Original Article

Eugenia Jambolana Used as Corrosion Inhibitor on Mild Steel in 1N Hydrochloric Acid Medium

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ABSTRACT

The inhibition efficacy of *Eugenia Jambolana* fruit peel (EJFP) extract on mild steel in 1N Hydrochloric acid with various exposure time (24 to 360hrs) and temperature (303 to 323K) are investigated by mass loss measurements. The value of inhibition efficiency is increased with increase of inhibitor concentration and rise in temperature is suggestive of chemisorption. The adsorption of EJFP onto the mild steel surface is found to follow the Langmuir adsorption isotherm. Both kinetic (activation energy and heat energy change) as well as thermodynamics parameters (adsorption of enthalpy, entropy and Gibbs free energy) are calculated and discussed in details. The characterization of alcoholic extract of inhibitor and corrosion products formed on the metal surface is analyzed by UV, FT-IR and XRD spectral studies.

Keywords: Mild steel, corrosion, inhibition, adsorption and free energy.

INTRODUCTION

Mild steel finds many applications in industries due to its easy of availability, fabrication, low cost and good tensile strength besides various other desirable properties. It suffers from severe corrosion when it comes in contact with acid solutions during cleaning, transportation, de-scaling, storage of acids and other chemical processes etc. The heavy loss of metal[1] whenever it contact with acids can be minimized to a great extent by the use of corrosion inhibitors. Most of the corrosion inhibitors are organic compounds [2] containing sulphur or nitrogen in their chemical constituents. It was found out that this kind of compounds is chemically adsorbed on the metal surface forming barrier for mass and charge transfer and consequently decreasing the rate of corrosion. Unfortunately, most of these compounds are harmful for both human being and environments [3,4]. The known hazardous effect of most synthetic corrosion inhibitors is the motivation for the use of some natural products. The plant extracts from the natural source have [5] most important because they are environmentally acceptable, inexpensive, readily available and renewable sources of materials, and ecologically acceptable. They are rich enough source of active molecules, which have noticeably high inhibition efficiency and hence termed as “Green Inhibitors” [6]. Some investigators [7-13] have been reported the successful use of naturally occurring substances to inhibit the corrosion of metals in various environments. In our present study, we have chosen eco-friendly bio-inhibitor, a green approach to prevent environmental pollution by harmful organic chemicals. The influence of *Eugenia Jambolana* fruit peel extract on mild steel in 1N Hydrochloric acid using mass loss measurements with different time and temperature have been investigated. The alcoholic extract of inhibitor and corrosion product on Brass in the presence of bio-inhibitor is characterized by UV, IR, and XRD studies

EXPERIMENTAL DETAILS

Stock solution of *Eugenia Jambolana* fruit peel (EJFP) extract

About 3 Kg of *Eugenia Jambolana* fruit was collected from in and around Western Ghats from which the peel was removed and dried in natural air condition for 5 to10 days. Then it was grained well and finely powdered. Exactly 50g of finely powdered dried material was taken in a round bottom flask and required quantity of ethyl alcohol was added to cover the powder completely. The RBF was covered with stopper and left it for about 48 hrs. Then the resulting paste was refluxed and it was filtered. The filtrate was collected and the alcohol was removed with the distillation unit. The obtained paste was boiled with activated charcoal (about 1g) to remove hung and the pure plant extract was collected and stored.

Properties of *Eugenia Jambolana*

Eugenia Jambolana fruit and seeds of this tree have long been used in Eastern traditional medicine, and used for the treatment of diabetes. It lowering blood sugar and researchers are investigating its potential as a male contraceptive. Wine and vinegar are also made from the fruit. It has a high source in vitamin A and vitamin C. The main phytochemical constituents present in *Eugenia Jambolana* [14] fruit peel is anthocyanins, delphinidin, petunidin, malvidin-diglucosides.

