A Dissertation thesis entitled

"SYNTHESIS AND CHARACTERIZATION OF METAL SUPER-HYDROPHOBIC SURFACES"

Submitted in partial fulfilment of the requirements For the award of the degree of

Master of Science

In

INDUSTRIAL CHEMISTRY

Submitted By

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Dedicated to

My BelovedFamily

Without their love, support and constant encouragement,
this would not have been possible

DECLARATION

We undersigned, hereby declare that the work assimilated in the dissertation thesis entitled **"**Synthesis and characterization of super-hydrophobic surfaces**"** has been carried out by us at Faculty of Science, Department of Industrial Chemistry, Atmiya University, Rajkot, Gujarat, India, under the supervision and Guidance of **Mr. Anand V. Khistariya & Dr. Mehul L. Savaliya Assistant Professor, Faculty of Science, Department of Industrial Chemistry, Atmiya University, Rajkot, Gujarat, India.**

To the best of our knowledge and belief, the work included in this thesis is quite original and has not submitted to any other Institution or University for theaward of any degree either in this or any other form.

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Contents

ABSTRACT

In this our dissertation work we prepared superhydrophobic surface on zinc, Aluminum and copper metals surfaces and on fabric surface. On metals surface we created superhydrophobic coating by etching and hydrothermal coting process. In this process we use KOH and NaOH use as etching solutions which creates microstructure on metal surfaces. Our coating material was stearic acid and lauric acid. After coating contact angles of surface with water droplets was measured with the help of image J capture software. Higher contact angle was 159.57° on aluminum surface by etching process, which shows superhydrophobic characteristics. Our Another work on fabric surface. In coating on fabric surface our coating method is novel and not reported yet. In this process contact angle is 153.56° degree, which shows superhydrophobic characteristics.

Key words: superhydrophobic, coating, metal, aluminium, zinc, copper, surface, morphology, characterization, contact angle.

