

Sapindus as potential green corrosion inhibitor of Aluminium and mild steel

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Master of Sciences in Chemistry

By

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Under the guidance

Of

Dr. Ashish Kumar



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Lovely Professional University, Punjab, India

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Sapindus as potential green corrosion inhibitor of Aluminium and mild steel



TOPIC APPROVAL PERFORMA

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Qualitative Assessment of Proposed Topic by PAC		
Sr.No.	Parameter	Rating (out of 10)
1	Project Novelty: Potential of the project to create new knowledge	7.67
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3	Project Academic Inputs: Project topic is relevant and makes extensive use of academic inputs in UG program and serves as a culminating effort for core study area of the degree program.	7.33
4	Project Supervision: Project supervisor's is technically competent to guide students, resolve any issues, and impart necessary skills.	8.33
5	Social Applicability: Project work intends to solve a practical problem.	8.33
6	Future Scope: Project has potential to become basis of future research work, publication or patent.	7.67

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Certificate

This is to certify that the dissertation-II entitled “SAPINDUS AS CORROSION INHIBITOR OF ALUMINIUM AND MILDSTEEL” submitted by Sahil Kumar to the Lovely Professional University, Punjab, India is a documentation of genuine literature review of coming research work approved under my guidance and is commendable of consideration for the honor of the degree of Master of Science in Chemistry of the University.

Supervisor

Dr. Ashish Kumar

Associate Professor

Declaration

I certify that,

- The work enclosed in this thesis is innovative and has been carried out by me under the guidance of my supervisor, Dr. Ashish Kumar
- The present work has not been submitted earlier to any other university for any degree
- I have been followed the guiding principle provided by the university in the preparation of the report
- Whenever I have used resources (such as data, theoretical representations, any figure, and text) from other sources, I have given due recognition to them by citing them in the report and providing their details in the bibliography.

Date:

Sahil Kumar

Acknowledgement

It is great pleasure for me to present the project report on “SAPINDUS AS CORROSION INHIBITOR OF ALUMINIUM AND MILDSTEEL”. Every work accomplished is a pleasure a sense of fulfillment. However many people always motivate, criticize and appreciate a work with their objective ideas and opinions. I would like to use this opportunity to thank all, who have directly or indirectly helped us to complete this dissertation-II.

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Lovely Professional University, Punjab

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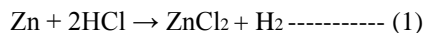
1. ABSTRACT

Corrosion is the major problem for metal. It damages the metal or steel in great extent, so we use the natural product as inhibitor to reduce the corrosion rate. The main motive to use the natural product is that, natural products are easily available and they are having many properties like antioxidant, antibiotic etc. Techniques include weight loss method, EIS, AFM, Infra red analysis, NMR and UV spectral analysis. Thermodynamic parameters shall also be calculated. The morphology of metal has shall be elucidated by SEM. And the theoretical parameters of inhibitor shall be done by using quantum chemical parameters.

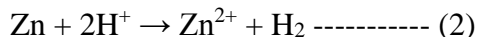
2. INTRODUCTION

2.1 DEFINITION OF CORROSION

Corrosion can be defined as the deterioration of metals by means of a chemical attack on its exposure to the environment. In present definition we are not talking about non metals ^{[1] [2]}. In the process of corrosion both oxidation and reduction takes place that may be termed as electrochemical ^[3]. For example, a vigorous reaction occurs, whenever the zinc metal is places in the solution of dilute hydrochloric acid (HCl); zinc dissolves and in this process hydrogen gas is evolved and the zinc chloride solution is formed. The reaction may be written as:

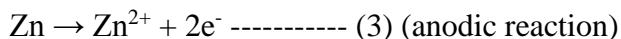


This reaction is written as

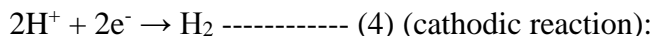


Equation (2) takes place in two steps first step is oxidation of zinc and second step is the reduction of hydrogen ions:

Oxidation:



Reduction

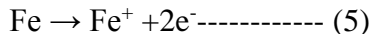


Reduction may be defined as the gain of electrons and oxidation is the loss of electron. Physical and chemical factors can limit the rate of electrochemical reaction. So, an electrochemical reaction is called as polarized ^{[4] [5]}. Wet corrosion usually takes place in aqueous conducting medium. This type of corrosion occurs when metals are immersed in a conducting liquid or when two dissimilar metals are immersed in a solution. According to the electrochemical theory of

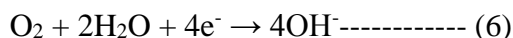
corrosion, the corrosion of metal like iron exposed to the environment may take place in three steps. [6]

- Formation of galvanic cells means the formation of anodic and cathodic regions.
- Oxidation corrosion taking place at anodic region
- Reduction reaction taking place at cathodic region

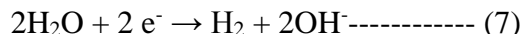
In anodic reaction the oxidation of metal for example, iron takes place with the loss of electrons.



Cathodic reactions on the other way depend upon the constituents of corrosion medium. If the solution is aerated or neutral, oxygen is reduced in presence of H₂O and OH⁻ ions.



If the solution is deaerated and almost neutral, H₂ is liberated along with OH⁻ ions.



If the solution is deaerated and acidic, H⁺ ions is reduced to hydrogen gas.



The metal ions formed at the anode react with the hydroxide ions and lead to the formation of metal hydroxide Fe (OH)₂. This gets further oxidized to hydrated ferric oxide.



2.2 CORROSION INHIBITORS

Corrosion inhibitor is described as the substances which are used to reduce the effect of corrosion from the metal surface. Inhibitors are very useful in the oil extraction and processing industries. Synthetic compounds may be the good corrosion inhibition property but they are very toxic in nature that was why we search or find some other corrosion inhibitors which are environment friendly. For example garlic extract, papaya leaves, beet root, banana peel, aloes extract etc. The compounds which are some properties like antioxidant of chlorophylls, phenols, caretenoids, are good corrosion inhibitors i.e. water hyacinth is good corrosion inhibitors.

2.3 TYPES OF CORROSION INHIBITORS

a) Anodic inhibitors

A protective oxide film on the metal which causing the anodic shifting of corrosion potential, done by the anodic inhibitors. This anodic shifting is responsible for forces the metal surface to the passivate region and they are termed as passivator. The examples of anodic inhibitors are chromates, nitrates, tungstate, and molybdates ^{[7][8]}

b) Cathodic inhibitors

The cathodic reaction rate is reduced with the help of cathodic poisons. Also the metal susceptibility is increased by that cathodic poison; to hydrogen induced since when the aqueous corrosion and the cathodic charging hydrogen are absorbed by metal. The corrosion rate is also reduced when the oxygen scavengers are reacted with dissolved oxygen. The example of oxygen scavengers are sulfite and bisulfate, they form sulphate when these are reacted with oxygen. ^[9]

c) Mixed inhibitors

Mixed inhibitors are the compounds that are used for film forming. They are responsible for formation of the precipitates on the surface of metal by that they block the cathodic as well as anodic sites. They are working in the process of decreasing the cathodic and anodic reactions. The salt of calcium in hard water having capacity to form the protective layer on the surfaces of water because the salt formation of calcium salt. This is due to the extent of calcium in hard water also magnesium metal is less in soft water. The example of the mixed inhibitors is phosphates and silicates. Sodium silicates are very much used in the domestic softeners of water to reduce the occurrence of rust in water. It also protect steel and brass in the aerated warm water. To the very effective inhibition phosphates also be used in great extent but for that phosphates will required the oxygen. Both phosphates and silicates are not afford degree of protection which is provided by the nitriles as well as chromates ^[10], hence in the non toxic additives silicates and phosphates are very effective.

d) Volatile corrosion inhibitors

By the processing of volatilization from the source the volatile corrosion inhibitor compounds are transported in the site where corrosion takes place. The basic compounds of volatile for example hydrazine and morpholine are run with help of steam to reduce the corrosion in the tube of condenser by neutralize the acidic carbon dioxide (CO₂). In the shipping containers; salt of hexamethylene amine, cyclohexylamine and salt of dicyclo-hexylamine are used. The condensation of the salt of these compounds occurs and they liberate the ions when they hydrolyzed by the presence of air or moisture. The volatile corrosion inhibitors are also called as vapor phase inhibitors (VPI).^[10]

2.4. DISADVANTAGES OF INHIBITOR

A) Disadvantages of anodic corrosion inhibitors

Anodic corrosion inhibitors have a serious disadvantage that at high concentrations the corrosion rate becomes high which is one of the reasons why monitoring systems are advisable when it comes to anodic protection.

Cathodic corrosion inhibitors reduce the cathodic reaction. It forms a protective barrier on the cathodic area by formation of some insoluble compounds that precipitate on the cathodic site^[11].

B) Disadvantages of cathodic corrosion inhibitors

Cathodic protection sometimes leads to the formation of atomic hydrogen which gets adsorbed on the protected metal and leads to hydrogen embrittlement of welds and materials with high hardness:

- Due to the formation of hydrogen ions, it leads to the disbondment of protective coating from protected surface.
- It also leads to cathodic shielding.

Volatile corrosion inhibitors: these are carried in a closed environment to the metal surface to be protected. As the metal surface comes in contact with VCI, the vapor of these salts condenses and is hydrolyzed by any moisture to liberate protective ions. Example of volatile corrosion inhibitors are morpholine and hydrazine.

C) Disadvantages of volatile corrosion inhibitors

A survey conducted on TOXNET, a database kept up by the National Institutes of Health on chemical wellbeing, suggests that about all Volatile Corrosion Inhibitors are to be perilous if the definition given by OSHA is to be considered. OSHA characterizes dangers regarding incorporate aggravations, activators, and combustibles. Importance to appropriately recognize unsafe compounds chemicals can't be exaggerated. Past the chemicals themselves, some VCIs and numerous solvents utilized as a part of these items emanate unstable natural mixes. Volatile corrosion inhibitors are declared to be dangerous components according to few governments. Endeavors have been brought in progress in numerous nations to fundamentally diminish them. Indeed, even the additives which are fused into some VCIs are harmful. ^[12]

2.5. TYPES OF CORROSION:

a) Uniform attack:

It is an electrochemical phenomenon in which the reactions start over entire surface of the metal at almost same rate. General corrosion results in leakage through the metal surface because it reduces the mechanical thickness of metal. Rusting steel in the presence of atmosphere is example of uniform corrosion and copper in sea water is also example of uniform corrosion. Steel in seawater is also suffered from the uniform corrosion but it also suffers from non uniform corrosion under some conditions. ^[13]



Figure1. Uniform corrosion.

(http://www.corrosionclinic.com/types_of_corrosion/uniform_corrosion.htm)

b) Galvanic Corrosion

When the conducting materials which are not similar are connected electrically and uncovered to an electrolyte, the galvanic corrosion occurs. The requirement of the galvanic corrosion will be as following:

Different metals(or other conductors for example graphite)

When there is the electrical contact with the two different conducting material.

When the corrosive material is come in contact with the dissimilar material.

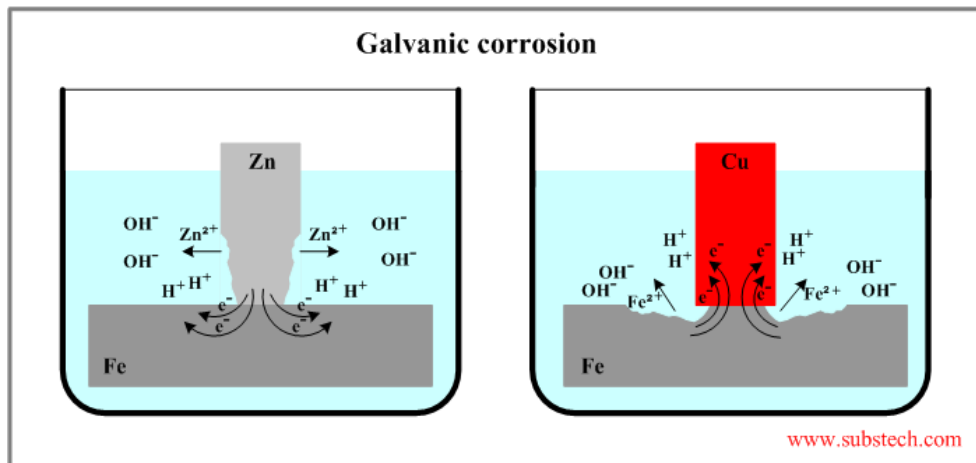


Figure 2: Galvanic corrosion

(http://www.substech.com/dokuwiki/doku.php?id=galvanic_corrosion)

c) Crevice corrosion:

In certain metals the surface is not uniform and consists of certain occluded regions called crevices. As this metal comes in contact with the environment, the environment of this region does not freely mix with the bulk environment and this difference leads to corrosive attack. Flanges, deposits, etc. are the example of crevice corrosion.



Figure 3. Crevice corrosion

(http://www.corrosionclinic.com/types_of_corrosion/crevice_corrosion.htm)

d) Pitting corrosion

Pitting corrosion is occurs on the small spots of metal surface at a high rate. The flaws present in the coating of metal surface are usually the place where pitting corrosion occurs. It is also common in corrosion resistant metals that form native oxides on their surface. Pits can be in form of cup-shaped or hemispherical. ^[14]

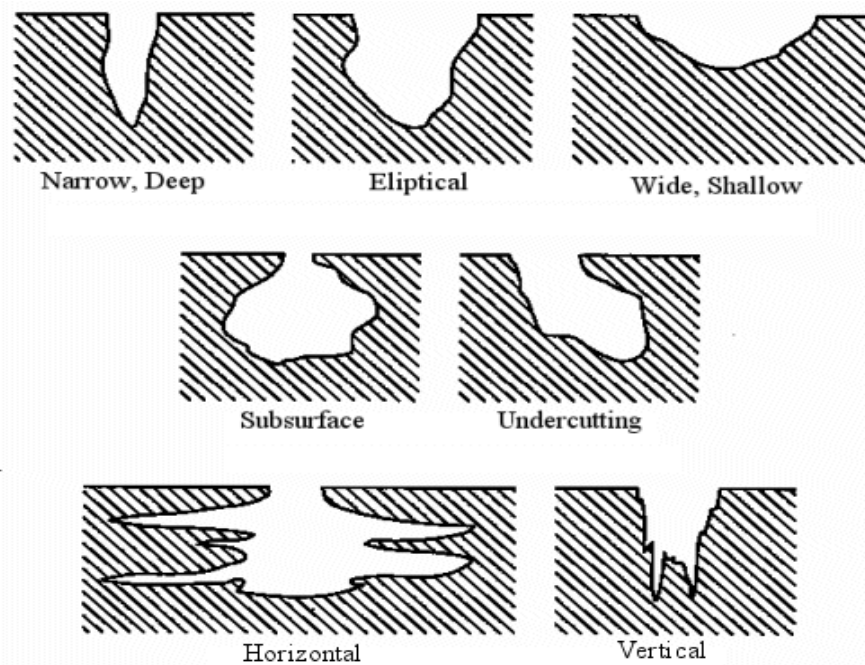


Figure 4. Pitting corrosion

(http://www.corrosionclinic.com/types_of_corrosion/pitting_corrosion.htm)

e) Intergranular corrosion

In some engineering alloys the surface of the metal is solidified by coating it with some melt consisting of mixture of elements. As a result of which there comes a difference between properties and the chemical composition of these solid crystals and the inside of metal surface. This result in the rapid corrosion between these crystals called intergranular corrosion.

