Natural Products as Environment Friendly Corrosion Inhibitor

Dissertation-II Report

Submitted by

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To

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Under the guidance

Of

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April, 2015

Certificate

This is to certify that the capstone project entitled 'Natural Products as Environment Friendly Corrosion Inhibitor', submitted by 'Palak' to the Lovely Professional University, Punjab, India is a documentation of genuine literature review of coming research work carried out under my supervision and is commendable of consideration for the award of the degree of Master of Science in Chemistry of the University.

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Supervisor

Dr. Ashish Kumar

Assistant 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.

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Date:

Acknowledgement

It is my great pleasure to present the project report on **"Natural Products as Environment Friendly Corrosion Inhibitor".** Every work skilled is pleasure wisdom. However a number of people always inspire, disparage and welcome a work with their objective ideas and opinions. I would like to employ this opportunity to thank all, who have helped us to complete this project.

Firstly, I would like to thank Dr. Ashish Kumar without whose support this could not be completed. I would like to express thank all people who give their precious time and comment to improve this project. I want to thank my university for providing us with assets.

At last I would like to express my deep gratitude to our head of department Dr. Ramesh Chand Thakur for providing all necessary facilities and encouraging.

Palak

Contents

Introduction

Corrosion is a process in which the metal reacts with the surrounding environment and undergoes decomposition or deterioration .Corrosion causes a lot of damage to metals in industries and other constructional systems. Much work has been done to minimize this corrosion.

Foe reducing the corrosion one of the best method is the use of inhibitors. The corrosion inhibitors can be a part of any plant or any natural compound which when used in acidic or alkaline media can help to prevent the process of corrosion. The inhibitors most commonly used are natural products which are cheap, easily available and environment friendly. The inhibitors are mainly used in acidic medium so as to prevent the loss of metal which occurs as a result of corrosion**.** The inhibitors containing hetero atoms like oxygen, sulphur, nitrogen are very effective as they get adsorbed on the surface of metal by blocking the active corrosion sites. The use of plant extracts has both environmental and economic benefit since they are low cost and biodegradable **[1-3].**

A corrosion inhibitor is a substance which when added to the metal, the metal surface adsorbs the molecules of corrosion inhibitor and this process of adsorption helps in preventing the corrosion. Natural products are considered as rich sources of naturally synthesized chemicals.

The corrosion inhibitors form various types of films by the process of adsorption. In this way it controls corrosion on the metal surface. Inhibitor films can be formed by various ways some of which include formation of a thin layer on metal surface, formation of heavy precipitates and adsorption.

The main function of the inhibitor is to form an adsorptive film on metal surface and hence acting as a barrier to prevent the access of ions in the corrosive environment on the metal surface.

Inhibitors are compounds that reduce the rate of corrosion of metals by been absorbed on the surface of metal either through (physical adsorption) or by (chemical adsorption) **[4-5].**

Review of Literature

- Work has been done by using the stem extract of Brahmi for Aluminium in 0.5 basic solution as an inhibitor for corrosion. Several techniques have been used which include potentiodynamic polarization, weight loss methods and EIS methods. By using potentiodynamic polarization it was seen that the extract of Brahmi reduced both anodic and cathodic reactions on surface of metal of aluminium in basic solution. The thermodynamic parameters like free energy and activation energy have also been evaluated **[6].**
- By using different techniques like spectroscopic (UV-V and FTIR) and weight loss at 30–60^{0}C work has been done on the stem and leaves extracts of Sida acuta in 1M H_2SO_4 on corrosion inhibition of mild steel. It was seen that the stem extracts and leaves of S. acuta inhibited the acid corrosion of mild steel. It was found that with increase in temperature the inhibition efficiency decreases and with increase in concentration of plant extract it also increases. Inhibitive effect was determined by Freundlich adsorption isotherm by the adsorption of components of plant extracts. Inhibition mechanism is resulted from the inhibition efficiency which is temperature dependent and from spectroscopic results **[7].**
- Work has been done on the corrosion of mild steel in 2M H_2SO_4 on water and alcoholic extracts of Medicago Sative (MS) using weight loss techniques.SEM is also used to support the obtained results. It was observed that with the increase of Medicago Sative concentration the inhibition efficiency increases. The water and alcoholic extracts of MS plant act as mixed type inhibitors with nearly the same efficiency. The inhibition action of M. Sative extracts was determined by adsorption on the surface of metal. It was seen that the adsorption follows Langmuir adsorption isotherm **[8].**
- By using various techniques like EIS, potentiodynamic polarization and weight loss the natural extract of Chenopodium Ambrosioides in H_2SO_4 has been studied for the corrosion inhibition of carbon steel. The results showed that the metal tested in 0.5M H_2SO_4 solution has a good inhibiting effect. From the potentiodynamic polarization measurements it was shown that it acts as a cathodic inhibitor. The results obtained from EIS measurements shown that with the extract's concentration of Chenopodium Ambrosioides, change in the impedance parameters takes place which is indicating the adsorption of molecules on the surface of carbon steel and helps in preventing the corrosion by forming a protective layer on the metal surface. It was found that with increase in temperature the efficiency decreases. The extract of Chenopodium Ambrosioides is found to follow the Langmuir adsorption isotherm. The thermodynamic parameters like enthalpy and activation energy were also being determined **[9].**
- By using electrochemical frequency modulation, potentiodynamic polarization and EIS techniques, the effect of inhibition of hydroxyethylcellulose in 3.5% NaCl solution was studied on corrosion of carbon steel. The results obtained from potentiodynamic polarization indicated that HEC could act as a mixed-type of

inhibitor. From EIS measurements the results obtained were investigated to model the process of corrosion inhibition through equivalent circuit. The data obtained from EFM technique were shown good agreement with EIS and potentiodynamic techniques. HEC follows the Langmuir adsorption isotherm. To investigate mechanism of inhibition thermodynamic parameter (ΔG^0_{ads}) and activation parameters (E_a^*, ΔH^* and ΔS^*) were calculated. SEM and EDX analysis were done to characterize the film formed on the surface of metal **[10].**

- By using standard gravimetric technique at 30–60^{0}C using extracts of Spondias mombin L was studied for the inhibition of aluminium in 0.5 M H_2SO_4.For the mechanism of inhibition the change of inhibition efficiency with respect to temperature was used. The results obtained indicated that the S. Mombin L. extract in acidic medium for corrosion of aluminium could act as an effective inhibitor. It was observed that as we increase the concentration of S. Mombin L. extract inhibition efficiency also increased and with temperature decreased. On addition of potassium iodide inhibition efficiency increased. It was found that for all the concentrations and temperatures adsorption was studied by Langmuir adsorption isotherm. The values obtained from the variation of inhibition efficiency with respect to temperature the activation parameters like Gibbs free energy, heat of adsorption and activation energy were calculated for determining the mechanism of physical adsorption **[11].**
- By hydrodistillation essential oil of aerial parts of Salvia aucheri Boiss.var. mesatlantica was studied and analyzed by GC and GC/MS. The oil was predominated by camphor (49.59%). By using measurements of weight loss and electrochemical measurements the inhibitory effect of the essential oil was studied in 0.5M H_2SO_4 on the corrosion of steel. It was found that in the presence of natural oil inhibition efficiency was increased and corrosion rate of steel is decreased. The temperature effect in 0.5 M H_2SO_4 in the range 303 to 343 K temp was studied with and without the inhibitor at 2 g/L and from it the activation energy have been calculated. It was found that the adsorption obey Langmuir's adsorption isotherm **[12].**
- By using EIS measurements, SEM, potentiodynamic polarization method and weight loss method in 1M H_2SO_4 and in 1 M HCl the inhibition effect of the corrosion of mild steel by Spirulina platensis has been studied in 303-323 K temperature range. It was found that the values of inhibition efficiency increased on increasing the concentration of inhibitor in both medium i.e. HCl and H_2SO_4. From weight loss data the results obtained matched well with that of polarization and impedance measurements. It was confirmed from the results of weight loss measurements at different temperatures that the type of adsorption is of physisorption and the adsorption follow Temkin isotherm. With the help of isotherm, entropy and the free energy of adsorption are determined **[13].**
- By using various methods like polarization resistance measurements, weight loss and potentiodynamic in 1M HCl the effect of Bifurcaria bifurcata extract was studied on the corrosion of steel. From the experimental data it was shown that Bb extract in acidic medium acts as good inhibitor and the extract was found to be mixed-type of inhibitor. It was shown that with increase in the concentration of Bb extract the value

of inhibition efficiency also increased. By UV-visible and infrared spectrophotometry in 1M HCl the corrosion inhibition of Bifurcaria bifurcata extract on carbon steel was studied to find out the bonding mechanism between the inhibitor and the surface of metal **[14].**

- By using different techniques like linear polarization, weight loss, EIS and potentiodynamic polarization in HCl solution the inhibition effect of the corrosion of mild steel by the Kalmegh extract (Andrographis paniculata) has been studied. It was found that on increasing the concentration of extract inhibition was also increased. The variation of immersion time, acid concentrations and effect of temperature has been studied in 1M HCl on the corrosion behaviour of mild steel. The inhibition process follows the Langmuir adsorption isotherm. By FTIR spectroscopy, the protective film formed on the surface of metal was analyzed. From the results obtained it was shown that the Kalmegh extract (Andrographis paniculata) in HCl medium could act as a good corrosion inhibitor for the corrosion of mild steel **[15].**

Scope of the study

Plant extracts are used as rich source of naturally synthesized chemical compounds as they can be directly extracted by various methods. They are also biodegradable and have low cost. In the present scenario, there is increase in awareness among society for protection of environment, so natural plant extracts are highly useful as effective corrosion inhibitors because they contains carbohydrates, alkaloids, amino acids, hetero atoms like N,S,O and aromatic rings which act as centres of adsorption. For exploring this, an attempt is made by us to use natural plant extracts of Gudmar Buti and Shahtoot as corrosion inhibitors on mild steel as they are non-toxic, cheap and biodegradable and in future they will be very helpful in preventing the corrosion as they can be used in making paints or polishes or by direct application.

Objectives

1. To study the effects of different natural products such as Gymnema Sylvestre and Morus Nigra as corrosion inhibitor on metal i.e. Mild Steel.
2. To study the effects of these corrosion inhibitors in acidic media.
3. To study the effects of inhibition on increasing/decreasing concentration, time and temperature.
4. To determine different activation parameters for the process of corrosion.
5. To validate the type of adsorption by various adsorption isotherms like Langmuir, Temkin, Frumkin etc.
6. To determine Quantum Chemical parameters for predicting the structure and molecule suitability of these plant extract as ideal corrosion inhibitors.

Materials and Research Methodology

Those plants which has medicinal properties and which contains hetero atoms we have selected as corrosion inhibitors:-

- Gudmar buti
- Shahtoot

Gudmar buti:-

Its botanical name is Gymnema Sylvestre and this herb is found throughout the world. This plant possesses sweet suppressing and antimicrobial activities. The leaves of this plant are used for the treatment of diabetes. The main active chemical constituent of this plant is Gymnemic acid. Gymnema Sylvestre is an antidiabetic plant and used in ayurvedic as well as in homeopathic systems of medicine. This plant has various beneficial effects such as antihelmentic, diuretic and anti-inflammatory. It is used for the treatment of various diseases like constipation, jaundice, cardiopathy, asthma, bronchitis etc.

Botanical name:-

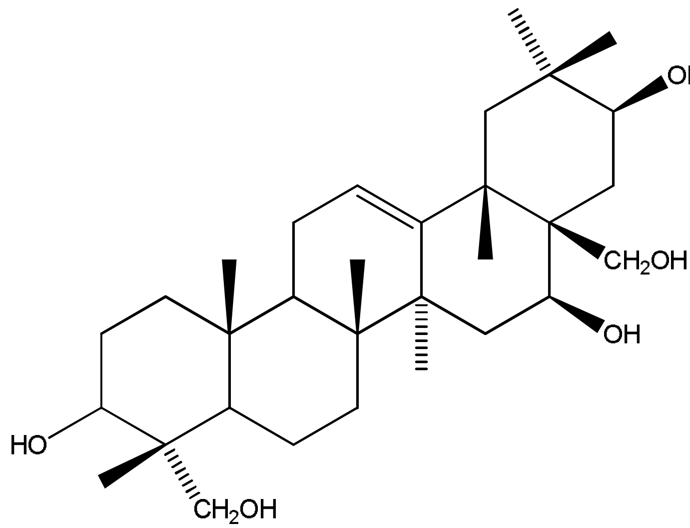
Gymnema sylvestre

Scientific classification:- It belongs to Kingdom- Plantae, Order- Gentianales. It is from Asclepidaceae family, Genus- Gymnema and species is G.Sylvestre.

