

A Preeminent inhibition approach towards carbon mild steel using fruit extract of *Physalis peruviana* in acidic medium: Electrochemical & Adsorption studies

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## Abstract

An effective corrosion inhibition hobby of carbon mild steel with the promising inexperienced inhibitor *Physalis peruviana* fruit peel extract changed into tested in 1 M  $H_2SO_4$  acidic solution by means of the usage of diverse strategies such as gravimetric, potentiodynamic polarization and electrochemical impedance spectroscopy. An growth in inhibition efficiency with the improved attention of the inhibitor *Physalis peruviana* fruit peel extract. It changed into realized that the inhibitor molecule had a greater high-quality inhibiting impact on carbon mild steel. It follows the effect of immersion time (2–8 hours) was discussed and the adsorption mechanism became fitted with the Langmuir adsorption and Freundlich adsorption isotherms. FTIR spectroscopy had been additionally hired to discover the modifications in practical organizations of the organic molecules of the extract.

**Keywords:** *Physalis peruviana* fruit peel extract (PPFPE), polarization measurements, charge transfer resistance, double layer capacitance and sulfuric acid, Mild carbon steel.

## 1. Introduction

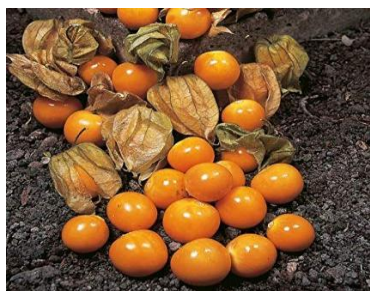
Mild steel is a low carbon steel alloy which is extensively used as constructional resource in numerous industries which include petroleum, meals, strength manufacturing, chemical industries because of its excessive mechanical power, clean fabrication and low cost [1]. The process of corrosion is common anywhere because of humid surroundings, the rate of corrosion is quite excessive in acidic media. in order to triumph over the most important difficulty of corrosion on carbon mild steel in an commercial and engineering purposes by using the usage of an inhibitors.

Inhibitors play an vital role in reducing or stopping the system of corrosion on moderate metal in an acidic media. A survey of literature well-known shows that numerous varieties of natural and inorganic compounds had been used for the protection of carbon slight metal. however, the usage of chemical inhibitors has been restricted because of being artificial chemical compounds,

tremendously costly, and toxic to the environment. therefore, it's far worthwhile to present attention in the direction of a totally cheap and environmentally safe studies for corrosion inhibition of carbon mild metallic in acidic media [2].

In this view, various plants such as *Tagetes erecta* (Marigold flower) extract [3], *Nicotiana tabacum* leaves extract [4], the extract of *Punica granatum* peel [5], *Centella asiatica* extract [6], *Spirulina platensis* [7], *Piper longum* extract [8], Leaves extract of *ananas sativum* [9] have been reported the effective inhibitor towards mild steel in acidic and alkaline medium by many researchers. *Physalis peruviana*, a plant species of the genus *physalis* in the nightshade family *Solanaceae*. The plant and its fruit are commonly called Cape gooseberry, goldenberry, pitchberry or *physalis*. The objective of this investigation is to evaluate the corrosion inhibition effect of PPFPE on carbon mild steel in 1M  $H_2SO_4$  solution. The inhibition performance is examined by potentiodynamic polarization

and electrochemical impedance spectroscopy.



**Fig.1. Images of *Physalis peruviana* fruit peel extract**

## 2. Experimental Methods

The *physalis peruviana* fruit was peeled out and the skin dried for a day, grind it to powder. Then 10 g of the powdered PPFPE was weighed and taken in a spherical bottom flask, 100ml of ethanol introduced and soak in it completely for at some point, same quantity of distilled water became brought and reflux it for 2hrs, switch the condensed extract and make it to evaporate to get a concentrated extract. furthermore, it could be used to synthesis and characterize.

The working electrode was made of carbon mild steel (for weight loss studies and surface morphology) and cylindrical rods (for electrochemical analysis) of composition (wt%) presented in Table.1.

