surfaces and in environmental applications to separate pollutants from water.

The use of superhydrophobic surfaces for oil-water separation is a promising technology that has the potential to significantly reduce the environmental impact of oil spills and improve the efficiency of oil recovery operations. By creating surfaces that selectively interact with oil and water, we can develop more effective and sustainable methods for oil-water separation.

1.5 References

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Chapter 2

Methodology and Characterization Techniques

Superhydrophobic coatings have garnered significant attention due to their ability to repel water and resist wetting. The unique properties of superhydrophobic surfaces, such as high water contact angles and low contact angle hysteresis, have found applications in a wide range of fields, including self-cleaning surfaces, anti-icing coatings, and microfluidic devices. Sponges, with their porous and highly absorbent nature, present an intriguing substrate for the deposition of superhydrophobic coatings.

Various methods have been developed to prepare superhydrophobic coatings on sponges, each offering distinct advantages and tailored for specific requirements. These methods encompass a diverse range of techniques. Each method employs different strategies to achieve the desired superhydrophobic properties on the sponge surface.The selection of an appropriate method for the preparation of superhydrophobic coatings on sponges depends on several factors, including the substrate material, desired coating thickness, roughness control, and the availability of specific chemicals and equipment. The ultimate goal is to create a durable and robust superhydrophobic coating that exhibits exceptional water repellency and self-cleaning properties while maintaining the underlying structure and functionality of the sponge material.

Here, we will explore and discuss in detail the various methods employed for the preparation of superhydrophobic coatings on sponges.

❖ **Electrospinning**

The electrospinning technique allows for the fabrication of continuous fibers with diameters in the range of a few nanometers. While this method is commonly utilized with polymers, it can also be applied to metals and ceramics, particularly when enhanced thermal stability is achieved using ceramics [1].

❖ **Solution immersion method**

The solution immersion method is a straightforward and uncomplicated deposition technique. It does not necessitate the use of specialized equipment, making it highly accessible and convenient. This method proves to be a time-saving approach to deposition, allowing for efficient coating or treatment of surfaces without the need for complex setups or procedures [2].

There are numerous methods available for preparing superhydrophobic surfaces, including the template method [1], etching method [1], electroless galvanic deposition method

[1], wet chemical reaction method [2], hydrothermal synthesis [2], phase separation method [2], plasma treatment method [2], casting method, and more. The selection of a specific method depends on various factors such as the substrate material, desired chemical composition, deposition parameters, and other specific requirements [In the case of preparing a superhydrophobic material, the solution immersion method or dip coating method is often chosen. This technique allows for the efficient coating of the material, resulting in the desired superhydrophobic properties. It is a practical and effective approach specifically tailored for the preparation of superhydrophobic material [4].

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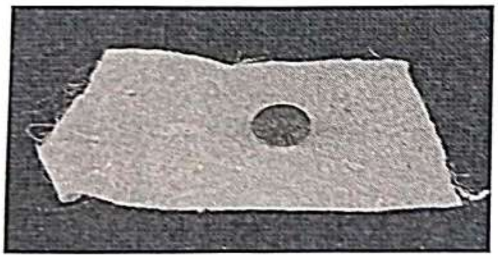
CHAPTER 3

EXPERIMENTAL WORK

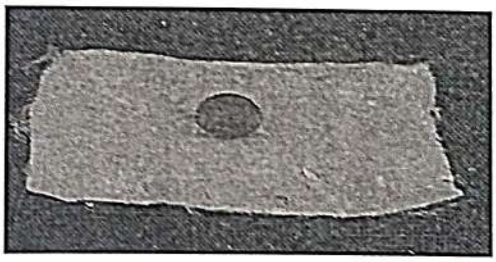
For dipping the process of coating superhydrophobicity on membrane of PCL- PS made by electrosping method, the initiate process is done by dissolving 0.5 gm of PS and 0.5 gm of PCL in 10 ml of dichloromethane by stirring. Subsequently, the prepared solution is used for electrospinning process. During the electrospinning process, it is imperative to maintain a flow rate of the PS-PCL solution at 1ml/h using a syringe pump. A high voltage of 15kv is applied between the needle and collector, with a needle diameter of 0.55mm. The distance between the needle and fiber collector is been fixed at 14 cm. As a fiber collector, rotating drum is covered covered by aluminum foil and it will maintain a constant rolling speed of 120 rpm.

