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Experimental and theoretical investigation of *Rosmarinus officinalis* leaves extracts as the corrosion inhibitor for mild steel in H_3PO_4 solution; synergistic effect

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ABSTRACT

The inhibition efficiency of Rosmarinus officinalis leaves extract (ROE) on the corroded mild steel in 1N Phosphoric acid has been investigated by the weight loss method and Potentiodynamic polarization methods at 303K-333K. The concentration of inhibitor increased with decreased in the corrosion rate compared to blank, it was also found that the inhibition efficiency increased synergistically in the presence of Potassium iodide. A Potentiodynamic polarization method shows that the studied inhibitor is the mixed type. The adsorption of inhibitor on mild steel surface has been found to obey's Temkin's, Frumkin, adsorption isotherm. Thermodynamic parameters reveal that the spontaneous process and exothermic in nature. The Surface morphology on the mild steel surface analyzed by FT- IR and SEM analysis. The electronic properties such as E_{HOMO}, E_{LUMO}, energy gap orbital's using Density Functional Theory at the B$_3$LYP/6-31G $_{++}$ (d, p) basis set with the inhibiting action of Rosmarinus Officinalis. Quantum chemical calculations confirmed the adsorption of the molecule on the surface.

Keywords: *Rosmarinus Officinalis*; Synergism; Adsorption; Thermodynamic Parameters; Density Functional Theory (DFT);

INTRODUCTION

Corrosion inhibitors are usually used in industry to decrease the corrosion rate of metals and alloys in making contact with aggressive environment. The majority of corrosion inhibitors is artificial chemicals, and very dangerous to the surroundings. Therefore, it is necessary to develop environmentally protected inhibitors. The recent trend is towards Eco-friendly inhibitors the majority of the usual products is non-hazardous ecological and convenient. Thus, recent researchers are focused on usual product as the corrosion inhibitor [1-3].

The improvement of the inhibition effectiveness of organic compound in the presence of a few "anions" mainly halide ions, have been accounted with us and other authors were recognized for a synergistic effect [4]. Raja *et al* were investigated to the naturally occurring substances to inhibit the metal surface in acidic and alkaline medium and the successfully reported to some plants extract's acts as a good inhibitor for some metal like Aluminium, mild steel, and Zinc. These parameters will supply insights keen on the mechanism of the interaction of the extraction mechanism with mild steel surface [5-6].In the present study is aimed at investigated the inhibitive and adsorption properties ROE extract for mild steel in 1N phosphoric acid. It is to discover the obvious, going on cheap and environmentally protected substance that could be used for inhibiting the corrosion of mild steel. The use of such product will establish, simultaneously, the economic and environmental goals [7-8].

MATERIALS AND METHODS

2.1. Materials

The Mild steel specimens (Fe-99.686, Ni-0.01, Mo-0.017, Cr-0.043, S-0.014, P-0.008, Si-0.005, Mn-0.196 and C-0.017%). Rectangular samples of area 5 cm x 1cm have been cut from a large sheet of mild steel. The mild steel specimens were abraded to mirror the finish, and let a hole on the corner. The papers ranging from 110 to 410-grade sand. They decreased with trichloroethylene specimens be dehydrated and stored in desiccators for further uses.

2.2. Preparation of plant extract

Water extract of (ROE) was prepared from the aerial part of a plant collected and dried in air and then ground. 50g of powder of ROE to soxhelt extraction using methanol (95%), the solvent has been removed by boiling at a constant temperature at 40^oC in a vacuum evaporator, finally the residue of ROE was collected

2.3. Weight loss methods

The weight loss measurements of the Mild steel specimens are completely immersed in the test solution of 1N H_3PO_4 with and without different concentration of ROE with the help of PTFE threads and a glass rod in 100ml beaker. The specimens were removed 3 hours revelation time, cleaned with water to eliminate any corrosion products and cleaned with acetone. After that, they were dried as well as reweighed. Mass loss capacity was carried out in 1N phosphoric acid with ROE in the concentration of 0.1mgs to 0.5mgs as inhibitor and the temperature between 303K, 313K, 323K, and 333K.