Preparation of specimen for mass loss measurements

Rectangular specimens of size 5 x 2 x 2 cm were cut from a parent sheet of Mild steel. The specimens were drilled a hole at one end and numbered by punching before the use of specimen, then the samples were pickled with picking solution, washed with water, rubbed with cotton cloth and dried. After pickling the samples were mechanically polished with 1/0 to 5/0 emery sheets and degreased with trichloroethylene then kept it for some time in desicators. These samples were used for the mass loss studies.

Mass loss method

In the mass loss measurements on Mild steel in triplicate were completely immersed in 50ml of the test solution in the presence and absence of the inhibitor. The metal specimens were withdrawn from the test solutions after an hour at 303K to 323K and also measured 24 to 360 hrs at room temperature. The Mass loss was taken as the difference in weight of the specimens before and after immersion using LP 120 digital balance with sensitivity of ±1 mg. The tests were performed in triplicate to guarantee the reliability of the results and the mean value of the mass loss is reported.

From the mass loss measurements, the corrosion rate was calculated using the following relationship.

$$\text{Corrosion Rate}(\text{mmpy}) = \frac{87.6\times W}{DAT} \quad \text{-------(1)}$$

Where, mmpy = millimeter per year, W = Mass loss (mg), D = Density (gm/cm^3), A = Area of specimen (cm^2), T = time in hours.

The inhibition efficiency (%IE) and degree of surface coverage (θ) were calculated using the following equations.

$$\%\ IE = \frac{W_1 - W_2}{W_1}\times 100 \quad \text{--------------------(2)}$$

$$\theta = \frac{W_1 - W_2}{W_1} \quad \text{--------------------(3)}$$

Where W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor respectively.

RESULTS & DISCUSSION

The values of corrosion rate and the percentage of inhibition efficiency is derived from mass loss measurements on mild steel in the presence and absence of EJFP extract in 1N Hydrochloric acid at various exposure time (24 to 360hrs) are shown in Table-1. The observed values are clearly indicates that in the absence of inhibitor the mass loss increased from 154 to 1300mgs from 24 to 360hrs exposure time. In the presence of EJFP extract the value of corrosion rate decreased from 3.5757 to 0.1625mmpy (24hrs) and 2.0123 to 0.5557 mmpy (360hrs) with increase of inhibitor concentration from 0 to 1000ppm. The maximum of 96.75% inhibition efficiency even after 24hrs exposure is mainly due to the phytochemical constituents such as Anthocyanins, delphinidin, petunidin, malvidin-diglucosides in the inhibitor molecule is adsorbed on the metal surface and shield completely to reduce the further dissolution of the electrode.

The inhibition efficiency of EJFP extract on mild steel in 1N Hydrochloric acid at temperature ranges from 303 to 323K is shown in Table-2. In the absence of inhibitor the value of mass loss increased from 372 to 572mgs and corrosion rate increased from 207.29 to 318.75mmpy at 303 to 323K. In the presence of inhibitor the value of corrosion rate decreased from 207.29 to 27.30mmpy and 318.75 to 30.09mmpy with increase of inhibitor concentration from 0 to 1000ppm at 303 and 323K. The maximum of 87, 89 and 90% inhibition efficiency is achieved at 303, 313 and 323K respectively. This is due to the adsorption of the active molecules present in the inhibitor molecules on the metal surface is more preferential than desorption process at high temperature. The value of inhibition efficiency is increased with rise in temperature is suggestive of chemisorption.

Effect of Temperature

The effect of temperature on the corrosion of mild steel in the presence and absence of EJFP extract was investigated using the Arrhenius equation.

$$CR = A\exp(-Ea/RT) \quad \text{--------------------(4)}$$

$$\log(CR2/CR1)=Ea/2.303R(1/T1-1/T2) \quad \text{----(5)}$$

where CR_1 and CR_2 are the corrosion rate at the temperature T_1 (303K) and T_2 (323K) respectively. The values of Corrosion rate obtained from the mass loss measurements are substituted in Equation (4) to obtain the values of Activation energy (E_a). The observed values of activation energy (E_a) are ranged from (03.9537 to 14.7981kJ/mol) for mild steel in 1N Hydrochloric acid environment containing various concentration of inhibitor. The average value of E_a obtained from the blank (17.5073kJ/mol) is higher than that of the values obtained in the presence various concentrations of EJFP extract suggests the adsorption takes place through chemically [15].