**Table.1. Chemical composition of the carbon steel specimens used in this study**

Element	C	S	Al	Cu	Mn	P	Si	Cr
Wt.	0.058	0.009	0.067	<0.005	0.28	0.02	0.01	<0.005

The rectangular coupon was used for weight reduction measurement, measuring 3.5cm x 2cm x 0.5 cm from the carbon slight metallic sheets, then floor with no. 600 emery paper, eventually polished and

not using a. 2000 emery paper accompanied by immediate rinsing with absolute acetone and repeat this after each immersion period with distinctive awareness. The weight loss approach changed into evaluated at one of a kind temperatures at room temperature through weighing the clean polished coupons before and after immerse in 1M H<sub>2</sub>SO<sub>4</sub> (in outside) in the absence and presence of numerous concentrations of an PPFPE inhibitor[10].

## 3. Result and discussion

### 3.1 Effect of PPFPE concentration on Corrosion rate and Inhibition efficiency

The weight loss approach for PPFPE were investigated inside the variety of a 100 -200ppm at 308K in 1M H<sub>2</sub>SO<sub>4</sub> medium. The corrosion charge and inhibition efficiency obtained inside the presence and shortage of PPFPE become listed in table 2. The inhibition performance increasing with increasing awareness of the inhibitor PPFPE about 95.65% at 200ppm. beyond this awareness, there may be no development inside the IE. It indicated that 200ppm is the most desirable awareness to get the most corrosion safety on carbon slight steel in 1M H<sub>2</sub>SO<sub>4</sub> [11]. Because of the presence of a few phytochemical elements inside the PPFPE has a functional organizations particularly C=O, -COOR and O-H, which can be electron rich and can be attributed to good inhibition performance.

### 3.2 Effect of Temperature of PPFPE on Carbon mild steel

The temperature performance of the PPFPE with different concentrations from 100ppm to 200ppm on carbon mild metal in 1M H<sub>2</sub>SO<sub>4</sub> values are given in table 2. From the table, it's far clean that inhibition performance decreases with boom in temperature from 95.65 to

86.02%. This suggests that the inhibitive / shielding layer formed as movie on steel surface changed into reduced in nature at higher temperatures because of desorption of the inhibitor molecules from the steel surface[12].

**Table.2 Corrosion rate and inhibition efficiency data obtained from weight loss measurements in acid solutions in the absence and presence of PPFPE**

Acid solution	Con. Inhibition	Corrosion Rate				%IE			
		308K	313K	323K	333K	308K	313K	323K	333K
1M H <sub>2</sub> SO <sub>4</sub>	Blank	3.35	4.56	5.82	7.32	-----	-----	-----	-----
	100 ppm	0.767	1.1601	1.668	2.325	77.08	74.55	71.34	68.23
	150 ppm	0.443	0.788	1.246	1.875	86.77	82.71	78.59	74.38
	200 ppm	0.1455	0.289	0.554	1.023	<b>95.65</b>	<b>93.66</b>	<b>90.48</b>	<b>86.02</b>

### 3.3.Activation parameters

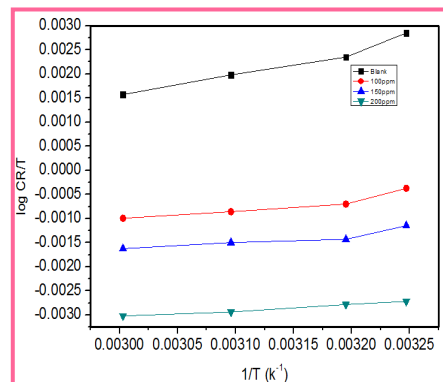
On plotting CR vs 1/T (Fig.2.) and logCR/T vs 1/T (Fig.3) gave a straight line with slope of  $-E_a/2.303R$  and  $-\Delta H^*/2.303R$ . From the straight line  $E_a$ ,  $\Delta H^*$ ,  $\Delta S^*$  values can be calculated.

