Eco-friendly Inhibitor (*Tribulus terrestris* L) for Mild Steel Corrosion in 1 N Phosphoric Acid

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The inhibition effect of *Tribulus terrestris* L alcoholic extract on mild steel corrosion in 1 N phosphoric acid has been studied by mass loss and polarization techniques between 303 and 333 K. The inhibition efficiency increased with increase in concentration of plant extract. The corrosion rate increased with increase in temperature and decreased with increase in concentration of inhibitor compared to blank. The adsorption of inhibitor on mild steel surface has been found to obey Temkin's adsorption isotherm. Potentiostatic polarization results revealed that *Tribulus terrestris* L extract act as mixed type inhibitor. The values of activation energy (Ea), free energy of adsorption (ΔG_{ads}), heat of adsorption (Q_{ads}), enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) were calculated. Surface analysis (FT-IR and SEM) was also carried out to establish the mechanism of corrosion inhibitor on mild steel corrosion in phosphoric acid medium.

Key Words: Mild steel, Phosphoric acid, Corrosion inhibition, Temkin's adsorption isotherm, Potentiostatic polarization, *Tribulus terrestris* L alcoholic extract.

INTRODUCTION

Phosphoric acid is a major chemical product, which has many important uses, especially in the production of fertilizers. Most of the acid is produced from phosphate rock by wet process. Generally nickel-base alloys and stainless steel are frequently used in many parts of the wet process and a considerable quantity of data has been published about the resistance of these materials to corrosion by phosphoric acid solution[1-4]. Most of the previous studies were focused on the inhibition of stainless steel or chromium-nickel steel in hydrochloric acid or phosphoric acid solutions using organic compounds containing nitrogen, sulphur and oxygen atoms as corrosion inhibitors[5,6]. The corrosion inhibiting property of these compounds is attributed to their molecular structure. These compounds contain π-electrons and heteroatom, which induce greater adsorption of the inhibition molecules onto the mild steel surface.

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Because of the toxic nature and high cost of some chemicals currently in use, it is necessary to develop environmentally acceptable and less expensive inhibitors. Natural products can be considered as a good source for this purpose. Extracts of naturally occurring products contain mixture of compounds and are biodegradable in nature, these compounds having nitrogen and sulphur as constituent atoms are studied as corrosion inhibitor in HCl medium[7]. Gunasekaran and Chaughan[8] studied the inhibition effect of *Zenthoxylum alatum* on the corrosion of mild steel in phosphoric acid medium. Abdel-Gaber and co-workers[9] studied inhibitive action of some plant extracts *e.g. Nigella sativa* L (Black cumin), *Phaseolus vulgrais* L (Kidney bean) and *Cymbopogon proximus* (Halfabar) on the corrosion of mild steel in sulphuric acid medium. Several works have been reported using such economical plant leaves extract of *Azadirachta indica* for mild steel in H_2SO_4[10], leaves extract of *Nypa fruticand* wurmb[11] and *Occinium viridis*[12], acid extract of *Alllium sativum* (Garllic)[13], *Foenum graecum*[14], aqueous extract of *Lawsonia inermis* (Henna)[15] and carboxymenthylchitoson[16] as inhibitors for mild steel in HCl medium. Literature survey revealed that not much work was done on the corrosion inhibition of mild steel in phosphoric acid solutions using naturally available plant extracts.

Tribulus terrestris L, is a member of the Zygophyllaceae family, is an annual plant native of Mediterranean region. It has pinnate leaves, yellow flowers and stellate shape carpel fruits. Extracts of this plant have been used traditionally in treating variety of diseases including hypertension, coronary heart diseases, ocular inflammation and infertility in both sexes.

The phytochemical components of *Tribulus terrestris* L alcoholic extract (TTAE) has been extensively studied and it is known to have steroidal saponins compounds[17,18], polysaccharides[19], tannins[20]. These compounds have been known for their medicinal properties like antifungal, antibacterial, antioxidant and most likely responsible for inhibiting corrosion.