The heat of adsorption on the surface of mild steel in the presence of EJFP in 1N HCl environment is calculated by the following equation.

$$Q_{ads} = 2.303R\,[\log(\theta_2/1\text{-}\theta_2)\text{-}\log(\theta_1/1\text{-}\theta_1)]\,(T_2T_1/T_2\text{-}T_1) \quad \text{----(6)}$$

Where R is the gas constant, $\theta_1$and θ_2 are the degree of surface coverage at temperatures T_1 and T_2 , respectively. The calculated values of Q_{ads} are (Table-3) are ranged from 22.853 to 15.320 kJ/mol. The positive values [16] are indicated that the adsorption of EJFP extract on mild steel is endothermic.

Other kinetics parameters such as enthalpy (ΔH) and entropy (ΔS) of activation of corrosion process may be evaluated from the effect of temperature. An alternative formulation of Arrhenius equation also called transition state (7).

$$CR= (RT/Nh)\exp(\Delta S/R)\exp(-\Delta H/RT) \quad \text{------------(7)}$$

Where h is the Planck's constant, N the Avogadro's number, R is the universal gas constant, ΔS the entropy of activation and ΔH the enthalpy of activation. A plot of log (CR/T) vs. 1000/T should give a straight line (Fig.1) with a slope of (−ΔH/R) and an intercept of [log(R/Nh)) + (ΔS/R)], from which the values of ΔS and ΔH were calculated and listed in Table-3. The positive sign of the enthalpy of activation reflects the endothermic nature of mild steel dissolution process. The increase of ΔS is generally [17] interpreted by increase in disorder taking place on going from reactants to the activated complex.

The observed data are tested graphically for fitting Langmuir isotherms on mild surface in the presence of EJFP inhibitor. The Langmuir adsorption isotherm can be expressed by the following equation

$$\log C/ = \log C - \log K \quad \text{------------------ (7)}$$

Here is the surface coverage, C is the concentration of the inhibitor and K is an adsorption coefficient. By plotting values of logC/ versus logC, linear plots are generated (Fig.2) and conforming that the experimental data fitted with the Langmuir adsorption isotherm for the adsorption of EJFP extract on mild steel surface mean that there is no interaction between the adsorbed species (i.e; adsorbate and adsorbent) in hydrochloric acid environment.

The free energy of adsorption (ΔG_{ads}) of EJFP extract on mild steel in 1N HCl are calculated by using equation 9

$$\Delta G_{ads} = -2.303\,RT\log(55.5\,K) \text{------------------ (9)}$$

Where R is the gas constant, T is the temperature, K is the equilibrium constant of adsorption of EJFP extract on the surface of mild steel. The values of K obtained from Langmuir adsorption isotherm are substituted into Equation 9 and the calculated values of ΔG_{ads} are recorded in Tables 4. The negative value ensures that the adsorption of inhibitor on the surface of mild steel is spontaneous and stable one [18].

Morphology Studies

UV spectrum

Figure 3 (a) & (b) shows that the UV visible spectrum of the EJFP extract and the corrosion product on the surface of Mild steel in the presence of EJFP extract in 1Hydrochloric acid. In the EJFP inhibitor, the UV absorption maximum of around 230nm and 445nm were obtained. However in the presence of inhibitor, one peak was shifted to lower wavelength region (352nm). The change of adsorption band from the above spectrum revealed that the strong co-ordination between the active group present in the inhibitor molecules and the metal surface.

FTIR- studies

The Figures 4 and 5 reflects that the FT-IR spectrum of ethanolic extract of EJFP and the corrosion product on Mild steel respectively. The observed stretching frequency and the corresponding band assignment were given in Table 5. These shifting frequencies suggested that the formation of barrier film on the metal surface which may confirm the co-ordination between inhibitor molecule and metal surface.