GRAPHICAL ABSTRACT

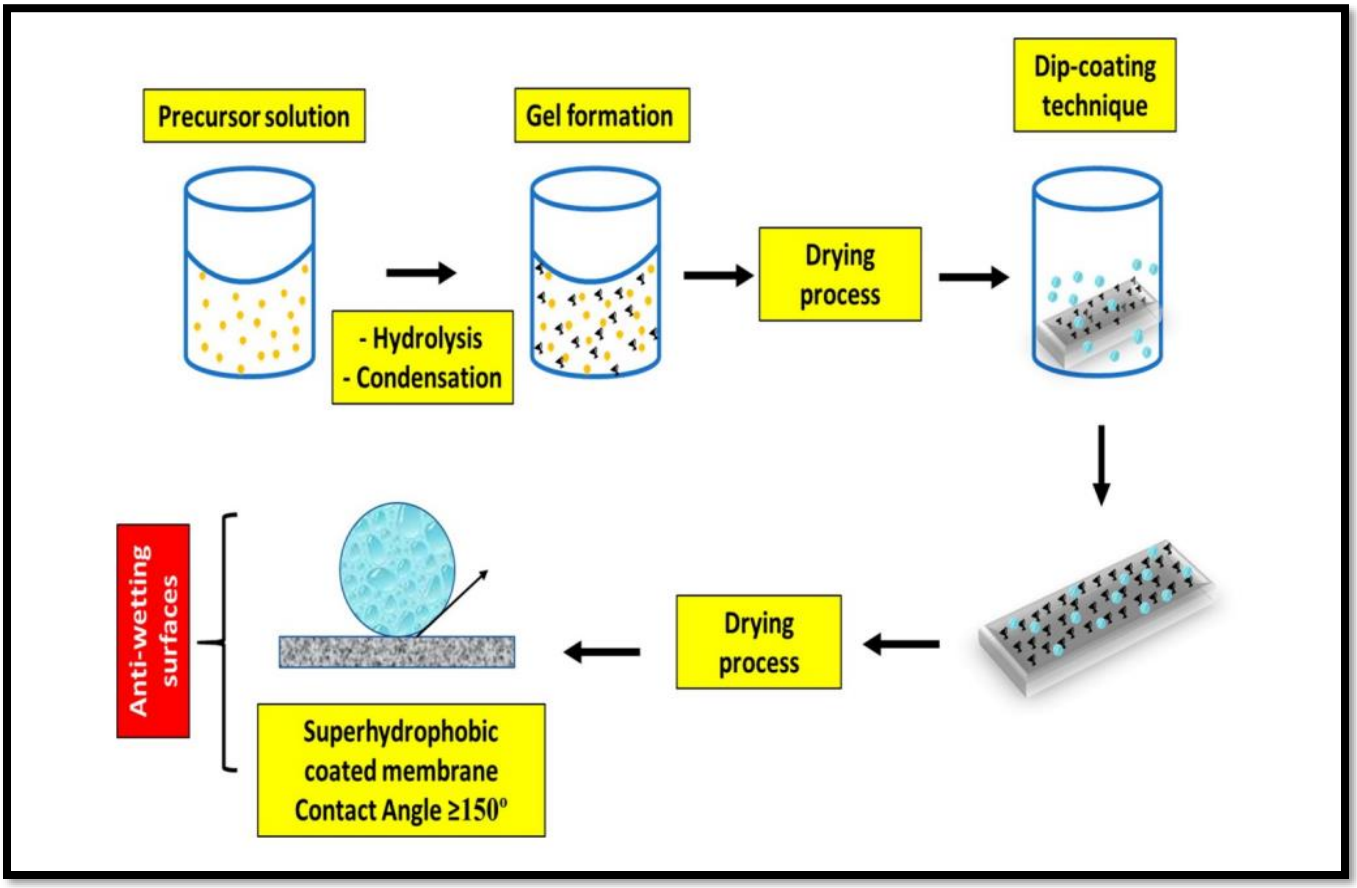

Figure 1. Schematic presentation of antiwetting and superhydrophobic coating s of various substrate by sol–gel processing and dip-coating technique.

INTRODUCTION

Superhydrophobic surfaces are extremely repellent to water and aqueous liquids and have received significant interest in recent years due to their applications in a wide variety of industries including energy production/transmission, transportation, agriculture, consumer products and medical devices. This interest is propelled by careful examination of natural repellent surfaces using cutting edge imaging and analysis methods which lead to a fundamental understanding of repellent surfaces and the capability to fabricate engineered repellent surfaces. Superhydrophobic surfaces shed water very easily and it is difficult to balance a water droplet on the surface.

Hydrophobic is surface that has ability to repeal water. The hydrophobicity was derived from two Greek word hydro which meanswater and Phobos that means fear. Thus, hydrophobic surface can be defined as material which tend to repeal water.

Generally hydrophobic surface can be measured by contact angle measurements technique. Contact angle between the droplet of water with the surface itself. If contact angle is less than 90° the surface is hydrophilic and droplet spread out far and water droplet do not roll-onsurface. If contact angle is 90° to 150° the surface is hydrophobic surface. Water droplet will flow easily and above 150° the surface is superhydrophobic surface which retails its spherical shape and difficultto wet the surface (As shown In Figure-2)

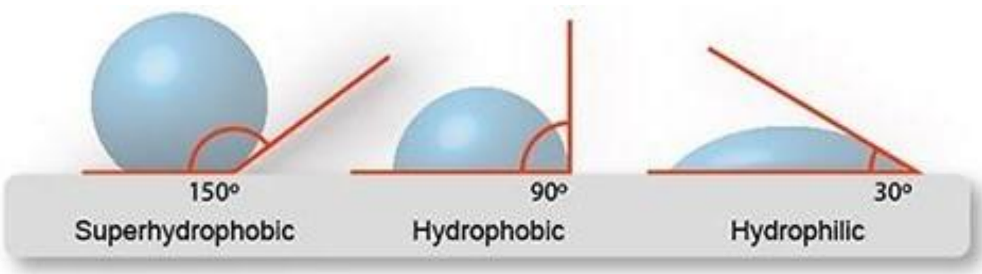

Figure-2 (Contact Angle)

In nature the hydrophobic properties can be seen on lotus leavesor Nelumbo. Dirt particles are picked up by water droplets due to the micro- and nanoscopic architecture on the surface, which minimize thedroplet's adhesion to that surface.

Figure-3
(water drop in Cloth)

Figure-4
(Super hydrophobic material)

Since the hydrophobicity is a new thought in front of the modern era, research on the superhydrophobic coating methods, recently, more and more attraction has been attracted to manufacture various devices with the help of superhydrophobic fabrication. Moreover, superhydrophobic surfaces have important technical potentials for a variety of uses because of their extreme anti-wetting properties. Dynamic effects for instance bouncing, splashing, rebound and fragmentation of a droplet on different types of polymer have been identified.

Reducing the contact of metal substrates with corrosive mediumis a very effective method for the corrosion protection. In nature, thereare many surfaces with special wettability, and super-hydrophobiclotus behaviour is particularly special. Inspired by the mysteriousnature, researchers have tried to apply super-hydrophobic surface technology to the field of metal corrosion protection and have proven that building superhydrophobic sur-face is a very effective way to blockcorrosive medium.

Solid surfaces with customized wetting properties could be usedfor a variety of applications such as self-cleaning, anti-fouling, anti- drag, water condensation, and water/oil separation. In addition, the efficiency of devices with such surface-wetting customized properties toward liquids is enhanced according to the existing environmental conditions.