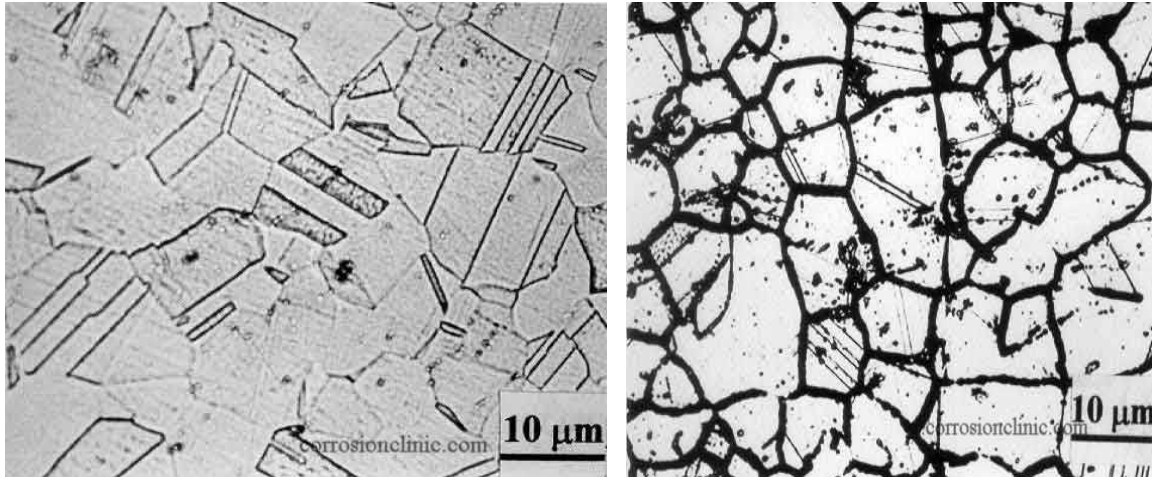


Figure 5. Intergranular corrosion

(http://www.corrosionclinic.com/types_of_corrosion/intergranular_corrosion_cracking.htm)

f) Selective leaching

Selective leaching is also known as dealloying. When dealloying is done it includes the leaching of one of the alloys which reduces the mechanical strength and leads to porous surface. Selective removal of zinc in brass alloy (dezincification) is the common example of selective leaching.



Figure 6. Selective leaching

(<http://sirius.mtm.kuleuven.be/Research/corr-o-scope/hcindex1/tutorial1.htm>)

g) Erosion corrosion

According to Derrick H. Lister, Erosion corrosion occurs as a result of high relative motion between the metal and the environment. Erosion corrosion leads to the formation of holes, cavities and grooves on the metal surface aligned in the direction of fluid.

The relative movement between a corrosive fluid and metal surfaces can help to decrease the corrosion rate of deterioration or attack on metal.

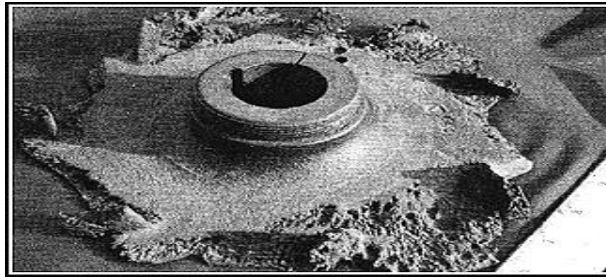


Figure 7. Erosion corrosion

(<http://advancedmaterialsassoc.com/faq-metals-corrosion-7.html>)

h) Environmentally induced corrosion

When some metals are exposed to chemically reactive atmosphere, formation of crack occurs due to the application of mechanical stress. Organic solvents, aqueous solutions have been known to be a main cause of this failure.

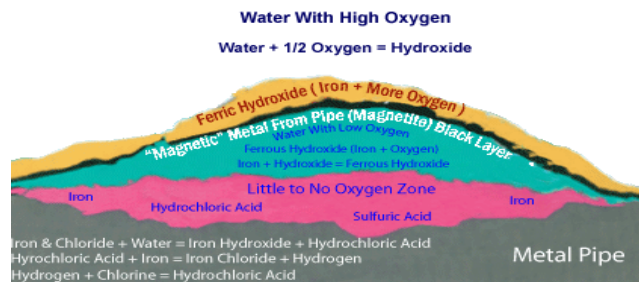


Figure 8. Environment induced corrosion

(<http://www.experts.com/Articles/Stress-Corrosion-Cracking-And-Intergranular-Corrosion-of-a-316Ti-Stainless-Steel-Preheater-Tube-By-Metallurgical-Technologies>)

3. PROBLEM BACKGROUND

3.1. LOSS DUE TO CORROSION

Corrosion is a noteworthy expense to industry in all countries. In 1949 H.H.Uhlig assessed the expense of corrosion of USA by summing materials and strategies expense identified with corrosion control. In USA, the Battelle-NBS study led in 1978 evaluated the aggregate direct corrosion cost utilizing monetary info/yield model. With the help of IO strategy Australia in the year of 1983 and Kuwait in the year of 1995 done their corrosion expense. In UK the study was directed in 1970 by collecting so as to utilize another strategy for information through meeting and studies of centered divisions. In Rajagopalan (India) in 1962 evaluated the expense of consumption with CSIR. The table beneath compresses the aggregate expense of corrosion of different countries and rate of GDP (GNP) of the individual countries. The table below clears the expense of corrosion shifts from 1.5 to 5.2 percent of GNP. ^[15]

Country	Total annually cost of corrosion(US\$)	Percentage of GNP	Reference
India	\$320 million	-	Rajagopalan, 1962
USA	\$5.5 billion	2.1	Uhlig, 1950
UK	£1.365 billion	3.5	Hoar, 1971
Japan	\$9.2 billion	1.8	Okamoto, 1977
USA	\$70 billion	4.2	Payer et al 1980
Australia	\$2 billion	1.5	Cherry and Skerry, 1983
Kuwait	\$1 billion	5.2	Kharafi et al, 1995
Finland	\$ 54 million	-	Linderborg, 1967

According industrial estimates, in the past 30 years, the corrosion cost to the industries is 3.1% of country's GNP. From the year 1999- 2001, the research is conducted by CC technologies laboratories Inc. with Federal Highway Administration (FHWA) under some cooperative agreement. In this research around \$276 billion per year direct cost of corrosion was determined,

which is 3.1% of the U.S. gross domestic product , of which infrastructure- related costs represent a sizeable portion.

3.2. PROTECTION OF STEEL AND IRON FROM CORROSION

In order to prevent corrosion many corrosion inhibitors are available, some of which can be discussed below:

A) Paints

Paints are usually the organic coatings which consist of some finely divided particles immersed in the primer. Paints contain polar compounds which augment the bonding of coating on the surface by facing their hydrophobic ends towards the environment. The inhibitors present in paints are lead oxide, lead azelate, calcium plumbate. Red lead for example preserves the physical properties o paints by deterring the local cells. Red lead Pb_3O_4 is the most commonly used paint for iron^[16]. Despite of the vast applications of paints in day to day life it does have some hazardous effects.

B) Disadvantages of paints (organic coatings)

Paints have a diverse effect on environment due to the presence of some additives such as lead and chromium. These are well known for their hazardous effects to the environment. Moreover, paint comes in the class of volatile corrosion inhibitors which consists of toxic fumes hazardous to the health and environment too.

C) Galvanization

Galvanization involves dipped iron or steel in a bath of molten zinc which thereby reduces its corrosion. Galvanization process in which of zinc-iron coating is produced due to the reaction between zinc and Fe in the steel. The temperature of the bath in which the metals are dipped varies from 440 to 460°C^[17] While galvanization seems to be a useful corrosion inhibition method, it has some disadvantages because it uses zinc and high amounts of zinc are being used in industries which affects the environment. Water is regularly the first to become contaminated where industrial plants don't filter their waste water. This may be a reason in the ascent of corrosive levels inside of water – effecting nearby widely plants and animals^[16]

D) Acid pickling

Pickling involves the removal of contamination by using acids like HCl. The major disadvantage of this process is that the hydrogen from the acid reacts with the surface and makes it brittle and causes cracks.

Owing to the disadvantages of the above mentioned corrosion inhibition method some alternative methods are used whereby the corrosion inhibitors used are less toxic. Numerous ecological principles are put forth in order to force, occupy specialists to utilize non-toxic compounds as an option. ^[18] This will lead us to search environment- friendly, cheap, renewable green corrosion inhibitors.

3.3. ENVIRONMENT CHANGES

A) Decreasing temperature

Corrosion rate can be controlled by the decreasing temperature. Under few conditions, temperature change has minor effect on the corrosion rate. In additional cases, the rate of corrosion is decrease by increasing in the temperature.

C) Decreasing velocity

It is a practical method to control the corrosion rate. Metal and alloys that passivity, like stainless steel, usually good resistance to flow medium than stagnant solution. High velocity rates occur due to the erosion corrosion effect.

D) Removing oxygen

In this case boiler feed water was deaerated by passing it through a large mass of scrap steel. Now a day this can be done by vacuum treatment, through the use of oxygen scavengers and inert gas sparging. It is the old technique to control the corrosion. ^[15]

4. LITERATURE SURVEY

4.1 SAPINDUS

Sapindus also called soap nut or reetha is one of the important trees of subtropical and tropical region of Asia. It is found in the plains of South Asia and Western Ghats. It is the medium sized tree having the height around 25m. This tree gives the greenish white flower and the fruits of this tree are solitary globose appears in the month of July- August. This fruits consist of saponins ranges from 6% to 10% of mass weight ^[20]. High level contents of sugar are also there in Sapindus. The saponins moiety is characterized as hederagenin group of glycosides ^[21]. The Sapindus consist of phenolic acid like cinnamic acid, protocatechuic acid, cis-p- coumaric acid , p- hydro benzoic acid and cinnamic acid. It is very useful or it is the effective ingredient in shampoos and cleansers.

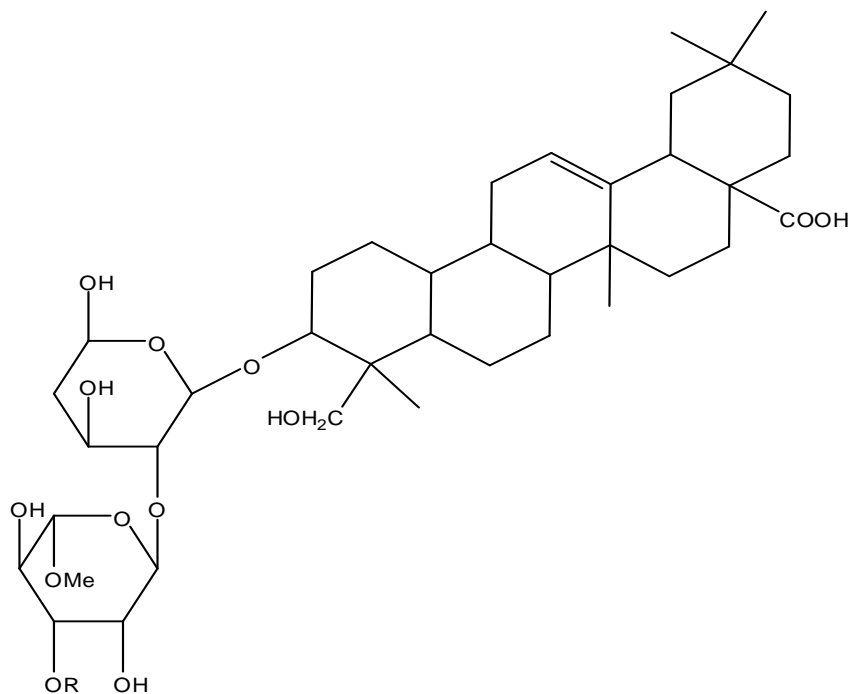


Figure1. Structure of Sapindus (Reetha)

4.2 PROPERTIES OF SAPINDUS:

a) Anti – Inflammatory Activity

The crude saponin which is isolated from the Sapindus is done by Takagi. It is utilizing by adjuvant arthritis which is present in rat and also utilizing by granuloma pouch. Vascular permeability, acetic acid (CH₃COOH) induced, writhing in mice are also be effected by these agents. The aqueous extract of *S. emarginatus* leaves for four different solvent such as aqueous, 1, 4- dioxin, acetone and methanol are showed activity of antibacterial against the pseudomonas testosterone and proteous. [22]

b) Cytotoxic activity

Cytotoxic effect of saponins is done by Kuo and co workers. From the galls of *S. mukorossi*, these saponins are isolated. The preliminary data tells that saponins [23] showed cytotoxic activity against human tumor cell lines.

C) Molluscidal activity

Huang checked the molluscidal activity of hederagenin saponins [24] which is isolated from *S. mukorossi* golden apple, including bacteria like canaliculata and pomacea.

d) Anti diabetic activity

The Anti hyperglycemic effect of alcoholic extract of *S. emarginatus* at different doses in glucose – loaded hyperglycemic and normal fasted rats is studied by S. Jeyabalan and coworkers. The level of glycosylated- hemoglobin, total hemoglobin, serum creatinine, and serum urea are showed by this study. The lipids profiles measured in alloxan induced diabetic rats which show anti- diabetic activity. [25]

E) Anti – hyperalgesic activity

The aqueous pericarps extract of fruits migraine hyperlgesic model is studied by *S. trifoliatius*. They tell that antagonism to dopamine D₂ might underlie the mechanism which is involved in the anti-hyperalgesic activity of the plant extract. [23]

Sapindus as potential green corrosion inhibitor of Aluminium and mild steel

S.No.	Metal	Inhibitor	References
1.	Mild Steel	4-Aminoantipyrine	[24]
2.	Iron and steel	Capsicum frutescens	[25]
3.	Steel	Soybean Oil	[26]
4.	Aluminium	HibiscusRosa-sinensis	[27]
5.	Mild Steel	Aquilaria Crassna	[28]
6.	Aluminium	Capparis decidua	[29]
7.	Steel	Ginger Extract	[30]
8.	Mild Steel	Butea monosperma	[31]
9.	Mild Steel	Musa sapientum	[32]
10	copper	pyrazolyindolenine	[33]
11.	Aluminium	Withania Somnifera	[34]
12.	Aluminium and cu	Ziziphus mauritiana	[35]
13.	Steel	sichuan pepper	[36]
14.	Mild Steel	Xylophia Ferruginea	[37]
15.	Aluminium	red onion	[38]
16.	Steel	Polyvinyl Pyrrolidone	[39]
17.	Steel	black pepper	[40]
18.	Steel	Opuntia-Ficus Indica	[41]
19.	Steel	Occimum viridis	[42]
20.	Mild Steel	Nypa fruticans	[43]
21.	Aluminium	Nypa Fruticans	[44]
22.	Steel	Pennyroyal oil	[45]
23.	Steel	lupine extract	[46]
24.	Aluminium	Ipomoea involcrata	[47]

Table 2: Work of steel and Aluminium with different extract

5. Objectives

1. To calculate the inhibition efficiency of Sapindus plant extract on the corrosion of mildsteel and Aluminium in acidic medium.
2. To study the adsorption isotherm involved in the contact between the metals and corrosion inhibitor.
3. To identify the mechanism involved in the process of corrosion inhibition of metal by using the Sapindus plant extract.
4. To estimate various thermodynamic parameter like Gibbs free energy, entropy, enthalpy and activation energy.
5. To calculate the quantum chemical parameter such as LUMO, HOMO and dipole moment of the Sapindus plant extract used as inhibitor for corrosion of Mildsteel and Aluminium
6. To calculate the corrosion rate from electrodynamic study like potentiodynamic study and electrochemical study.
7. To calculate the adsorption energy of inhibitor by Monte Carlo simulations.

6. RESEARCH METHEDOLOGY

6.1 Weight loss method:

By this method we shall be able to evaluate the surface coverage and inhibition efficiency of inhibitors. This technique involves the specimen to be tested for its weight loss by using weighing balance of sensitivity of ± 0.01 mg. The specimen (metal) is treated with acid and variety of concentrations of the inhibitors and the weight loss is seen in the specimen before it is immersed in the acid solution and after immersion for some specific time. The concentration of inhibitor in this technique is taken in mgL^{-1} . By using this technique the inhibition efficiency as well as surface coverage can be measured by the following formulae: ^[48]

$$\theta = IE\% / 100$$

$$IE\% = W(0) - W(1) / W(0) \times 100$$

Here

$W_{(1)}$ = average weight loss with the inhibitor

$W_{(0)}$ = average weight loss without the inhibitor

$$CR = 87.6 \times w / AtD$$

Here

W (mg) = the mild steel weight loss

A = the coupon area (cm²)

t = the time of exposure

D = the mild steel density (g/cm³)

6.2 Electrochemical measurements:

Electrochemical experiment can be done by the consisting of three electrode cell. The three electrodes are saturated calomel electrode, platinum counter electrode, which is attached with the luggin capillary. Luggin capillary acts as the reference electrode. The Luggin capillary tip is kept near to working electrode, to minimize the ohmic contribution. To embed the working electrode Teflon holder is used having the epoxy resin with area 0.785cm².^[49]

The potential of potentiodynamic polarization curves was started from cathodic potential of 250mV to anodic potential of +250 mV vs. OCP at a sweep rate of started rate of 1mV sec⁻¹. Inhibition efficiency η_p (%) is written as:

$$\eta_p (\%) = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \times 100$$

Where

I_{corr}^0 = corrosion current density without inhibitor.

I_{corr} = corrosion current density with inhibitor respectively.