After the preparation of membrane, the process of dip coating starts with mixture of solute and solvent, such as PDMS (polydimethylsiloxane) and hexane at a constant weight ratio of 10:1.The solution is prepared by solvent (hexane) and solute (PDMS), adding 20ml solvent and 1.2ml solute. The mixture is stirred for 30 min.

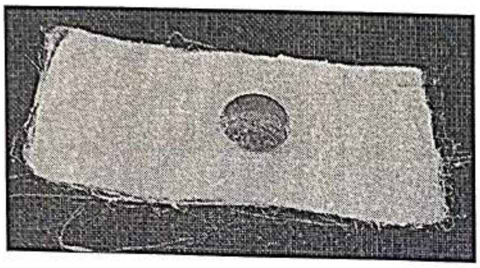
After the solution is prepared the dipping process starts for samples such as 10 sec dipping and 1 min air dry gives us 1 cycle, minimum 3-4 samples are been collected for the test of superhydrphobicity . The sample 1 contain 1 cycle, sample 2 contain 3 cycles, sample 3 contain 6 cycles, sample 4 contain 9 cycles, etc. The sample 3 of 6 cycle is taken for further process which is dried in the hot air oven, after that process the wettability of the sample is been tested .



SAMPLE 1



SAMPLE 2



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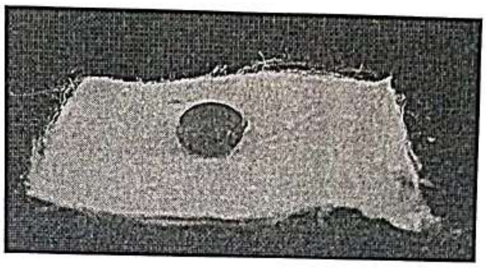

SAMPLE 4

OIL-WATER SEPARATION

Here the oil water separation will be performed by using the PCL-PS membrane which is coated by superhydrophobic layer. Here the superhydrophobicity will repel the water and absorb the oil from the solution that is mixture of oil and water. For the process oil and water are mixed at proportion of 10ml oil and 10ml water. Here we have used two types of oil that are disel and hexan . For the practical we have used the pouring method that means the mixture of oil and water are poured from angle of 45degree at the membrane which is fixed at the container. Here we can see the the separation of oil and water the membrane is oreophilic which absorbs oil and not water. The absorbed oil is given out from the other side and collected in the measuring cylinder. The process is carried for both the oils and the oil water separation has been done.