XRD spectrum

The Corrosion product scraped from the mild steel surface after immersion was examined by XRD studies (Fig:6). It may be assigned mainly the combination with the rich amount of Fe_2O_3 and $FeCl_3$. This result reveals that the co-ordination between the active molecules in the inhibitor and Fe in mild steel.

CONCLUSION

Results obtained from the experimental data shows EJFP as effective inhibitor for the corrosion of mild steel in 1N Hydrochloric acid. The inhibition efficiency of EJFP is increased with increase of inhibitor concentration and maximum of 95 and 75% even after 24 and 360hrs exposure time. In temperature studies the value of inhibition efficiency is increased with rise in temperature is suggestive of chemisorption. The adsorption of EJFP extract on mild steel surface was found to obey with Langmuir adsorption isotherm. The adsorption process is spontaneous, endothermic and accompanied with a increase in entropy of the system from thermodynamic point of view. The introduction of EJFP extract into 1N Hydrochloric acid solution results in the formation of a protective film on the mild steel surface to effectively protects steel from corrosion. *Eugenia Jambolana* ethanolic extract is a as effective corrosion inhibitor and can be replace toxic chemicals

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Table 1. Corrosion behavior of mild steel in 1N HCl containing various concentration of EJFP extract after 24 to 360hrs exposure time

Exposure time (hrs)	Concentration of inhibitor (ppm)	Mass loss (mgs)	Corrosion rate (mmpy)	Surface coverage (θ)
24	0	154	3.5757	---
	10	22	0.5108	0.85
	50	17	0.3947	0.88
	100	14	0.3251	0.90
	500	5	0.1161	0.96
	1000	7	0.1625	0.95
72	0	402	3.1113	---
	10	267	2.0665	0.33
	50	264	2.0433	0.34
	100	210	1.6253	0.47
	500	175	1.3544	0.56
	1000	232	1.7956	0.42
120	0	504	2.3405	---
	10	416	1.9318	0.17
	50	365	1.6950	0.27
	100	343	1.5928	0.31
	500	261	1.2120	0.48
	1000	339	1.5742	0.32
168	0	693	2.2987	---
	10	435	1.4429	0.37
	50	398	1.3202	0.42
	100	368	1.2206	0.46
	500	317	1.0515	0.54
	1000	347	1.1510	0.49
264	0	1024	2.1615	---
	10	415	0.8760	0.59
	50	387	0.8169	0.62
	100	357	0.7536	0.65
	500	280	0.5910	0.73
	1000	331	0.6987	0.67
360	0	1300	2.0123	---
	10	475	0.7353	0.63
	50	400	0.6192	0.69
	100	370	0.5727	0.71
	500	336	0.5201	0.74
	1000	359	0.5557	0.72

Table 2. Corrosion behavior of Mild steel in 1N Hydrochloric acid containing various concentration of EJFP extract at 303 to 323K.

Temperature (K)	Concentration of inhibitor (ppm)	Mass loss (mgs)	Corrosion rate (mmpy)	Surface coverage (θ)
303	0	372	207.297	---
	10	189	105.320	0.49
	50	125	69.656	0.66
	100	86	47.923	0.76
	500	57	31.763	0.84
	1000	49	27.305	0.87
313	0	502	279.740	--
	10	201	112.007	0.60
	50	156	86.931	0.69
	100	109	60.740	0.78
	500	73	40.679	0.85
	1000	52	28.977	0.89
323	0	572	318.748	---
	10	212	118.137	0.63
	50	161	89.717	0.72
	100	117	65.198	0.79
	500	82	45.694	0.85
	1000	54	30.091	0.90

Table 3. Thermodynamics and activation parameters for mild steel in 1N HCl in the absence and in the presence of EJFP extract.