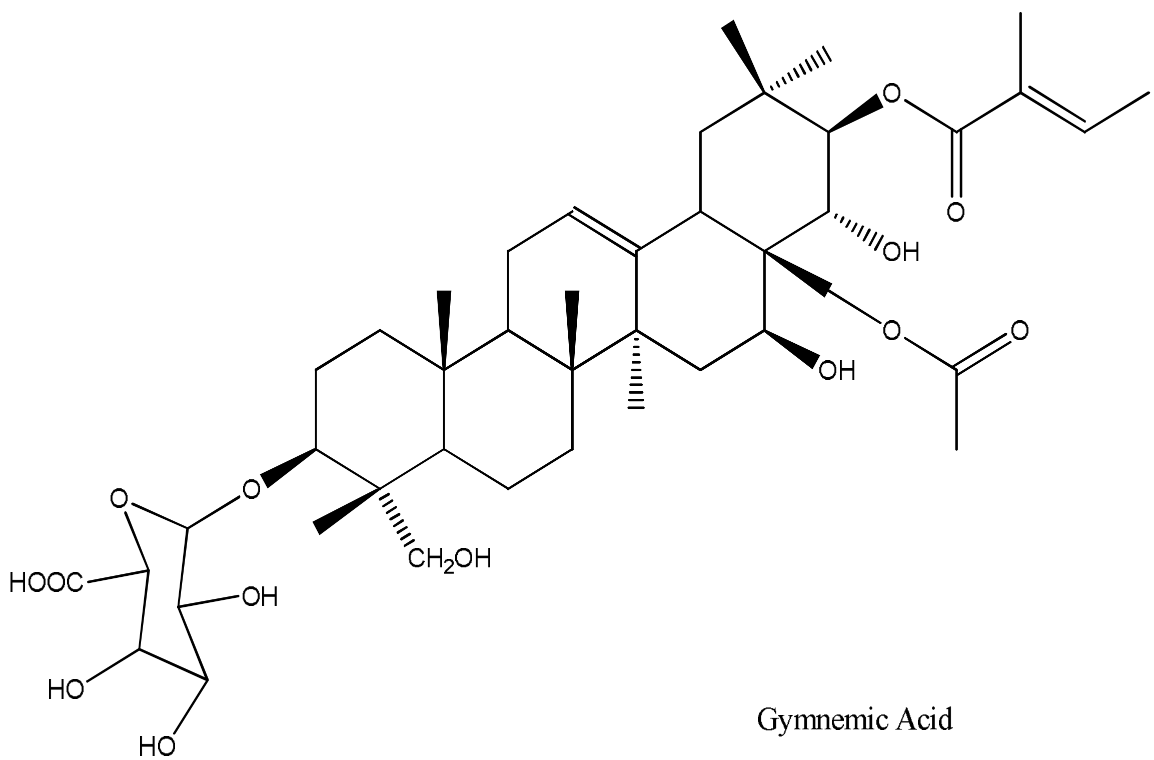
Chemical constituents:-

The leaves of Gymnema sylvestre contain triterpene saponins belonging to oleanane and dammarene classes in which dammarene saponins are gymnemasides while oleanane saponins are gymnemic acids and gymnemasaponins. The leaves also contains chlorophyll, tartaric acid, carbohydrates, formic acid, resins, butyric acid, cellulose(22%), inositole alkaloids, organic acid(5.5%), albumin, calcium oxalate(7.3%), anthraquinone derivatives, lignin(4.8%), parabin. The active constituents are gymnestogenin, gymnemic acid and gymnemanol **[16].**

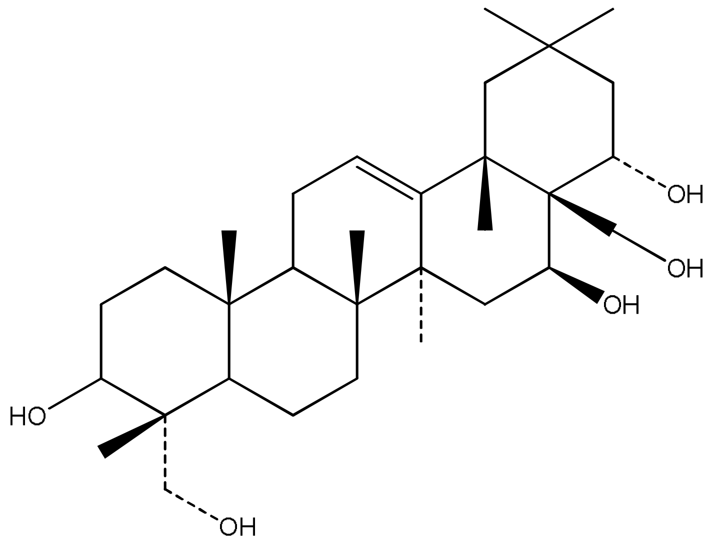
Structures:-



Gymnestogenin



Gymnemic Acid



Gymnemanol

Sahtoot:-

Botanical name :-

Morus nigra called black mulberry or blackberry

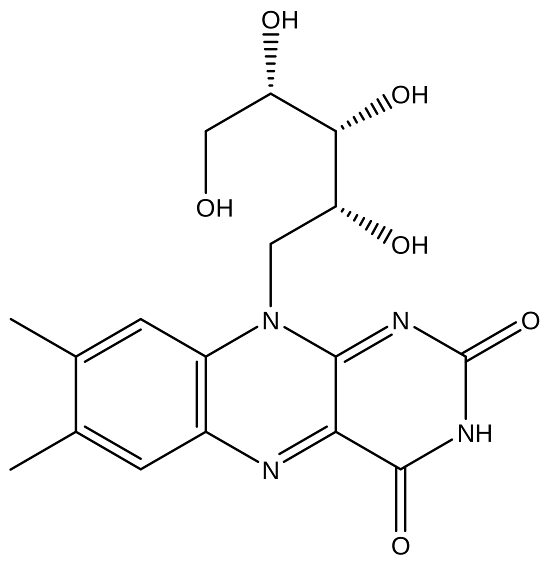
Scientific classification:-

It belongs to the Plantae kingdom and of Rosales order. Its species is M.nigra, containing genus Morus and its tribe is Moreae.

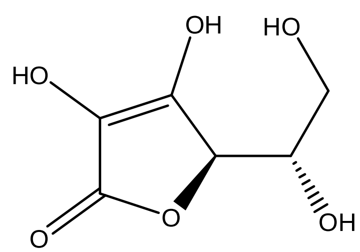
Chemical constituents:-

The fruits of mulberry were rich in total phenol and alkaloid contents containing values of (880±7.20)–(1650±12.25) mg per 100 g fresh weight and (390±.22)–(660±5.25) mg/100 g fresh weight. Almost all the morus species ascorbic acid (Vitamin C) in the range of (15.20±1.25) to (17.03±1.71) mg per 100 g fresh weight (FW) and also contains niacin(Vitamin B_3),low riboflavin(Vitamin B_2). The macro elements in sufficient quantities are (K, Ca, Mg, and Na). The main element Potassium concentration ranges from (1270±9.36) to (1731±11.50) mg per 100 g, while the quantities of Ca, Na, and Mg were (440±3.21)–(576±7.37), (260±3.86)–(280±3.50) and (24±3.51)–(360±4.20) mg per 100 g **[17].**

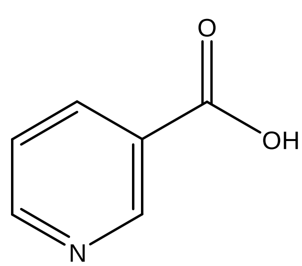
Structures:-



Riboflavin



Ascorbic acid



Niacin

Results and Discussion

Experimental work:-

In the present study we will try to find use of those plants which have medicinal values i.e. Sahtoot, Gudmar buti as corrosion inhibitors by following studies (depending upon the availability of instruments):-

- Inhibition
- Weight Loss Method
- Fourier Transform Infrared Spectroscopy(FTIR)
- Adsorption isotherms
- Quantum Chemical Calculations
- Scanning Electron Microscopy (SEM)

Materials:- Gudmar Buti and Shahtoot leaves powder, Hydrochloric acid, Acetone, Sodium Bicarbonate, Mild Steel Sheets, Emery papers (400-1200 grade), Steel cutter, Driller, Beakers (100 ml), Glass rod, round bottom flask, condenser, heating mantle.

Experimental Procedure:-

We have prepared HCl solutions of different molarities like 1M , 2M ,3M, 4M, 5M etc. and one of the solution i.e. 2M HCl is taken as standard solution. We have used mild steel as metal for corrosion inhibition. Then we have prepared the aqueous extracts of leaves of Gudmar Buti and Shahtoot inhibitors and effect of these corrosion inhibitors will be studied at different concentrations, temperature and time. The aqueous extract is prepared by taking the leaves of the inhibitors in 800 mL of water and refluxes it for 6-8 hrs. The results include the variations of both in presence and absence of inhibitor with respect to temperature, time and concentration. At high temperature and high concentration it was seen that the mild steel decomposes. The inhibition efficiency will be seen from various adsorption isotherms which will include Temkin, Langmuir and Frumkin adsorption isotherms. The mechanism of inhibition and various thermodynamic parameters like activation energy, enthalpy, entropy and free energy etc. will also be deduced.

Weight loss study:-

Mild steel has been purchased from market and cut into the rectangular shape of about (2.5 cm × 2.0 cm) and scrubbed with emery paper (400-1200 grades). These sheets were weighed and immersed in conical flask containing 100 ml of different concentrations of HCl with and without the addition of extract. After different intervals of time, the specimens were taken out from the conical flask, washed with sodium bicarbonate and acetone, then air dried followed by oven dry and finally weighed. The corrosion rate (C_R) of acid and inhibitor (in mg cm^{-2}) was determined as:

$$C_R\ (mm/y) = 87.6W/at\ D$$

Where t represents the immersion time, W represents the weight loss of mild steel, D represents the density of mild steel in (g cm^{-3}) and a represents the total area of mild steel. By using the below equation, the efficiency of inhibition on mild steel can be calculated as:

$$\eta\ (\%) = C_R - C_{R\ inh} / C_R * 100$$

Where $C_{R\ inh}$ and C_R represents the corrosion rates in presence and absence of inhibitor **[18-19].**

Quantum chemical calculations:-

The adsorption and mechanism of inhibition was determined by using quantum chemical calculations of different molecules of inhibitor in the extracts by using different methods like B3LYP, DFT and all the calculations were done with the help of Gaussian 03.The factors E_{HOMO}, E_{LUMO}, ΔE (LUMO-HOMO) and (μ) dipole moment are responsible for the electronic interaction of molecules of inhibitor with the surface of metal. Frontier orbital theory was used for determining the adsorption centres of the molecules of inhibitor. It was found that the lower value of E_{LUMO} indicates the higher probability that the molecule would accept electrons. For higher inhibition efficiency lower values of ΔE were concerned **[20-21].**

Adsorption isotherm:-

The adsorption isotherms are used to provide information about the mechanism involved in the process of corrosion inhibition. From the below equation, θ i.e. surface coverage can be calculated as:

$$\theta = C_R - {}^{inh}C_R / C_R$$

Where ${}^{inh}C_R$ is the corrosion rate of mild steel in presence of inhibitor and C_R represents the corrosion rate of mild steel in absence of inhibitor. By using weight loss data, the θ values were fit to various isotherms like Temkin, Langmuir and Frumkin. It was found that the better result was obtained with Langmuir isotherm. On plotting graph between (C/θ) vs θ, a straight line was obtained for Langmuir isotherm with regression coefficient R^2 almost equal to 1 **[22-23].**

<u>Thermodynamic activation parameters:-</u> A straight line has been obtained by the plot between the logarithm of corrosion rate vs. 1000/T and the (E_a) was calculated as:

$$\ln (C_R) = -E_a/RT + A$$

The values obtained from slope was being used for determining the values of E_a for both in presence and absence of inhibitor in 2M HCl from the slope by plotting the values obtained.