6.3 Electrochemical impedance spectroscopy^[50]

The measurement of EIS can be done by the corrosion potential which is denoted by E_{corr} with frequency from 100,000 to 0.1 Hz. The result of EIS is exposed in the diagram called Nyquist and the electrical equivalent circuit for the system was obtained along with the charge transfer resistance which is donated by R_{ct} value. In this method the IE % is calculated by the formula:

$$IE\% = \frac{R_{ct(0)} - R_{ct(I)}}{R_{ct(0)}} \times 100$$

Here $R_{ct(0)}$ = charge resistance transfer of mild steel without inhibitor

$R_{ct(I)}$ = charge resistance transfer of mild steel having the inhibitor.

6.4 Potentiodynamic polarization:

This technique is used in order to know the values of corrosion potential denoted by E_{corr} , current densities which are denoted by I_{corr} , anodic tafel slopes and cathodic tafel slopes denoted as β_a and β_c , and surface coverage denoted by θ and inhibition efficiency as functions of inhibitor concentration measured from the curves. The curve fitting equation which is written below is used for calculation of the corrosion current.

$$I = \left[\exp\left(\frac{2.3\Delta E}{\beta_a}\right) - \exp\left(\frac{-2.3\Delta E}{\beta_c}\right) \right]$$

From the value of I_{corr} we calculate the inhibition efficiency by the following relationship:

$$\mu\% = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \times 100$$

Here

I_{corr}^0 = corrosion current density not having corrosion inhibitor.

I_{corr} = corrosion current density having corrosion inhibitor. [51]

6.5 Surface adsorption and morphology analysis

The optimum concentration of extracts is calculated by using Gamry instrument 600 AC. Voltametry is used to understand the nature of mild steel's surface adsorption. Bode plot is the method used to identified the maximum frequency of sample. The final and initial range of potential was set at 1V to -1V with voltage at 0.01. The evaluation of surface morphology of steel specimen is done by scanning electron microscope. [52]

6.6 Scanning Electron Microscopy

When the metal is immersed in the HCl and H₂SO₄ solution in presence and absence in the of the inhibitor for 1 hr then the mild steel specimen is taken out and washed by the distilled water and dry it and finally use SEM. The SEM study can be done by LEO435 VP instrument at an accelerating voltage of 5KV and 500 × magnifications. [53]

6.7 AFM STUDY

The analysis of AFM can be done by using the NT-MDT multimode AFM, Russia controlled by solver scanning probe microscope controller. The single beam cantilever having resonance frequency in the range of 240-255 kHz in semi –contact mode with corresponding spring constant of 11.5Nm⁻¹ containing NOVA program was used for image interpretation. The scanning area of AFM is 10μm × 10μm. [54]

6.8 Quantum chemical calculations

In order to find the HOMO, LUMO and dipole moment of the inhibitors Gaussian software shall be used. This program runs by using density function theory method. In this case the value of E_{HOMO} should be high and E_{LUMO} should be low so that the value of total energy becomes decreases hence the electron can easily transfer from HOMO to LUMO. This indicate the inhibitor have efficiency to control the corrosion

6.9 Monte Carlo Simulations

Monte Carlo simulation using the adsorption locator and forcite codes implemented in the material studio 6.0 software from accelrys Inc. USA was adopted to compute the adsorption energy of interaction between Sapindus and Al and Fe surfaces. For the whole simulation procedure the compass force field was used to optimize the structure of all component of the system of interest. The simulations were carried out in the simulation boxes ($42\text{\AA} \times 42\text{\AA} \times 55\text{\AA}$) having $\alpha=90.00$; $\beta=90.00$ and $\gamma=90.00$ with periodic boundary condition in order to simulate a representative part of an interface devoid of any arbitrary boundary effects. The Al (111) planes were next enlarged to a (10*10) super cell. After that, a vacuum slab of 50 thickness was built above the surface to convert the system to 3D periodicity. The optimized inhibitor using the Forcite code was then added near the surface of Fe (110) and a Monte Carlo simulation annealing procedure was carried out.

7. Result and Discussion:

7.1 Weight loss method

Aluminium coupon is dipped in the HCl solution of 1M for 1 hrs. The copper metal coupon is also dipped in the variety of ppm solutions of inhibitor in the 1M solution of HCl. This process is done to check the weight loss of coupon in acid and the weight of coupon with inhibitor. The weight loss can be done in the acid variation this can be done to check which molarity will be suitable for Aluminium for 1hr. Inhibition variation is also done to check which ppm solution is helpful to decrease the corrosion rate. The corrosion efficiency can be checked at different temperature and time. The difference of the weight loss of both of the coupon decides the efficiency of the inhibitor in copper metal. To calculate the corrosion efficiency following equation is used:

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$$IE\% = W(0) - W(I) / W(0) \times 100$$

Where, W (0) and W(I) is the initial and the final weight of Aluminium coupon respectively and $\eta\%$ is the inhibition efficiency.

Acid Variation with Aluminium:

Concentration	Initial weight	Final weight	weight loss	%Age weightloss
0.1	0.3151	0.3150	0.0001	0.03173
0.2	0.3132	0.3130	0.0002	0.0638
0.4	0.3223	0.3213	0.0010	0.3102
0.5	0.2874	0.2832	0.0042	1.4613
0.6	0.2833	0.2671	0.0162	5.7183
0.8	0.2956	0.1830	0.1126	38.0920
1	0.3493	0.1148	0.2345	67.1342
1.2	0.2800	0.0592	0.2208	78.8571

Table 3: Acid variation of Aluminium metal for 1 hr

The reaction in case of 1.2M HCl is very high at 25°C. So the monitoring of reaction is difficult for further processes so we took the 1M standard for further studies. As the concentration of the HCl is increases the corrosion rate is increase as seen above table.

Inhibitor Variation

Further studies of inhibitor are done by preparing the inhibitor solutions in ppm. This can be done carefully in the HCl solution of 1M because our standard set of HCl is 1 M. the variation of inhibitor is taken from 400ppm to 4000ppm.

Concentration	Initial Weight	Final weight	Weight Loss	% wt loss	Inhibition Efficiency
400	0.3152	0.2726	0.0426	13.5152	83.0075
800	0.3128	0.2793	0.0335	10.7097	86.6374
1000	0.2930	0.2778	0.0152	5.1877	93.9369
1500	0.2970	0.2839	0.0131	4.4107	94.7746
1600	0.2959	0.2904	0.0055	1.8587	97.8061
1800	0.2713	0.2666	0.0047	1.7323	98.1252
2000	0.2750	0.2710	0.0040	1.4545	98.4044
3000	0.2931	0.2899	0.0032	1.0917	98.7235
4000	0.2871	0.2866	0.0005	0.1741	99.8005
Blank	0.3670	0.1163	0.2507	68.3106	0

Table 4. Inhibition efficiency in different ppm solution if inhibitor

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From the table it was clearly seen that as the concentration of Aluminium is increased the corrosion rate is decreased it is due to the higher adsorption on the surface of metal takes place vice versa in case of blank no adsorption takes place so the corrosion rate is higher. The percentage efficiency is 98.40 at 2000ppm which is our standard ppm solution.

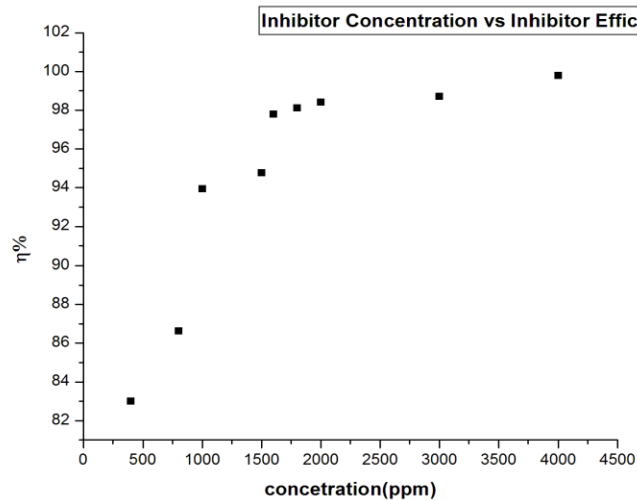


Figure2: Graph between percentage Vs concentration of Sapindus in HCl.

Effect of time:

TIME		Initial weight	Final weight	Weight loss	%age weight loss	Inhibition Efficiency
10	Blank	0.3248	0.3242	0.0006	0.1847	66.6666
	inhibitor	0.2847	0.2845	0.0002	0.0702	
20	Blank	0.3070	0.2996	0.0074	2.4104	86.4864
	inhibitor	0.3004	0.2994	0.001	0.3328	
40	Blank	0.2820	0.2097	0.0723	25.6382	95.2973
	inhibitor	0.3002	0.2968	0.0034	1.13257	
60	Blank	0.2910	0.0930	0.198	68.0412	98.4848
	inhibitor	0.2750	0.2720	0.003	1.0909	
80	Blank	0.2733	0.0292	0.2441	89.3157	79.1069
	inhibitor	0.3130	0.2620	0.051	16.2939	

Table5: variation of efficiency with time.

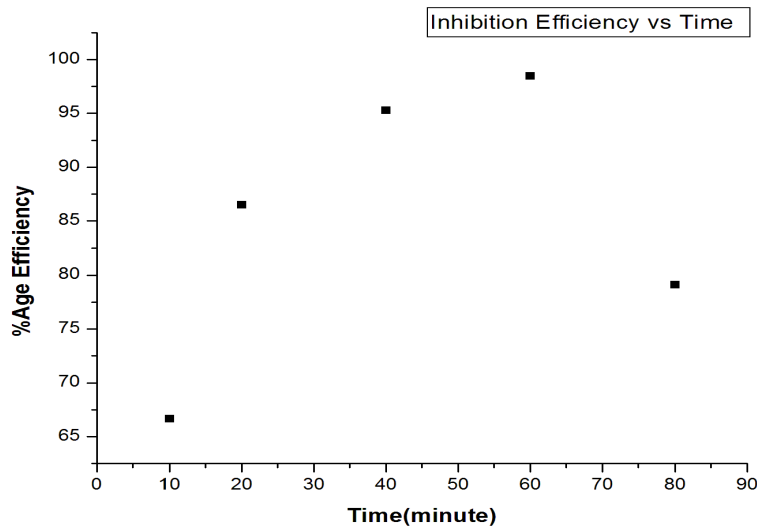


Figure 3: Graph between percentage efficiency Vs Time

From the above table and graph it shows that as the time is increased the efficiency of Sapindus is also increased but at the certain time the effect of Sapindus is not as much efficient because at a certain temperature the adsorption layer of molecule on the metal surface is decreased so the corrosion rate is increased.

Effect of temperature:

Weight loss measurement of Aluminium is carried out in temperature from 293 to 308K in the presence and absence of Sapindus of 2000ppm solution in 1M HCl. So by this data we get the activation energy as well as the absorption of Sapindus will be evaluated.

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Temperature		Initial weight	Final weight	Weight loss	%age weight loss	Inhibition Efficiency
20	Blank	0.3343	0.1099	0.2244	67.1253	99.1532
	Inhibitor	0.3005	0.2986	0.0019	0.6322	
25	Blank	0.3231	0.1023	0.2208	68.3379	98.3242
	Inhibitor	0.3476	0.3439	0.0037	1.0644	
30	Blank	0.3071	0.0905	0.2165	70.5177	88.9176
	Inhibitor	0.2960	0.2720	0.024	8.1081	
35	Blank	0.2977	0.0726	0.2250	75.5962	86.3141
	Inhibitor	0.2878	0.2570	0.0308	10.7018	
45	Blank	0.2881	0.0461	0.242	83.9982	69.8347
	Inhibitor	0.2638	0.1908	0.073	27.6724	

Table 6: Inhibition efficiency at different temperature

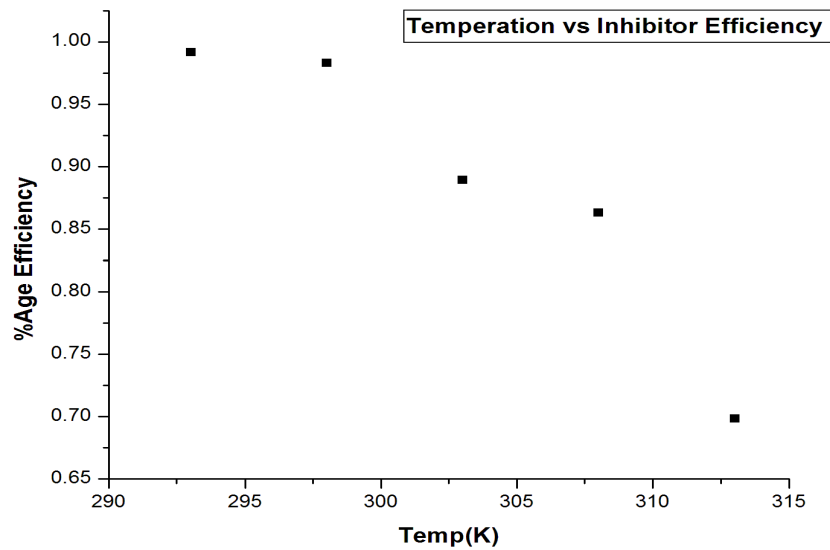


Figure 4: Graph between percentage efficiency Vs temperature.

The plot above show the variation of inhibitor of optimum concentration of Sapindus at different Temperature during 1 hour of immersion time.

Corrosion rate is calculated by the formula below:

$$C_R = \frac{87.6 \times \text{weight loss (mg)}}{\text{Surface Area of Specimen (cm}^2\text{)} \times \text{time (h)} \times \text{density of specimen (g cm}^{-3}\text{)}}$$

Calculation of corrosion rate is listed below:

Temperature		Initial weight	Final weight	Weight loss	Corrosion Rate
20	Blank	0.3343	0.1099	0.2244	0.9100
	Inhibitor	0.3005	0.2986	0.0019	0.0077
25	Blank	0.3231	0.1023	0.2208	0.8954
	Inhibitor	0.3476	0.3439	0.0037	0.0150
30	Blank	0.3071	0.0905	0.2165	0.8782
	Inhibitor	0.2960	0.2720	0.0240	0.0973
35	Blank	0.2977	0.0726	0.2250	0.9127
	Inhibitor	0.2878	0.2570	0.0308	0.1249
45	Blank	0.2881	0.0461	0.2420	0.9814
	Inhibitor	0.2638	0.1908	0.0730	0.2960

Table 7: Values of corrosion rate w.r.t temperature.

The inhibition efficiency is decreased and the corrosion rate is increased as the temperature is increased. This case is done because the desorption of inhibitor which is absorbed on the metal surface due to which greater surface area of Aluminium is come in contact with the environment and the corrosion rate is increased.

Adsorption isotherm tells the interaction of inhibitor molecule on the surface of metal. The surface coverage of different concentration at different temperature will helps to get the isotherm plot.

Langmuir isotherm, $\frac{\theta}{1-\theta} = K_{ads} C$

Freundlich isotherm, $\theta = K_{ads} C$

Here C is the concentration and θ is the surface coverage and K_{ads} is the equilibrium constant.

Langmuir absorption is the method to check the behavior of adsorption of Sapindus molecule on the surface of metal of Aluminium. The graph is plotted in between the $\log C/\theta$ vs. $\log C$.

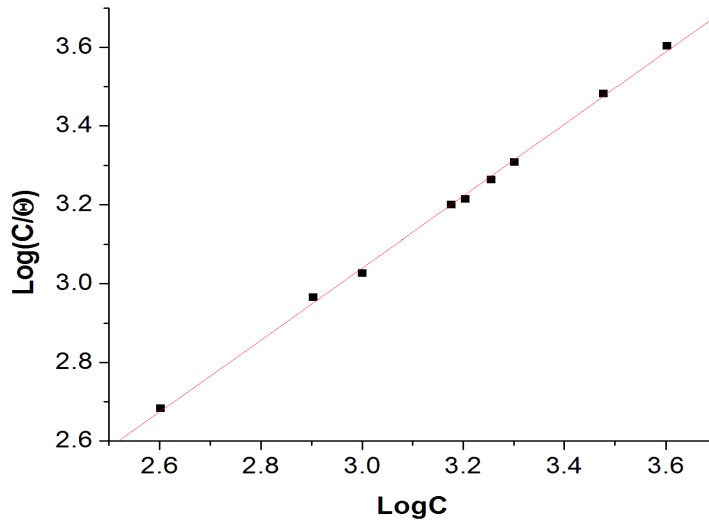


Figure 5: Arrhenius plot for solution containing Sapindus and 1M HCl.