2.4. Potentiodynamic polarization

The polarization measurement has been taken by the assist of three electrode system working electrode as mild steel specimen of 5cm x 1cm. An area which was bare and the rest being covered with red lacquer, a rectangular pit foil as the counter electrode and the reference electrode as standard calomel electrode. A time period of 10-15 minutes was given for every testing to attain the steady state open the circuit potential. The polarization agreed from a cathodic potential of -800 MV to an anodic potential -200mV at a sweep rate of 1mV.

$$\text{IE}\ (\%) = \frac{\text{Icorr} - \text{I}{*}\text{corr}}{\text{ICorr}} \times 100 \text{ ------------------ } \{1\}$$

Where I_{corr} and I^*_{corr} are corrosion current in the absence and presence of an inhibitor.

2.5. Computational methods

The Density Functional Theory is one of the most significant theoretical representations and used to investigate the characteristics of the inhibitor/surface mechanism. The DFT method of B_3LYP version uses three parameters functional (B_3), combination of HF with DFT exchange conditions associated with the accurate correlation functional of Lee, Yang and Parr (LYP) was used to carry out Quantum mechanics calculations. The optimization, geometry structure of vibration analysis of the inhibitor was carried out the Gaussian 09 software package of $B_3LYP/6\text{-}31G_{++}$ (d, p) level of theory.

RESULTS AND DISCUSSION

3.1. Weight loss method

For weight loss experiments, mild steel specimens were immersed in 1N H_3PO_4 solution (100ml) for an optimized time period (3 hours). An effect observed and analyzed by comparing the data obtained without and with different concentration of ROE. Corrosion Rate was calculated using the following equation

$$\text{CR} = \frac{87.6 \times \text{W}}{\rho \times \text{A} \times \text{T}} \text{ -------------------------- } \{2\}$$

Where, W = weight loss in mg, ρ = density (7.51 g/cm^3 for mild steel) of material used, A = area in cm^2 and t = exposure time in hours.

$$\text{IE (\%)} = \frac{\text{Wu}-\text{Wi}}{\text{Wu}} \times 100 \text{ ---------------------- } \{3\}$$

$$\Theta = \frac{\text{Wu}-\text{Wi}}{\text{Wu}} \text{ ---------------------------- } \{4\}$$

Where Wu and W_i are the corrosion rates of mild steel in the absence and presence of inhibitor correspondingly at the similar temperature. Table 1 shows the increasing value of inhibition efficiency with an increase in concentration of inhibitors and decreased the temperature from 303K to 333K in 1N phosphoric acid shown in Fig.1.

Table 1: Corrosion performance of the mild steel in 1N phosphoric acid with ROE at various temperatures (303K -333K)

S.no	Conc. (mgs)	303K CR (mmpy)	I.E(%)	313K CR (mmpy)	I.E (%)	333K CR (mmpy)	I.E (%)	353K CR (mmpy)	I.E (%)
1	Blank	62.6496		113.8623		143.2268		293.1602	
2	0.1	33.3543	46.92	45.5346	68.59	61.5033	56.63	158.6053	46.26
3	0.2	28.3229	54.23	35.4569	74.32	46.1248	68.23	140.9456	52.16
4	0.3	24.6822	56.24	30.3547	87.02	38.7786	73.49	98.3385	66.28
5	0.4	20.2655	58.96	22.5142	83.44	32.1678	77.92	85.4256	71.61
6	0.5	19.3654	65.35	18.5369	86.39	28.8326	80.42	64.6841	78.45