Wetting properties of a solid surface can be manipulated by introducing physical and/or chemical modifications to the surface.Roughening magnifies wetting properties by the degree of increase in the actual surface area compared to the corresponding apparent Area [2],[3]

In recent years, a considerable amount of work has been carried out to study the Mechanisms and principles of super-hydrophobicity. Ithas been found that the micro-geometry and low surface-energy chemical composition of solid surface are two key factors to decide thecontact angle (CA) and rolling angle of water droplets on the surface. A series of preparation methods, including template methods, chemical etching, oxidation, electrodeposited, and sol-gel methods, etc., have been emerged. But there are some serious flaws including environmental pollution, high costs, complex process and so on. In thisstudy, a superhydrophobic surface is successfully fabricated on metal surfaces like copper, zinc, and aluminium surfaces.

RESEARCH & DEVELOPMENT:

Dettre and Johnson discovered in 1964 that the super- hydrophobic lotus effect phenomenon was related to rough hydrophobic surfaces, and they developed a theoretical model based on experiments with glass beads coated with paraffin or TFE telomer. Theself-cleaning property of super-hydrophobic micro-nanostructured surfaces was reported in 1977.

Perfluoroalkyl, perfluoropolyether, and RF plasma formed super-hydrophobic materials were developed, used for electro-wetting and commercialized for bio-medical applications between 1986 and 1995. Other technology and applications have emerged since the mid- 1990s[4].

A durable super-hydrophobic hierarchical composition, applied in one or two steps, was disclosed in 2002 comprising nano sized particles ≤ 100 nanometers overlaying a surface having micrometer sized features or particles ≤ 100 micrometers. The larger particles wereobserved to protect the smaller particles from mechanical abrasion. In recent research, super- hydrophobicity has been reported by allowing alkyl ketene dimer (AKD) to solidify into a nano structured fractal surface.

Many papers have since presented fabrication methods for producing super- hydrophobic surfaces including particle deposition, sol-gel techniques, plasma treatments, vapor deposition and casting techniques. Current opportunity for research impact lies mainly in fundamental research and practical manufacturing. Debates have recently emerged concerning the applicability of the Wenzel and Cassie–Baxter models.

In an experiment designed to challenge the surface energy perspective of the Wenzel and Cassie–Baxter model and promote a contact line perspective, water drops were placed on a smooth hydrophobic spot in a rough hydrophobic field, a rough hydrophobic spot in a smooth hydrophobic field, and a hydrophilic spot in a hydrophobic field[5].

Experiments showed that the surface chemistry and geometry at the contact line affected the contact angle and contact angle hysteresis,but the surface area inside the contact line had no effect. An argumentthat increased jaggedness in the contact line enhances droplet mobilityhas also been proposed[6].

Many hydrophobic materials found in nature rely on Cassie's lawand are biphasic on the submicrometer level with one component air. The lotus effect is based on this principle. Inspired by it, many functional superhydrophobic surfaces have been prepared.

An example of a bionic or biomimetic super-hydrophobic material in nanotechnology is nanofin film. One study presents avanadium pentoxide surface that switches reversibly between super hydrophobicity and super hydrophilicity under the influence of UV radiation[7]. According to the study, any surface can be modified to thiseffect by application of a suspension of rose-like V_2O_5 particles, for instance with an inkjet printer. Once again hydrophobicity is induced by interlinear air pockets.

The UV effect is also explained. UV light creates electron-holepairs, with the holes reacting with lattice oxygen, creating surfaceoxygen vacancies, while the electrons reduce V^{5+} to V^{3+}. The oxygenvacancies are met by water, and it is this water absorbency by thevanadium surface that makes it hydrophilic. By extended storage in thedark, water is replaced by oxygen and hydrophilicity is once again lost .A significant majority of hydrophobic surfaces have their hydrophobic properties imparted by structural or chemicalmodification of a surface

of a bulk material, through either coatings orsurface treatments. That is to say, the presence of molecular species(usually organic) or structural features results in high contact angles ofwater. In recent years, rare earth oxides have been shown to possess
intrinsic hydrophobicity.

The intrinsic hydrophobicity of rare earth oxides depends on surface orientation and oxygen vacancy levels and is naturally more robust than coatings or surface treatments, having potential applications in condensers and catalysts that can operate at high temperatures or corrosive environments.

APPLICATION & POTENTIAL APPLICATIONS:

- Hydrophobic concrete has been produced since the mid-20thcentury.

- Active recent research on superhydrophobic materials might eventually lead to more industrial applications.

- A simple routine of coating cotton fabric with silica [8] or titanium [9] particles by sol-gel technique has been reported, which protectsthe fabric from UV light and makes it superhydrophobic.

- An efficient routine has been reported for making polyethylene superhydrophobic and thus self-cleaning [10]. 99% of dirt on sucha surface is easily washed away.

- Patterned superhydrophobic surfaces also have promise for lab- on-a-chip microfluidic devices and can drastically improve surface-based bioanalysis [11].