Both (ΔH*) and (ΔS*) were determined as:

$$C_R = RT/Nh\ \exp(\Delta S^*/R)\ \exp(-\Delta H^*/RT)$$

By plotting a graph between log (C_R/T) vs. 1000/T, the value of ΔH^* was determined from the slope ($-\Delta H^*/R$) and the value of ΔS^* was calculated from intercept [(ln (R/Nh)) + ($\Delta S^*/R$)].

$K_{ads,}$ equilibrium constant and ΔG^o_{ads} values at various temperatures were determined as:

$$\mathbf{K = \theta / C\,(1-\theta)}$$

$$\mathbf{\Delta G^0_{ads} = -RT\ ln\ (55.5\ K_{ads})}$$

In the above equation the value 55.5 represents the concentration of water in solution in mol/L**.** The ΔG^0_{ads} having negative values indicate the spontaneity of the adsorption of molecules of inhibitor on the metal surface **[24-25].**

Weight loss measurements

Shahtoot:-

The values of weight loss in 2M HCl in the presence of Shahtoot inhibitor is shown below in table 1. It was found that as we increase the concentration of inhibitor efficiency of inhibitor also increases.

Table 1: Values of weight loss measurement in 2M HCl for mild steel at various concentrations of inhibitor

Inhibitor concentration (ppm)	Weight loss (mg cm^{-2})	η%	C_R(mm/y)	θ
Blank	103.3	-	35517.64	-
50	36.2	64.95	12446.65	0.6495
100	29.5	71.44	10142.99	0.7144
200	24.3	76.47	8355.069	0.7647
400	17.8	82.76	6120.174	0.8276
600	15.3	85.18	5260.599	0.8518
800	11.2	89.15	3850.896	0.8915

Effect of immersion time:-

In below figure the change of inhibition efficiency with respect to time in HCl is shown. It is observed that with increase in time inhibition efficiency increased. The result obtained showed that the film formed on the surface of mild steel had good inhibition efficiency.

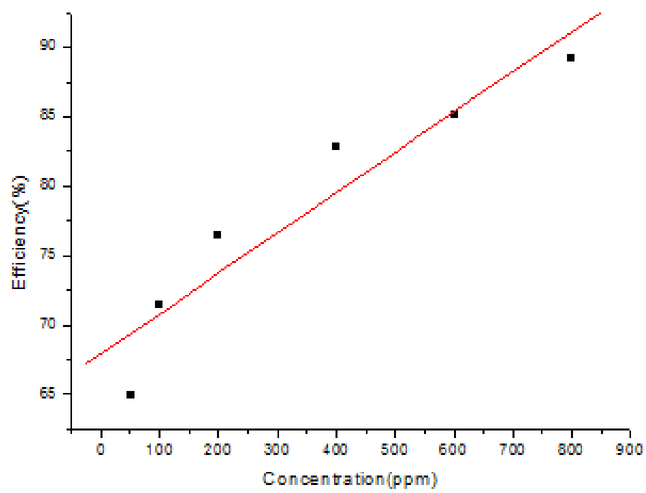


Figure (1)

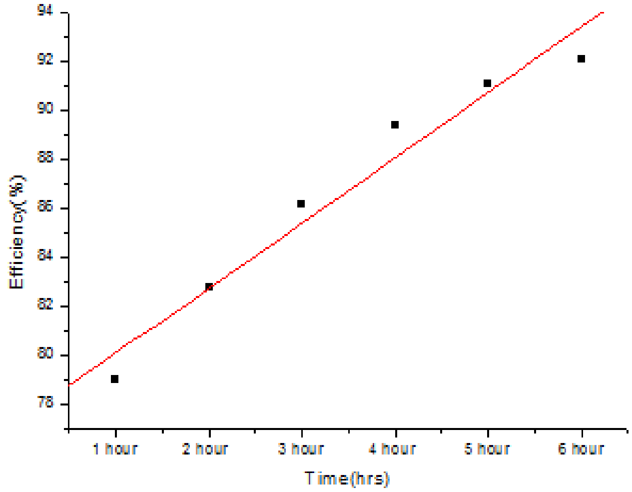


Figure (2)

Effect of Temperature:-

To find out the adsorption of shahtoot and activation parameters in acidic medium for corrosion of mild steel, measurements of weight loss were carried out in 298-313K temp in the presence and absence of shahtoot during immersion time 2h at specific concentration as shown in below figure. It was found that with increase in temperature efficiency decreases at a particular concentration **[26-27].**

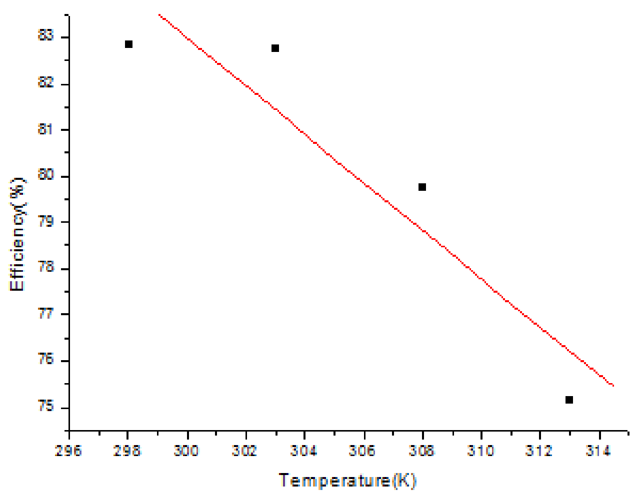


Figure (3)

Table 2: Thermodynamic parameters in 2M HCl for mild steel in presence and absence of inhibitor [28-29]

Inhibitor concentration (ppm)	E_a (kJ/mol^{-1})	ΔH (kJ/mol^{-1})	ΔS (J mol^{-1} K^{-1})
Blank	7.965	5.36	-16.77
400	26.614	24.31	-11.00

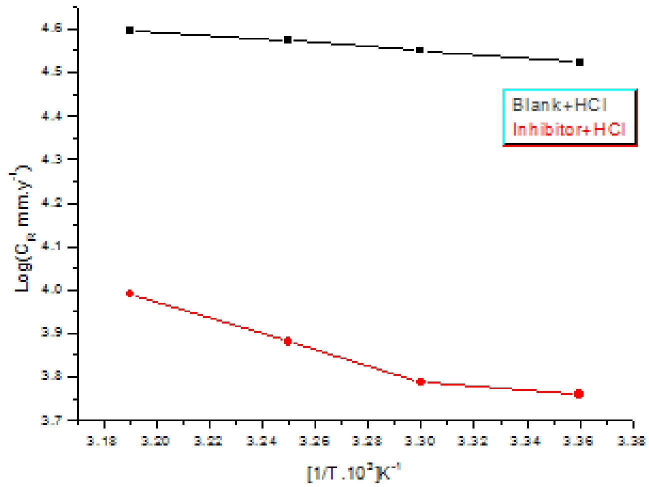


Figure (4)

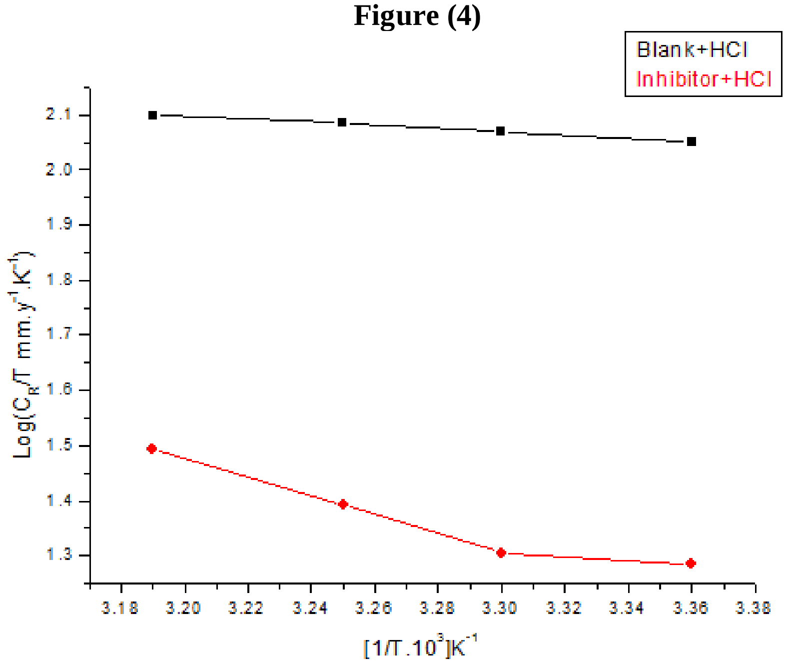


Figure (5)

Table3: Standard Gibb's free energy of adsorption in 2M HCl for mild steel in absence and presence of Shahtoot at various temperatures [30]

Temperature (K)	ΔG^0_{ads} (kJ mol^{-1})
298	-24.0509
303	-23.9646
313	-19.1012
323	-12.6318

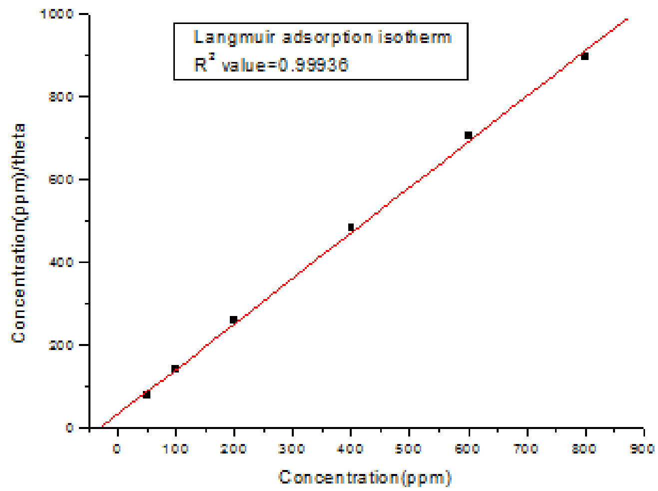
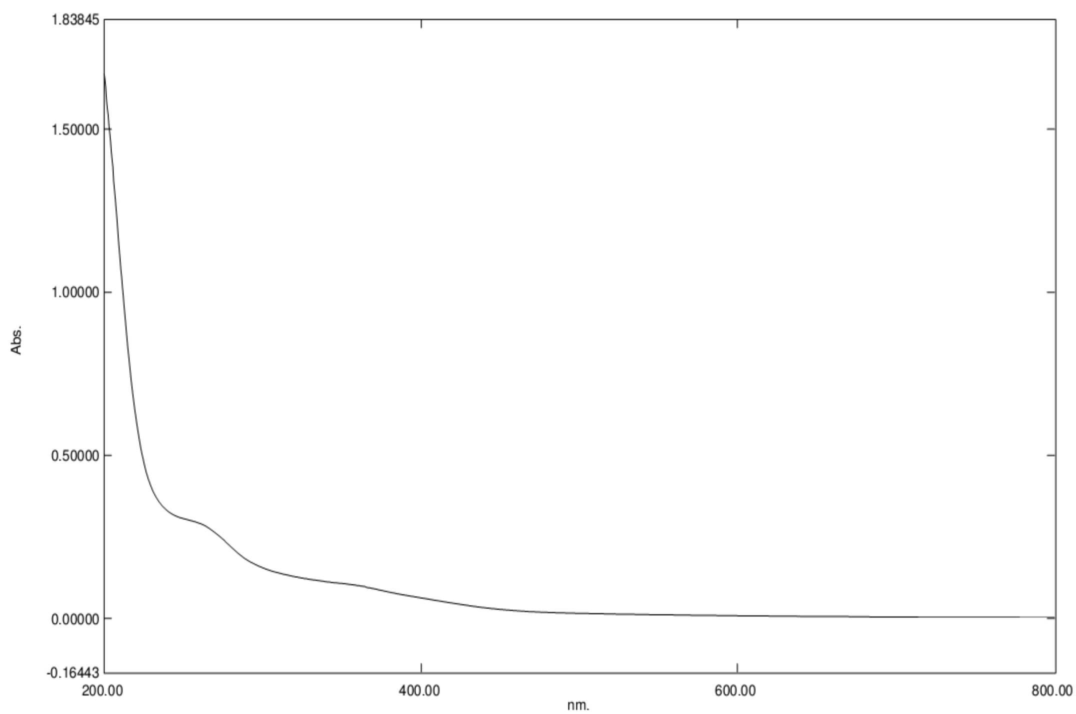