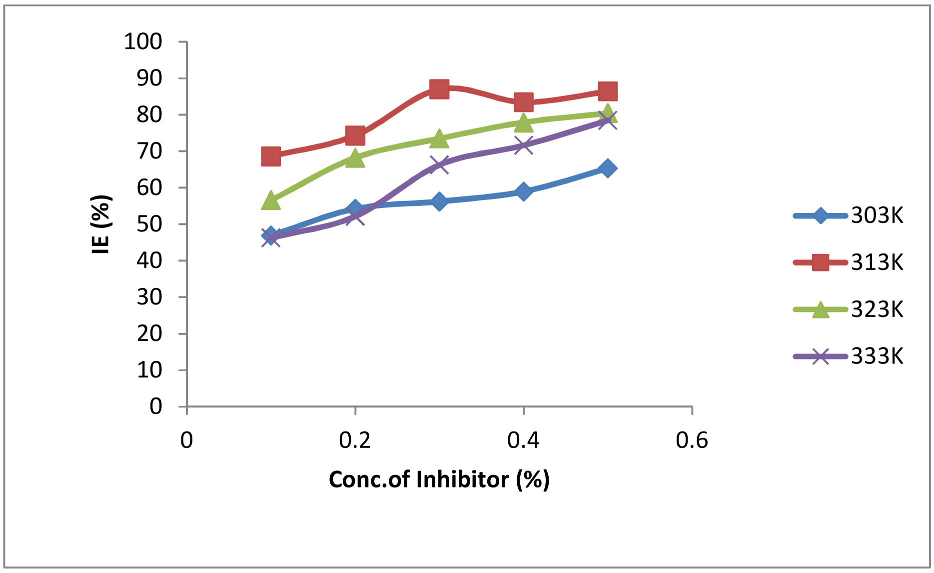


Figure 1: Corrosion behaviour of mild steel in 1N phosphoric acid with ROE at various temperatures (303K -333K)

3.2. Synergistic effect

It was reported that the addition of halides to the corrosion system along with inhibitor, significantly diminishes the corrosion of the metal. So in the present study the synergistic effect of KI was studied against corrosion on mild steel in H_3PO_4. The synergistic factor S was calculated by the equation

$S= (1-I_{1+2}) / (1-I'_{1+2})$

Where $[I_{(1+2)} = I_1 + I_2]$ I_1 is the inhibitor efficiency of the potassium iodide. I_2 is the inhibitor efficiency of the Rosmarinus officinalis. I' is measured inhibitor efficiency for ROE with KI. The ROE solution was added 10^{-2} M KI indicates that increased the inhibitor efficiency due to the synergistic effect. Table 2 shows that the maximum value of inhibitor efficiency of ROE in the presence of KI was 95.79% at 0.5 % ROE +10^{-2} M KI.

Table 2: Synergistic effects of KI

Temp.(K)	**Cons / of the inhibitor (%)**	**CR(mmpy)**	**IE(%)**
303K	Blank	62.6496	
	0.1	33.3543	46.92
	0.2	28.3229	54.23
	0.3	24.6822	56.24
	0.4	20.2655	58.96
	0.5	19.3654	65.35
Synergism Consideration of KI			
Cons / of ROE +KI (%)	**CR (mmpy)**	**IE(%)**	**S**
Blank+x10^{-2} M	18.3352	60.99	
0.1x10^{-2}M	16.5501	71.76	2.525
0.2x10^{-2}M	14.4584	77.76	1.4952
0.3x10^{-2}M	12.4183	86.9	1.353
0.4x10^{-2}M	0.9834	92.2	1.3042
0.5x10^{-2}M	0.8412	95.79	1.3222

3.3. Potentiodynamic polarization curves

Table 3 shows the addition of ROE shows that the fewer negative values of corrosion potential shifts. The Tafel slopes value of anodic and cathodic, (ba and bc) is slightly altered, corresponding to the behaviour reflects the plant's extract's capability of inhibiting the corrosion of mild steel in 1N H_3PO_4 change solution (Fig.2.). Adsorption molecules on both anode and cathode are consequently, the extract act through the mixed type inhibition [9].

Table 3: Potentiodynamic polarization parameters for a mild steel in 1N H_3PO_4 with ROE

				Tafel Slope mV/D		
S.NO	**Conc.of ROE(mgs)**	**Ecorr (V)**	**Icorr(mA/cm^2)**	**ba**	**bc**	**IE(%)**
1	blank	-0.51	3.57	78	122	-
2	0.1	-0.515	1.46	75	127	59.1
3	0.2	-0.497	0.97	76	128	72.8
4	0.3	-0.495	0.76	75	127	78.71
5	0.4	-0.498	0.55	77	129	84.5
6	0.5	-0.509	0.34	75	129	90.4