So, in this present investigation, the corrosion of mild steel in 1 N phosphoric acid solution in the absence and presence of TTAE at 303 to 333 K has been studied by mass loss and polarization techniques. It is aimed to predict the corrosion rate, inhibition efficiency on mild steel corrosion and the thermodynamic feasibility of inhibition *via* surface coverage on mild steel by adsorbed TTAE at various temperatures. The adsorption characteristic of TTAE was studied in order to access the mechanism of corrosion inhibition and the adsorption isotherm (s).

EXPERIMENTAL

Preparation of specimens: Mild steel specimens were cut to size of 5 cm × 1.5 cm from the mild steel sheets having the following percentage composition as shown below. The surface of specimens were polished with emery papers ranging from 110 to 410 grades and degreased with trichloroethylene specimens were dried and stored in vacuum desiccators containing silica-gel.

Composition of mild steel:

Element	Fe	Ni	Mo	Cr	S	P	Si	Mn	C
Composition (%)	99.686	0.013	0.015	0.043	0.014	0.009	0.007	0.196	0.017

Preparation of plant extract: Water extract of *Tribulus terrestris* L was prepared by the aerial part of plant collected and dried in air and then grained. 50 g of grained powder subjected to Soxhlet extraction using methanol (95 %). The solvent can be removed by boiled at constant temperature at 40 ºC in vacuum evaporator, finally the residue of TTAE was collected. From the TTAE residue the various concentration of inhibitor solution (1, 2, 3, 4 and 5 mgs) was prepared. All the solutions were prepared with AR grade chemicals in double distilled water.

Weight loss measurement: Polished specimens were initially weighed in an electronic balance. After that the specimens were suspended with the help of PTFE threads and glass rod in 100 mL beaker containing acid in the presence and absence of TTAE. The specimens were removed after 4 h exposure period, washed with water to remove any corrosion products and finally washed with acetone. After that they were dried and reweighed. Mass loss measurements were carried out in 1 N phosphoric acid with TTAE in the concentration range of 1 to 5 mgs as inhibitors and the temperature between 303 and 333 K for an immersion period of 4 h. Mass loss measurements were performed as per ASTM method described previously[21,22].

Potentiostatic polarization measurements: Polarization measurements were carried out in a conventional three-electrode cell. Mild steel strips coated with lacquer except for an exposed area of 1 cm^2 were used as the working electrode. The saturated calomel electrode and the platinum foil were used as reference and counter electrodes, respectively. The potentiostatic polarization measurement was carried out using BAS-100, a model instrument. The potential of the test electrode was measured with respect to SCE, platinum electrode was used as auxiliary electrode and the experiment was carried out at 303 to 333 K.

Surface analysis: The mild steel specimens were exposed in 100 mL of 1 N phosphoric acid solution having 5 mgs of plant extract for 3 h at room temperature and washed with distilled water then dried. The nature of film formed on the surface of the metal specimens was analyzed by FT-IR and SEM. The dried specimens were scratched off and the resultant powder mixed with KBr (1:100 ratio) to prepare pellets, then the pellets was introduced into Fourier Transfer Infra-Red spectrophotometer FT-IR, 8400's Shimadzu, Japan to analyze the sample.

RESULTS AND DISCUSSION

Mass loss studies: Table-1 shows the value of inhibition efficiency [IE %], surface coverage (θ) and corrosion rate obtained at different concentration of the inhibitors in 1 N phosphoric acid solution for an immersion period of 3 h. From the mass loss value, the inhibition efficiency [IE %] and surface coverage (θ) were calculated using the following equation[23].

$$IE(\%) = \frac{Wu - Wi}{Wu} \times 100 \tag{1}$$

$$\theta = \frac{Wu - Wi}{Wu} \tag{2}$$

TABLE-1
CORROSION PARAMETERS FOR MILD STEEL IN 1 N PHOSPHORIC ACID
WITH *Tribulus terrestris* L ALCOHOLIC EXTRACT (TTAE) FROM
MASS LOSS AND POLARIZATION STUDIES