The slope of this graph is 0.99925 which is equal to 1. This will show that the Langmuir desorption isotherm will be obeyed for the adsorption of Sapindus on the metal.

The activation energy or the activation parameter is calculated by the Arrhenius equation given below:

$$C_R = A \exp\left(\frac{-E_a}{RT}\right)$$

Where, A is the pre-exponential factor, T is the temperature, R is the gas constant, and E_a is the activation energy.

The activation energy is calculated by the graph between $\text{Log}C_r$ and $1000/T$. By this graph we calculate the slope and then apply the formula to calculate the activation energy E_a .

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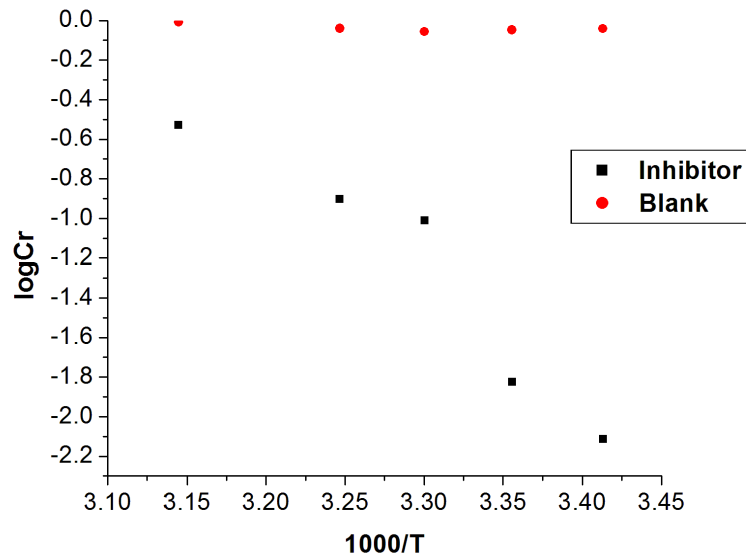


Figure 6: Graph between 1000/T Vs log Cr.

S.No.	Inhibitor	Slope	Ea(KJmol ⁻¹)
1.	Blank	-0.12853	2.4609
2.	Sapindus	-6.1371	117.4927

Table 9: Values of activation energy of blank and Sapindus immersed in 1 M HCl.

Due to the physical barrier created by the adsorbed inhibitor molecules for charge and mass transfer the value of the activation energy is high as compared to the blank activation energy.

To calculate the enthalpy of activation following formula is used:

$$\ln \frac{Cr}{T} = \left(\frac{-\Delta H}{R} \right) \cdot \frac{1}{T} + \left(\frac{\ln R}{Nh} + \frac{\Delta S}{R} \right)$$

Here,

ΔH = enthalpy of activation.

ΔS = entropy of activation.

R= gas constant.

N= Avogadro's number.

h= plank's constant.

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This equation is called as Eyring equation.

A plot of $\ln Cr/T$ vs. $1/T$ gave a straight line with slope value of $(-\Delta H/R)$ and an intercept value of $(\frac{\ln R}{Nh} + \frac{\Delta S}{R})$ which was used to calculate the value of ΔH and ΔS .

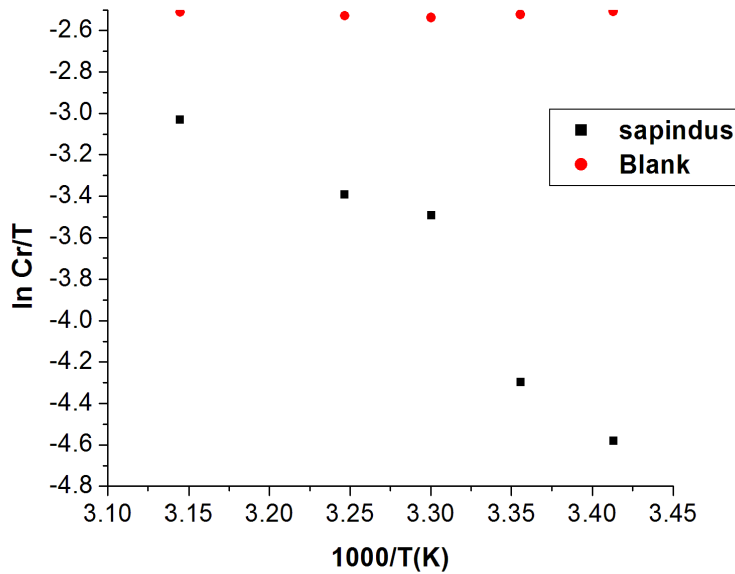


Figure 7: Graph between $1000/T$ Vs $\ln Cr/T$

To calculate the value of K_{ads} with respect to Langmuir isotherm. The formula is:

$$K_{ads} = \frac{\theta}{Cr(1-\theta)}$$

The value of K_{ads} for inhibitor at 298K is written below:

S.No.	Inhibitor	concentration	θ	CR	Kads
1.	Sapindus	2000ppm	0.9832	0.0150	1.2610

Table 10: Values of corrosion rate and K_{ads}

Sapindus as potential green corrosion inhibitor of Aluminium and mild steel

The standard free energy of adsorption equation gives the relation between the ΔG°_{ads} and K_{ads} . the equation is:

$$\Delta G^{\circ}_{ads} = -2.303RT \log(55.5K_{ads})$$

Here the 55.5 value is the molar concentration of water in solution having unit mol/l.

Form the value of ΔG°_{ads} and ΔH°_{ads} we calculate the ΔS°_{ads} with the following equation:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads}$$

S.No.	Inhibitor	ΔH_{ads}	ΔS_{ads}
1.	Blank	0.033755	-
2.	Sapindus	49.91493	343.3506

Table11: Activation parameter obtained for Aluminium in 1m HCl in the absence and presence of Sapindus.

The value of ΔG_{ads} for Sapindus is -10.181kJ/mol. The negative value tells the spontaneity of the adsorption as well as the stability of adsorbed layer which is made by the Sapindus on the metal surface. The ΔG_{ads} value is -20kJ/mol or less negative due to electrostatic interaction between the inhibitor and the charged metal surface (i.e. Physisorption). The values of ΔG_{ads} around -40 kJ/mol or more negative indicate that a charge sharing or transferring from organic species to the metal surface occurs to form a coordinate type of bond (i.e. Chemisorptions). The calculated values of ΔG_{ads} suggest a strong interaction between the inhibitor and the surface of Aluminium, this interaction involves chemisorptions.

The dissolution of Aluminium is endothermic in nature due to the positive value of ΔH°_{ads} and the higher positive value in presence of inhibitor than in blank is an evidence of slower dissolution of metal in presence of inhibitor.

The disordering increases which is the driving force for inhibitor adsorption on Aluminium surface due to the positive value of ΔS°_{ads} .

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Acid variation with Steel

It is also used in weight loss method to analyze whether the Sapindus is helpful to inhibit the corrosion of steel or not. In case of steel, coupon is dipped in the 5M H₂SO₄ solution, and the Sapindus is used as 2000ppm in H₂SO₄. The process used is same as in case of Aluminium.

Concentration	Initial Weight	Final weight	Weight Loss	% wt loss
1	1.4312	1.401	0.0302	2.1101
2	1.4607	1.4065	0.0542	3.7105
3	1.4529	1.3598	0.0931	6.4078
4	1.5132	1.3596	0.1536	10.1504
5	1.2219	0.9902	0.2317	18.9622
6	1.3634	1.0497	0.3137	23.0086
7	1.2734	0.9616	0.3118	24.4856
8	1.3114	0.8279	0.4835	36.8689
9	1.3751	0.8610	0.5141	37.3863
10	1.4206	0.7762	0.6444	45.3611

Table 12: Acid variation of steel metal for 2 hr.

From the table it is clearly seen that as the concentration of H₂SO₄ is increased the weight loss is also increased because the acidity of acid increase the corrosion of metal and vice versa.

Concentration	Initial Weight	Final weight	Weight Loss	% wt loss	Inhibition Efficiency
400	1.3951	1.3565	0.0386	2.7668	83.5394
800	1.3373	1.3000	0.0373	2.7892	84.0938
1000	1.2374	1.2170	0.0204	1.6486	91.3006
1500	1.2502	1.2327	0.0175	1.3997	92.5373
1600	1.3604	1.3416	0.0188	1.3819	91.9829
1800	1.4749	1.4553	0.0196	1.3289	91.6417
2000	1.313	1.2959	0.0171	1.3023	92.7078
blank	1.2219	0.9902	0.2317	18.9622	1.1940

Table13: Inhibition efficiency in different ppm solution of inhibitor

Sapindus as potential green corrosion inhibitor of Aluminium and mild steel

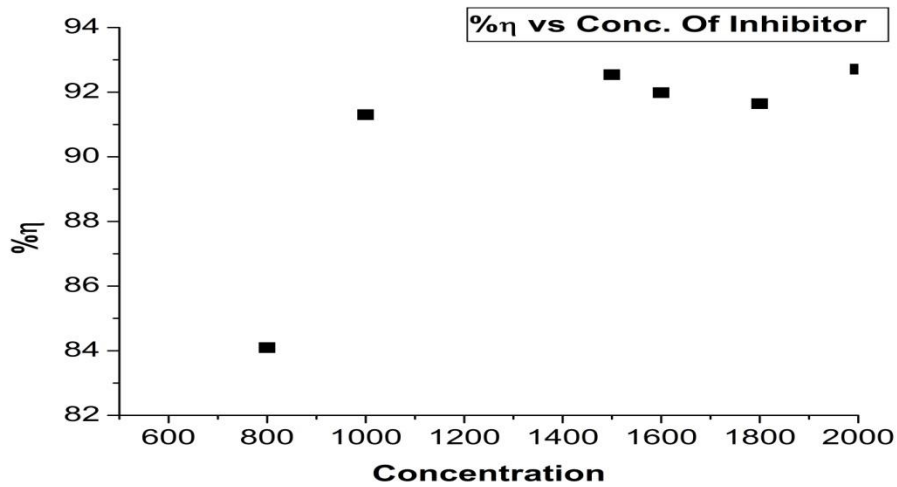


Figure7: Graph between percentage efficiency Vs concentration of Sapindus.

From the above table and graph as the concentration of inhibitor is increased the corrosion rate is decrease because the inhibitor will adsorb on the surface of metal that will help to decrease the corrosion on the metal.

Effect of Time:

TIME		Initial weight	Final weight	Weight loss	%age weight loss	Inhibition Efficiency
1	Blank	1.4998	1.3806	0.1192	7.9477	92.6174
	Inhibitor	1.306	1.2972	0.0088	0.6738	
2	Blank	1.3685	1.0204	0.3481	25.4366	91.1519
	Inhibitor	1.2835	1.2527	0.0308	2.3996	
3	Blank	1.4242	0.9377	0.4865	34.1595	88.9003
	Inhibitor	1.3375	1.2835	0.054	4.0373	
4	Blank	1.4552	1.2174	0.2378	16.3413	89.6131
	Inhibitor	1.5583	1.5336	0.0247	1.5850	

Table 14: Calculate the inhibition efficiency of Sapindus (1000ppm in H₂SO₄) at different time.

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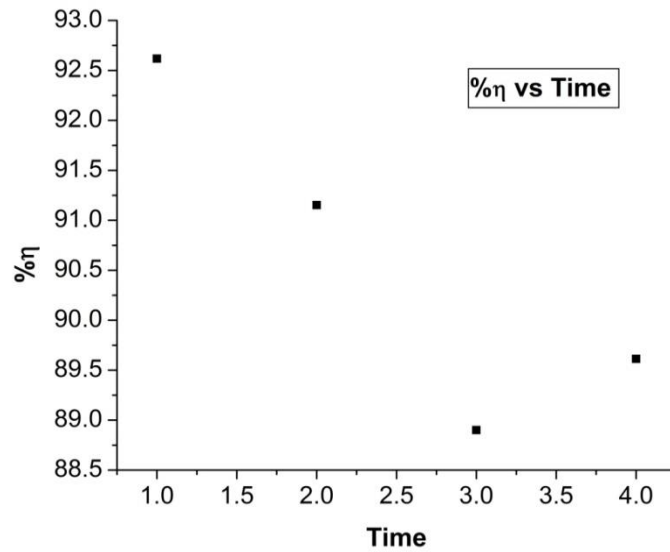


Figure 8: Graph between percentage efficiency Vs Time.

From the above table and graph it is clearly shown that as the time is increased the inhibition efficiency is decreased because the absorption of inhibition on the metal surfaces is decreased in increases of time.

Effect of Temperature:

Temperature		Initial weight	Final weight	%age weight loss	Corrosion Rate	Inhibition Efficiency
20	blank	1.4765	1.4189	3.9011	0.0401	73.2638
	inhibitor	1.4632	1.4478	1.0524	0.0107	
25	blank	1.2681	1.1356	10.4487	0.0922	87.0182
	inhibitor	1.4033	1.3861	1.2256	0.0119	
30	blank	1.4417	1.1734	18.6099	0.1868	91.0920
	inhibitor	1.2992	1.2753	1.8395	0.0166	
35	blank	1.4486	0.8856	38.8651	0.3921	79.6802
	inhibitor	1.4182	1.3038	8.0665	0.0796	

Table15: Variation of inhibition efficiency w.r.t temperature by weight loss method.

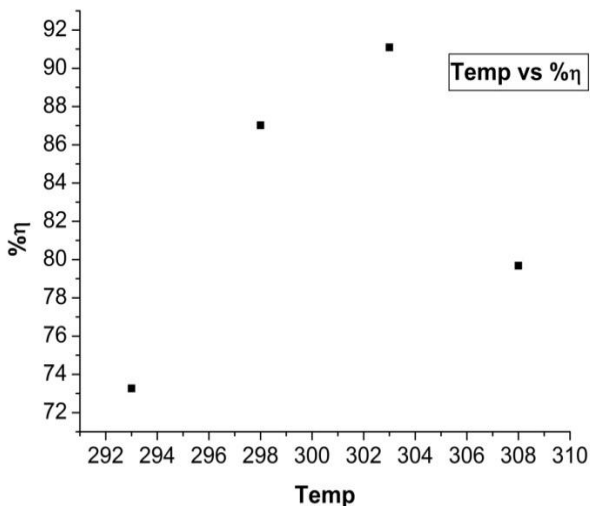


Figure 9: Graph between percentage efficiency Vs temperature

Weight loss measurement of steel is carried out in temperature from 293 to 308K in the presence and absence of Sapindus of 1000ppm solution in 5M H₂SO₄. By the temperature variation we calculate the thermodynamic parameters as mentioned in case of Aluminium above.

The inhibition efficiency is decreased and the corrosion rate is increased as the temperature is increased. This case is done because the desorption of inhibitor which is absorbed on the metal surface due to which greater surface area of steel is come in contact with the environment and the corrosion rate is increased.

Adsorption isotherm tells the interaction of Sapindus molecule on the surface of steel. The surface coverage of different concentration at different temperature will helps to get the isotherm plot.

$$\text{Langmuir isotherm, } \frac{\theta}{1-\theta} = K_{\text{ads}}C$$

$$\text{Freundlich isotherm, } \theta = K_{\text{ads}}C$$

Here θ is the surface coverage, C is the concentration and K_{ads} is the equilibrium constant.

Langmuir absorption is the method to check the behavior of adsorption of Sapindus molecule on the surface of steel. The graph is plotted in between the $\log C/\theta$ vs $\log C$.

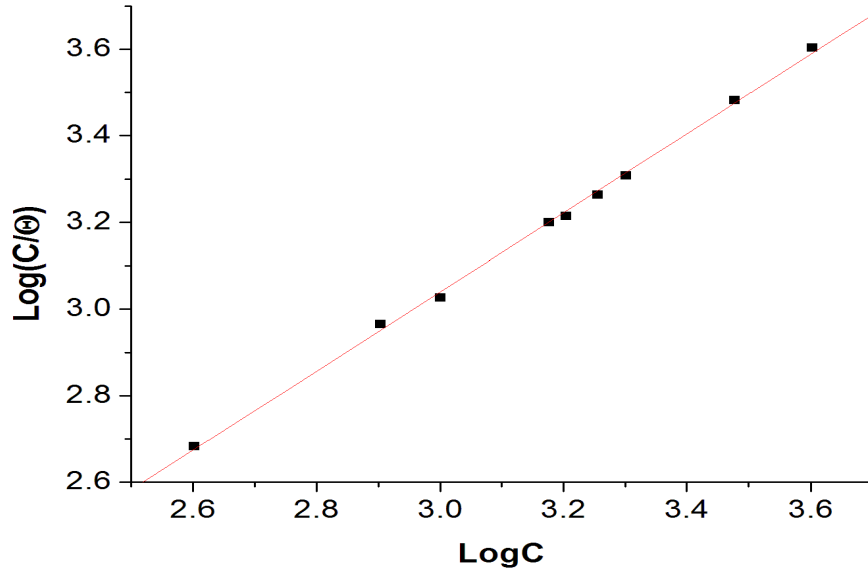


Figure 10: Graph between Log C Vs Log(C/θ)

The slope of this graph is 0.99925 which is equal to 1. This will show that the Langmuir desorption isotherm will be obeyed for the adsorption of Sapindus on the metal.