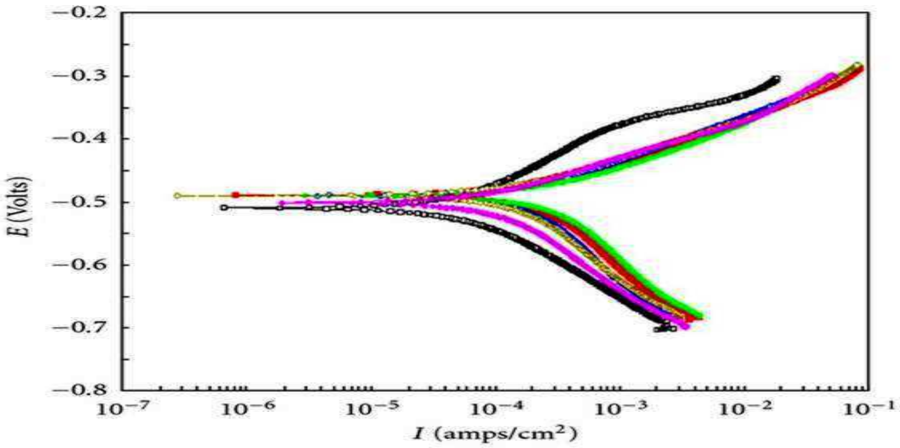


Figure 2: Potentiodynamic polarization for mild steel in 1N H_3PO_4 containing various concentrations of the ROE

3.4. Thermodynamic parameters

Table 4 shows that the values of energy of activation (Ea) for mild steel in 1N phosphoric acid with and without ROE from 303K to 333K.

$$\mathrm{Log}\left(\frac{P2}{P1}\right) = \mathrm{Ea}/2.303\mathrm{R}\left[\frac{1}{T1} - \frac{1}{T2}\right] \text{ ------------------------ } \{5\}$$

Hence P_1 and P_2 are corrosion rates of mild steel at the temperatures T_1 (303K) and T_2 (313K) respectively.

Heat adsorption ($Q_{(ads)}$) can be calculated by the equation.

$$Q\ (ads) = 2.303R\log\left[\frac{\theta2}{1-\theta2} - \frac{\theta1}{1-\theta1}\right] \times \frac{T1 \times T2}{T2-T1} \qquad \text{-------------}\ \{6\}$$

Hence θ_1 and θ_2 are surface coverage of the inhibitor at the temperatures T_1 (303K) and T_2 (313K) by the different additives.

The free energy of adsorption [$\Delta G_{(ads)}$] was calculated from the following equation

$\Delta G_{(ads)}$ = -RT ln (55.5K) ----------------------- {7}

And K is given by
K=θ /C (1- θ) -------------------------------- {8}

Where θ is surface coverage on the metal surface, C is the concentration of ROE inhibitor in mole/lit and K is the equilibrium constant [10].

The enthalpy of adsorption (ΔH) by the equation
ΔH=Ea-RT ------------------------------- {9}

The entropy of adsorption (ΔS) was calculated using the equation
ΔG=ΔH-TΔS ------------------------------ {10}

The values of Ea>80 KJ/mol indicate chemical adsorption whereas Ea <80 KJ/mol infer physical adsorption. The activation energy values support the fact that ROE is physisorption. The values of $\Delta G_{(ads)}$ around -20 KJ /Mol or lower are consistent with the electrostatic interaction between organically charged molecules and charged metal (physisorption). The negative value of free energy of adsorption (ΔG_{ads}) for ROE point outs that the adsorption of the metal surface was a spontaneous process and adsorption could be physisorption. The enthalpy of adsorption (-ΔH) indicates that the exothermic in nature. The adsorption of entropy (+ΔS) point out that reaction was spontaneous process.

Table 4: Thermodynamic parameter for a mild steel in 1N phosphoric acid with ROE at various temperatures (303K -333K)

S.no	Conc. (mgs)	Ea KJ/mole	ΔH KJ/mole	ΔS KJ/mole	Q (abs) KJ/mole	ΔG_{ads} KJ/mole			
						303K	313K	323K	333K
1	Blank	47.09	-2.42	-	-	-	-	-	-
2	0.1	24.54	-2.49	0.0432	33	-15.6	-18.47	-17.68	-17.07
3	0.2	18.68	-2.5	0.0399	61.73	-14.59	-17.4	-17.16	-15.81
4	0.3	16.31	-2.502	0.0372	123.05	-13.78	-18.53	-17.84	-10.91
5	0.4	8.29	-2.51	0.0357	200.67	-13.33	-17.04	-17.4	-16.21
6	0.5	3.44	-2.515	0.0356	401.59	-13.32	-17.06	-16.44	-16.53

3.5. Adsorption isotherms

The adsorption isotherms are used to study the mode of adsorption and the characteristic of adsorption of inhibitor on the mild steel surface. In the present study the Temkin and Frumkin isotherm. The value of surface coverage calculated from weight loss measurements shows in Table-1.The surface coverage value for the ROE fitted into Temkin , Frumkin adsorption model which has the form

Exp (-2 α θ) = KC

Frumkin adsorption isotherm can be expressed by the following equation.