Figure (6)

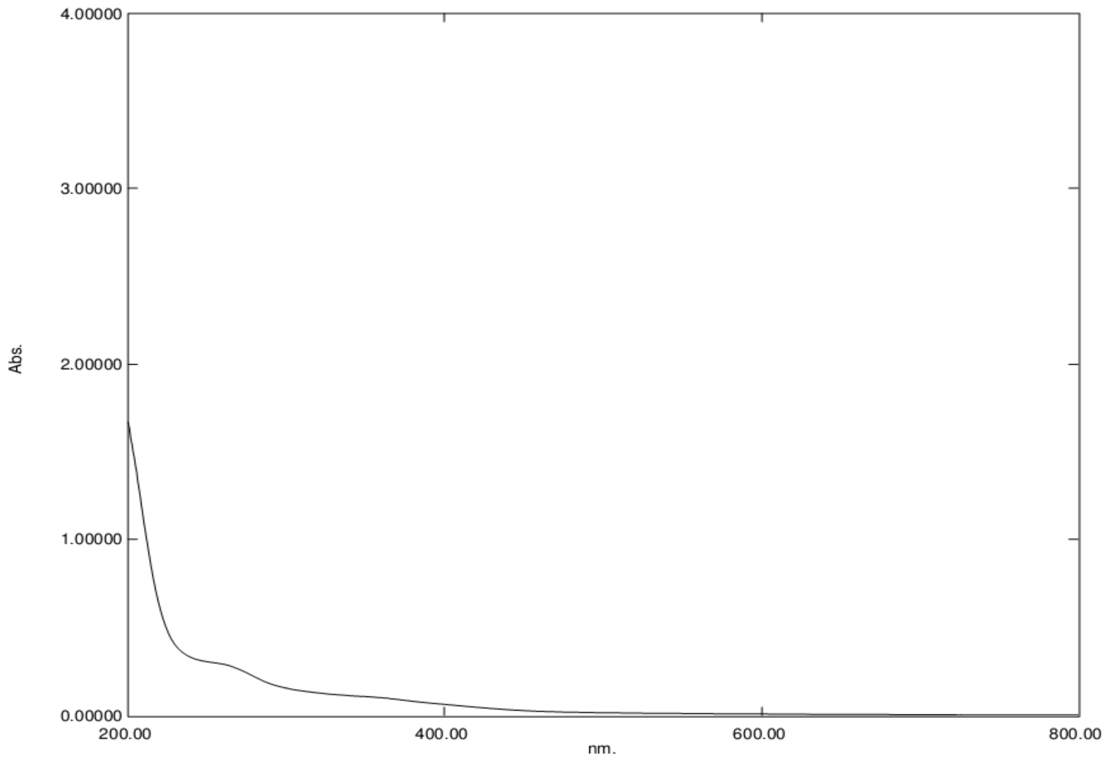
Morphology:-

UV study:-

Sahtoot Inhibitor:-



Steel+Sahtoot Inhibitor:-



Weight loss measurements

Gudmar Buti:-

The weight loss data obtained with and without Gudmar buti inhibitor is shown in table 4. It was found that as we increase the concentration of inhibitor efficiency of inhibitor also increases.

Table 4: The values of weight loss in 2M HCl for mild steel at various concentrations of Gudmar Buti inhibitor [31]

Inhibitor concentration (ppm)	Weight loss (mg cm^{-2})	η%	C_R (mm/y)	θ
Blank	103.2	-	35483.256	-
50	75.8	55.62	26062.314	0.5562
100	55.4	61.82	19048.182	0.6182
200	64.0	70.64	22005.12	0.7064
400	86.1	79.94	29603.763	0.7994
600	89.9	81.68	30910.317	0.8168
800	100.5	82.36	34554.915	0.8236

Effect of immersion time:-

The change of inhibition efficiency with respect to time in HCl is shown in figure (2). It is found that with increase in the values of inhibition efficiency decreases. The result obtained showed that the film formed on the surface of mild steel had good inhibition efficiency.

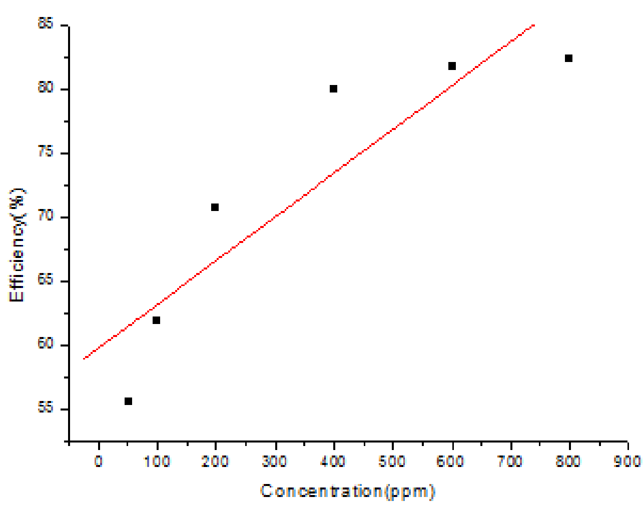


Figure (1)

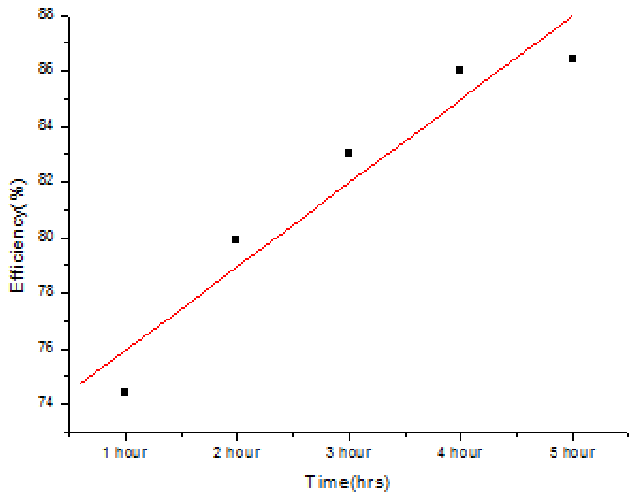


Figure (2)

Effect of Temperature:-

Weight loss measurements were carried out in acidic medium in 296-318 K temp in the presence and absence of Gudmar Buti during immersion time 2h at specific concentration as shown in figure (3) to find out the adsorption of Gudmar Buti inhibitor and activation parameters for the corrosion of mils steel. It was found that with increase in temperature efficiency decreases at a particular concentration of inhibitor.

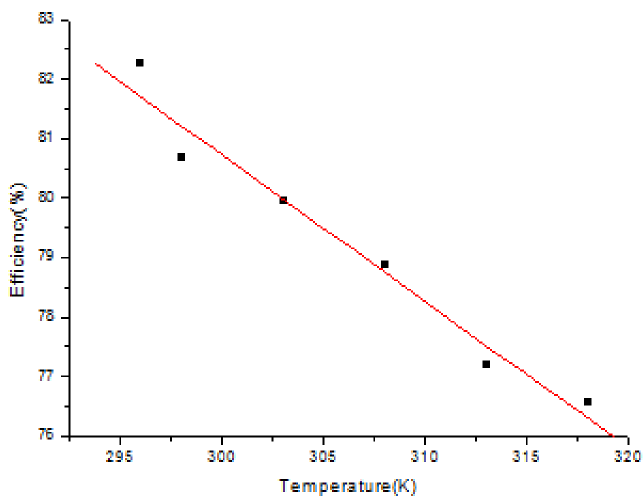


Figure (3)

Table 5: The values of thermodynamic parameters in 2M HCl for mild steel in presence and absence of Gudmar Buti inhibitor

Inhibitor concentration(ppm)	E_a (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Blank	541500	5.36	-16.85
400 ppm	1372218	31.78	-7.20

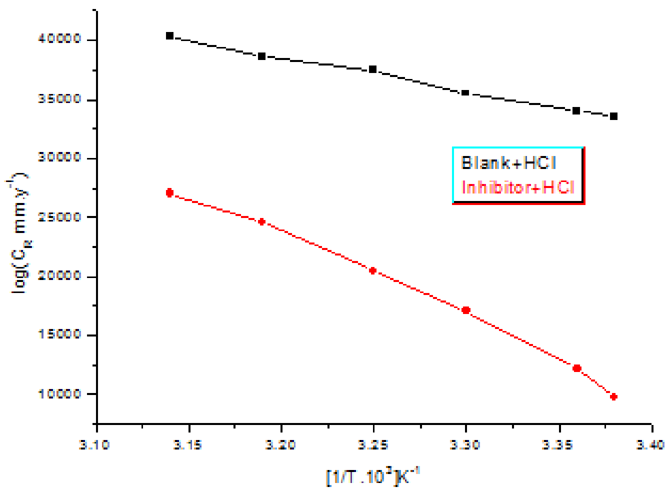


Figure (4)

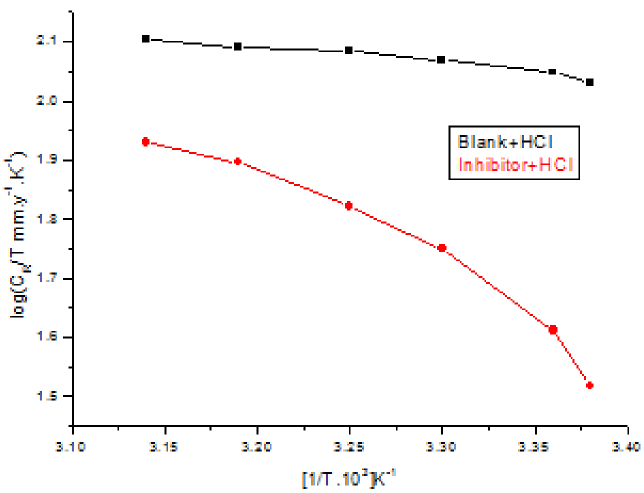


Figure (5)

Table 6: In 2M HCl Standard Gibb's free energy of adsorption for mild steel in presence and absence of Gudmar Buti inhibitor at various temperatures

Temperature (K)	ΔG^0_{ads} (kJ mol^{-1})
296	-22.9721
298	-20.5249
303	-19.7282
308	-18.3831
313	-16.2001
318	-15.5079

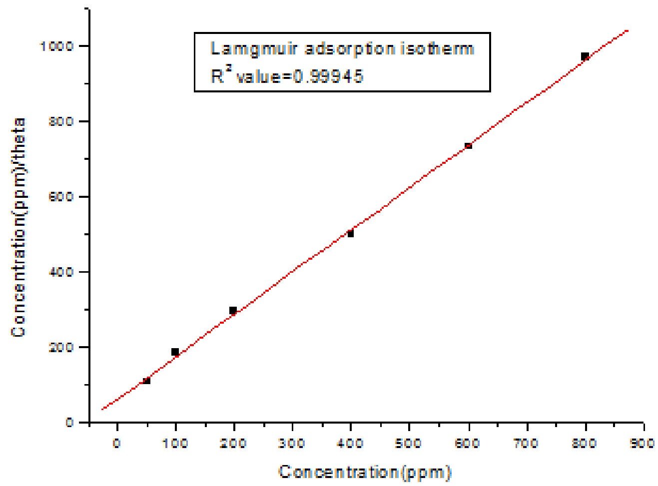
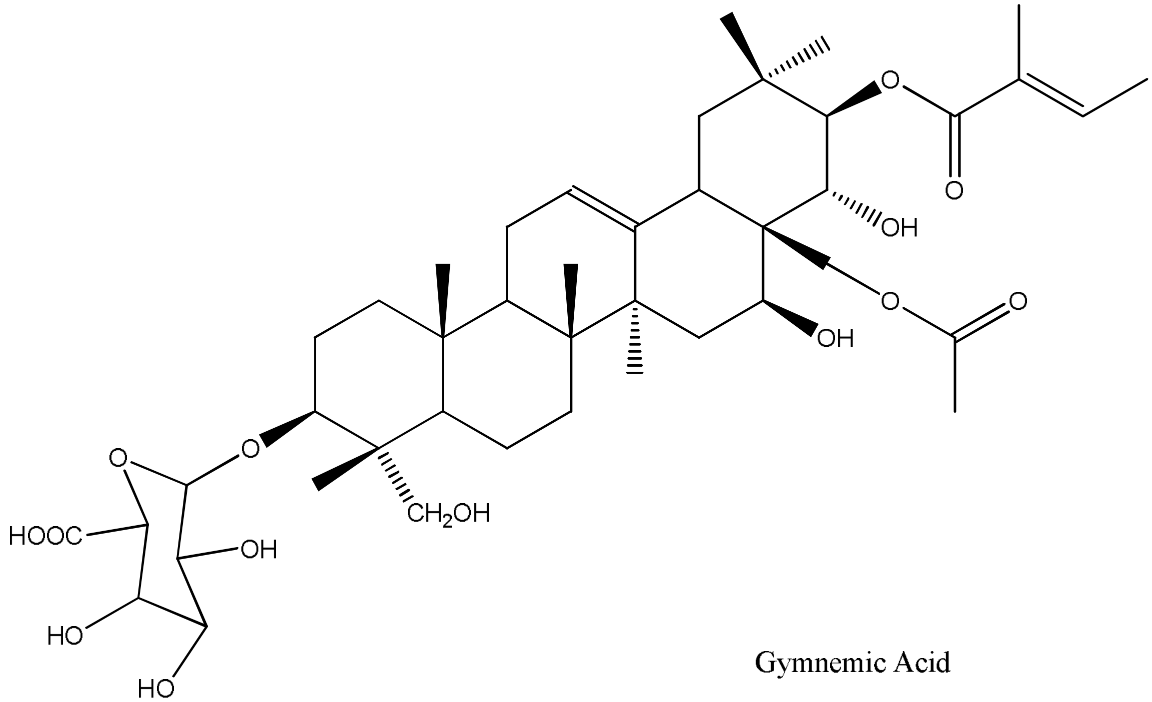