The activation energy or the activation parameter is calculated by the Arrhenius equation given below:

$$C_R = A \exp\left(\frac{-E_a}{RT}\right)$$

Where, T is the temperature, A is the pre-exponential factor, R is the gas constant, and E_a is the activation energy.

The activation energy is calculated by the graph between $\log C_R$ and $1/T$. By this graph we calculate the slope and then apply the formula to calculate the activation energy E_a .

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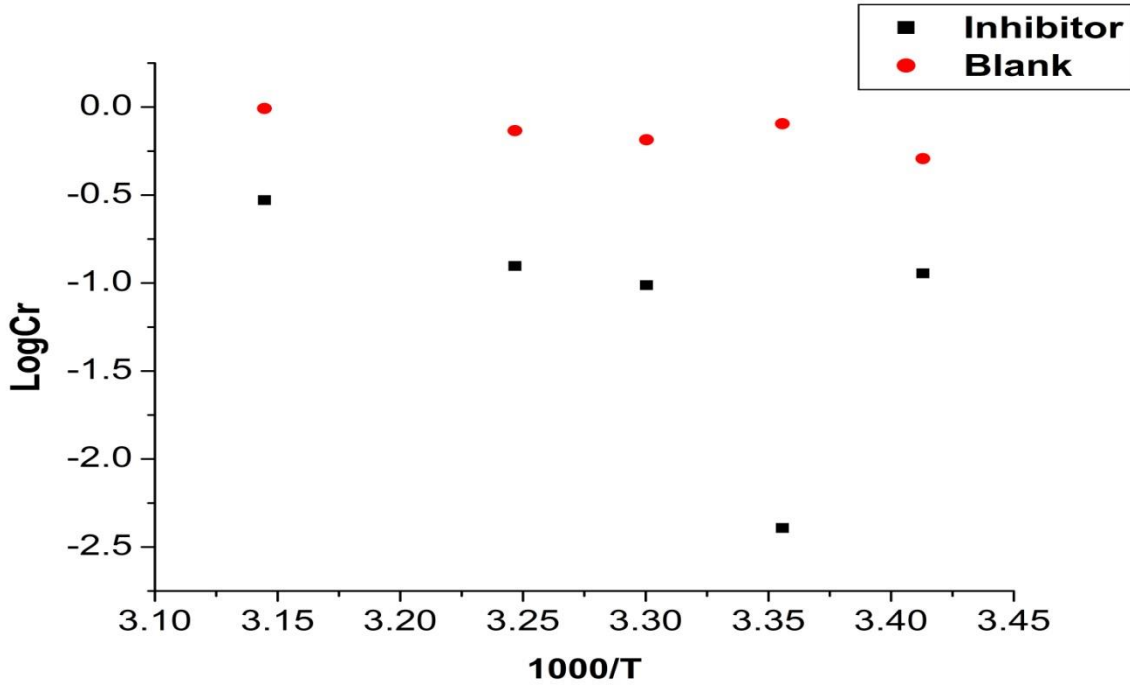


Figure 11: graph between 1000/T vs LogCr

S.No.	Inhibitor	Slope	Ea(KJmol ⁻¹)
1.	Blank	-0.83905	16.065
2.	Sapindus	-3.66538	70.189

Table16: Values of activation energies of blank and Sapindus

Due to the physical barrier created by the adsorbed inhibitor molecules for charge and mass transfer the value of the activation energy is high as compared to the blank activation energy.

To calculate the enthalpy of activation following formula is used:

$$\ln \frac{Cr}{T} = \left(\frac{-\Delta H}{R} \right) \cdot \frac{1}{T} + \left(\frac{\ln R}{Nh} + \frac{\Delta S}{R} \right)$$

Here,

ΔH = enthalpy of activation.

ΔS = entropy of activation.

R= gas constant.

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N= Avogadro's number.

h= plank's constant.

This equation is called as Eyring equation.

A plot of $\ln Cr/T$ vs. $1/T$ gave a straight line with slope value of $(-\Delta H/R)$ and an intercept value of $(\frac{\ln R}{Nh} + \frac{\Delta S}{R})$ which was used to calculate the value of ΔH and ΔS .

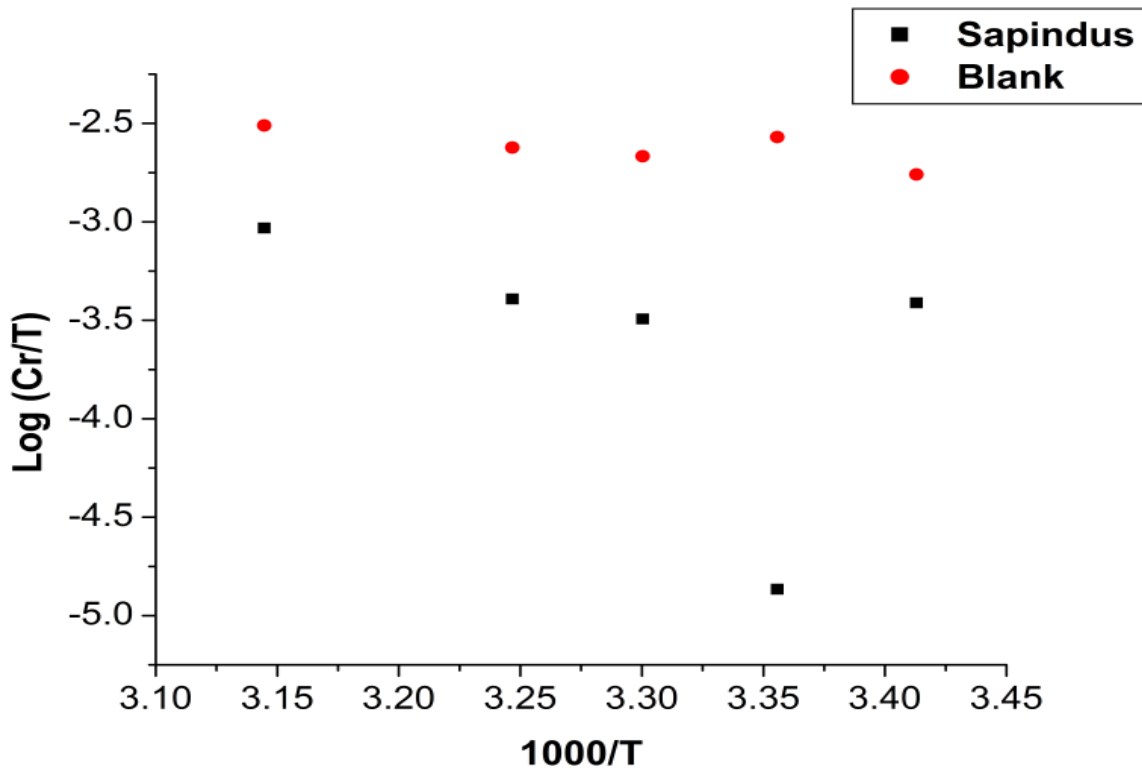


Figure 12: Graph between Log (Cr/T) Vs 1000/T.

To calculate the value of K_{ads} with respect to Langmuir isotherm. The formula is:

$$K_{ads} = \frac{\theta}{Cr(1-\theta)}$$

S.No.	Inhibitor	concentration	Θ	CR	Kads
1.	Sapindus	2000ppm	0.8508	0.0973	1.3038

Table 17: Values of corrosion rate and K_{ads} .

Sapindus as potential green corrosion inhibitor of Aluminium and mild steel

The standard free energy of adsorption equation gives the relation between the ΔG°_{ads} and K_{ads} the equation is:

$$\Delta G^{\circ}_{ads} = -2.303RT \log(55.5K_{ads})$$

Here the 55.5 value is the molar concentration of water in solution having unit mol/l.

Form the value of ΔG°_{ads} and ΔH°_{ads} we calculate the ΔS°_{ads} with the following equation:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads}$$

S.No.	Inhibitor	ΔH_{ads}	ΔS_{ads}
1.	Blank	5.873508	-
2.	Sapindus	29.37178	35.69531

Table18: Activation parameter obtained for steel in 5M H₂SO₄ in the absence and presence of Sapindus.

The value of ΔG_{ads} for Sapindus is -10.786kJ/mol. The negative value tells the spontaneity of the adsorption as well as the stability of adsorbed layer which is made by the Sapindus on the metal surface. The ΔG_{ads} value is -20kJ/mol or less negative due to electrostatic interaction between the inhibitor and the charged metal surface (i.e. Physisorption). The values of ΔG_{ads} around -40 kJ/mol or more negative indicate that a charge sharing or transferring from organic species to the metal surface occurs to form a coordinate type of bond (i.e. Chemisorption). The calculated values of ΔG_{ads} suggest a strong interaction between the surface of steel and the Sapindus, this interaction involves chemisorptions.

The dissolution of Aluminium is endothermic in nature due to the positive value of ΔH°_{ads} and the higher positive value in presence of inhibitor than in blank is an evidence of slower dissolution of metal in presence of inhibitor.

The disordering increases which is the driving force for inhibitor adsorption on Aluminium surface due to the positive value of ΔS°_{ads} .

7.2 Electrochemical studies:

7.2.1 Potentiodynamic polarization studies:

Polarization curves of the iron electrode in 1M HCl and 5M H₂SO₄ solution in the presence and absence of Sapindus with different ppm solution or concentration. By this we can check various electrochemical parameter like corrosion potential (E_{corr}), corrosion current densities (I_{corr}), and tafel slopes. I_{corr} or corrosion current densities are used to calculate the inhibition efficiency. The tafel plot describes that as the inhibitor concentration is increased the corrosion rate densities is decreased. This suggest that reduction of electrochemical rate due to the formation of barrier layer over the surface of steel and Aluminium metal. The hydrogen evolution mechanism cannot be modifying by the addition of Sapindus in the presence of 1M HCl and 5M H₂SO₄ this is suggested by the parallel cathodic tafel lines. The shifting of the anodic lines is may or may be not due to the adsorption of inhibitor on the surface of Aluminium and steel metal. It is also clear that the shifting of the cathodic region in the corrosion potential value due to the fact that $\beta_c > \beta_a$. The surface coverage (θ) was calculated by:

$$\theta = \frac{I_{\text{corr}}(\text{blank}) - I_{\text{corr}}(\text{inhibitor})}{I_{\text{corr}}(\text{blank})}$$

Here $I_{\text{corr}}(\text{blank})$ is the corrosion current density of without inhibitor and $I_{\text{corr}}(\text{inhibitor})$ is the corrosion current density with inhibitor.

conc	I_{corr}	$\times 10^{-3}$	IE	(-)E _{corr}	Ba(mV/dec)	Bc(mV/dec)
1000	2.02×10^{-3}	2.0200	93.0344	0.7390	4.4840	5.0150
2000	1.37×10^{-3}	1.3700	95.2756	0.7820	6.9410	22.2000
3000	6.12×10^{-4}	0.6120	97.8896	0.7700	6.9930	8.0910
4000	5.08×10^{-5}	0.0508	99.8248	0.7370	7.2120	9.4570
blank	2.90×10^{-2}	29.0000		0.7000	4.4890	4.5150

Table19: Corrosion parameters of Aluminium in 1M HCl in the presence of Sapindus at 298K

If $b_a > b_c$, it suggest that anodic disintegration process is more preferred and inhibitor will go about as an anodic type of inhibitor and If $b_c > b_a$, then cathodic disintegration process is more preferred and inhibitor will go about as a cathodic type of inhibitor. In the present studies, the values of E_{corr} remain almost constant, indicating the mixed type of inhibitor. It is clear from the table that both cathodic and anodic slopes are affected in presence of inhibitor, it can therefore

be assumed that Sapindus gets adsorbed by inhibiting the corrosion of Al in HCl solution by precipitation of chloride salt on both cathodic and anodic sites of metal oxide surfaces.

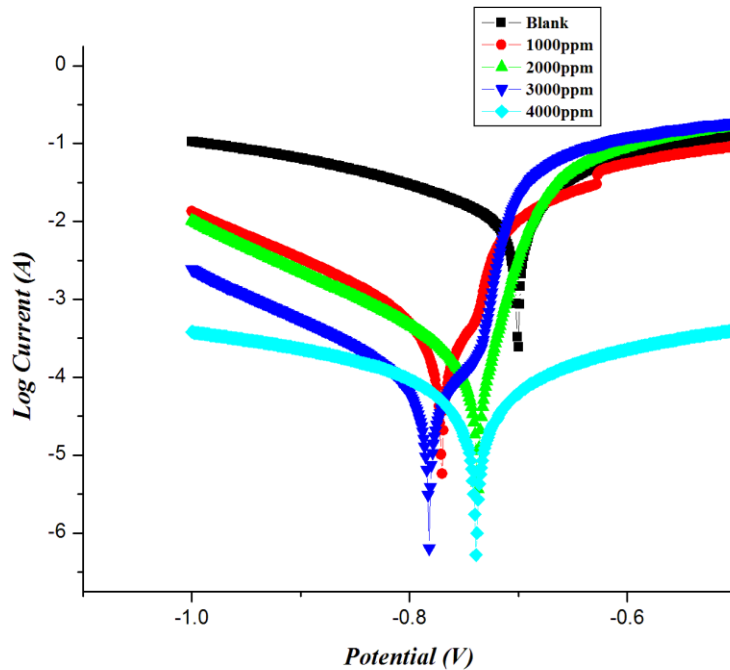


Figure 13: Tafel polarization curves for Aluminium in 1 M HCl in the presence of Various concentrations of Sapindus at 298 K.

7.2.2 Electrochemical impedance spectroscopy (EIS):

The Aluminium metal and steel metal corrosion from the HCl is explored by the EIS at 298K after immersion of 1hr. By EIS we can calculate the two fold layer capacitance (C_{dl}) and charge transfer resistance value (R_{ct}). By measuring the width of semicircle and the two fold layer capacitance, calculation of charge transfer resistance. The following equation is help to do that:

$$C_{dl} = 1/2\pi f_{max} R_{ct}$$

Here, f_{max} is the frequency where imaginary part of impedance i.e., Z'' has maximum magnitude.

Also the corrosion inhibition efficiency is calculate by the following equation:

$$\eta_{EIS} (\%) = (R_{ct} \text{ inhibitor} - R_{ct} \text{ acid} / R_{ct} \text{ inhibitor}) \times 100$$

Here

$R_{ct} \text{ inhibitor}$ = charge transfer resistance exhibited by Aluminium in the presence of Sapindus in 1M HCl,

Rct blank= charge transfer resistance exhibited by Aluminium in the absence of Sapindus in 1M HCl,

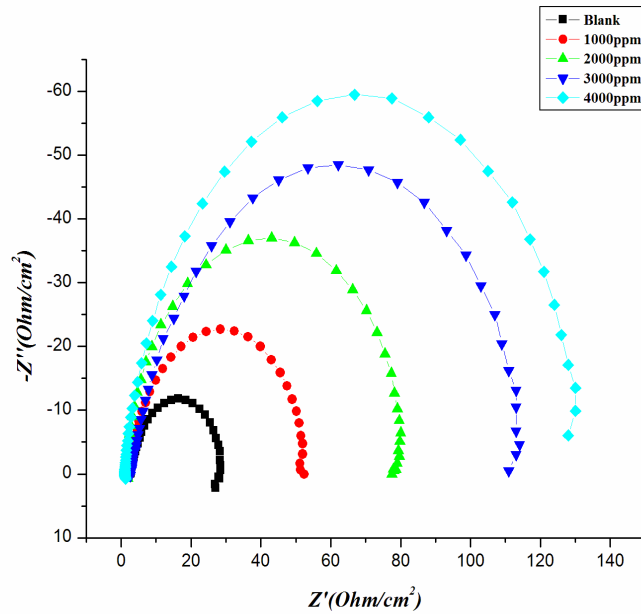


Figure14: Nyquist plot for Aluminium 1M HCl without and with various concentration of Sapindus.