Temp. (K)	Conc. of TTAE (mg)	Mass loss studies			Polarization measurement				
		Corrosion rate (mmpy)	Surface coverage (θ)	Inhibition efficiency (%)	E_{corr} *vs.* SCE (mV)	I_{corr} $(\mu A/cm^2)$	Tafel constant (mV/decade)		IE (%)
							b_a	$-b_c$	
303	Blank	159.2502	–	–	-460	260	55	110	–
	1	56.6663	0.6442	64.42	-465	55	42	100	78.85
	2	34.1286	0.7857	78.57	-480	50	45	95	80.77
	3	23.9742	0.8495	84.95	-482	47	45	95	81.92
	4	19.0704	0.8802	88.02	-485	42	50	90	83.85
	5	12.6806	0.9204	92.04	-480	35	45	85	86.54
313	Blank	182.7291	–	–	-465	610	50	120	–
	1	92.0828	0.4961	49.61	-490	255	40	122	58.20
	2	77.3713	0.5766	57.66	-460	210	45	110	65.57
	3	50.7718	0.7221	72.21	-470	171	40	90	71.97
	4	42.3016	0.7685	76.85	-465	143	35	95	76.56
	5	26.8472	0.8531	85.31	-460	122	40	80	80.00
323	Blank	217.0558	–	–	-475	1050	65	135	–
	1	131.3628	0.3948	39.48	-480	565	58	130	46.19
	2	106.0512	0.5114	51.14	-480	465	60	118	55.71
	3	91.9342	0.5764	57.64	-482	375	55	105	64.29
	4	77.4704	0.6431	64.31	-470	260	65	100	75.24
	5	43.2923	0.8005	80.05	-480	245	60	95	76.67
333	Blank	271.7408	–	–	-480	1600	90	140	–
	1	169.7018	0.3755	37.55	-480	890	80	125	44.38
	2	142.4088	0.4759	47.59	-485	746	80	115	53.38
	3	124.9235	0.5403	54.03	-490	610	75	125	61.88
	4	109.0232	0.5988	59.88	-485	520	72	110	67.50
	5	99.7605	0.6329	63.29	-485	465	75	105	70.94

where Wu and Wi are the corrosion rates for mild steel in the absence and presence of inhibitor respectively at the same temperature.

It could be seen from the table that the addition of inhibitor to the acid had reduced the corrosion rate. The inhibition efficiency increased with increase in concentration of inhibitors and decreased with increase the temperature from 303 to 333 K in 1 N phosphoric acid.

Thermodynamic parameters

Energy of activation (Ea): Table-2 shows that the calculated values of activation energy (Ea) for mild steel corrosion in 1 N phosphoric acid with and without inhibitor from 303 to 333 K. Energy of activation (Ea) was calculated from the slopes of plots of log p *versus* 1/T in Fig. 1 and also calculated from Arrhenius equation[24].

TABLE-2

THERMODYNAMIC PARAMETERS FOR MILD STEEL CORROSION IN 1 N
PHOSPHORIC ACID WITH *Tribulus terrestris* L ALCOHOLIC EXTRACT (TTAE)