**Table.3. Activation parameters of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of PPFPE**

Concentration	$E_a$ (KJ/mol)	$\Delta H^*$ (KJ/mol)	$\Delta S^*$ (J/mol/K)
Blank	26.03	94.53	-197.586
100 ppm	54.32	44.50	-197.580
150 ppm	66.04	68.11	-197.581
200 ppm	121.45	76.40	-197.583

The consequences acquired suggests that the PPFPE acted as inhibitor through growing activation strength of slight steel dissolution with the aid of creating a barrier to mass and fee transfer by means of their adsorption on the slight metal surface. From table.3. it's far clear that entropy of activation accelerated within the presence of PPFPE as compared to the

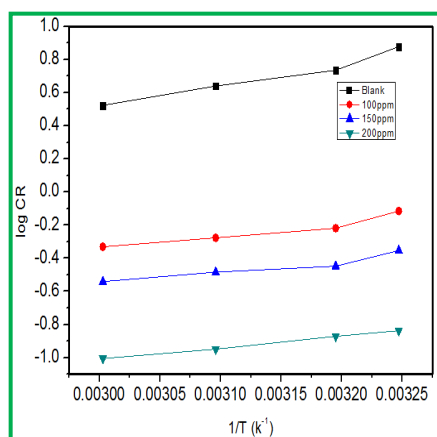
1M H<sub>2</sub>SO<sub>4</sub> answer. The fine signal of  $\Delta H^*$  displays endothermic nature on carbon mild metal dissolution method and it requires more electricity to obtain the energetic state or equilibrium state [13].



**Fig.2. Arrhenius plots for log CR vs 1/T for steel in 1M H<sub>2</sub>SO<sub>4</sub> at different concentrations of PPFPE**

Due to the presence of PPFPE inhibitor, the rate determining step is the discharge of H<sup>+</sup> ions to form adsorbed hydrogen atoms. The surface is protected with the presence of an inhibitor, there was a retard inside the corrosion discharge of hydrogen

ions on metallic surface. It shows that the entropy of activation ( $\Delta S^*$ ) in the presence of PPFPE inhibitor, which in turn increases inside the disordering of reactant to activated complex[14].



**Fig.3.** Transition plots for log CR/T vs 1/T for steel in 1M H<sub>2</sub>SO<sub>4</sub> at different concentrations of PPFPE

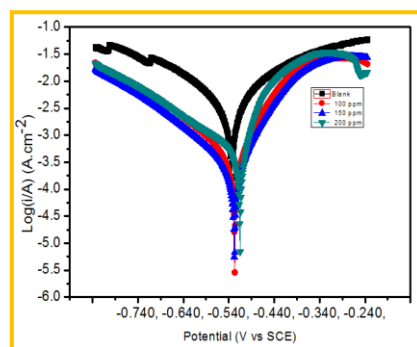
### 3.4 Potentiodynamic polarization studies

An electrochemical parameters including corrosion capacity ( $E_{corr}$ ), cathodic and anodic Tafel slopes ( $b_c$  and  $b_a$ ) and corrosion present day density ( $I_{corr}$ ) were acquired by means of extrapolation of the anodic and cathodic areas of the Tafel plots and its inhibition performance is listed in table.4. it's miles obvious that the cost of  $b_a$  changed with growth in the presence of PPFPE whereas more said exchange takes place inside the values of  $b_c$  indicating that both anodic and cathodic reactions are effected however impact on the cathodic reactions is extra prominent.

Fig.4. shows the cathodic and anodic polarization plots of mild steel immersed in 1M H<sub>2</sub>SO<sub>4</sub> at 308 K in the absence and presence of different concentrations of PPFPE. In the addition of inhibitor PPFPE that reduced the anodic dissolution reactions and retarded the hydrogen evolution reactions on the cathodic sites. The shift in the anodic Tafel

slope ( $b_a$ ) is due to the inhibitor molecules adsorbed on the metal surface. An inhibitor can be classified as an anodic or cathodic type when the change in  $E_{corr}$  value is larger than 85 mV [15].