- In pharmaceuticals, hydrophobicity of pharmaceutical blends affects important quality attributes of final products, such as drug dissolution and hardness. Methods have been developed to measure the hydrophobicity of pharmaceutical materials

LITERATURE REVIEW

Wettability

The wettability of a surface is typically characterized by aliquid's contact angle and contact angle hysteresis on the surface. The wettability of non-textured (e.g., smooth) surfaces is fundamental to theunderstanding of all repellent surfaces and the focus of the earliest wetting analyses. For a smooth surface, Young's relation defines the equilibrium contact angle ϴ for a liquid:[12]

$$\cos\Theta = \frac{\gamma SV - \gamma SL}{\gamma_{LV}}$$

Here, γ_{SV} is the solid surface energy, γ_{LV} is the liquid surface tension and γ_{SL} is the solid-liquid interfacial energy. Young's equation arises from the force balance for a liquid droplet contacting a non-textured, non-reactive (e.g., no strong chemical bonds formed due to interactions between liquid and solid) solid surface and can be visualized in Figure4 The contact angle is defined as the angle between the tangent to the liquid-vapor interface and the tangent to the liquid-solid interface at thetriple phase contact line, measured through the liquid. For a given liquid, a lower solid surface energy will result in higher contact anglesthan a higher solid surface energy. Therefore, lower surface energy materials are preferred for repellent-surfaces. The lowest surface energy materials are typically fluorinated or per fluorinated materials.

A surface with θ > 90° is considered to be hydrophobic and a surface with θ < 90° is considered to be hydrophilic.

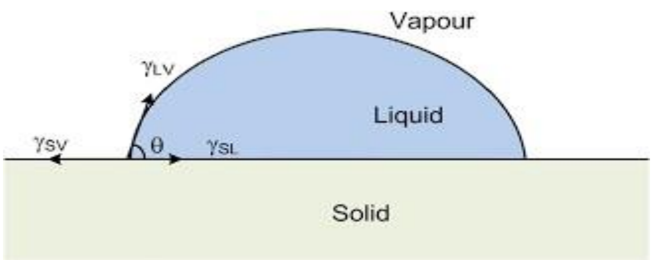

Figure – 5

The highest observed water contact angle on even the lowest γ_{SV} non- textured surface is θ ≈130°. Higher contact angles can be achieved withtextured surfaces.

Chemical etching is one of the most common techniques used in the above-mentioned studies. However, chemical etching can involve acidic or toxic solutions, which lead to a higher cost of fabrication andhazardous conditions. A combination of two simple and environmentally friendly techniques such as mechanical sanding and treatment with boiling DI water to introduce a hierarchical surface withboth micro and nanoscale roughness characteristics has not been reported yet. In addition, the effects of various sandpaper grit sizes, isotropy/anisotropy of roughness, and various time periods of treatmentwith boiling water on the water and oil CA have not been investigated.In recent years, a few studies have used mechanical sanding to roughensolid's surfaces for modifying their wetting properties. Mechanical sanding as a simple and environmentally friendly technique that has been used for centuries primarily for smoothening surfaces, as well as roughening, has been overlooked in spite of its potential in rougheningsurfaces at micro and submicron scales. In addition, surfaces were usually randomly sanded, and the effects of directional-sanding as wellas sandpaper grit sizes on the shape of microstructures have not been addressed yet.

METHODOLOGY

Materials/chemicals: Aluminium , copper and zinc sheets, cotton piece, sand paper, Acetone, Distilled water, KOH, NaOH, Stearic acid,Ammonia solution, Deionized water, Paraffin wax, Ethanol. (All chemical are 95% to 99% pure, obtained from Rankem)

Etching process [1]:

Aluminium, zinc, and copper substrate cleaned with acetone and D.W. Then aluminium, zinc, and copper were immersed in a mixture of 10gm/litre KOH in D.W. Solution for 5-60 min. KOH solution roughed the aluminium and zinc surfaces. Subsequently, aluminium, zinc, and copper substrate were rinsed with D.W. & Ethanol. Finally, they were immersed in 20gm/litre ethanol solution of lauric acid/stearicacid for 30minute & then they were dried in air for 20hour. stearic acid here lowered the surface energy of aluminium and zinc surfaces.

Figure-6(Zinc)

Figure-7(Aluminium)

Etching process [2]:

Aluminium, zinc, and copper substrate cleaned with acetone and D.W. Then aluminium, zinc, and copper were immersed in a mixtureof 10gm/litre KOH in D.W. Solution for 5-60 min. KOH solution roughed the aluminium, zinc, and copper surfaces. Subsequently, aluminium and copper substrate were rinsed with D.W. & Ethanol. Finally, they were immersed in 20gm/litre ethanol solution of lauricacid for 30minute & then they were dried in air for 20hour. Lauric acid/stearic acid here lowered the surface energy of aluminium and copper surfaces.