Sr.no	Conc. of inhibitor(ppm)	E_a ($kJmol^{-1}$)	Q_{ads} ($kJmol^{-1}$)	ΔH ($kJ\ mol^{-1}$)	ΔS ($Jk^{-1}mol^{-1}$)
1.	0	17.507	---	6.5019	8.5795
2.	10	04.672	22.8530	0.9007	11.3281
3.	50	10.298	10.4296	3.3768	10.4412
4.	100	12.525	06.3576	4.3391	10.2044
5.	500	14.798	03.1895	5.3188	9.97861
6.	1000	03.953	15.3202	0.5910	12.0980

Table 4. Langmuir adsorption parameters for the adsorption of EJFP extract on mild steel in 1N Hydrochloric acid

Adsorption Isotherms	Temperature (Kelvin)	Slope	K	R^2	ΔG_{ads} kJ/mol
	303	0.87906	0.3983	0.9981	-2.3194
Langmuir	313	0.91215	0.3038	0.9997	-3.1001
	323	0.92212	0.2728	0.9998	-3.4885

Table 5. FT- IR spectrum of the corrosion product on Mild steel in the presence of ethanolic extract of EJFP as an inhibitor in Acid environment

Frequency(cm^{-1}) Pure extract of EJFP	Frequency(cm^{-1}) Extract adsorbed on mild steel	Band Assignment
3106.05	3359.77	-OH in alcohol
1681.81	1726.17	C-O in carbonyl
1404.08	1448.44	C=C in aromatic ring
1274.56	1286.43	C-O in ether
898.77	921.91	C-H bending in alkene
----	649.97	C-Cl in chloroalkane

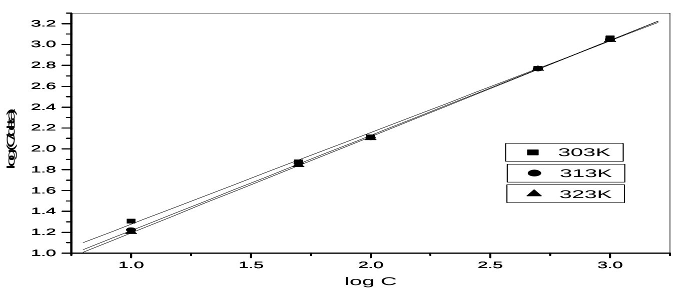

Figure.1. Langmuir isotherm for the adsorption of EJFP inhibitor on mild steel in 1N Hydrochloric acid.

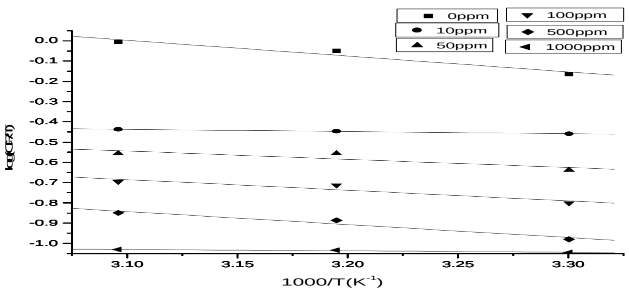

Figure.2. The relation between log(CR/T) and 1/T for different concentrations of EJFP extract on mild steel in 1N Hydrochloric acid.

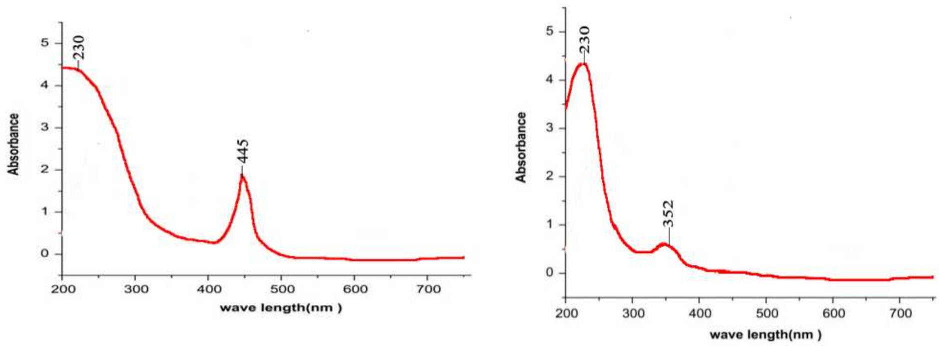

Figure.3. UV spectrum of (a) ethanolic extract of EJFP, (b) the corrosion product on mild steel in 1N HCl in the presence of EJFP extract