Conc. of TTAE (mg)	Ea from eqn. 1 (KJ/mol)	Ea from plot (KJ/mol)	$-\Delta G_{ads}$ (KJ/mol)				Q_{ads}	ΔH (KJ/mol)	ΔS (KJ/mol/k)
			302K	313K	323K	333K			
Blank	14.95	15.60	–	–	–	–	–	10.79	–
1	30.68	32.10	29.01	28.39	28.19	28.84	-15.09	26.52	0.1812
2	39.95	38.54	29.05	27.43	27.60	28.06	-4.59	35.80	0.2099
3	46.17	45.74	29.11	28.05	27.21	27.65	1.99	42.01	0.2292
4	48.76	49.27	29.05	27.94	27.19	27.51	8.29	44.60	0.2377
5	57.69	55.86	29.63	28.82	28.75	27.30	11.66	53.53	0.2724
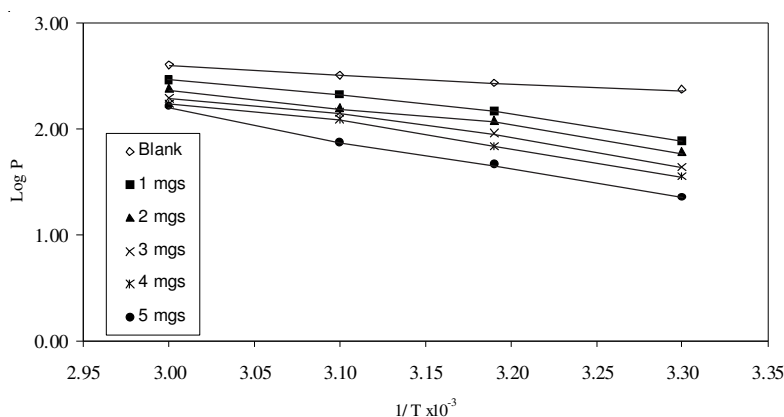
Fig. 1.   Arrhenius plot for corrosion in 1 N phosphoric acid with *Tribulus terrestris* L
alcoholic extract (TTAE)

$$\log \frac{P_2}{P_1} = \frac{Ea}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{3}$$

where P_1 and P_2 are the corrosion rates at temperatures T_1 and T_2, respectively. The Ea values were found to be 30.68 KJ/mol and 14.95 KJ/mol in 1 N phosphoric acid with and without TTAE respectively.

The addition of plant extract increases the activation energy as reported by Gunasekaran and Chaughan[25] for metal dissolution reaction indicating that this plant extract hinders metal dissolution. Bentiss *et al.*[26] explained that the Ea value increased in the presence of plant extract may be interpreted as physical adsorption (weakening) that occurs in the first stage, that is important because it is the proceeding stage of chemisorption of plant extract on mild steel. But Szauer and Brand[27] revealed that the increase in Ea can be attributed to an appreciable decrease in the adsorption of the inhibitor on mild steel surface with increase in temperature. A corresponding increase in the corrosion rate occurs because the greater area of the metal that is frequently exposed to acid environment.

Table-2 shows that the Ea values for 1 N phosphoric acid containing TTAE are found to be higher than that of without inhibitor. These higher values of Ea indicate that the addition of plant extract hinders metal dissolution and also indicate that, decrease in the adsorption of inhibitor on mild steel surface with increase in temperature The Ea values are calculated from the slopes of Arrhenius plot and by using eqn. 3 are almost similar.

Free energy of adsorption: The free energy of adsorption (ΔG_{ads}) at different temperatures was calculated from the following equation[24].

$$\Delta G_{(ads)} = -RT \ln (55.5\ K) \tag{4}$$

where K is given by

$$K = \frac{\theta}{C(1-\theta)}$$

where θ is surface coverage on the metal surface, C is concentration of inhibitor in mol/L and K is equilibrium constant. 55.5 is concentration of water (mol/L).

Bouklah *et al.*[28] explained generally the values of ΔG_{ads} upto -20 KJ/mol are consistent with characteristic interaction between charged molecules and charged metal surface (physisorption). While those around -40 KJ/mol or higher[26, 28] or smaller[17,29] are associated with chemisorption[14] as a result of sharing or transferring of electrons from organic molecules to the metal surface.

The free energy of adsorption (ΔG_{ads}) in 1 N phosphoric acid with TTAE on mild steel calculated from the eqn. 4 from 303 to 333 K. From Table-2 the negative free energy values (ΔG_{ads}) ranging from -29.63 to -27.19 KJ/mol indicate that the adsorption of the inhibitor is spontaneous and also adsorption of plant extract (TTAE) on mild steel is chemically adsorbed in phosphoric acid medium attributed to the donation of π electron by aromatic rings or non-bonding electron pair of compounds (hetero atoms) present in plant extract.