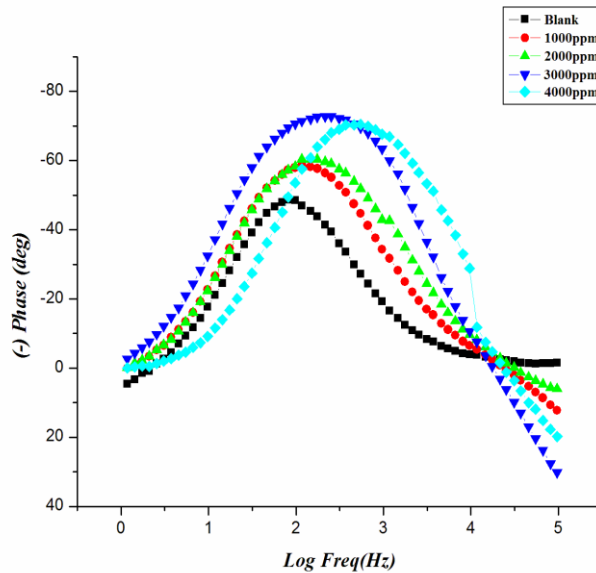


Figure15: Bode plot (Log Freq. (Hz) vs (-) Phase(deg)) for aluminium in 1M HCl in the presence and absence of Sapindus.

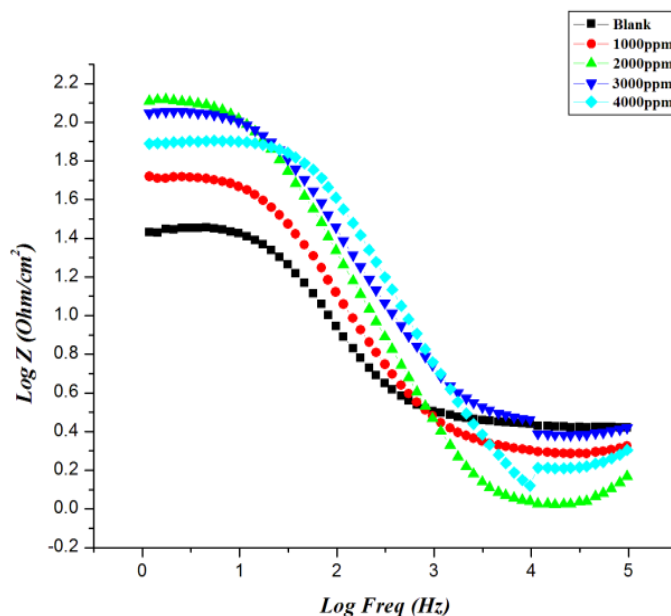


Figure16: Bode plot (log freq (Hz) vs. LogZ (Ohm/cm²)) for Aluminium in 1M HCl in presence and absence of Sapindus.

Conc	rct in	rct bl	fmax in	fmax bl	IE	c blank(μF)	C inhi
					Rct in- rctbl/rctin*100	1/2πfmaxRct	
1000	50.24	3.868	46.5	1.828	92.3009	22520.48	68.1612
2000	77.22	3.868	37.5	1.828	94.9909	22520.48	54.9894
3000	112.12	3.868	21.2	1.828	96.5501	22520.48	66.9917
4000	130.32	3.868	14.3	1.828	97.0319	22520.48	85.4462

Table20: Impedance parameters for the corrosion of Aluminium in 1 M HCl in the presence of Sapindus

From the table it is clearly seen that as the concentration is increasing charge transfer resistance is also increasing this will help to decrease the corrosion current for aluminium in 1M HCl.

7.3 Quantum chemical results

From the optimized structure of lowest energy of conformer we get all quantum chemical parameter. By the frontier molecular orbitals, reactivity of inhibitor is calculated. Chemical

reactivity is strongly determined by the interaction of the HOMO and the lowest unoccupied molecular orbital (LUMO) of the interacting species, this is established by frontier molecular orbital theory. Other quantum chemical parameters were calculated to have more insight into the reactivity of Sapindus. The EHOMO is often associated with the electron donating ability of a molecule and a higher EHOMO energy value indicates higher tendency of the molecule to donate electron(s) to the appropriate acceptor molecule with low energy and empty/partially filled molecular orbital.

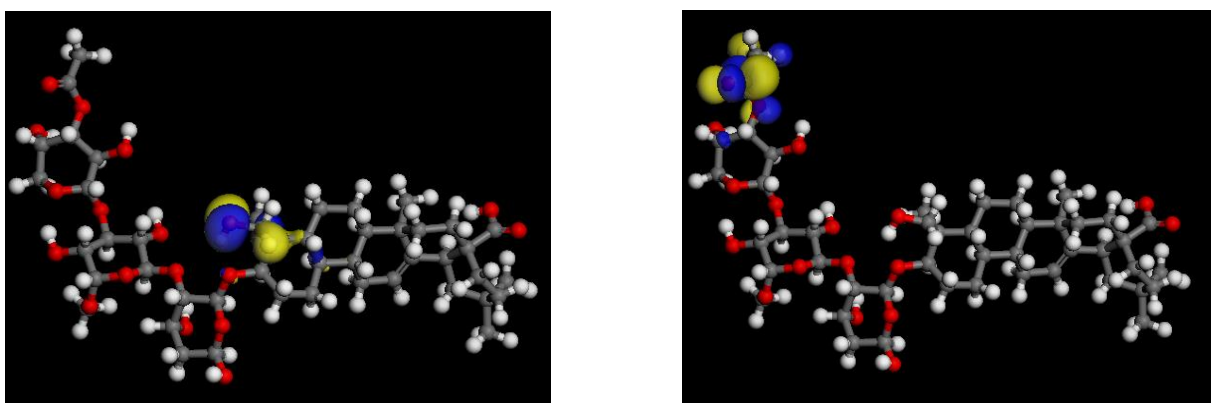


Figure 17: Highest occupied molecular orbital (HOMO) and Lowest unoccupied molecular orbital (LUMO) for the studied compound (Sapindus)

Type of inhibitors	E-HOMO	E-LUMO	ΔE
Sapindus	-5.44	-1.21	4.23

Table 21: Calculated quantum chemical parameters for Sapindus.

The results reported in Table shows the estimated values of quantum chemical parameters. Molecules with large value of ΔE (ELUMO– EHOMO) are highly stable and associated with low reactivity, while molecules with small values of ΔE are generally highly reactive. A molecule with a small value of ΔE is easily polarized and can therefore be easily adsorbed on the metal surface, resulting in appreciably good inhibition efficiency. The dipole moment (μ) is another index that is often used for the prediction of relative ability of corrosion inhibitors. It is the measure of polarity in a bond and is related to the distribution of electrons in a molecule. Inhibitors with high dipole moment tend to form strong dipole–dipole interactions with the metal, resulting in strong adsorption on the surface of the metal and therefore leading to greater inhibition efficiency. However, a survey of literature shows that in most cases, experimental inhibition efficiencies do not always correlate with dipole moments..

7.4 Monte carlo stimulation:

Monte Carlo studies reveal that adsorption energy of the Sapindus is far higher than that of water molecules thereby, suggesting the formation of protective layer.

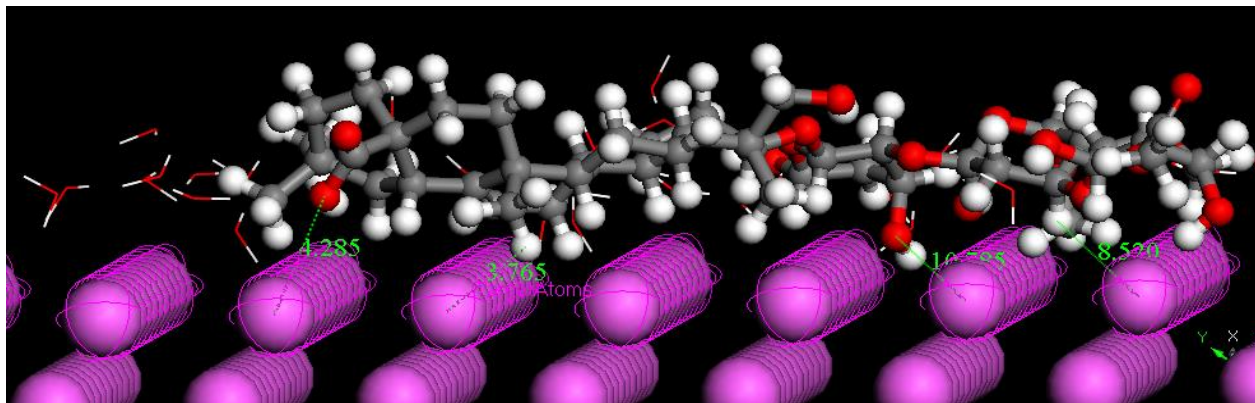


Figure 18: The most stable low energy configuration for the adsorption of sapindus on Al(111)/50H₂O system obtained using the Monte Carlo simulation, side view

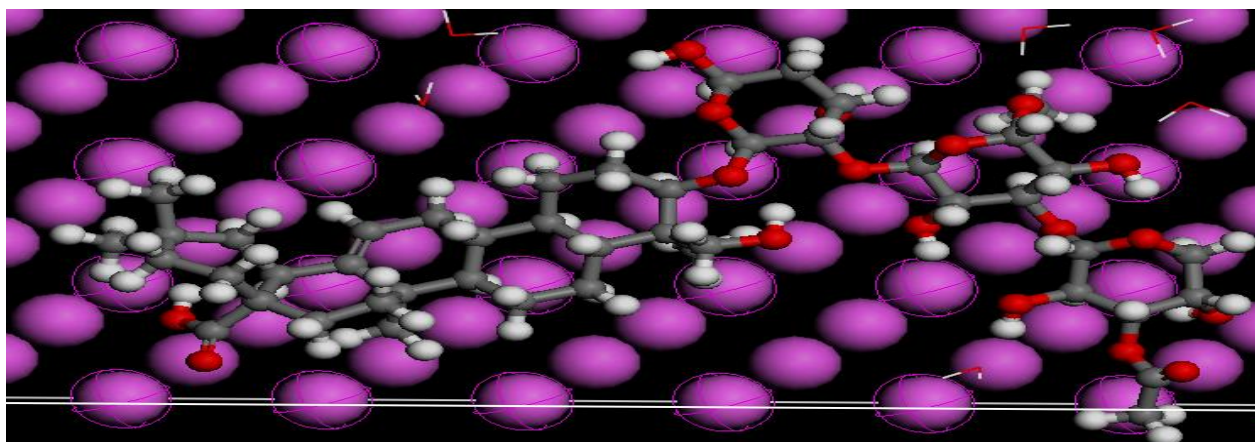


Figure 19: The most stable low energy configuration for the adsorption of sapindus on Al(111)/50H₂O system obtained using the Monte Carlo simulation, top view

Type of inhibitors	Total energy	Adsorption energy	Rigid adsorption energy	Deformation energy	sapindus : dEad/dNi	H ₂ O : dEad/dNi
Al(111)/Sapindul/50 H ₂ O	-503.19	-519.10	-534.17	15.07	-130.80	-1.74

Table 22: Monte Carlo simulation Results of corrosion inhibitors interaction on Al(111) in aqueous phase (Kcal/mol).

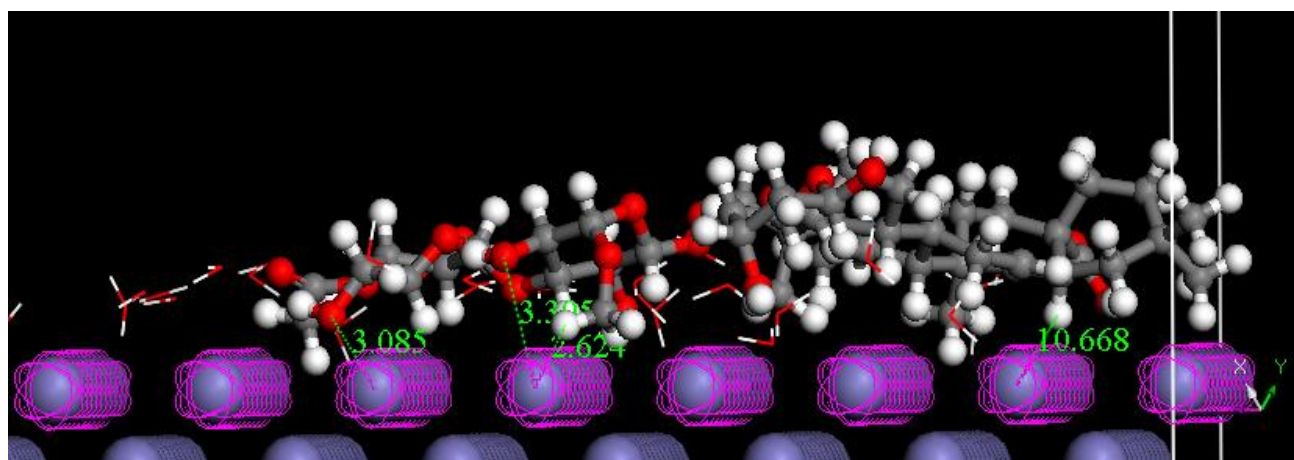


Figure 20: The most stable low energy configuration for the adsorption of sapindus on Fe(110)/50H₂O system obtained using the Monte Carlo simulation, side view

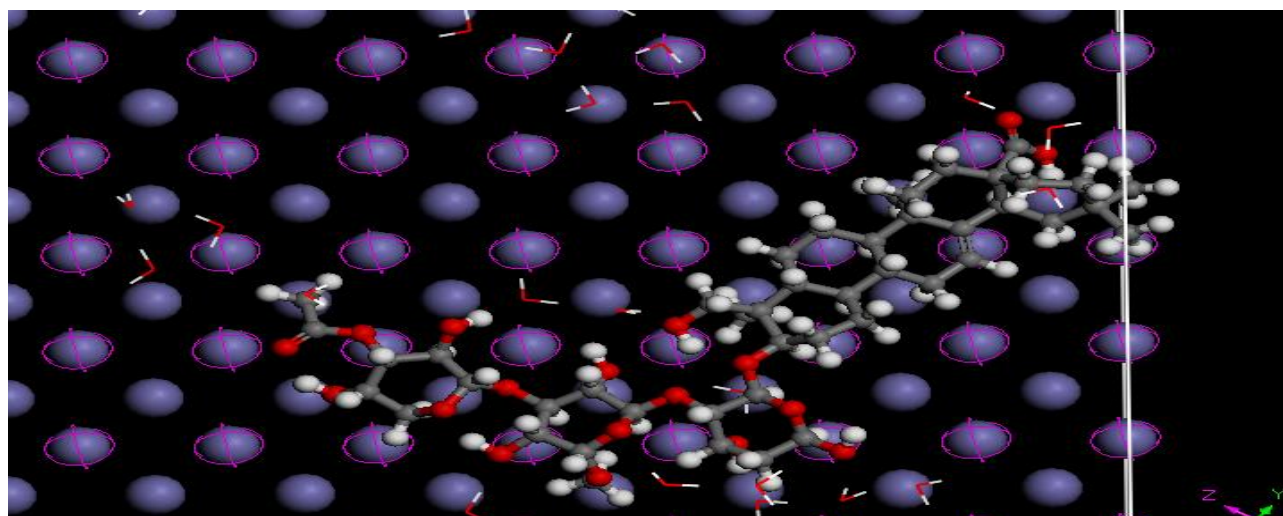


Figure 21: The most stable low energy configuration for the adsorption of Sapindus on Fe(110)/50H₂O system obtained using the Monte Carlo simulation, top view

Sapindus as potential green corrosion inhibitor of Aluminium and mild steel

Type of inhibitors	Total energy	Adsorption energy	Rigid adsorption energy	Deformation energy	Sapindus	H2O : dEad/dNi
Fe(110)/Sapindus/50 H2O	-606.65	-622.56	-638.30	15.74	-191.76	-4.52

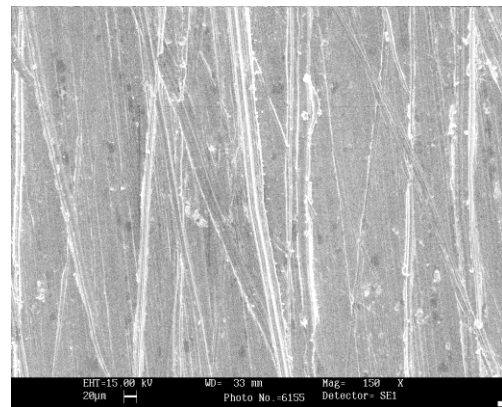
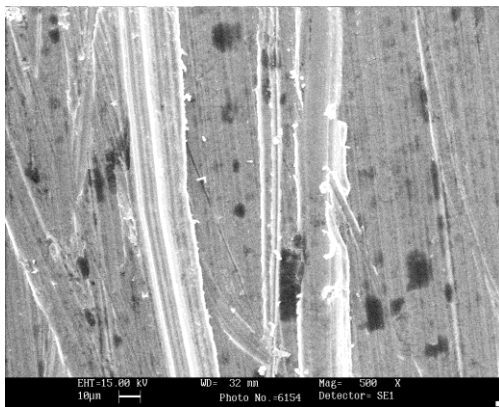
Table 23: Monte Carlo simulation Results of corrosion inhibitors interaction on Fe(110) in aqueous phase (Kcal/mol)

7.4 Scanning electron microscopy (LEO435 VP)

The surface morphology of the plain Aluminium surface or plain steel and Aluminium or steel in 1M HCl and H₂SO₄ respectively or the Sapindus with acids is exhibited in figures. It is clear that the surface of Al and steel with acid having large number of cavities and the disintegrated surface are there because of the corrosion. But when these metal is dipped in Sapindus with respective acid solution the defensive covering of the inhibitor is there so the smoothening of metal surface takes place.