Log [C x (θ/ (1-θ)] = 2.303 log K + 2 α θ

Where α is molecules interaction parameter, θ is surface coverage, K is equilibrium constant C is the concentration of ROE K is related to the free energy of activation from the equation -7. An organic molecules having polar groups are adsorbed on the metal surface may interact by mutual repulsion and attraction and this may be advocated as the reason for the departure of the slope values from unity. The number of active sites of the surface occupied by one molecules of the inhibitor is given by the value of (1/y). A straight line was obtained when the surface coverage was plotted against log C for the inhibitor are show in Fig-3.The plot of IE against log C are shown in Fig -4.The linearly shows that the adsorption of the inhibitor on the mild steel surfaces follows Frumkin, Temkin isotherm models. It is found to provide the best description of the adsorption behaviour with the regression coefficient R^2 almost unity (0.9) as shown in Fig.3, Fig.4 [11].

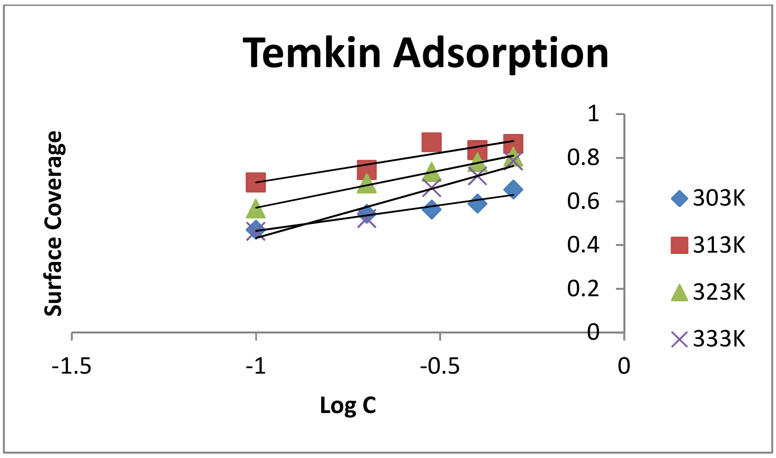


Figure 3: Tempkin's adsorption isotherm for of mild steel in 1N H_3PO_4 with ROE

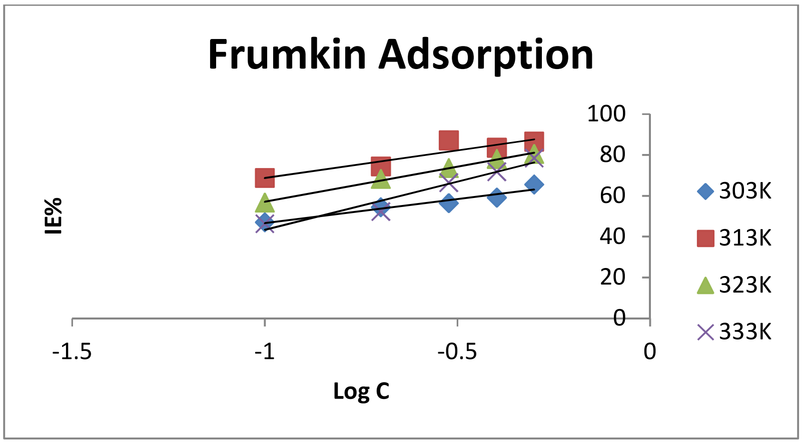


Figure 4: Frumkin adsorption isotherms for of mild steel in 1N H_3PO_4 with ROE

3.6. Computational details

The Density Functional Theory (DFT) is analyzed for the inhibitor/surface interaction, The experimental data in Figure.5(a-g), 6(a-g) and 7(a-g) show the optimized geometry, E_{HOMO} and E_{LUMO} density distribution and total energy. The electrostatic potential for ROE molecules was obtained using the DFT at $B_3LYP/6\text{-}31G_{++}$ (d, p) level.