Etching process [3]:

Aluminium, zinc, and copper substrate cleaned with acetone and D.W. Then aluminium, zinc, and copper were immersed in a mixture of 10gm/litre NaOH in D.W. Solution for 5-60 min. NaOH solution roughed the aluminium and zinc surfaces. Subsequently, aluminium, zinc, and copper substrate were rinsed with D.W. & Ethanol. Finally, they were immersed in 20gm/litre ethanol solution of lauric acid for 30minute & then they were dried in air for 20hour. Lauric acid here lowered the surface energy of aluminium and zinc surfaces.

Hydrothermal method [1]:

First aluminium, zinc, and copper substrates were polished with different grades of metallographic sandpaper to remove the surface oxide film. Then aluminium, zinc, and copper substrates were ultrasonically (fig. 11) cleaned with acetone, deionized water andethanol respectively and dried with warm air. Cleaned aluminium, zinc,and copper substrates were etched in 10 wt. % Ammonia solution (100ml) at room temperature for 20hr, and then washed with deionizedwater. Next aluminium, zinc, and copper substrates were placed in **AUTOCLAVE** (fig. 12) for 120°C for 2hr. Containing 60ml NaOH solution (0.2mol L^{-1}). Finally, substrates were immersed in an ethanol solution of stearic acid (0.1mol L^{-1}) at room temperature for 2hr. Prepared samples were rinsed with absolute ethanol, dried with warm air.

Hydrothermal method [2]:

First aluminium, zinc, and copper substrates were polished with different grades of metallographic sandpaper to remove the surface oxide film. Then aluminium, zinc, and copper substrates were ultrasonically cleaned with acetone, deionized water and ethanol respectively and dried with warm air. Cleaned aluminium, zinc, and copper substrates were etched in 10 wt. % Ammonia solution (100ml) at room temperature for 20hr, and then washed with deionized water. Next aluminium, zinc, and copper substrates were placed in **MUFFLE FURNACE (**fig. 11) for 120°C for 2hr. Containing 60ml naoh solution(0.2mol L^{-1}). Finally, substrates were immersed in an ethanol solutionof stearic acid (0.1mol L^{-1}) at room temperature for 2hr. Preparedsamples were rinsed with absolute ethanol, dried with warm air. **(NOTE:** Side effect of muffle furnace showing in figure 12.)

Figure-8
(Ultrasonic cleaner)

Figure-9
(Autoclave)

Figure-10
(Metal deeping)

Figure-11
(Furnace)

Figure-12
(Side effect of muffle furnace)

Coating on fabric:

First of all, take wax & ethanol in the ratio of 1:10 in gm. Then heating at 80℃ with stirring for 16-20 min. When solution was cleared then add solution of lauric acid in ethanol of 0.04gm/ml. Then dip cotton piece in this solution for 20hr. Then wash cotton piece with ethanol and dry in oven for 3hr at 75℃ − 80℃

RESULTS AND DISCUSSION

1) Without coating process:

First of all, metal surfaces (e.g., aluminium, copper and zinc.) washed with ethanol (95% pure, obtained from Rankem) and distilled water. Then after one drop of water impact on plain aluminium surface,zinc surface and copper surface with the help of micro-injection technique. Then after surface has been characterized with the help of contact angle with the Image J capture software. After measuringcontact angle, we will be observed water drops spread and stick on themetal surface.

SURFACE ANGLE WITHOUT COATING:

Table-1

Surfaces	Solvent	Contact angle [1]	Contact angle [2]	Contact angle [3]	Average
Aluminum	Water	56.39°	58.16°	57.95°	57.50°
Zinc	Water	67.57°	69.36°	69.04°	68.65°
Copper	Water	43.03°	42.07°	41.98°	42.36°
Fabric	Water	62.97°	64.43°	65.38°	64.26°

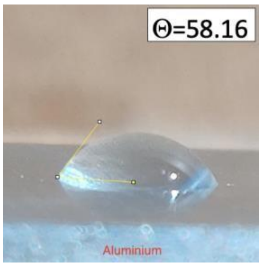

Figure-13
(Alluminium)

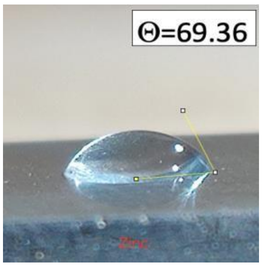

Figure-14
(Zinc)

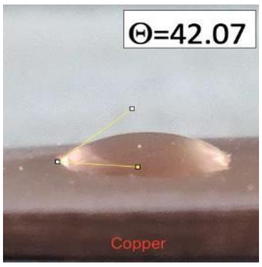

Figure-15
(Copper)

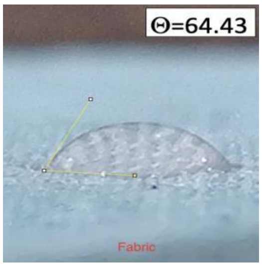

Figure-16
(Fabric)

2) With coating process:

(a) Etching process

(i)Etching process [1]:

Table-2

Coating Method	Coating Material	Surface	contact angle [1]	contact angle [2]	contact angle [3]	average
Etching	Steric acid	Aluminum	127.89°	126.74°	125.39°	126.67°
Etching	Steric acid	Zinc	133.95°	134.45°	136.04°	134.81°

(i)Etching process [2]:

Table-3

Coating Method	Coating Material	Surface	contact angle [1]	contact angle [2]	contact angle [3]	average
Etching	Lauric acid	Aluminum	157.67°	158.53°	158.72°	158.31°
Etching	Lauric acid	Copper	76.98°	77.22°	78.53°	77.57°

(i)Etching process [3]:

Table-4

Coating Method	Coating Material	Surface	contact angle [1]	contact angle [2]	contact angle [3]	average
Etching	Lauric acid	Aluminum	158.57°	159.99°	160.17°	159.57°
Etching	Lauric acid	Zinc	125.86°	127.54°	127.03°	126.81°

Etching process:

In all these etching processes (1), (2), and (3) method of coating is same but using different types of chemical. In etching process (1) and (2) metals substrate immersed in KOH solution to create roughness onsurface while in etching process (3) metals immersed in NaOH solution. Etching process (1) coating material is stearic acid while in process (2) and (3) coating material is lauric acid

Characterization by contact angle measurement technique, in etching process (1) average contact angle of Aluminum surface with water is 126.67° and zinc surface is 134.81° these each angle is greaterthan 90° so each surface is hydrophobic surface. In etching process (2)average contact angle of Aluminum surface with water is 158.31° and for copper surface it is 77.57° in this process copper contact angle is less than 90° so it does not show hydrophobic characteristics, while in aluminum surface contact angle is greater than 150° so it shows superhydrophobic characteristics. In etching process (3) average contact angle of Aluminum surface with water is 159.57° and for zinc it is 126.81°. so, both surface show hydrophobic characteristics but aluminum show superhydrophobic characteristics.

(b)Hydrothermal method

(i) Hydrothermal method [1]:

Table-5

Coating Method	Coating Material	Surface	contact angle [1]	contact angle [2]	contact angle [3]	average
Hydrothermal	Stearic acid	Aluminum	156.7°	158.3°	158.8°	157.95°
Hydrothermal	Stearic acid	Zinc	151.7°	152.9°	153.0°	152.56°
Hydrothermal	Stearic acid	Copper	138.3°	137.2°	136.7°	137.42°

In this hydrothermal process (1) auto clave is use for give temperature and pressure while in hydrothermal process (2) muffle furnace is use to give high temperature around 200°C

In hydrothermal process 1 average contact angle of Aluminum zincand copper surfaces is 157.95°, 152.56°, and 137.4° respectively. Aluminium and zinc show superhydrophobic characteristics while copper surface show hydrophobic characteristics.

(c)Coating on fabric:

Table-6

Coating Material	Surface	contact angle [1]	contact angle [2]	contact angle [3]	average
Lauric acid	Fabric	154.93°	153°	152.76°	153.56°

COMPARISON WITH VARIOUS METHOD

Comparison with various method on Aluminium surface withcoating:

Table-7

Coating Method	Coating Material	Solvent	contact angle [1]	contact angle [2]	contact angle [3]	average
Etching [1]	Steric Acid/KOH	water	127.89°	126.74°	125.39°	126.67°
Etching [2]	Lauric acid/KOH	Water	157.67°	158.53°	158.72°	158.31°
Etching [3]	Lauric acid/NaOH	Water	158.57°	159.99°	160.17°	159.57°
Hydrothermal[1]	Stearic acid/NaOH	water	156.78°	158.20°	158.88°	157.95°

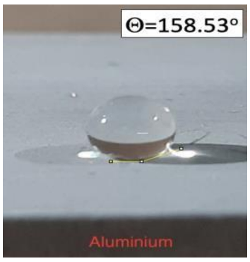

Figure-17
(Alluminium)

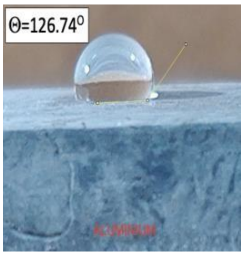

Figure-18
(Zinc)

Figure-19
(Copper)

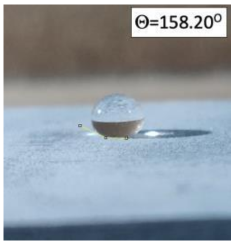

Figure-20
(Fabric)

In etching process aluminum surface was treated with KOH and NaOH and coating material was lauric acid and stearic acid. By characterization by contact angle measurement technique and got different contact angle. In etching process (3) maximum contact angle observed was 159.57°, use of coating material was lauric acid but in etching process (1) coating material was stearic acid but contact angle less as compared to etching process (3). But in Hydrothermal process use of coating material was stearic acid and contact angle was 157.95°it was very similar to etching process (2) and (3) (as shown in table 7)

Therefore, we conclude that the coating material stearic acid give superhydrophobic surface in hydrothermal method as compared to etching method.