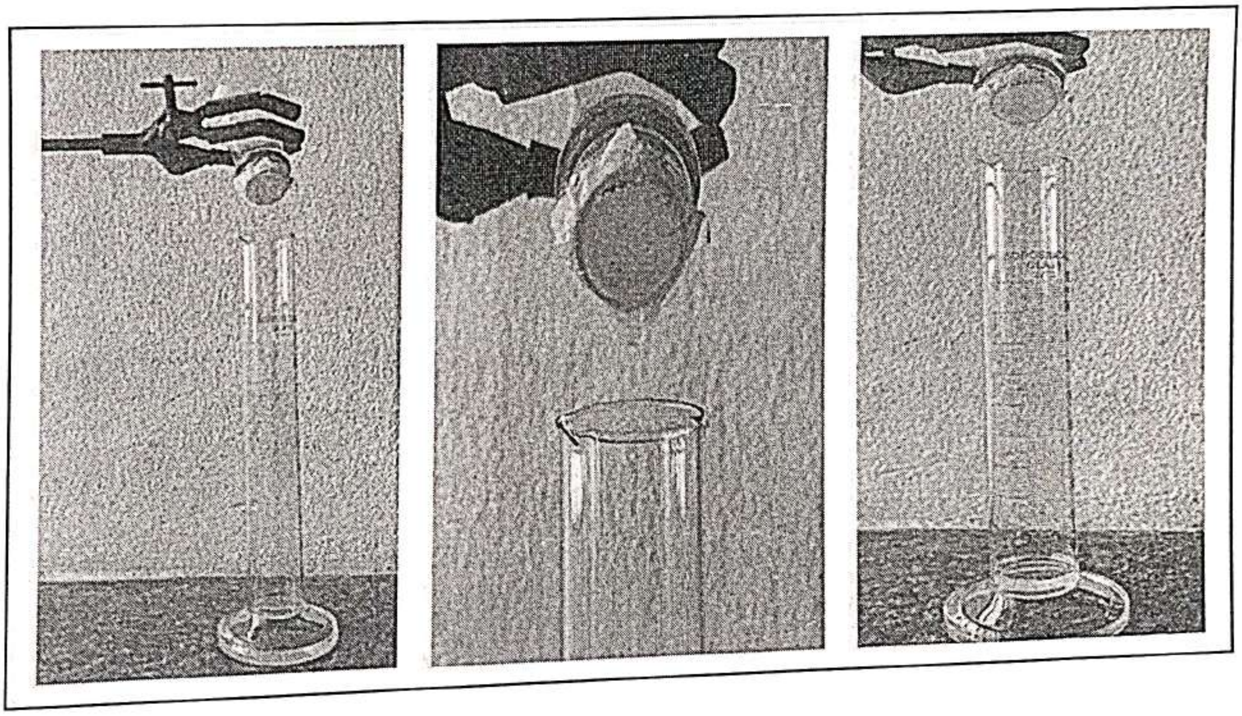

Fig. oil-water separation setup

CHAPTER 4

RESULT AND DISCUSSION

Wettability :

To evaluate the hydrophobicity of the coated membrane, an investigation was conducted by varying the contact angle. Variation in contact angle with different quantities of coating.

Sr. No.	Samples	Contact angle
1	S1	128.71°
2	S2	152.23°
3	S2	142.74°

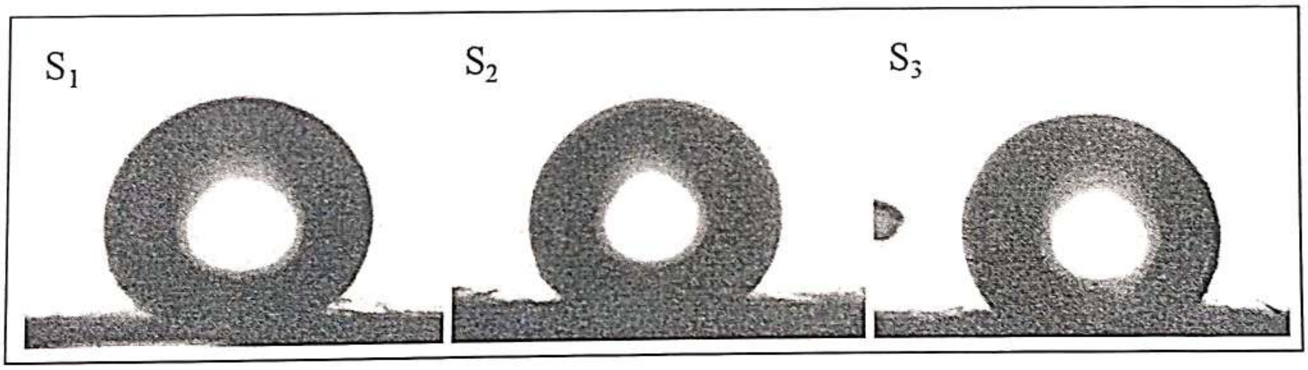

Fig. wettability of prepared samples

OIL WATER SEPARATION EFFICIENCY:

Oil	**Mixture with 10ml water**	**Collected**	**Efficiency (%)**
Disel	10ml	9.7ml	97
Hexane	10ml	9.8ml	98

CHAPTER 5

CONCLUSION

To address the persistent issue of oil leakages and spills, we have developed a simple yet effective method to separate oil from oil-water mixtures. Our approach capitalizes on the hydrophobic properties of membrane, utilizing it in conjunction with a porous surface—specifically, a PS-PCL membrane. By coating and modifying the membrane and polystyrene, we have successfully enhanced its ability to repel water and attract oil. The quantity of solution used in the coating process plays a significant role in determining the hydrophobicity of the membrane. Through our experiments, we observed that increasing the amount of solution resulted in higher contact angles and improved water repellency. While the hydrophobic coating demonstrates commendable performance, it is crucial to consider the mechanical durability of the coated membrane. We conducted adhesive tape tests to assess the coating's ability to withstand mechanical stress. The results revealed a decrease in the contact angle from 142.5° to 128.8° after ten tests, indicating potential limitations in the coating's long-term effectiveness under mechanical strain. The oil water separation gives in result to the minimum loss of oil in the water and maximum water is taken out from the mixture. The research gives effective results of oil water separation.