Sapindus with Aluminium:

Pure Aluminium sample:



Sapindus as potential green corrosion inhibitor of Aluminium and mild steel

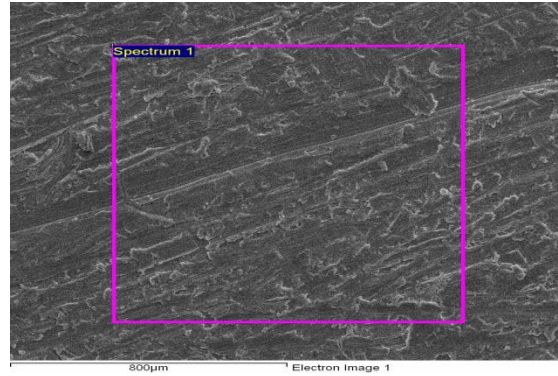
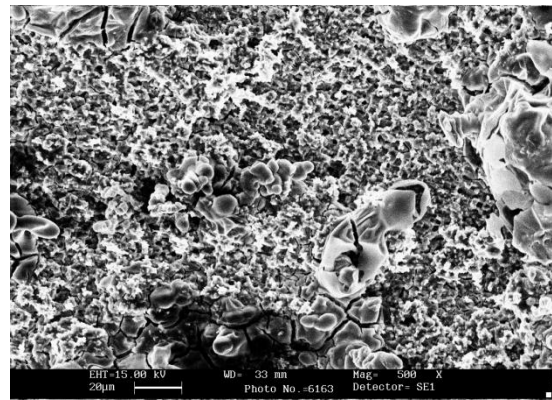
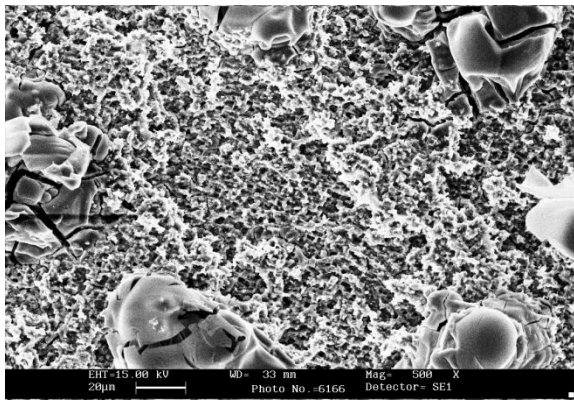


Figure 22: SEM images of polished Aluminium.

Above figures clearly shown there is not any cavity in the pure Aluminium. This is the polished Aluminium because the scratches are seen which are arises because of polishing.

Blank : In blank the Aluminium is treated with 1M HCl for a period of 1 hr. The surface of metal is corroded as seen below the large number of cavities is there.



Sapindus as potential green corrosion inhibitor of Aluminium and mild steel

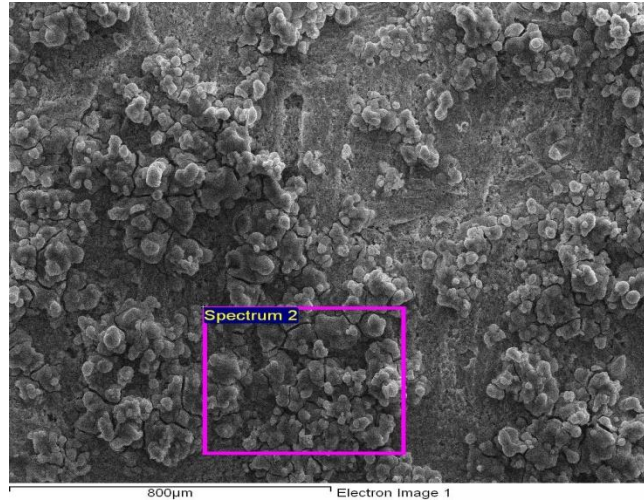


Figure 23: SEM images of Aluminium with 1M HCl.

Inhibitor: when the Aluminium is dipped in 2000ppm solution of Sapindus in HCl, the cavities is decreases as shown in the blank solution. The surface of Aluminium is smoother rather than balnk. This shows that the Sapindus reduce the corrosion rate

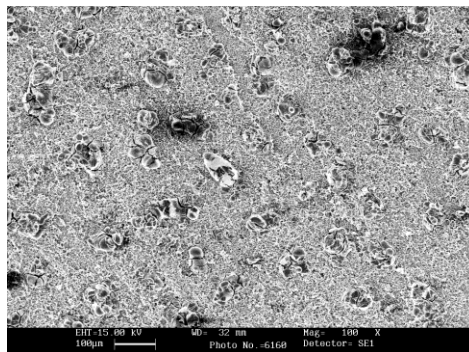
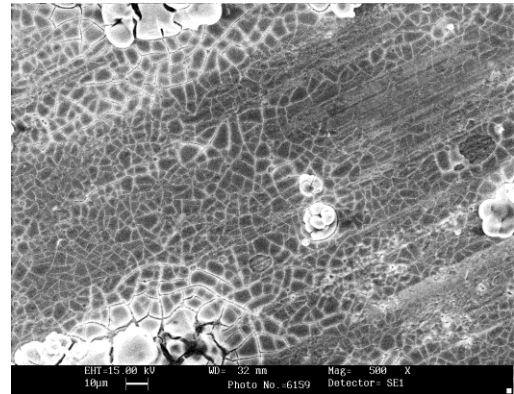
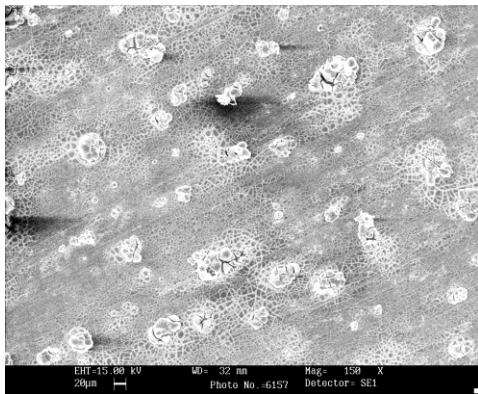


Figure 24: SEM images of Aluminium with Sapindus in 1M HCl.

Results with steel:

Pure steel:

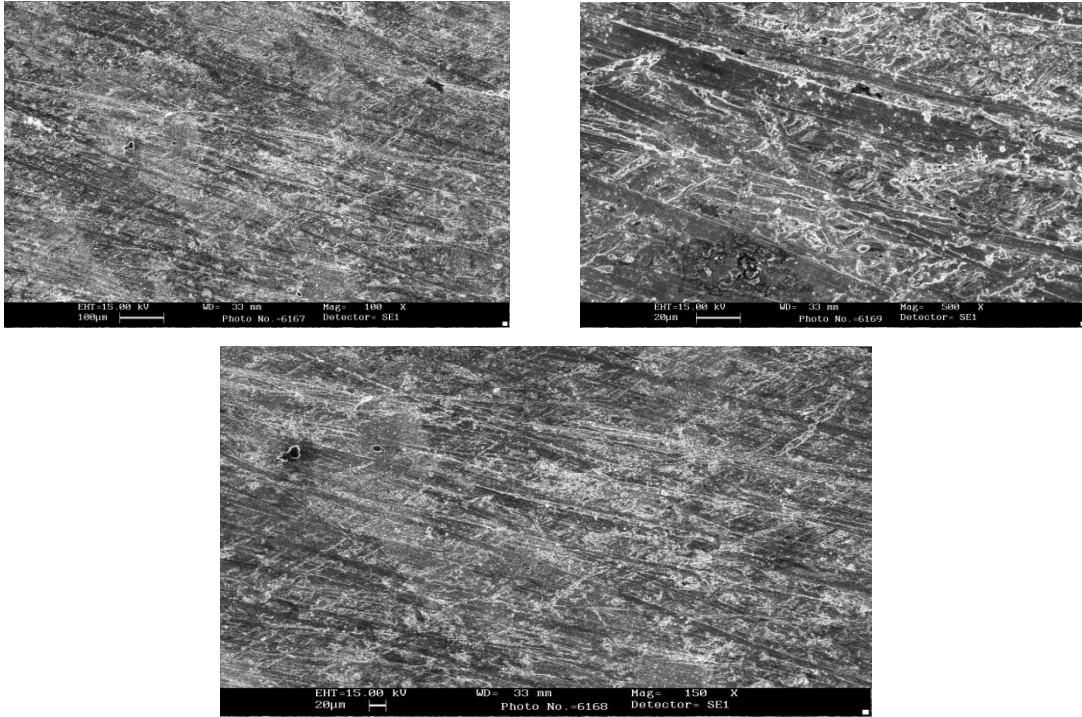
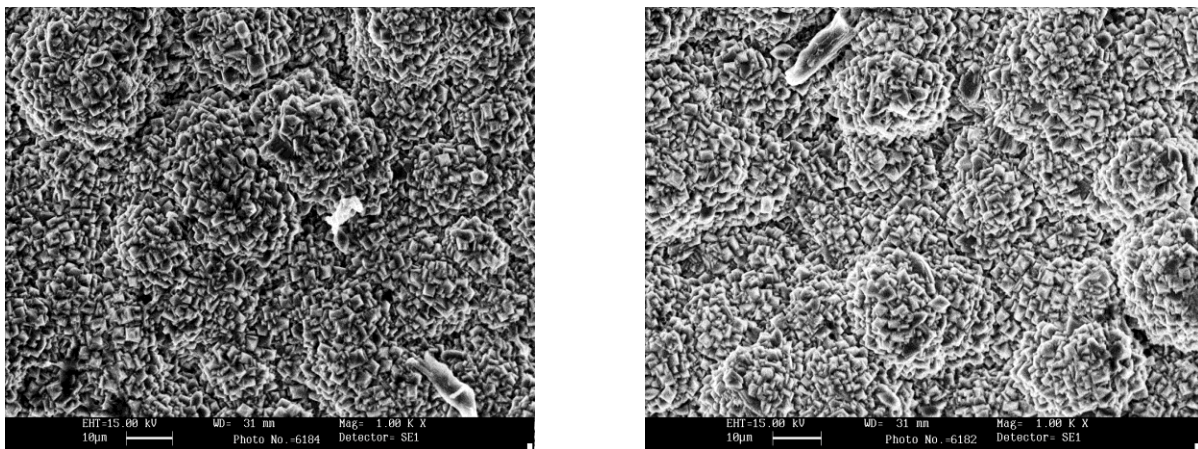


Figure 25: SEM images of polished Steel

Blank:



Sapindus as potential green corrosion inhibitor of Aluminium and mild steel

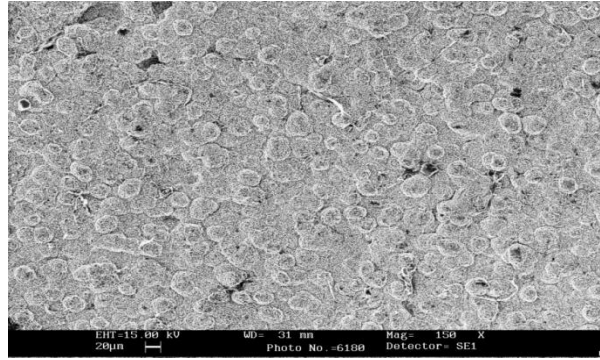


Figure 26: SEM images of steel with 5M H₂SO₄

Inhibitor:

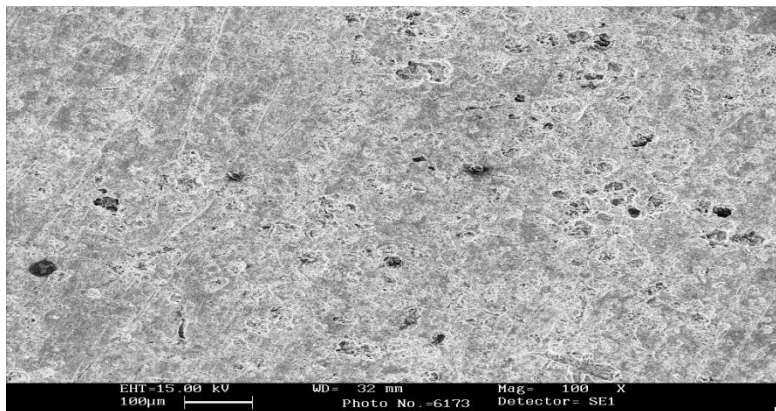
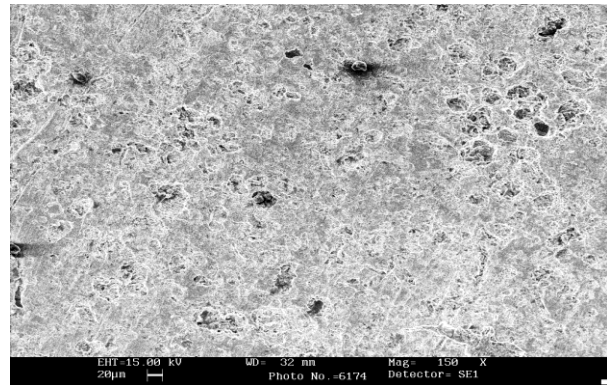
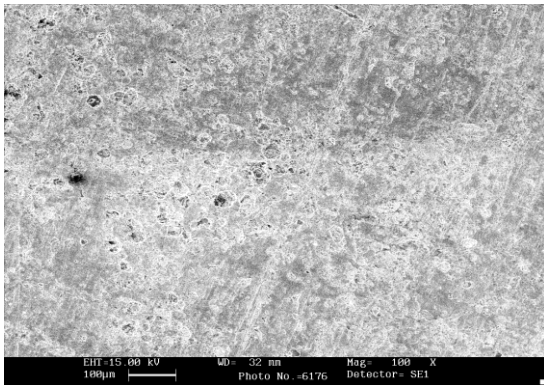


Figure 27: SEM images of steel with inhibitor solution of 5M H₂SO₄.

In the above figures the figures clearly shown that in case of steel Sapindus does job perfectly it helps to inhibit the corrosion rate in high rate. The cavity is decreases in case of inhibitor so we can say in both cases Sapindus is good inhibitor in steel as well as steel.

7.5. Atomic force Microscopy (NT-MDT-INTEGRA)

In atomic force microscopy we can predict the morphology of the metal and steel with or without Sapindus.