Lamgmuir adsorption isotherm
R² value=0.99945
Concentration(ppm)/theta
Concentration(ppm)
0
200
400
600
800
1000
0
100
200
300
400
500
600
700
800
900

Figure (6)

Gudmar Buti constituents- Quantum Chemical Calculations

1. <u>Gymnemic acid:</u>



Gymnemic Acid

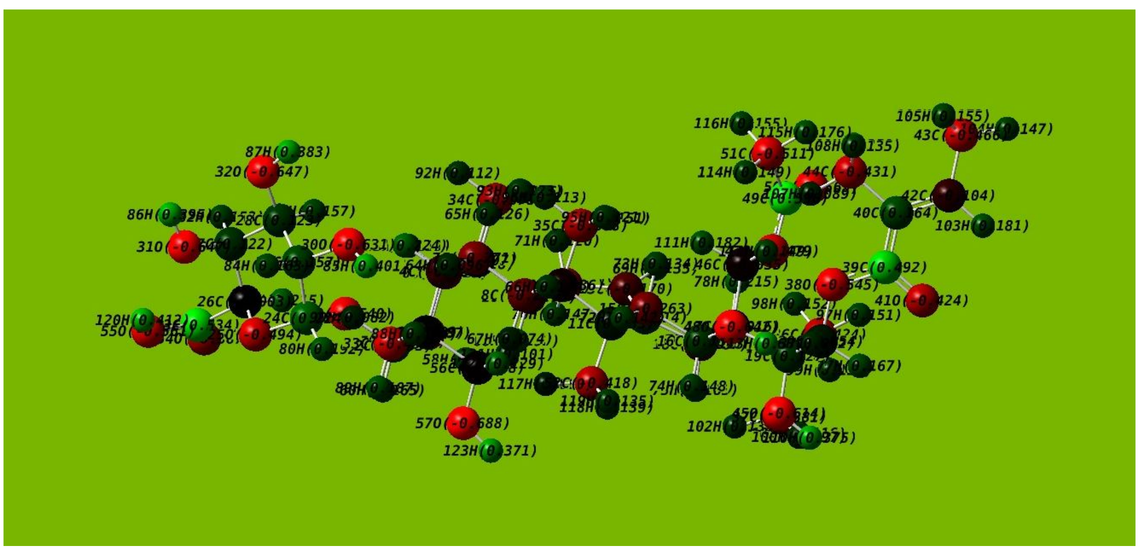


Figure (a)

Figure (a) Optimized molecular structure with Mullikan charges of the active constituent (Gymnemic acid) of Gudmar extract

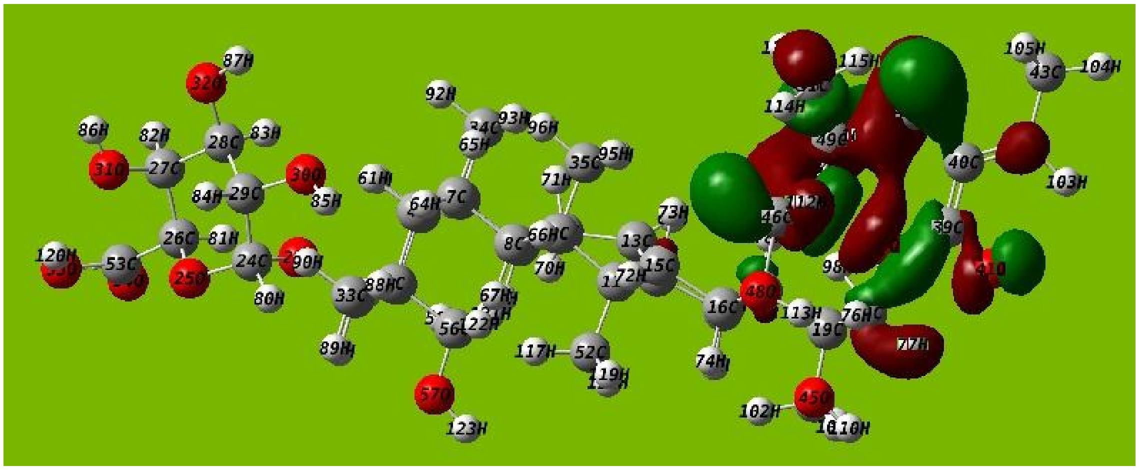


Figure (b): A

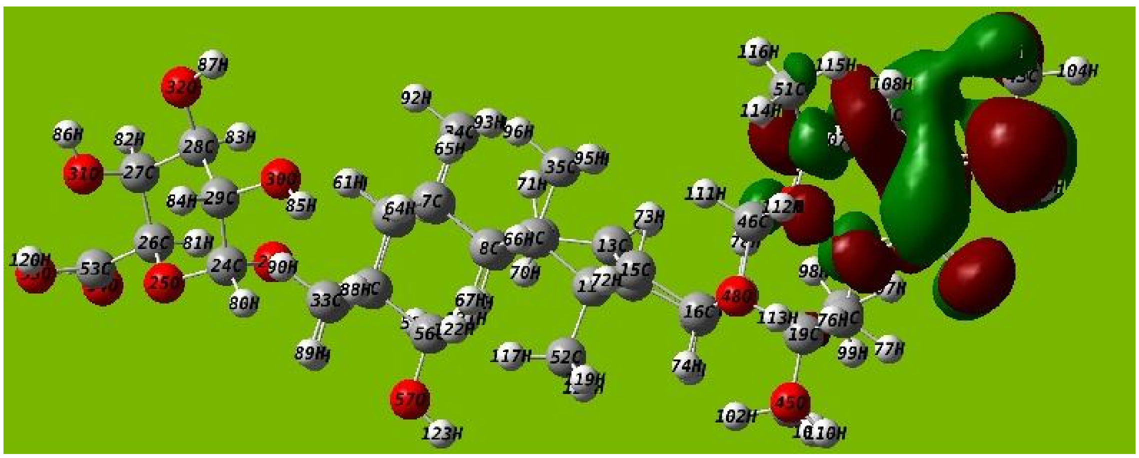


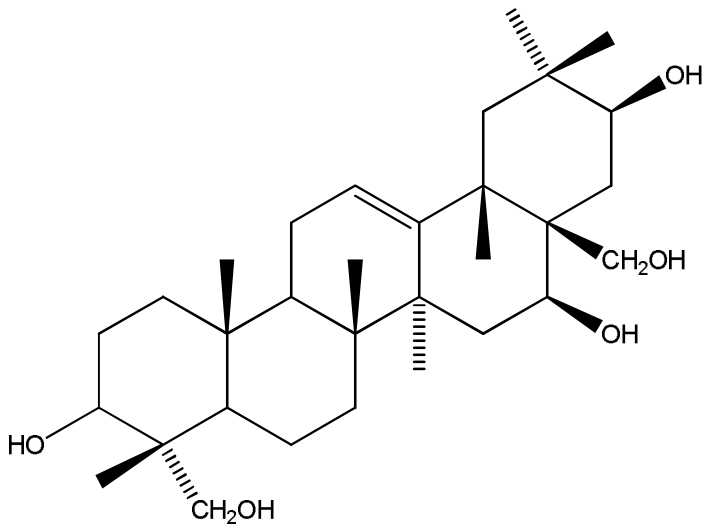
Figure (b): B

Figure (b): The frontier molecular orbital density distribution of the active constituent (Gymnemic acid) of Gudmar extract (A) HOMO (B) LUMO

Table 1: Calculated Quantum chemical parameters of Gymnemic Acid

Quantum Parameters	**Gymnemic Acid**
HOMO(hartree)	**-0.16383**
LUMO(hartree)	**-0.05571**
ΔE LUMO-HOMO(hartree)	**0.10812**
Dipole moment (μ)	**10.60**

2.<u>Gymnestogenin:</u>



Gymnestogenin

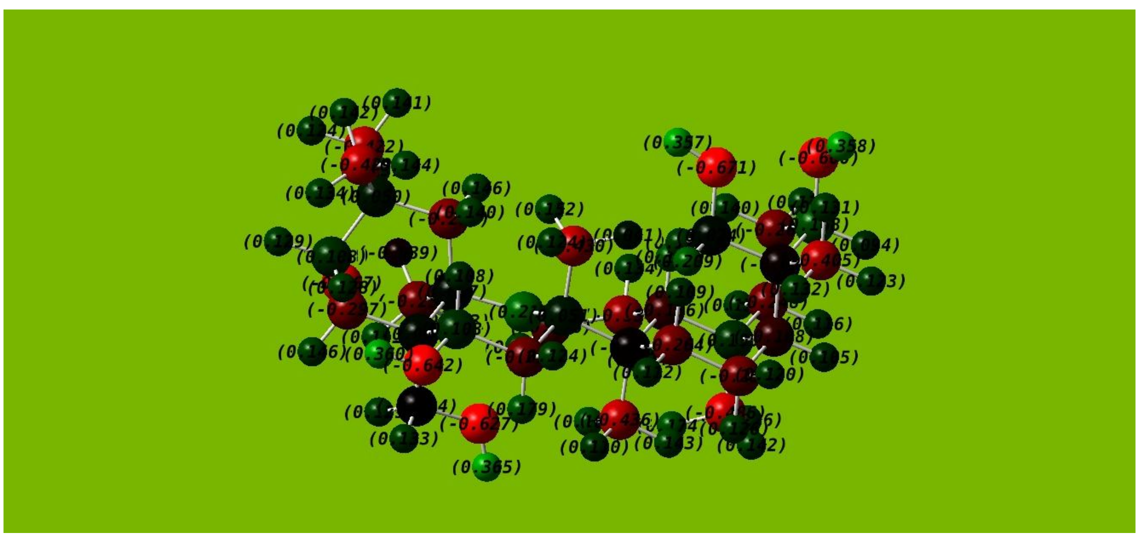


Figure (c)

Figure (c): Optimized structure with Mullikan charges of the active constituent (Gymnestogenin) of Gudmar extract