The Quantum chemical parameters obtained from the calculations which were accountable for the efficiency of inhibitors, such as the highest occupied molecular orbital energy. The lowest unoccupied molecular orbital, energy gap (ΔE), dipole moment (μ), and total energy are calculated in Table 5. The inhibition effect of the inhibitor compound is usually ascribed to the adsorption of the molecule on the metal surface. The adsorption strength can be either physisorption or chemisorptions. The energy of the highest occupied molecular orbital E_{HOMO} measures the tendency towards the donation of an electron by a molecule. Increasing values of E_{HOMO} make adsorption possible consequently enhance the inhibition efficiency by influencing its transfer to the adsorbed layer. The highest E_{HOMO} value of ROE indicates good inhibition efficiency [12].

Table 5: Quantum chemical parameters for ROE

S.No	Quantum Parameters	C1	C2	C3
1	E_{HOMO}	-0.27157au	-0.32299au	-0.29424au
2	E_{LUMO}	-0.05655au	-0.05355au	-0.04421au
3	ΔE	-0.21502au	-0.26944au	-0.25003au
4	Dipole movement(Debye)	5.9858(debye)	8.5516(debye)	4.3486(debye)
5	Total energy(TE)	0.08314 au	-0.15922au	0.159364au

The energy gap $\Delta E = E_{LUMO} - E_{HOMO}$ plays a significant role in the reactivity of the inhibitor molecule towards the adsorption on the metal surface. The inhibition efficiency value was found to increase with the decrease in the ΔE value [13-14]. The total energy calculated by the quantum chemical methods is also beneficial parameters. The total energy (TE) is composed of the internal, potential and kinetic energy.

The total energy of ROE is a unique function of the charge density. In addition to charge, transfer one might also take into consideration the simple electrostatic potential that might influence the ability of the inhibitor to interact with the metal surface. The molecular electrostatic potential surface for each molecule presented in Fig.5g, 6g, and 7g. It will be useful to examine the E_{HOMO} and E_{LUMO} for these studied molecules because the relative classifying of occupied and virtual orbital gives a reasonable size of excitation properties and also the ability of electron-hole transport. This is fairly good agreement with the theoretical and experimental observation, suggesting that ROE molecules have high inhibition efficiency.

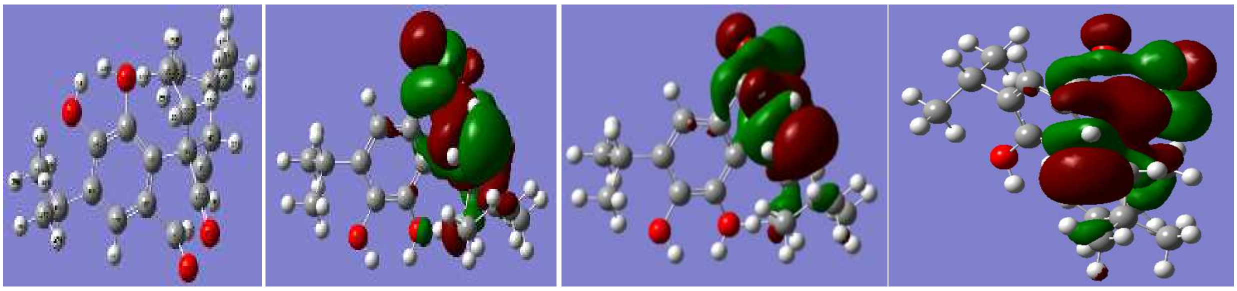


Fig 5a **Fig 5b** **Fig 5c** **Fig 5d**

Figure 5: a) Optimize structure of carnosol (C1) b) HOMO c) LUMO d) HOMO-LUMO

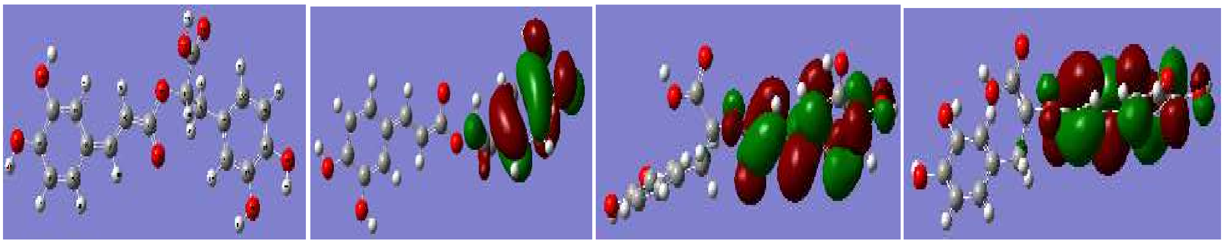


Fig 6a **Fig 6b** **Fig 6c** **Fig 6d**

Figure 6: a) Optimize structure of Ros-marinic acid (C2) b) HOMO c) LUMO d) HOMO-LUMO