Heat of adsorption (Q_{ads}): The values of heat of adsorption Q_{ads} were calculated using the following equation[30]

$$Q_{ads} = 2.303R \log\left[\left(\frac{\theta_2}{1-\theta_2}\right) - \left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{T_1 \times T_2}{T_2 - T_1} \tag{5}$$

where θ_1 and θ_2 are degrees of surface coverage at temperature T_1 and T_2 by the different additives.

Oguzie[30] explained that the negative values of Q_{ads} also signify that the degree of surface coverage decreased with rise in temperature and positive values of Q_{ads} means the physical adsorption equilibrium is usually rapid and the process readily reversible whereas in chemisorption, the occurrence of chemical reaction at the metal surface makes the process relatively slow and not readily reversible. From Table-2 it is evident that in all the cases, the Q_{ads} values are ranging from -15.09 to 11.66 KJ/mol with TTAE. The higher negative values of heat of adsorption also show that the inhibition efficiency decreased with rise in temperature.

Enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS): The enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) were also calculated from the following equations[31,32].

$$\Delta H^{\circ} = E_a - RT \qquad\qquad (6)$$
$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad\qquad (7)$$

The thermodynamic data obtained in this study are shown in Table-2. It could be seen from the table that the activation energy increased linearly with increasing the efficiency of inhibitor.

Bentiss *et al.*[26] revealed that the positive sign of enthalpies (ΔH) reflects the endothermic nature of the steel dissolution process, which means dissolution of mild steel in acid medium is difficult. Adeyen[33] described that if the heat of adsorption (ΔH_{ads}) < 10 KJ/mol the adsorption is probably physisorption and if (ΔH_{ads}) > 10 KJ/mol the adsorption is probably chemisorption. Therefore, the enthalpy of adsorption (ΔH_{ads}) values indicates that the plant extract strongly adsorbed on mild steel is chemisorption.

In authors view, the adsorption of inhibitor is not considered only physical or chemical adsorption phenomenon in this case. Physical adsorption that occurs in the first sage, then according to hard and soft acid base theory, inhibitors are chemisorbed on the surface of mild steel by sharing of an electron pair of hetero atoms present in plant extract with *d*-orbital of iron forming covalent bond, leading to the positive vale of ΔH_{ads}[17].

It's also observed that ΔS values increased with increase the efficiency of inhibitors. This is opposite to the expectation, since the adsorption is an exothermic process and is always accompanied by decrease in entropy. Ateya *et al.*[24,34] has described this situation as the adsorption of the organic compound leads to desorption of water molecules from the surface. While the adsorption process is believed to be exothermic and associated with a decrease in entropy of the solute, the opposite is true for the solvent. Therefore, this gain in entropy that accompanied the substitutional adsorption process is attributed to the increase in solvent entropy.

Adsorption isotherms: The electrochemical process on the metal surface are likely to be closely related to the adsorption of the inhibitors[35] and the adsorption is known to depend on the chemical structure of the inhibitors[36-37]. The adsorption of the inhibitors molecules from aqueous solutions can be regarded as quasi-substitution process[36] between the organic compound in the aqueous phase, $org_{(aq)}$ and water molecules at the electrode surface, $H_2O_{(s)}$.

$$Org_{(aq)} + xH_2O_{(s)} = org_{(aq)} + xH_2O_{(s)}$$
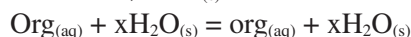
where x (the size ratio) is the number of water molecules displaced by one molecule of inhibitor.

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The most frequently used are those of Langmuir, Frumkin, Parsons, Temkin, Flory-huggins and Bockris -Swinkels[38-40]. All these isotherms are of the general form:

$$f(\theta, x) \exp (-a\,\theta) = K\,C$$

where $f(\theta, x)$ is the configurational factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm[41].