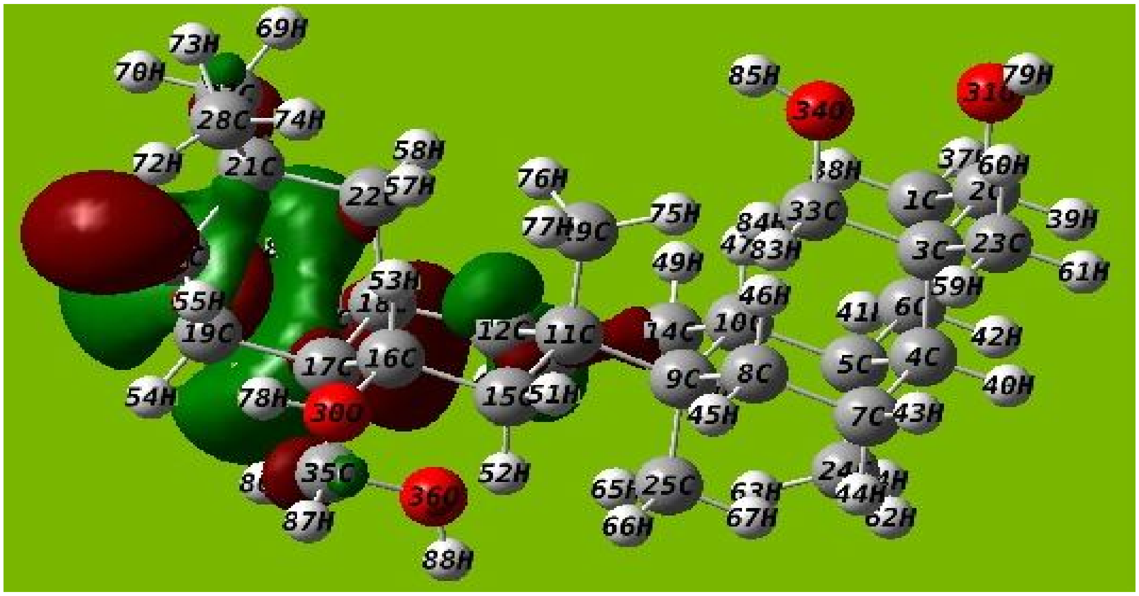


Figure (d): A

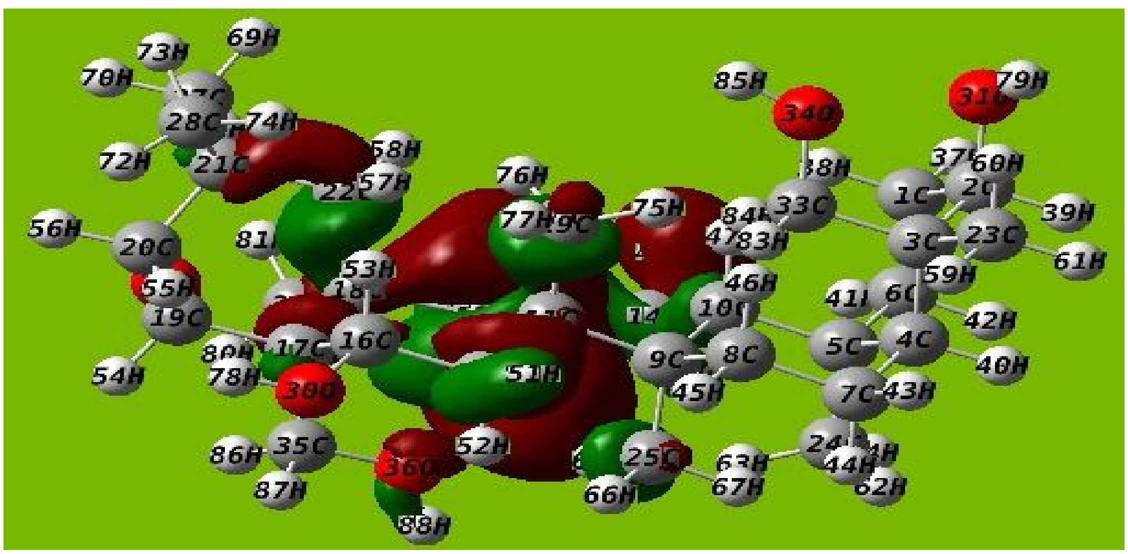


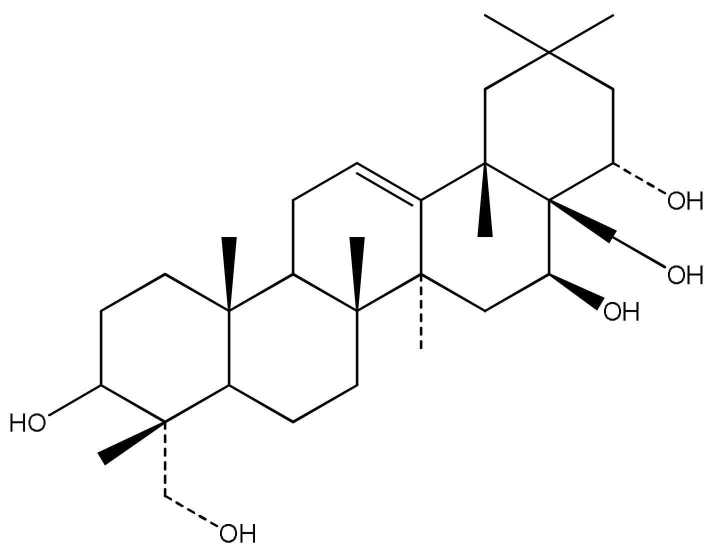
Figure (d): B

Figure (d): The frontier molecular orbital density distribution of the active constituent (Gymnestogenin) of Gudmar extract (A) HOMO (B) LUMO

Table 2: Calculated Quantum chemical parameters of Gymnestogenin

Quantum Parameters	Gymnemic Acid
HOMO(hartree)	**-0.12872**
LUMO(hartree)	**0.03469**
ΔE LUMO-HOMO(hartree)	**0.16341**
Dipole moment (μ)	**4.7120**

3. Gymnemanol :



Gymnemanol

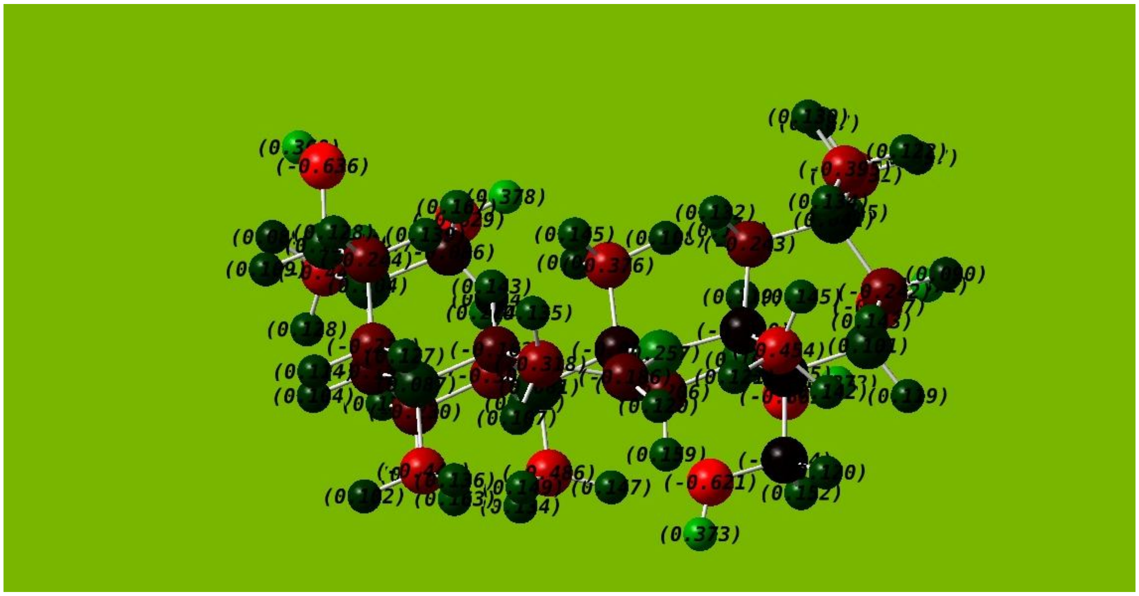


Figure (e)

Figure (e): Optimized molecular structure with Mullikan charges of the active constituent (Gymnemanol) of Gudmar extract

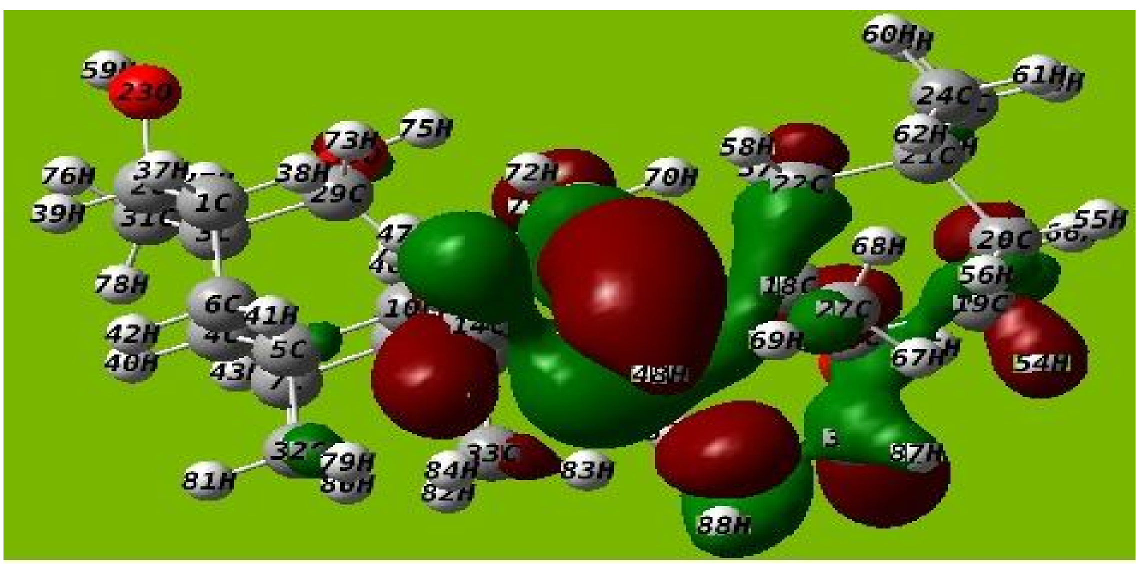


Figure (f): A

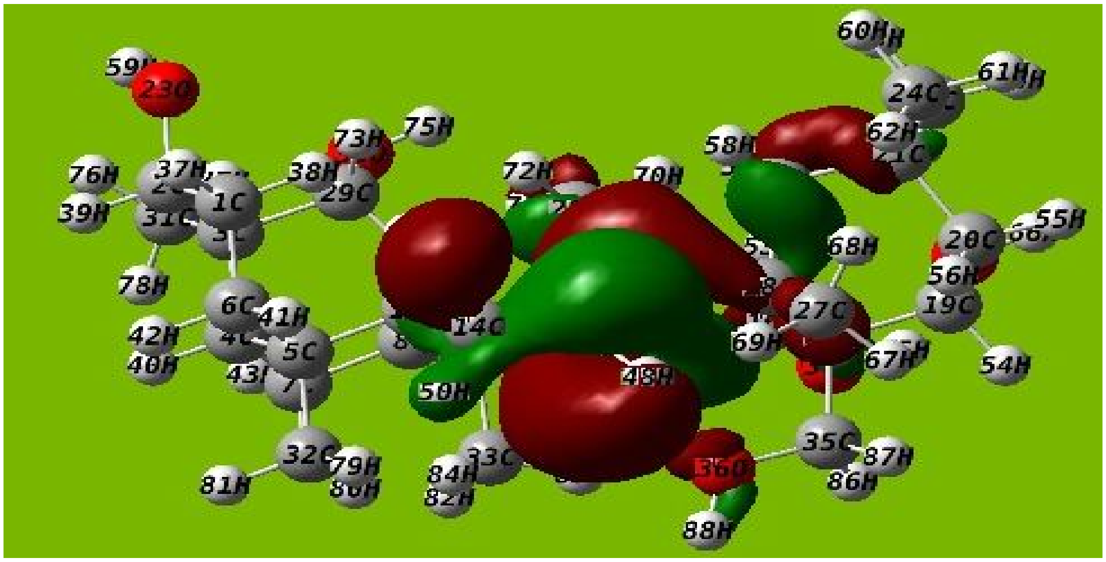


Figure (f): B

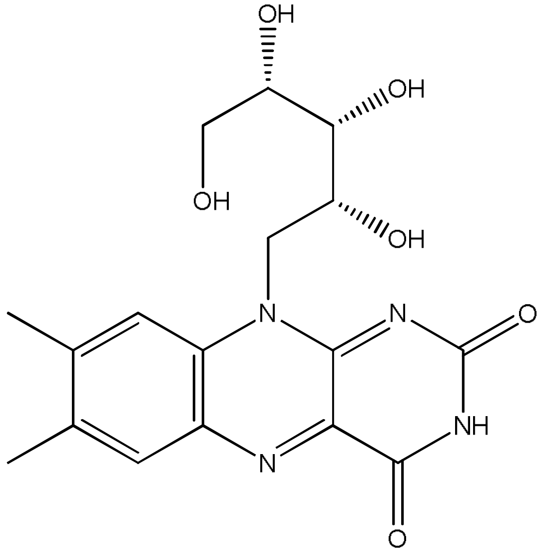
Figure (f): The frontier molecular orbital density distribution of the active constituent (Gymnemanol) of Gudmar extract (A) HOMO (B) LUMO