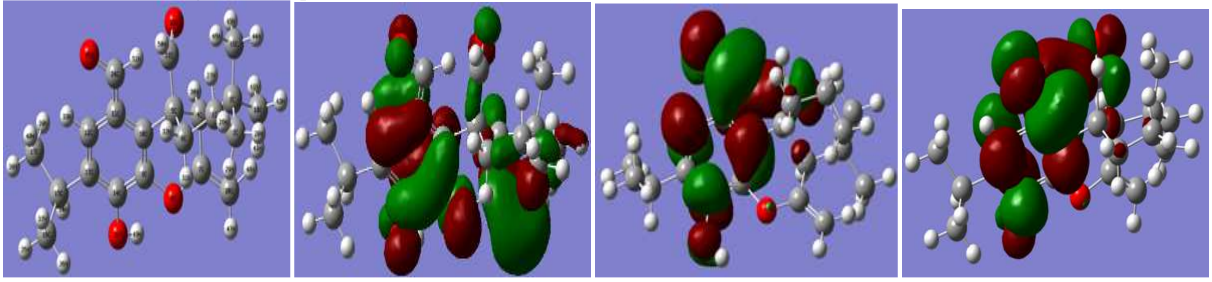


Fig 7a **Fig 7b** **Fig 7c** **Fig 7d**

Figure 7: a) Optimize structure of carnosic acid (C3) b) HOMO c) LUMO d) HOMO-LUMO

3.7. FT-IR Analysis

The broad peaks between 3200cm^{-1} to 3600cm^{-1} assigned to the presence of superficial absorbed water, (stretching mode of an OH). The peak appeared at 3420cm^{-1} corresponds to –OH group. The peaks at 2989, 2887& 2819 cm^{-1} correspond to stretching vibration of aliphatic and aromatic C-H. The peaks at 1753, 1681, 1489, 1309 & 1188cm^{-1} correspond to stretching vibration of C=O; aromatic substituted C=C (Aromatic ring), stretching vibration of the ether linkage (C-O) and stretching vibration of C-O. Shifting of the stretching frequency of C-O shows that there is a shifting of the electron cloud density of O atoms to co-ordinate with the metal surface to form metal plant extract complex. Then the peaks between 400 and 700 cm^{-1} are primarily due to Fe_2O_3 Fig.8. which indicates that the corrosion product contains ROE. FT-IR spectra revealed the physisorption of the studied extract on metal surface.

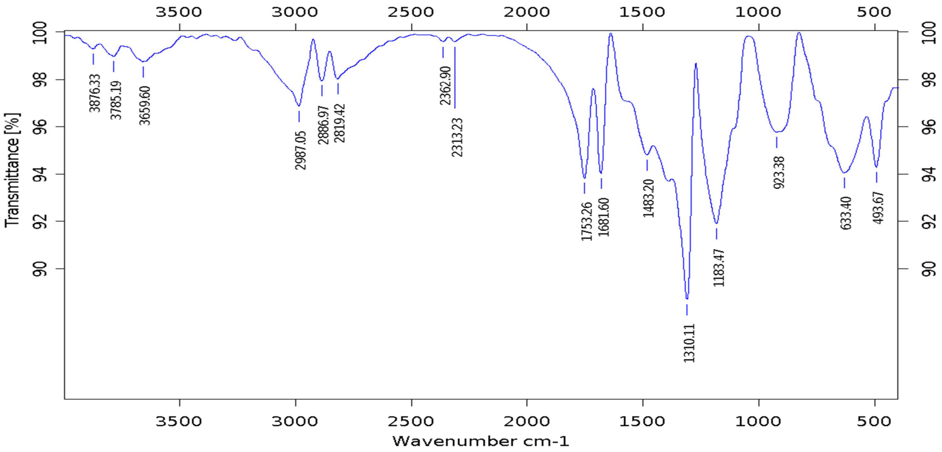
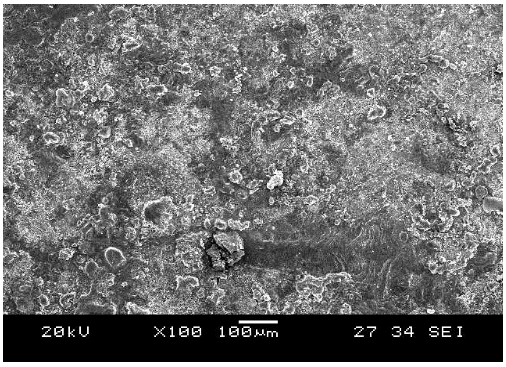