Comparison with various method on Copper surface withcoating:

Table-8

Coating Method	Coating Material	Solvent	contact angle [1]	contact angle [2]	contact angle [3]	average
Etching [2]	Lauric acid/KOH	Water	76.98°	77.22°	78.53°	77.57°
Hydrothermal [1]	Stearic acid/NaOH	Water	138.32°	137.16°	136.78°	137.42°

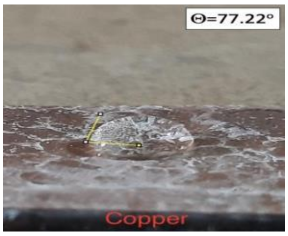

Figure-21
(Copper)

Figure-22
(Copper)

In etching process , copper surface was treated with KOH and coating material was lauric acid.in this method contact angle of water droplet with surface is 77.57° which indicates that the surface was hydrophilic in nature because it was less than 90°, but in Hydrothermalprocess coating material was stearic acid and treated with NaOH it gives 137.42° contact angle which was higher than 90° and show hydrophobic characteristics.

Finally concluded that etching process is not suitable to give hydrophobic surface on copper surface but hydrothermal process giveshydrophobic surface on copper surface

Comparison with various method on Zinc surface with coating:

Table-9

Coating Method	Coating Material	Solvent	contact angle [1]	contact angle [2]	contact angle [3]	average
Etching [1]	Steric acid	Water	133.95°	134.45°	136.04°	134.81°
Etching [2]	Lauric acid	Water	125.86°	127.54°	127.03°	126.81°
Hydrothermal [1]	Stearic acid	Water	151.78°	152.92°	153.00°	152.56°

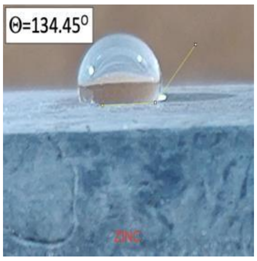

Figure-23
(Zinc Surface)

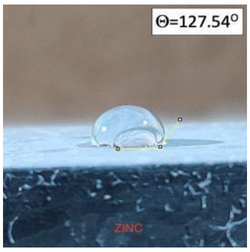

Figure-24
(Zinc Surface)

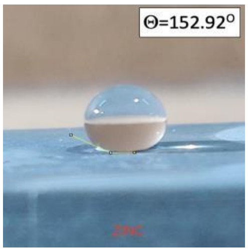

Figure-25
(Zinc Surface)

In Etching process (1) coating material on zinc surface was stearicacid and give contact angle 134.81° which shows hydrophobic characteristics and in etching process (2) coating material was lauric acid and gives contact angle 126.81° there for stearic acid was more suitable coating material than lauric acid but in Hydrothermal process zinc surface was coated with stearic acid and give 152.56° contact angle which shows superhydrophobic characteristics. That's why for zinc surface hydrothermal process is more suitable to create superhydrophobic coating.

Fabric surface with coating:

Table-10

Coating Material	Solvent	contact angle [1]	contact angle [2]	contact angle [3]	Average
Lauric acid	Water	154.93°	153°	152.76°	153.56°

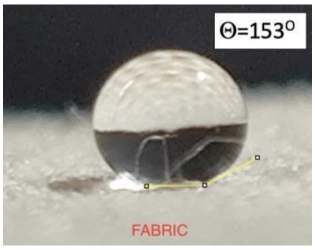

Figure-25
(Fabric)

CONCLUSION

In Summary, drop impact on plain metal surface (Aluminium, zinc & copper) and fabric surface was examined and as a result stickiness andspreading of droplets was observed due to the small static contact angle.After coating different solvent and coating material, contact angle weremeasured as a result we will observed maximum contact angle at 159.99° in etching Process with lauric acid coated surface. And it is very high compare to plain metal surface. which shows superhydrophobic surfaces.

Then after we have observed other parameters on coated metal surfacelike spreading, stickiness, fragmentation of water droplet and oscillation or dynamic behaviour of water droplet. As a result we will see minimum (Three) bounce observed in etching and hydrothermal both method in aluminium and zinc coated surface. In coated surface water drop are bounce like elastic ball due to presence of small pillars of solvent and coating material, rough surface of metal and high contactangle. And also in fabric surface we observed 153°. And it is very highcompare to plain fabric. Which shows superhydrophobic surface.

Finally to conclude, contact angle of water droplet is increase when hydrophobicity of the surface is increase and contact time of water droplet is reduce. And it is applicable to industrial purpose.