<u>Table 3: Calculated Quantum chemical parameters of Gymnemanol</u>

Quantum Parameters	**Gymnemic Acid**
HOMO(hartree)	-0.18798
LUMO(hartree)	0.02781
ΔE LUMO-HOMO(hartree)	0.21579
Dipole moment (μ)	5.2097

Shahtoot constituents -Quantum Chemical calculations

1. Riboflavin:



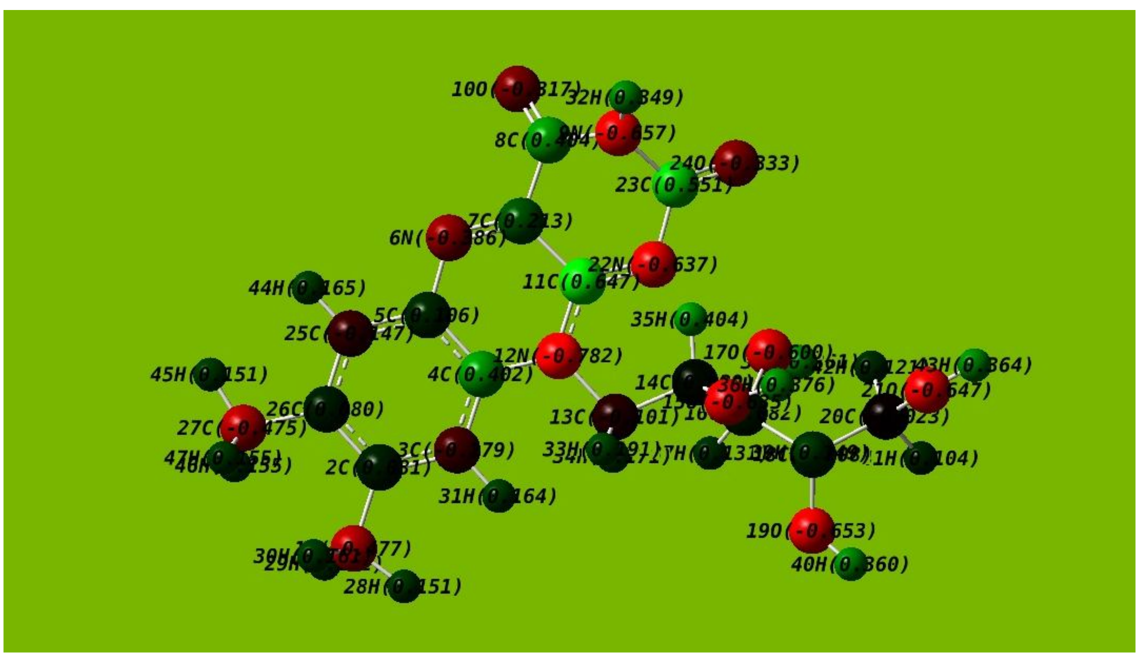


Figure (g)

Figure (g): Optimized molecular structure with Mullikan charges of the active constituent (Riboflavin) of Shahtoot extract

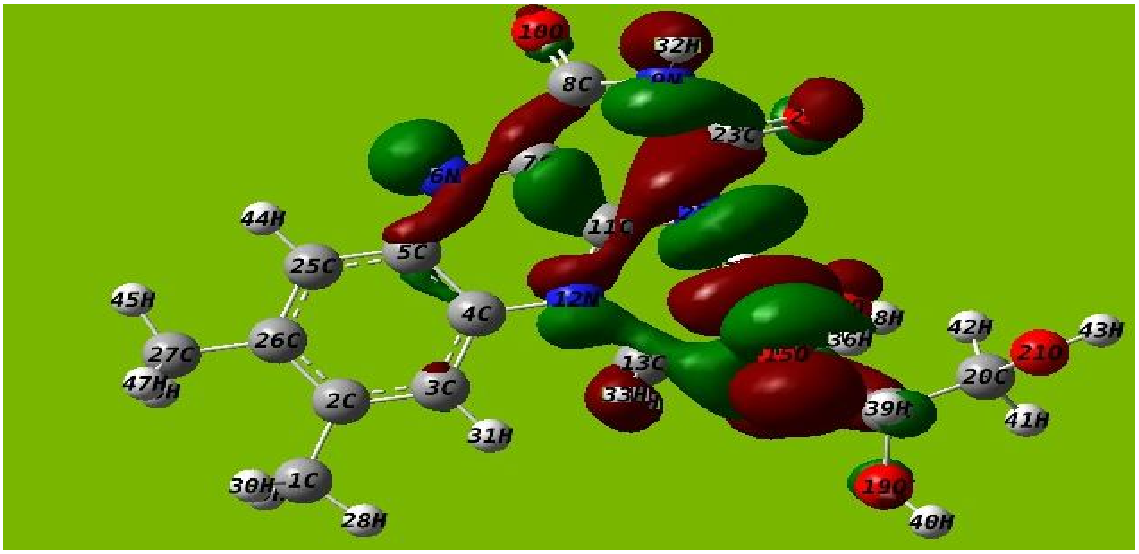


Figure (h): A

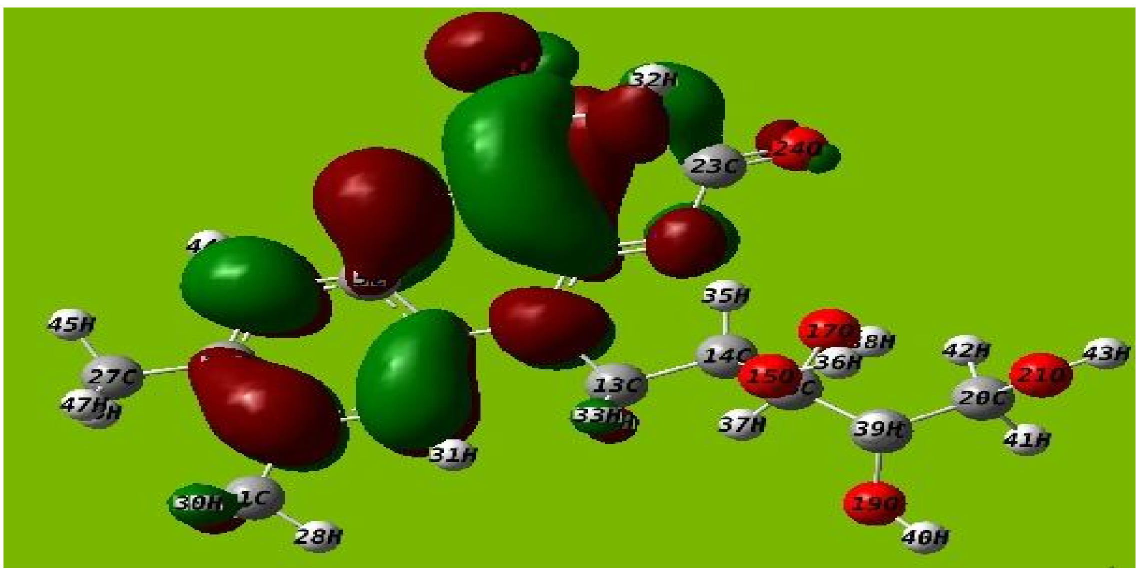


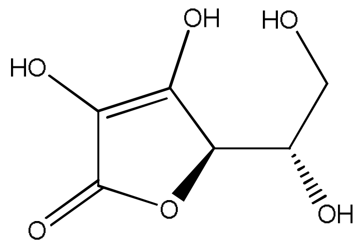
Figure (h): B

Figure (h): The frontier molecular orbital density distribution of the active constituent (Riboflavin) of Shahtoot extract (A) HOMO (B) LUMO

Table 1: Calculated Quantum chemical parameters of Riboflavin

Quantum Parameters	**Riboflavin**
HOMO(hartree)	**-0.16422**
LUMO(hartree)	**-0.10264**
ΔE LUMO-HOMO(hartree)	**0.06158**
Dipole moment (μ)	**6.47**

2. Ascorbic acid:



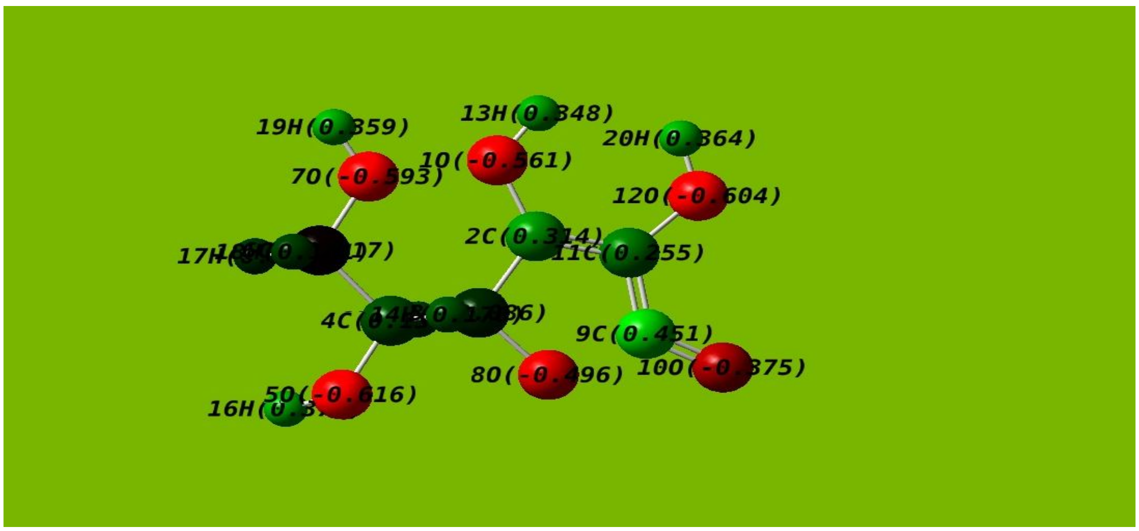


Figure (i)

Figure (i): Optimized molecular structure with Mullikan charges of the active constituent (Ascorbic acid) of Shahtoot extract