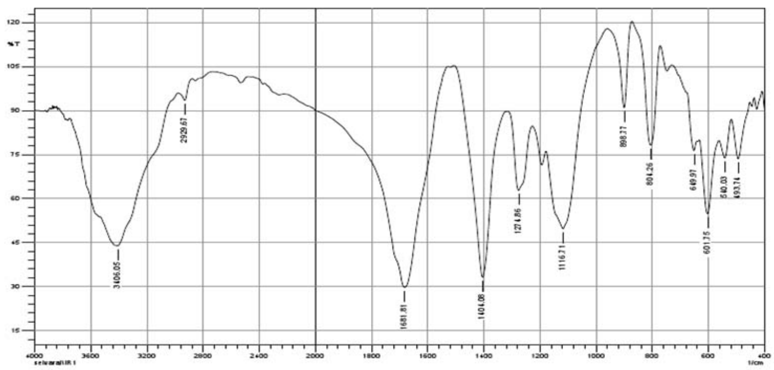

Figure.4. FT-IR spectrum of ethanolic extact of *Eugenia Jambolana fruit* peel.

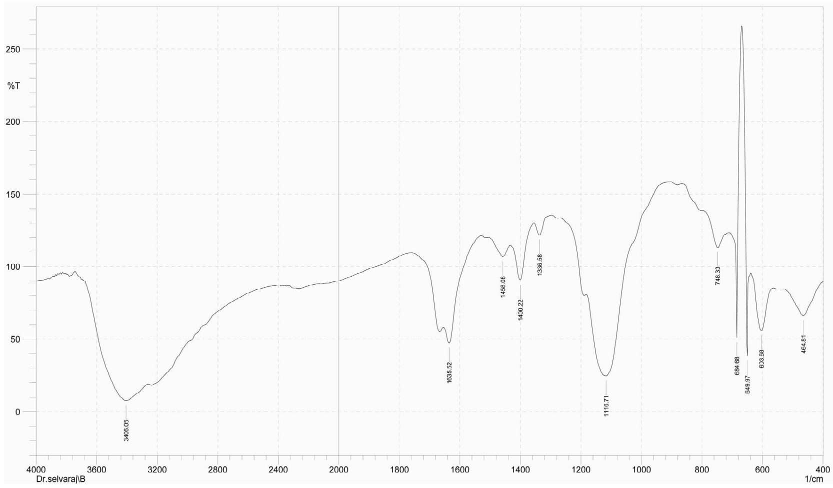

Figure.5. FT-IR spectrum for the corrosion product on mild steel in the presence of EJFP extract with 1N Hydrochloric acid

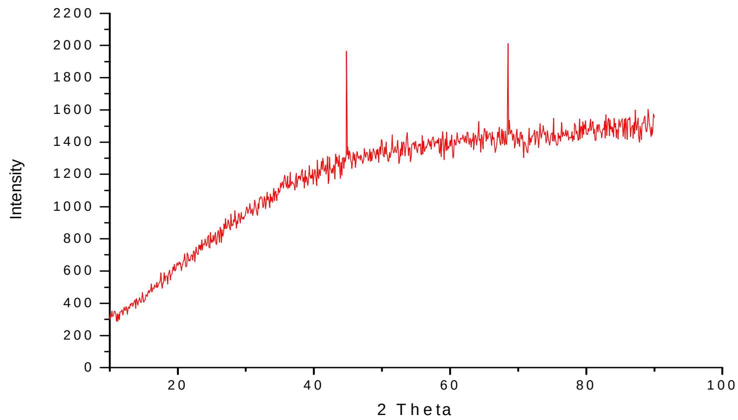

Figure.6. XRD spectrum of the corrosion product on mild steel surface in the presence of EJFP extract in 1N Hydrochloric acid.