The mechanism of inhibition of corrosion is generally believed to be due to the formation and maintenance of a protective film on the metal surface. The plot of surface coverage (θ) obtained by mass loss method *versus* log C at different concentrations of the inhibitors shows a straight line indicating that the adsorption of the inhibitor from acid on mild steel surface follows the Temkin's adsorption isotherm. This also points out that the corrosion inhibition by these compounds is being a result of their adsorption on the metal surface. Fig. 2 shows the Temkin's adsorption isotherm plots for TTAE with 1 N phosphoric acid.
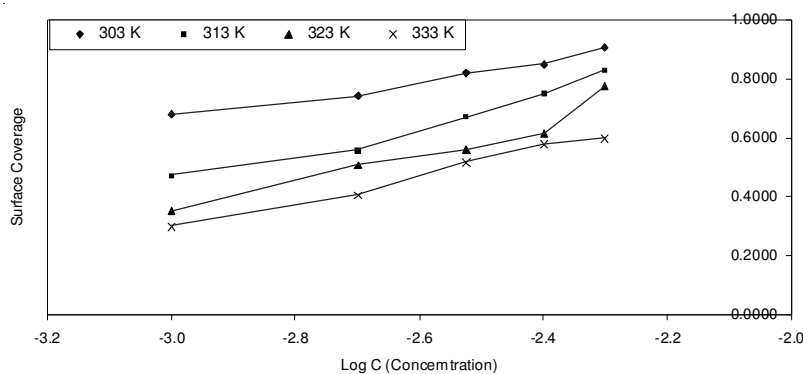

Fig. 2.   Tempkin's adsorption isotherm for corrosion behaviour of mild steel in 1 N phosphoric acid with TTAE
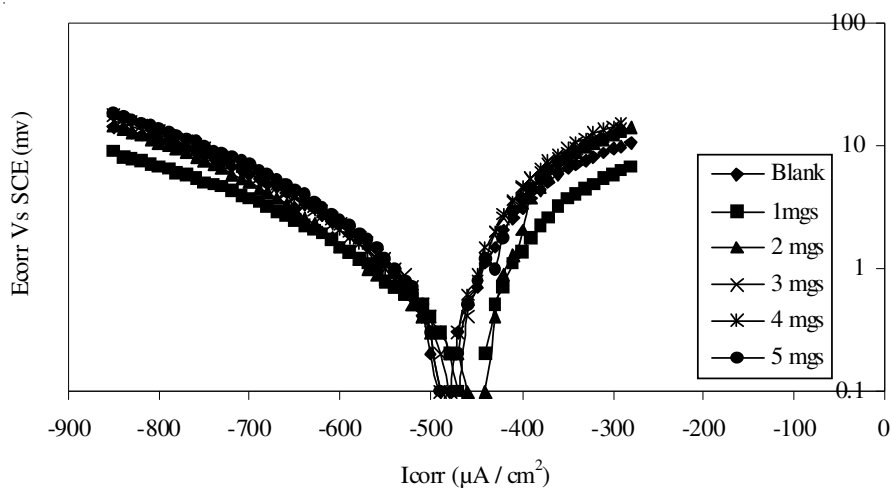

Fig. 3. Typical potentiostatic curves for mild steel in 1 N phosphoric acid with TTAE

Surface analysis

FT-IR: The peak values obtained from FT-IR analysis are shown in Table-3. The broad peaks between 3500 to 3200 cm^{-1} assigned to the presence of a superficial absorbed water, stretching mode of an OH and/or NH[9]. The peaks at 2929 and 2858 corresponds to stretching vibration of aliphatic and aromatic C-H. The peaks at 1670, 1654, 1560, 1527,1122 and 1091 cm^{-1} corresponds to stretching vibration of $R_2C=N$; $C=O$; aromatic substituted $C=N$, $C=C$ (aromatic ring), stretching vibration of ether linkage (C-O) and stretching vibration of C-O, respectively. This shows that the plant extract contains mixture of compounds. Almost all the peak observed for plant extract is also noticed on mild steel immersed in 1N phosphoric acid with 5 mg of plant extract.