Pure Aluminium:

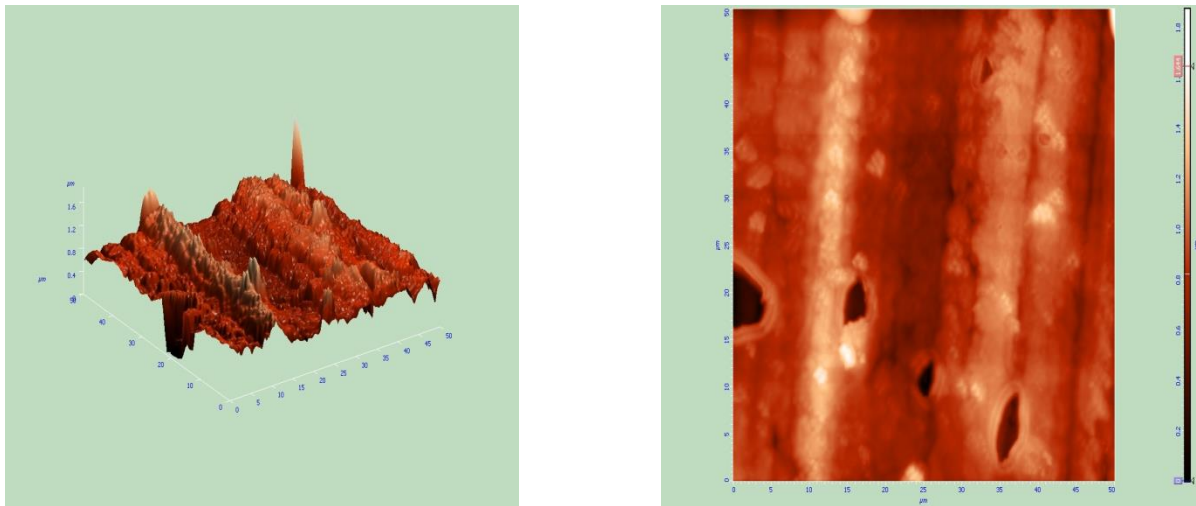


Figure 28: Atomic Force Microscopy of polished Aluminium.

Blank :

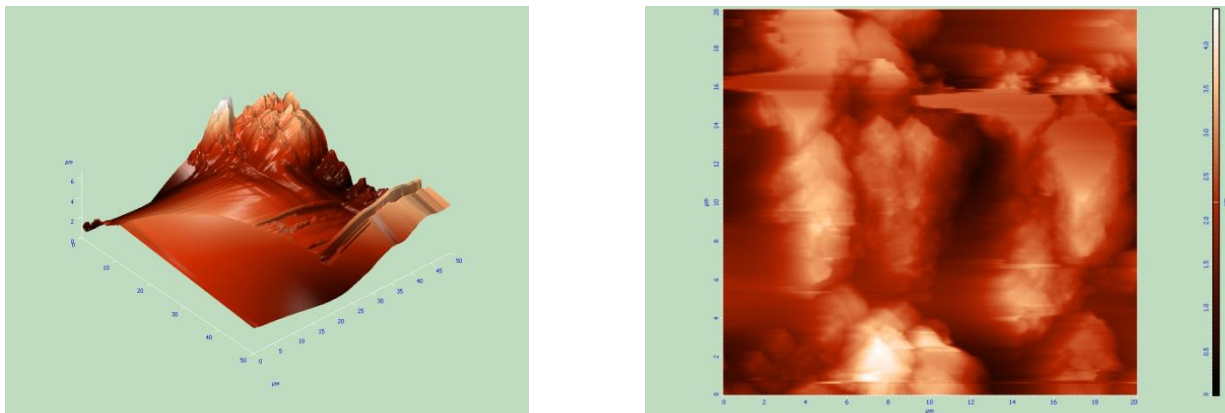


Figure 29: Atomic force microscopy of steel with 1M HCl.

In blank the surface show the irregular topology due to the 1M HCl attack. It shows the large mountain on the surface of the steel.

Sapindus with Aluminium:

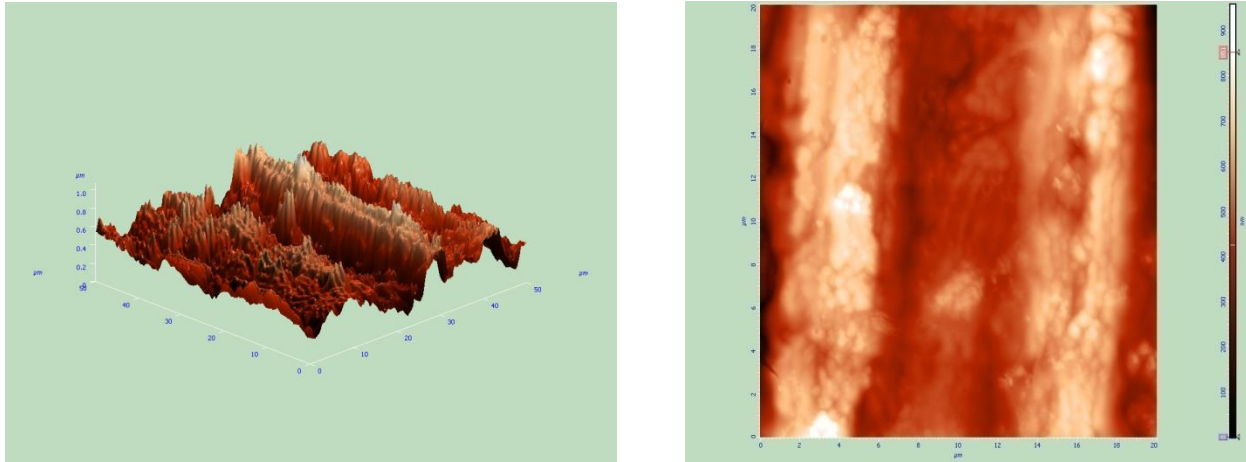


Figure 30: Atomic force Microscopy of Aluminium with Sapindus having 1M HCl.

In case of inhibitor the mountain is not too high it shows that the Sapindus inhibit the corrosion rate.

Sr.No.	Pure	Blank	Inhibitor
Roughness (Ra)	141.544nm	827.89nm	147.165nm

Table23: Roughness values of pure, blank, inhibitor Aluminium with 1M HCl.

Pure Steel

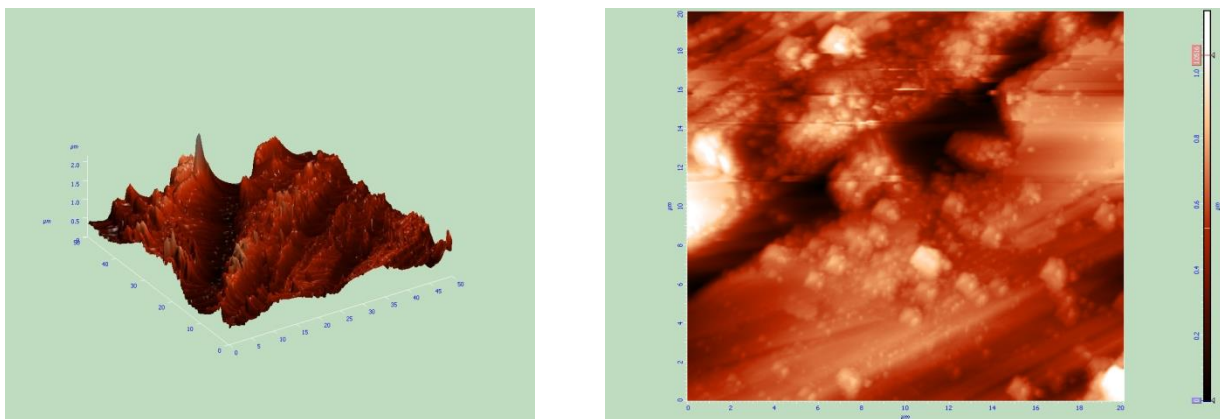


Figure 31: Atomic force microscopy of Polished Steel

Blank steel:

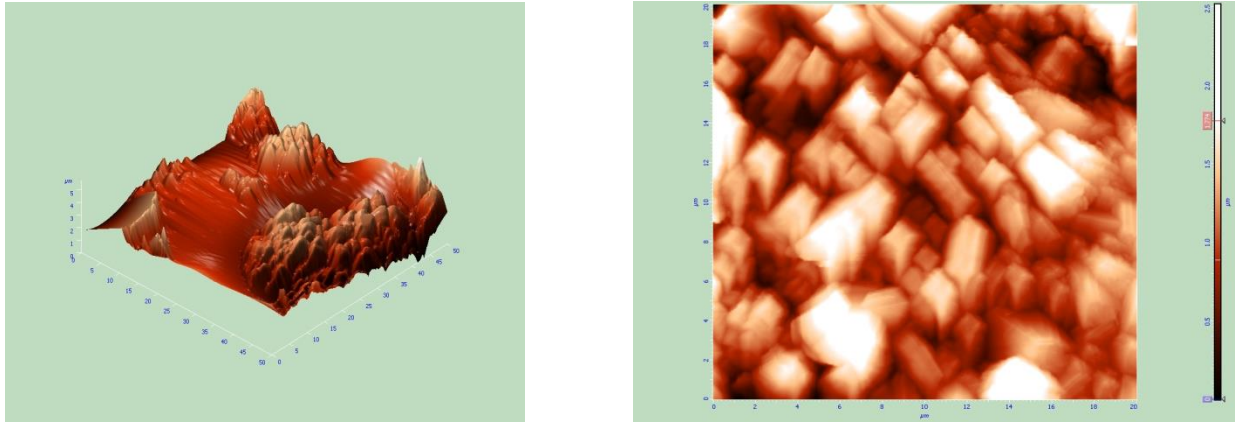


Figure 32: Atomic force microscopy of steel in 1M H₂SO₄.

Steel with Sapindus:

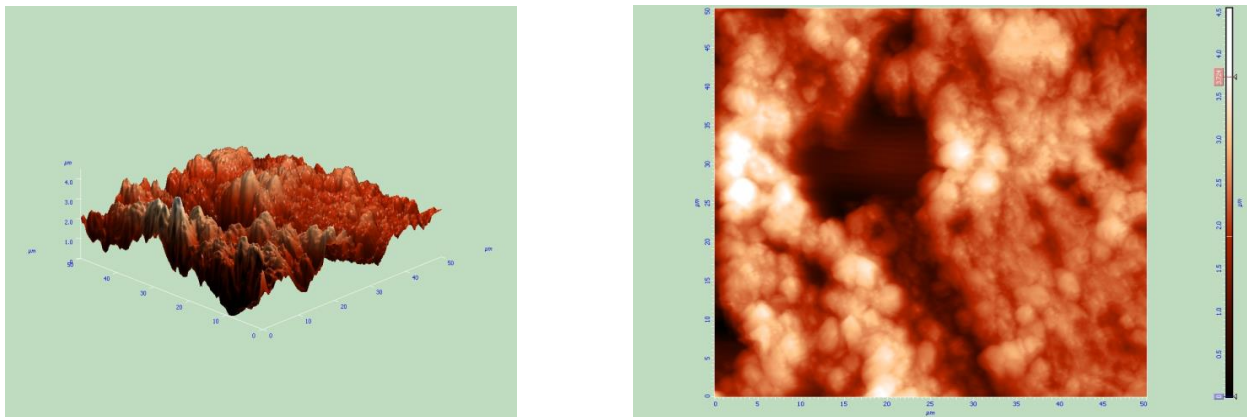


Figure 33: Atomic force Microscopy of steel with Inhibitor with 5M H₂SO₄

S.NO.	Pure Steel	Blank	Inhibitor
Roughness	202.831nm	763.286nm	285.001nm

Table 24: Table shows the roughness of blank, Pure and inhibitor steel in 5M H₂SO₄ .

7.6 FTIR/UV analysis (SHIMADZU UVPC 1800):

For the IR analysis the Aluminium is dipped in solution of Sapindus with water and without Sapindus .This process is done about 24 hrs and after 24hrs. After that the Aluminum coupon is picking from the solution. Then the solution is evaporating on the hot water bath. Then the precipitation formed this precipitation is allowed for IR. Same process is takes place in case of UV.

Sapindus as potential green corrosion inhibitor of Aluminium and mild steel

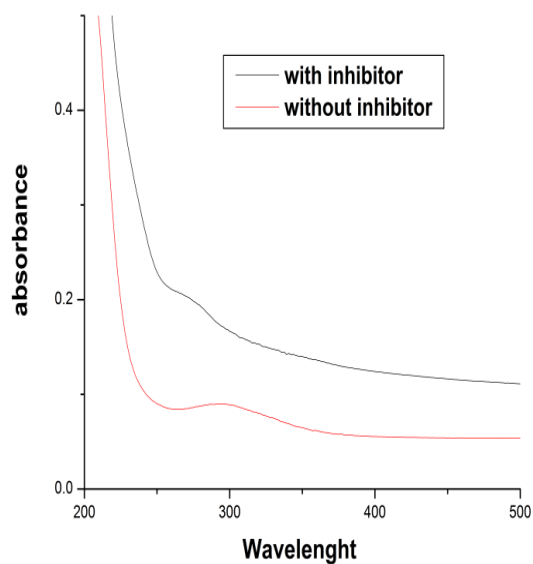


Figure 34: UV spectra of Sapindus before and after Aluminium immersion.

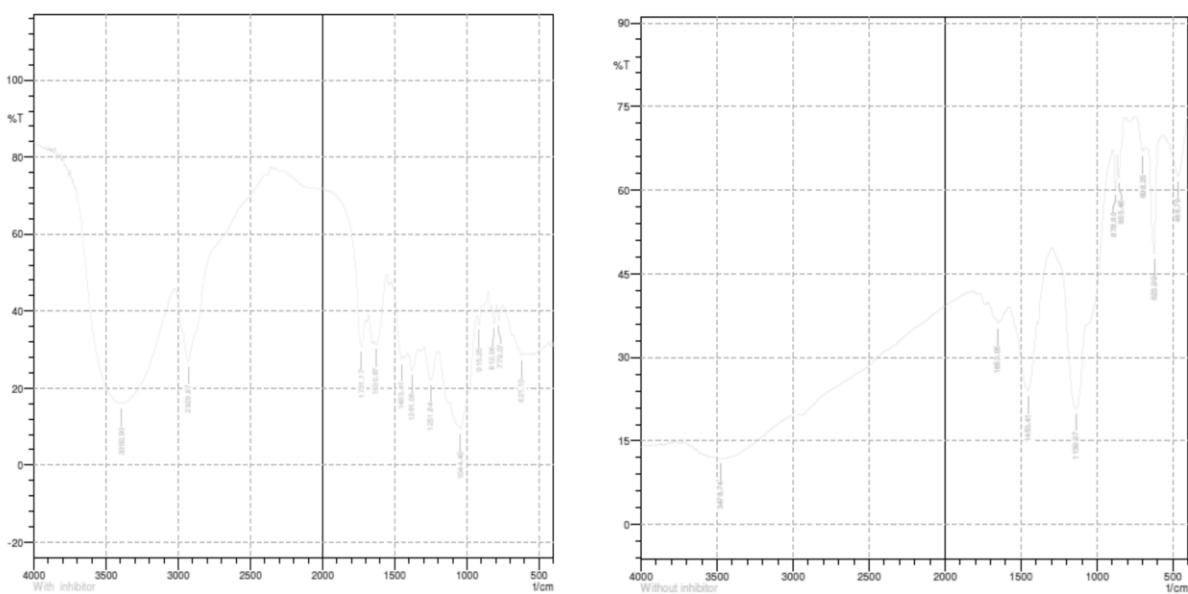


Figure 35: FTIR spectra of Sapindus before and after Aluminium immersion.

In figure a)

C=O stretching= 1731.17

Hydrogen bond O-H stretching=3392.9

Ester C=O Stretch =1731.05

C-O stretch= 1630.87

In figure b)

O-H stretching =3478.74

C=O stretching=1653.05

H-C-H bend =1500-1400

8. Conclusion:

Corrosion inhibition properties of Sapindus investigated on aluminium in 1 M HCl and 5M H₂SO₄ using spectroscopic techniques, electrochemical methods, quantum chemical calculations and Monte Carlo simulations. The following conclusions were drawn from the results:

1. Sapindus studied in this work showed good inhibition efficiency of 98.324% for aluminium corrosion in 1M HCl at 2000ppm and the inhibition efficiency with steel is 91.3006.
2. Potentiodynamic polarization study showed that the Sapindus is a mixed type inhibitor and The EIS study revealed that Sapindus form protective film on aluminium surface and steel surface. The experimental results showed that the studied Sapindus adsorbs spontaneously on aluminium surface and conform to the Langmuir adsorption isotherm.
4. SEM images also confirmed the formation of protective film by Sapindus on aluminium and steel surface.
5. FTIR spectra revealed the occurrence of chemical interactions between Sapindus and Aluminium or steel.
6. Quantum chemical parameters such as the EHOMO, ELUMO, and dipole moment agree with experimental results.
7. Monte Carlo studies reveal that adsorption energy of the Sapindus is far higher than that of water molecules thereby, suggesting the formation of protective layer.
8. AFM reveals the difference of roughness between pure, blank and inhibitor Sample that shows the roughness of the metal and tells the 3D structure of the surface of metals.

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