In the addition of the PPFPE in the concentration variety from a 100 - 200 ppm, decreases the  $I_{corr}$  ranges from 1.48 to  $2.368 \times 10^{-1} \mu A / cm^2$  in 1M H<sub>2</sub>SO<sub>4</sub> and inhibition performance increases from 70.16 to 95.22 in 1M H<sub>2</sub>SO<sub>4</sub>. The maximum displacement become 60 mV cathodically whilst in comparison to the clean. This shows that the PPFPE reduces the corrosion charges predominantly by means of hydrogen evolution of moderate metal.



**Fig.4.** Tafel plot of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> in the presence of PPFPE

**Table.4.** Tafel polarization for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> solutions containing PPFPE

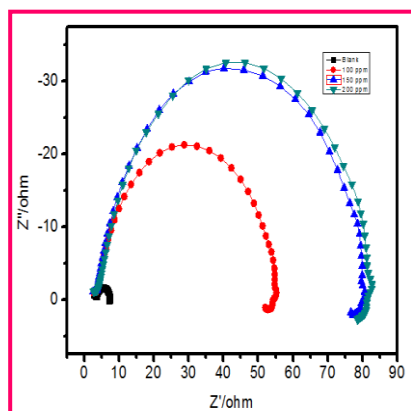
Concen tration	$E_{corr}$	$I_{corr} (10^{-6})$	$b_c$	$b_a$	% IE
Blank	0.6	$4.961 \times 10^{-3}$	0.1622	0.176	-
100 ppm	0.6	$1.480 \times 10^{-3}$	0.1496	0.087	70.16
150 ppm	0.6	$5.461 \times 10^{-4}$	0.1466	0.082	88.9
200 ppm	0.6	$2.368 \times 10^{-4}$	0.1432	0.077	95.22

### 3.5 Electrochemical Impedance Spectroscopy (EIS)

Nyquist plots for carbon slight steel inside the presence and absence of an inhibitor PPFPE with special concentrations proven in table.5 & Fig.5. The corrosion technique of carbon moderate metallic in acidic solution

inside the presence of PPFPE become investigated at 308K the usage of EIS after exposure of half-hour time. The obtained impedance spectra with depressed inhibitor concentration of PPFPE which suggests that it controls corrosion of carbon mild steel.

Reputedly from those plots the impedance which response carbon moderate metal in clean solution substantially exchange after the addition of PPFPE inhibitor in corrosion answer. This suggests that the impedance substrate will increase with an boom in awareness of the inhibitor. at the addition of PPFPE inside the awareness variety of one hundred-two hundred ppm, from the attention to an acid answer there ia an increase of  $R_{ct}$  from 52.742  $\Omega\text{cm}^2$  to 83.23  $\Omega\text{cm}^2$  in 1M  $\text{H}_2\text{SO}_4$  and reduces the Cdl cost from  $0.03 \times 10^{-3} \text{ F/cm}^2$  to  $1.19 \times 10^{-4}$  in  $\text{H}_2\text{SO}_4$ .



**Fig.5.**Nyquist plot of mild steel in 1M  $\text{H}_2\text{SO}_4$  in the presence and absence of PPFPE

**Table.5.**AC impedance parameters for mild steel in 1M  $\text{H}_2\text{SO}_4$  solutions containing PPFPE

Concentration	R left	$R_{ct}$	$C_{dl}$	% IE
Blank	3.162	4.360	$0.0365 \times 10^{-3}$	-
100 ppm	3.336	52.74	$3.0185 \times 10^{-3}$	91.73
150 ppm	3.097	81.71	$1.9485 \times 10^{-3}$	94.66
200 ppm	3.074	83.23	$1.9130 \times 10^{-4}$	94.76

The outcomes showed that the  $R_{ct}$  will increase with increasing awareness of the

inhibitors [17]. it is attributed to the formation of protecting film on the metallic / solution. The lower in Cdl might be due to the lower in nearby dielectric steady or an increase in the thickness of the protecting layer at the electrode surface.

### 3.6 Adsorption isotherm of PPFPE

A plot of C towards  $C/\theta$  showed a straight line (Fig.6) indicating that adsorption follows the Langmuir adsorption isotherm in addition to plotting  $\log C$  towards  $\log \theta$  indicating that the adsorption follows Freundlich adsorption isotherm proven in Fig.7 The linear relationships suggested that the adsorption of inhibitors obeyed Langmuir adsorption isotherm and Freundlich adsorption isotherm. From the intercept of the straight lines, the values of  $K_{ads}$  have been calculated and are summarized in table 6.