TABLE-3
FT-IR PEAK VALUES FOR PLANT EXTRACT, MILD STEEL IN H_3PO_4 AND
MILD STEEL IN H_3PO_4 WITH PLANT EXTRACT (TTAE)

FT-IR peak values				
Mild steel in H_3PO_4	Plant extract (TTAE)	Mild steel in H_3PO_4 with plant extract	Possible groups	Ref. No.
3000-3500	-	-	Stretching mode of O-H (from adsorbed water)	8, 45
-	3342	3344	O-H/N-H (from plant extract)	8, 9, 45
-	2929	2923	Aliphatic C-H	8, 9, 45
-	2858	2852	Aromatic C-H	8, 9, 45
-	1670	1670	$R_2C=N$	8, 9, 45
-	1654	1654	$C=O$	8, 9, 45
1610	-	-	Iron phosphate	8, 9
-	1560	1560	Aromatic substituted $C=N$	8, 9
-	1527	1527	$C=C$ (Aromatic ring)	8, 9, 45
-	1388	1373	Plane bending vibration of OH	40
1272	-	1272	Stret. $P=O$	8, 9
-	1122	-	Stret. vibration of ether linkage (C-O)	42, 45
-	1091	-	C-O	41
1024	-	-	Iron phosphate	8, 9
-	-	1018	Fe-plant extract complex/ salt	8, 9
663		663	γ-Fe_2O_3	8, 9
Peaks between 700-400 cm^{-1} mainly due to Fe_2O_3				8, 9

The stretching frequency of C-O shift from 1091 to 1018 cm^{-1} due to electron cloud density shift from O atoms to co-ordinate with Fe^{2+} to form iron plant extract complex[42-46]. The peaks at 1272 cm^{-1} (P=O) and 1018 cm^{-1} (P-O-Fe) indicates iron phosphate complex. Then the peaks between 400 and 700 cm^{-1} are mainly due to Fe_2O_3[8].

Scanning electron microscope: Surface of polished mild steel specimen immersed in 1 N phosphoric acid in the presence of plant extract (5 mg) were examined

using scanning electron microscope model Jeol 6360, Japan. Fig. 4a and 4b shows the surface photograph of mild steel specimens immersed in 1 N phosphoric acid in the absence and presence of plant extract, respectively. In the case of blank, the corroded metal surface with etched grain boundaries and corrosion products are clearly seen in Fig. 4a. But in the presence of plant extract there is formation of adsorbed layer of inhibitors on the metal surface as seen in Fig. 4b.
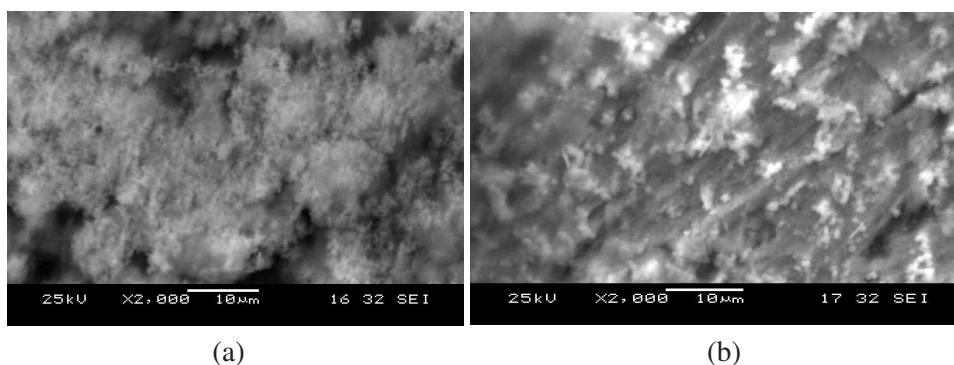

(a)   (b)

Fig. 4. SEM analysis of (a) Mild steel in 1 N phosphoric acid (b) Mild steel in 1 N phosphoric acid with TTAE

Potentiostatic polarization studies: The Polarization behaviour of mild steel functioning as cathode as well as anode in the test solution is shown in Fig. 3 for 1 N phosphoric acid with TTAE extract at room temperature (303 K). The electro-chemical data obtained are shown in Table-1. It is evident that TTAE bring about considerable polarization of cathode as well as anode. It was therefore inferred that the inhibitive action is of a mixed type. The non-constancy of Tafel slopes for different inhibitor concentration revealed that the inhibitor act through their inter-ference in the mechanism of the corrosion processes at the cathode as well as anode. The i_{corr} values were decreased with increasing concentration of the inhibitors which indicate that the corrosion process is controlled by adding TTAE.