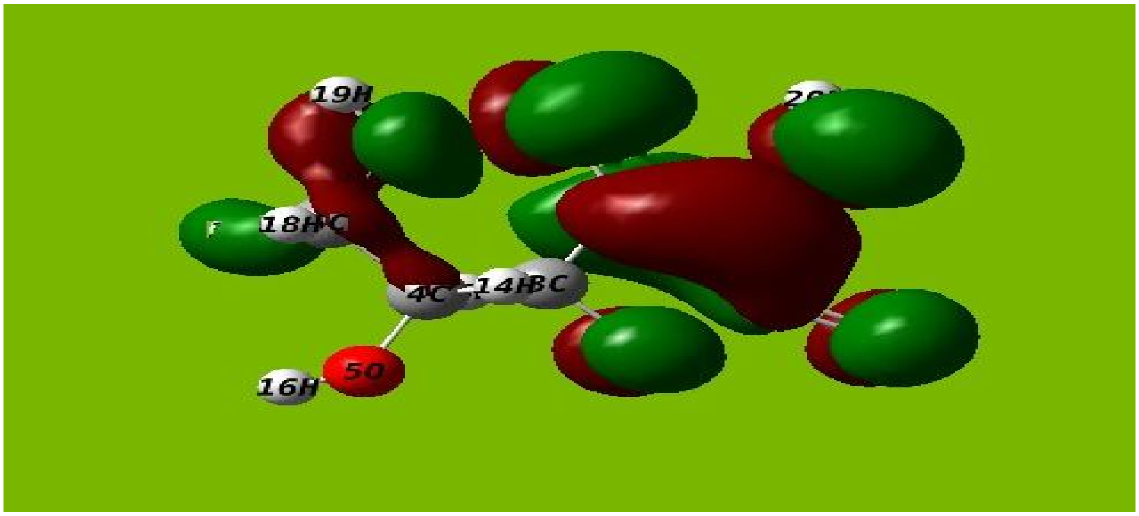


Figure (j): A

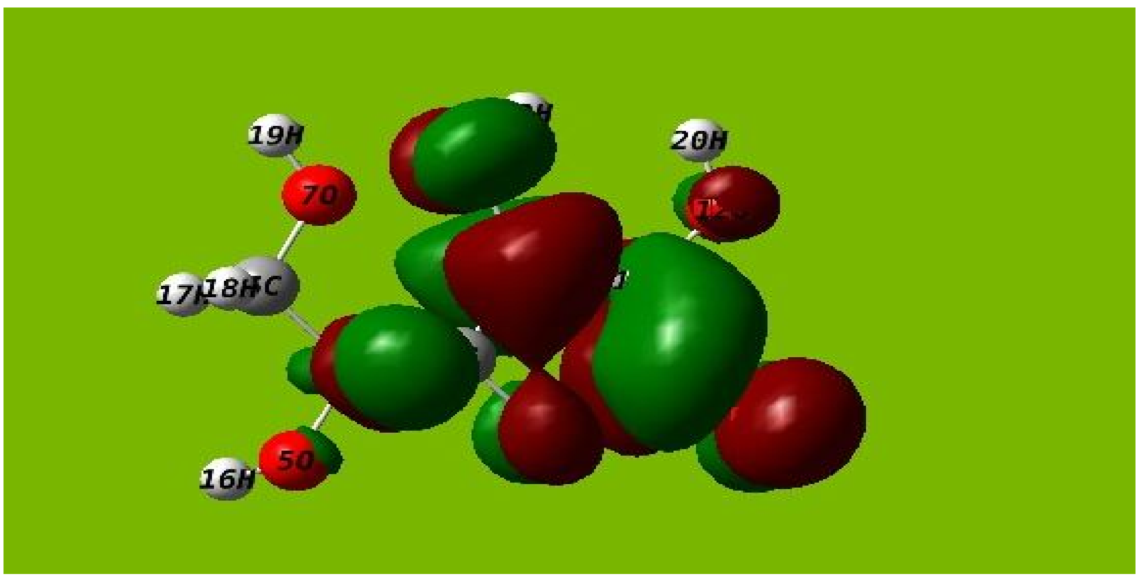


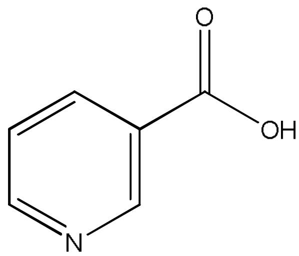
Figure (j): B

Figure (j): The frontier molecular orbital density distribution of the active constituent (Ascorbic acid) of Shahtoot extract (A) HOMO (B) LUMO

Table 2: Calculated Quantum chemical parameters of Ascorbic acid

Quantum Parameters	Ascorbic acid
HOMO(hartree)	**-0.21983**
LUMO(hartree)	**-0.04023**
ΔE LUMO-HOMO(hartree)	**0.1796**
Dipole moment (μ)	**9.1651**

3. Niacin:



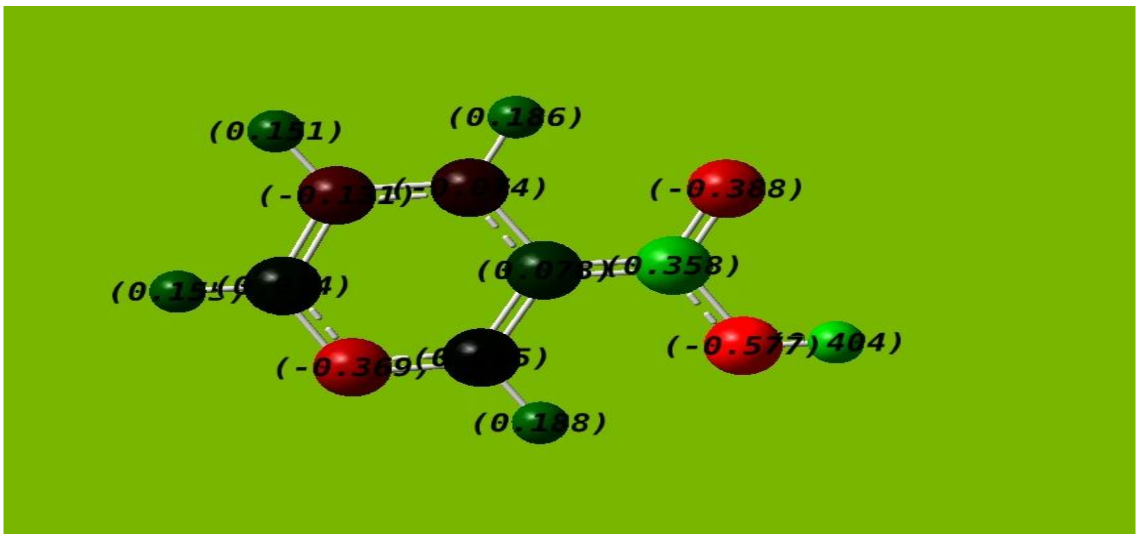


Figure (k)

Figure (k): Optimized molecular structure with Mullikan charges of the active constituent (Niacin) of Shahtoot extract

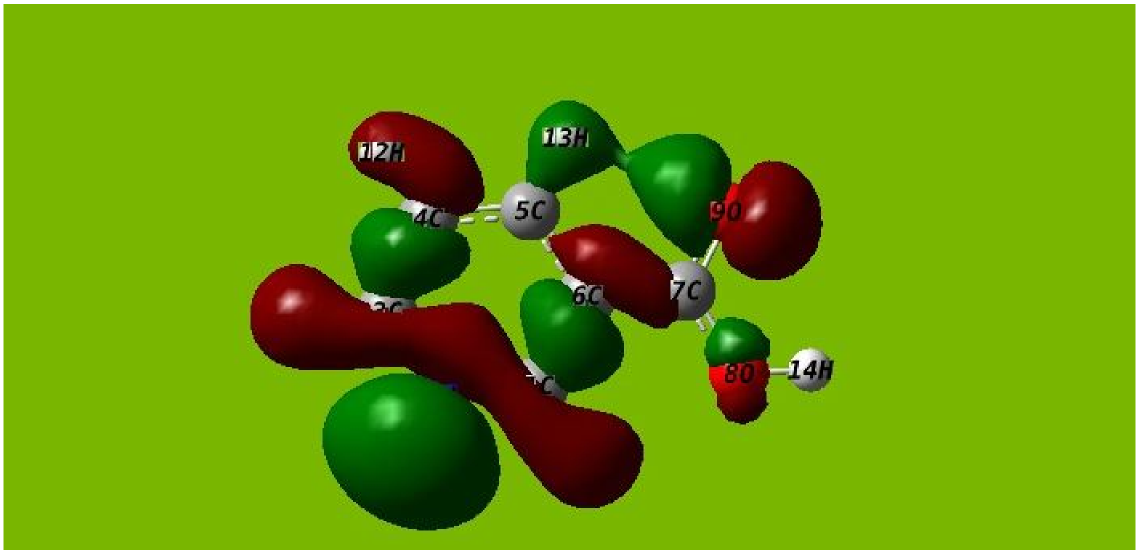


Figure (l): A

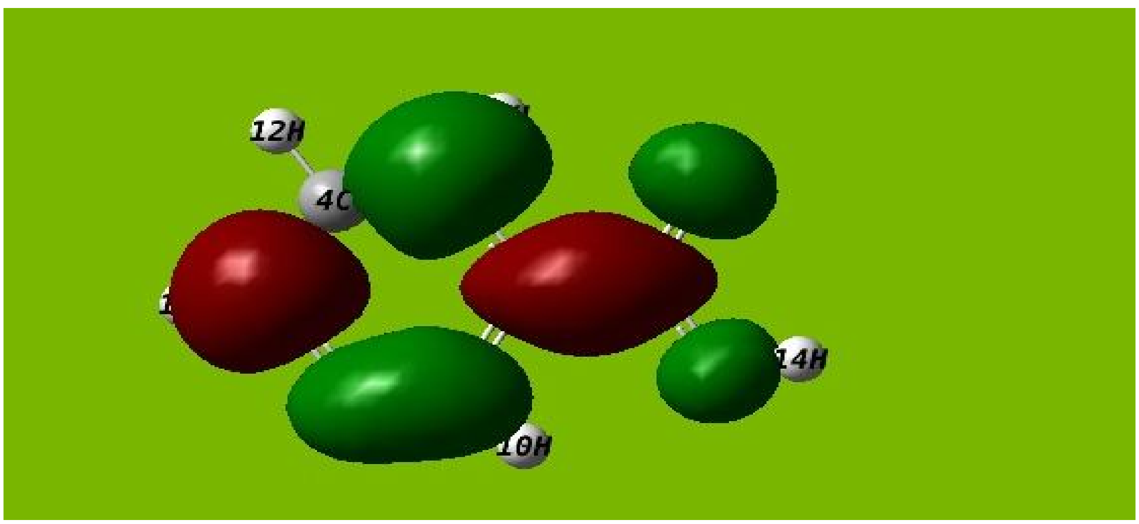


Figure (l): B

Figure (l): The frontier molecular orbital density distribution of the active constituent (Niacin) of Shahtoot extract (A) HOMO (B) LUMO

<u>Table 3: Calculated Quantum chemical parameters of Niacin</u>

Quantum Parameters	Niacin
HOMO(hartree)	-0.25762
LUMO(hartree)	-0.07102
ΔE LUMO-HOMO(hartree)	0.1866
Dipole moment (μ)	0.6614

The frontier molecular orbital density distribution of Gymnemic acid, Gymnestogenin, Gymnemanol present in Gudmar leaves extract are shown in figure (b),(d),(f) respectively and that of Riboflavin, Ascorbic acid, Niacin which are present in Shahtoot leaves extract are shown in figure (h),(j),(l) respectively. The factors that affect the electronic interaction of molecules of inhibitor with the surface of metal are E_{HOMO}, E_{LUMO}, ΔE (E_{LUMO}-E_{HOMO}) and (μ) dipole moment. To find out the adsorption centres of the molecules of inhibitor which are responsible for the interaction with the atoms of metal surface frontier orbital theory is used. The inverse relation of orbital energy difference with respect to stabilization energy is shown by the frontier molecular orbitals. The higher probability that the molecule would accept electrons is indicated by the lower values of E_{LUMO}. The high inhibition efficiency is shown by the lower values of ΔE because to remove an electron from the last occupied orbital energy will be low. The higher values of dipole moment (μ) will show accumulation of the inhibitor on the surface layer.

The adsorption of active constituents of extracts is shown by the donor acceptor interactions between π-electrons of multiple bonds and free electron pairs of hetero atoms. Planarity of molecules must also be considered for the adsorption of organic compounds on the surface of metal. The inhibitors which not only give electrons to metal atoms but also contains unoccupied higher energy orbitals so that they can accept electrons from d-orbital of metal atom for strong bonding interaction. The adsorption of constituents of extracts is shown by the inhibition of mild steel in 2M HCl **[32-34].**

Conclusion

Natural inhibitors are being used as good inhibitors for most of the metals going under corrosion as they are environment friendly, low cost and non-toxic and also they contain hetero atoms like O, N, S which work as good corrosion inhibitors. The plant extracts has environmental benefit as they are biodegradable.

By using weight loss method on mild steel in HCl solution the inhibition effect of Sahtoot and Gudmar Buti extract was being investigated. The inhibitor Sahtoot and Gudmar Buti has a good inhibition effect in 2M HCl for the corrosion of mild steel. The results obtained from weight loss measurements showed that with increase in the concentration of extracts the inhibition efficiency also increases while it decreases with rise in temperature. The high inhibition efficiencies of leaves extract of Shahtoot and Gudmar Buti show the adherent adsorption of the molecules of inhibitor on the mild steel surface.

The adsorption of molecules of inhibitor on the surface of mild steel in 2M HCl followed Langmuir adsorption isotherm with regression coefficient (R^2=0.99936).The negative values of ΔG^0_{ads} showed that the adsorption is spontaneous and followed Langmuir adsorption isotherm.

The structure and electronic parameters had been obtained using computational methodology of quantum chemistry to find out the optimized molecular structures of the active constituents of extracts and frontier molecular orbital density distribution **[35].**

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