REFERENCES

1. A. Khistariya, r. Nigmatullin and f. Gao, dynamic behaviours of water droplet impacting antiwetting plant leaves research, journal of chemical science, vol. 9(2), april (2019), 16-23.
2. Wenzel, r. N. 1936. "resistance of solid surface to wetting by water." Ind. Eng. Chem. 28: 988-94.
3. Cassie, a. B. D. And baxter, s. 1944. "wettability of porous surfaces."Trans. Faraday soc. 40: 546-51.
4. Barthlott, wihelm, c. Neinhuis, the purity of sacred lotus or escape from contamination in biological surface, vol. 1(8), april (1997), 202
5. Gao, lc; mccarthy, how wenzel and cassie were wrong, langmuir, vol. 23(7), 2007, 3762-3765.
6. Chen, w; fadeev, alexander y.; hsieh, meng che; oner, didem; youngblood, jeffrey; macarthy, tho,as j., ultrahydrophobic and ultralyophoic surface: some comments and examples, langmuir, vol. 15(10), 1999, 3395-3399.
7. Lim, ho sun; kwak, donghoon; lee, dong yun; lee, seung goo; cho, kilwon, uv-driven reversible switching of a roselike vanadium oxide film between superhydrophobicity and superhydrophilicity, journal of the american chemical society, vol. 129(14), april (2007), 4128-4129.
8. Xue, chao-hua; jia, shun-tian; zhang, jing; tian, li-qiang; chen, hong-zheng;wang, preparation of superhydrophobic surfaces on cotton textiles, science and technology of advanced materials, vol. 9(3), january (2016).
9. Xue, chao-hua; jia, shun-tian; hong-zheng; wang, superhydrophobic cottonfabrics prepared by sol-gel coating of tio_2 and surface hydrophobization, science and thechnology of advanced material, vol. 9(3), january (2016).
10. Yung, zhiqing; chen, hong; zhang, jide; zhao, dejian; liu, yuejun; zhou, xiaoyuan; li, song; shi, pu; tang, jianxin; chen, preparation and characterization of self-cleaning stable superhydrophobic linear low- density polyethylene, science and technology of advance materials, vol. 9(4), january (2016).
11. Ressine, anton; marko-varga, gyorgy; laurell, thomas, porous silicon protein microarray technology and ultra/superhydrophobic states for improved bioanalytical reasout., biotechnology annual review., (2007),149-200.
12. Young t (1805) an essay on the cohesion of fluids. Philos trans r soclond 95:65–87.
13. H. Vahid, d.m. afsaneh, r. Pradeep, n. Michael, beyond wenzel and cassie- baxter: second-order effects on the wetting of rough surfaces, langmuir 30 (2014) 9423e9429.
14. W. Qafsaouia, m.w. kendig, h. Perrot, h. Takenoutic, coupling of electro- chemical techniques to study copper corrosion inhibition in 0.5 mol l^{-1} nacl by 1-pyrrolidine dithiocarbamate, electrochim. Acta 87 (2013)348e360.
15. C.w. peng, k.c. chang, c.j. weng, m.c. lai, c.h. hsu, s.c. hsu, y.y. hsu, w.i. hung, y. Wei, j.m. yeh, nano-casting technique to prepare polyaniline surface with biomimetic superhydrophobic structures for anticorrosion application, electrochim. Acta 95 (2013) 192e199.
16. J. Han, q.j. xu, w. Liu, y.l. min, etching and heating treatment combined approach for superhydrophobic surface on brass substrates and the conse- quent corrosion resistance,

corrosion sci. 102 (2016) 251e258.
17. D. Yu, j. Tian, j. Dai, x. Wang, corrosion resistance of three-layer super- hydrophobic composite coating on carbon steel in seawater, electrochim. Acta 97 (2013) 409e419.
18. Y. Yang, j. Liu, c. Li, l. Fu, w. Huang, z. Li, fabrication of pompon- like and flower-like sno microspheres comprised of layered nanoflakes by anodic electro crystallization, electrochim. Acta 72 (2012) 94e100.
19. M.j. nine, m.a. cole, l. Johnson, d.n.h. tran, d. Losic, robust super- hydrophobic graphene-based composite coatings with self-cleaning and corrosion barrier properties, acs appl. Mater. Interfaces 7 (2015) 28482e28493.
20. J. Wang, d. Li, l. Qi, y. Xi, z. Ying, x. Jing, m. Zhang, fabrication ofhydrophobic surface with hierarchical structure on mg alloy and its corrosion resistance, electrochim. Acta 55 (2010) 6897e6906.
21. C.y. yang, s.i. chuang, y.h. lo, h.m. cheng, j.g. duh, p.y. chen,stalagmite-like self-cleaning surfaces prepared by silanization of plasma- assisted metal-oxide nanostructures, j. Mater. Chem. 4 (2016) 3406e3414.
22. T. Wang, j. Cui, s.s. ouyang, w.h. cui, s. Wang, a new approach to understand the cassie state of liquids on superamphiphobic materials, nanoscale 8 (2016) 3031e3039.
23. Mozalev, h. Habazaki, j. Hubalek, the superhydrophobic properties of self- organized microstructured surfaces derived from anodically oxidized al/nb and al/ta metal layers, electrochim. Acta 82 (2012) 90e97.