Mechanism: The composition and the structure of the films formed on iron remains subjects of continued interest from FTIR studies on the oxides of iron revealed the presence of Fe_2O_3 in solutions irrespective of the nature of the iron substrate.

At the interface of iron and electrolyte, the dissolution of iron can be written as:

$$Fe + H_2O \longleftrightarrow FeOH_{ads} + H^+ + e^-$$
$$FeOH_{ads} \longrightarrow FeOH^+ + e^-$$
$$FeOH^+ \longrightarrow Fe^{2+} + OH^-$$
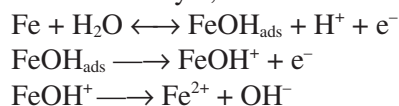
At medium and high concentrations of phosphoric acid, precipitation of iron-phosphate occurs at interface.

$$6H_3PO_4 + 3Fe \longrightarrow 3Fe(H_2PO_4)_2 + 3H_2$$
$$3Fe(H_2PO_4)_2 \longrightarrow Fe_3(PO_4)_2 + 4H_3PO_4$$
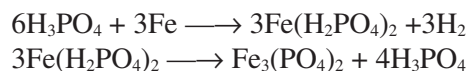
However, this precipitation can be weakly observed when the mild steel is treated with phosphoric acid solutions with low concentration. The formation of insoluble phosphate depends on the metal ions present in solutions at interface, concentration of metal ion in the solution and the reactivity of metal surface. Gunasekaran and Chaughan[8] explained that as soon as the plant extract interact with dissolving iron to form an organo-metel complex (Fe-PE) and forms a layer.

$$Fe^{2+} + PE \longrightarrow [Fe\text{-}PE]$$

This layer reacts with phosphate ions to form a layer of $FeHPO_4/FeH_2PO_4$. This reaction takes place in series with the formation of Fe-PE, since it is mediated or catalyzed by this compound, as is observed by the increased rate of formation of iron phosphates. After certain period, the formation of iron phosphate results in a dense layer and formation of Fe-PE will less. This was reflected by FT-IR analysis of mild steel immersed in 1 N phosphoric acid containing 5 mg of plant extract[8].

Conclusion

The following conclusions were made from the studies: (1) Corrosion rates of mild steel in 1 N phosphoric acid decreased with increasing concentration of *Tribulus terrestris* L alcoholic extract (TTAE). (2) The inhibition efficiency increased with respect to the concentration of inhibitor and decreased with rise in temperature from 303 to 333 K. (3) The maximum inhibition efficiency of TTAE was found to be 92.04 and 86.54 % in 1 N phosphoric acid at 5 mg of inhibitor from mass loss studies and polarization measurement respectively at 303 K. (4) The inhibition efficiency obtained from mass loss and polarization measurement showed fairly good agreement. (5) Energy of activation (Ea) values indicated that the addition of plant extract hinders metal dissolution and also indicated that, decrease in the adsorption of the inhibitor on mild steel surface with increase in temperature. (6) The negative value of ΔG_{ads} indicated that the TTAE is chemically adsorbed and spontaneous adsorption of inhibitors on the surface of mild steel. (7) The higher negative values of heat of adsorption also showed that the inhibition efficiency decreased with rise in temperature. (8) The high positive enthalpy values of adsorption (ΔH_{ads}) evident that the plant extract strongly adsorbed on mild steel is probably chemisorption. (9) The gain in entropy that accompanied by the substitutional adsorption process was attributed to the increase in solvent entropy. (10) It is found that the TTAE acting as mixed type inhibitor. (11) The adsorption of TTAE on mild steel surface from the acid solution followed Temkin's adsorption isotherm. (12) FT-IR and SEM analysis showed the presence of compounds in the plant extract react with metal ion to form the layer of inhibitor on the metal surface.

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