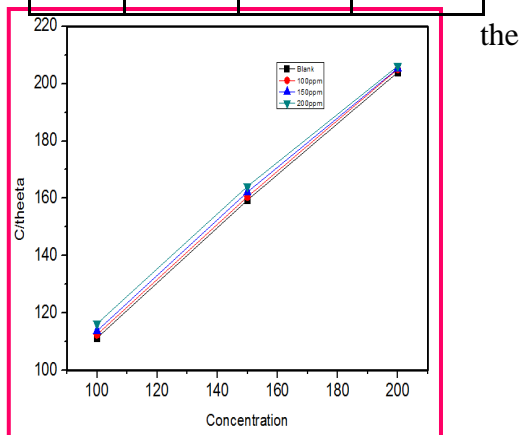
The standard free energy of adsorption  $\Delta G_{ads}^0$  and the equilibrium constant ( $K_{ads}$ ) are related by the following equation:  $\Delta G_{ads}^0 = -RT \ln (55.5 \times K_{ads})$  The negative values of  $\Delta G_{ads}^0$  clearly indicated that spontaneous adsorption of PPFPE on mild steel surface took place through physical adsorption mechanism [18].

In the present investigation the calculated values of  $\Delta G_{ads}^0$  round -2.7 kJ/mol & 1.9kJ/mol , indicating that the adsorption mechanism of PPFPE in 1M  $\text{H}_2\text{SO}_4$  solution on the studied temperatures may be a physisorption, which was constant with electrostatic interaction between a charged molecule and a charged metallic. the heat of adsorption and entropy of adsorption are important parameters for information the adsorption of an natural inhibitors at steel/solution interface. the heat of adsorption ( $\Delta H_{ads}$ ) is calculated using the van't Hoff equation:  $\ln K_{ads} = -\Delta H_{ads}/RT + \text{constant}$ .

All the calculated thermodynamic parameters are listed in table.6. Values of  $\Delta H_{ads}$  had been negative discovered that



Temperature (K)	$K_{ads}$	$-\Delta G^{\circ}_{ads}$ (KJmol <sup>-1</sup> )	$R^2$ value
308	0.05179	2.704	0.99907
313	0.04874	2.590	0.99905
323	0.04314	2.345	0.99774
333	0.03642	1.948	0.99706



adsorption of PPFPE inhibitor on carbon slight metal became an exothermic technique leads that an efficiency inhibition is lower at high temperature.

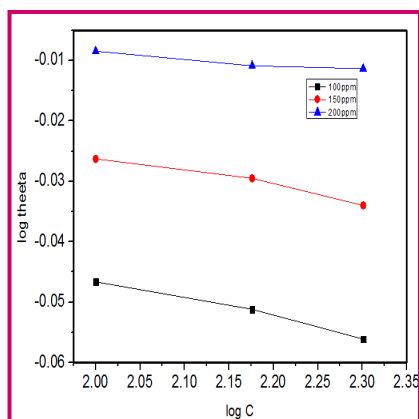


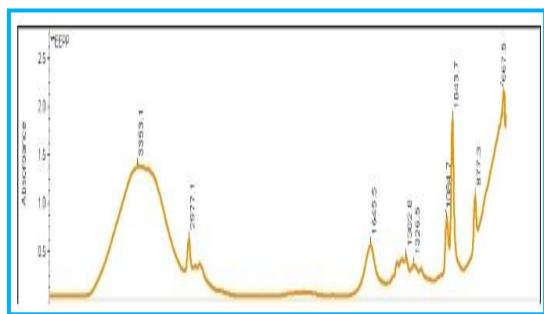
Fig.6. Langmuir adsorption isotherm for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> containing different concentrations of PPFPE at 303–333 K

Fig.7. Freundlich adsorption isotherm for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> containing different concentrations of PPFPE at 303–333 K