Figure 8: FT-IR spectrum of Mild steel in 1N Phosphoric acid with ROE

3.8. SEM analysis

SEM images were taken in order to study the changes of mild steel in 1N H_3PO_4 with and without of the ROE (Fig.9. and Fig.10). The micrographs of the mild steel samples after exposure to the corrosive environments shows different morphologies both portrayed severely damaged surface due to the formation of corrosion products. No pits and cracks were observed in the micrographs after immersion of inhibitors in the corrosive media expects polishing lines. The metal surface was homogeneously enclosed with the inhibitor molecules accordingly forming a protecting film.



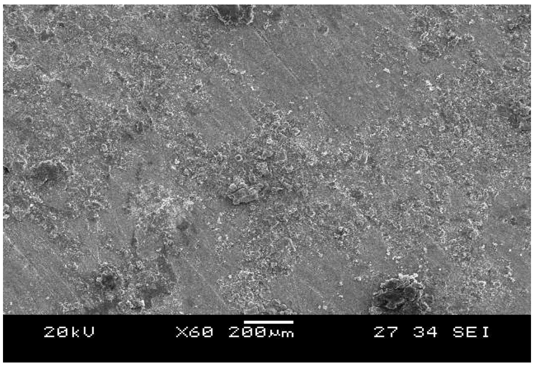


Figure 9: SEM analysis of Mild steel in 1N H_3PO_4 with ROE Figure 10: SEM analysis of Mild steel in 1N H_3PO_4 ROE

3.9. Mechanism of corrosion inhibition

The inhibitor was combined with the Fe^{2+} ions on the mild steel surface and forming the iron– inhibitor complexes:

$Fe \rightarrow Fe^{2+} + 2e^-$

$Fe^{2+} + Inh_{(ads)} \rightarrow [Fe - Inh]^{2+}_{(ads)}$

The results obtained so far suggest that the components of the extract from ROE exhibited good inhibition efficiency during mild steel corrosion in 1N H_3PO_4 solution. Owing to the complex chemical composition of the ROE, it is quite difficult to assign the inhibiting effect to a particular constituent. Del Bano M.J, *et al* 2003 was reported that phytochemical constituents of the ROE is due to the presence of Flavonols, carnosic acid, Ros-marinic acid, carnosol, anthocyanins, terpenoid, alkaloids which are active constituents of most green inhibitors . The adsorption of the inhibitor molecules is due to the donor–acceptor interaction between π electrons of donor atoms (O) and aromatic rings of inhibitors and the vacant d-orbital of the acceptor [15-16]. The negatively charged species of inhibitor molecules were adsorbed to the positively charged iron surface.

CONCLUSION

The inhibition efficiency of ROE increases with increase in the concentration and decrease with temperature. The Inhibition efficiency of ROE was increased by adding KI due to cooperative adsorption of the inhibitor. The weight loss and Potentiodynamic polarization were shown good agreement with the inhibition efficiency. The $\Delta G_{(ads)}$ values were negative suggest that they were strongly adsorbed on the metal surface by a spontaneous process and exothermic in nature. Adsorption models, Temkin, Frumkin fit well which was noted from the correlation coefficient values of (R^2=0.9). The DFT studies revealed the inhibitive action of ROE, which has been obtained from the ΔE values. FT-IR and SEM analyses were shown that compounds in the plant extract react with the metal ion to form the layer of inhibitor on the metal surface. Thus, ROE was proving to be an efficient, Eco-friendly and low cost inhibitor.

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