Table.6. Thermodynamic parameters for the adsorption of PPFPE on the mild steel in 1M H<sub>2</sub>SO<sub>4</sub> solutions

### 3.7. Analysis of FT-IR spectra

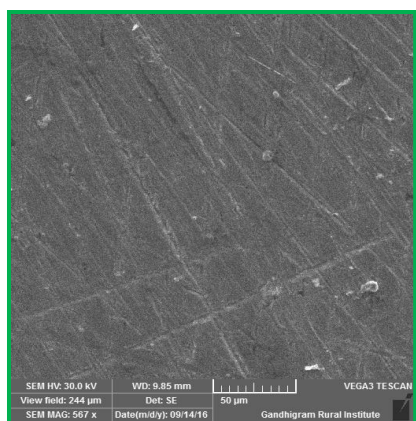
The FT-IR spectrum of PPFPE is shown in Fig.8. The peak maximum recorded at 667.5, 877.3, 1043.7, 1326.5, 1382.8, 1645.5, 2977.1 and 3353.1cm<sup>-1</sup>. The peak in the range of 3000- 3500 cm<sup>-1</sup> corresponds to strong stretching mode of O-H. The sharp peak at 1000- 1500 cm<sup>-1</sup> is attributed to C=O (acid or in ester). This indicates that it has coordinated with Fe<sup>2+</sup> formed on the metal surface resulting in the formation of Fe<sup>2+</sup> PPFPE complex on the metal surface. The spectrum of the PPFPE adsorbed surface films suggests that these functional groups are directly involved in iron-inhibitor interactions, thus confirming the proposed adsorption of some phytochemicals constituents of PPFPE on the carbon mild steel.



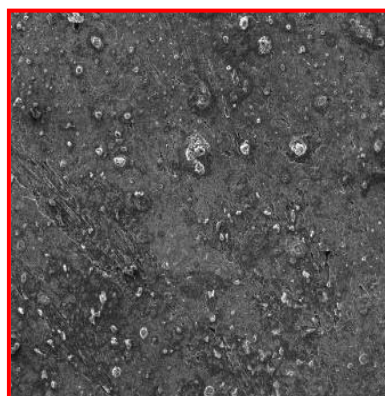
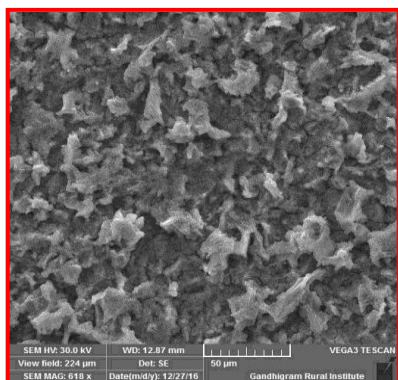
**Fig.8. FT-IR Spectra of PPFPE**

### 3.8 SEM Surface Examination

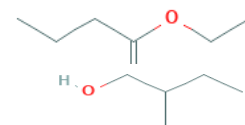
The specimens for floor morphological examination were immersed in 1M H<sub>2</sub>SO<sub>4</sub> containing gold standard concentration of inhibitors (200ppm) and the test solution for 2 h. Then, they were removed rinsed quick with acetone and dried. The evaluation turned into accomplished on a Scanning Electron Microscope[ 20].



**Fig.9a. SEM image of polished mild steel**



**Fig.9c. SEM image of mild steel after interact with PPFPE**



On close statement of the SEM photographs, the specimens immersed in the 1M H<sub>2</sub>SO<sub>4</sub> with the inhibition of PPFPE are in higher situations with smooth surfaces whilst compared with the ones of corroded difficult and coarse uneven surfaces of carbon mild metal immersed in 1M H<sub>2</sub>SO<sub>4</sub> alone. This statement indicated that corrosion charge is remarkably decreased in the presence of the inhibitors[21]. This might be due to the adsorption of inhibitor molecules on the metallic surface as a protective layer.

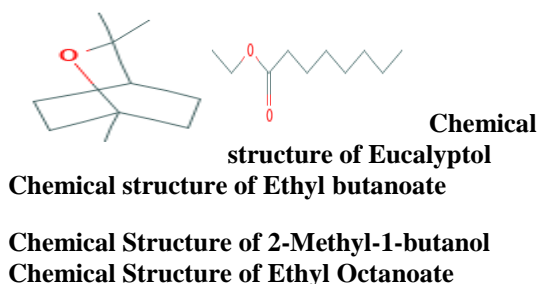
### 3.9. GCMS spectrum of PPFPE

GCMS analysed and tabulated the major constituents in *Physalis peruviana* fruit peel extract, which has shown in table .7 and the chemical structure of maximum composition has shown in Fig.10. These are responsible for the corrosion inhibition action on carbon mild steel in 1M H<sub>2</sub>SO<sub>4</sub>.

**Table.7. The Chemical constituents of *Physalis peruviana* fruit peel extract**

Name of the Compound	Molecular formula	Molecular weight	%Peak area
1-Hexanol	C <sub>6</sub> H <sub>14</sub> O	102	6.87

Eucalyptol	C <sub>10</sub> H <sub>18</sub> O	154	6.67
Ethyl butanoate	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	116	6.47
Ethyl octanoate	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	172	4.01
2-Methyl-1-butanol	C <sub>5</sub> H <sub>12</sub> O	88	3.10



**Fig. 10. Structure of the major constituents of PPFPE**

The synthesized PPFPE show a good performance due to the large size of the constituents which covers the surface and act as a protective film and thus retarding the corrosion. The adsorption of main constituents PPFPE attributed to the presences of O atoms, carboxyl groups enhances the inhibition efficiency.

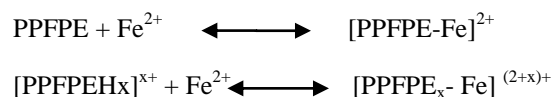
From the experimental and theoretical results the effect of PPFPE in 1M H<sub>2</sub>SO<sub>4</sub> solution can be explained as follows



The neutral inhibitor may be adsorbed on metal surface via physisorption mechanism involving the displacement of water molecules from metal surface on the basis of donor acceptor interaction between pi- electrons and vacant d-orbitals of iron.

In acidic media solution, PPFPE exist as either as neutral molecule or in the form of cation (protonated PPFPE). On the other hand, the protonated PPFPE may be adsorbed through electrostatic interactions between the positive molecules and adsorbed sulphate ions. Thus the metal

complexes of Fe<sup>2+</sup> and PPFPE or protonated PPFPE may be formed as



These complexes are adsorbed on the carbon mild steel surface to form a protective film on metal surface. It revealed that the PPFPE is found to be a mixed type inhibitor for carbon mild steel in 1M H<sub>2</sub>SO<sub>4</sub>.

#### 4. Conclusion

The inhibitor PPFPE were acts a good inhibitor for corrosion of carbon metallic in 1M H<sub>2</sub>SO<sub>4</sub> solution. Inhibition efficiency will increase with growing inhibitor concentration of PPFPE and reduce with boom in temperature. The activation power will increase with boom within the inhibitor attention. Enthalpy of activation reflects the endothermic nature of carbon moderate metal dissolution system. Entropy of activation increases with increasing inhibitor attention. growth in sickness of the gadget. Gibb's loose electricity, enthalpy and entropy of adsorption indicate that the adsorption system is spontaneous because of the poor value and the adsorption procedure became an endothermic in nature. The inhibitor molecules adsorbed at the steel surface via physical adsorption. Polarization curves indicated that the PPFPE act as combined type inhibitor in acidic solution, which the impedance facts suggest became completed through adsorption of the PPFPE extract species at the carbon mild steel surface. The adsorption of PPFPE are nicely described via Langmuir adsorption and Freundlich adsorption isotherm underneath all of the various temperatures. SEM famous the formation of a smooth floor on moderate metallic within the presence of PPFPE, because of the presence of phytochemicals constituents within the inhibitor probably because of the formation of an adsorptive



movie of electrostatic character. Further it be useful for the analysis of antimicrobial properties towards pathogens.

## 5. Acknowledgement

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