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Effect of Alcoholic Extracts of Tribulus Terrestris on the Corrosion Inhibition of mild steel in H_2SO_4 Solution

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ABSTRACT

The corrosion inhibition efficacy of alcoholic extract of stem, leaves and fruits of plant Tribulus Terrestris for mild steel in H_2SO_4 has been studied in relation to the concentration of inhibitor and temperature by mass loss method. Inhibition efficiency increases with inhibitor concentration but decreases with increase of temperature. The thermodynamic parameters revealed that the inhibition of corrosion is due to adsorption of the inhibitor on the metal surface. The negative free energy values shows spontaneity of the adsorption process with the assumption of Langmuir adsorption isotherm.

Introduction

All Corrosion of metal is a major industrial problem and many current corrosion control methods use coating and conversion layers which contain toxic and environmentally hazardous synthetic material [1-3]. Because of the toxic nature and high cost of chemicals there is a great need to develop a non-toxic, environmentally acceptable and less expensive replacement that is compatible with current industrial technologies. Natural substances can be considered as a good source for this purpose. The use of Natural products as corrosion inhibitors have been reported by several investigators. Numerous naturally occurring products such as Prosopis juliflora [4], Eugenia jambolans [5], Lawsonia [6], Citrullus Colocynthis [7], Swertia aungustifolia [8], Ficus religeosa [9], heena [10], Acacia Senegal [11] and calotropis [12] plant extracts have been evaluated as effective corrosion inhibitors. In the present work, an attempt has been made to study the influence of varying concentration of alcoholic extracts of fruits, leaves and stem constituents of plant Tribulus Terrestris on the corrosion rate of mild steel in sulphuric acid. The Tribulus Terrestris plant belongs to the zygophyllaceae family. Tribulus Terrestris is an annual creeping herb commonly known as Puncture vine [13, 14] widespread in large area of India, China, eastern Asia, and extends into western Asia and southern Europe. The phytocmpound of *Tribulus Terrestris* has been extensively studied and it is known to have tannins [15] steroidal saponins compounds [16,17] and Polysaccharides [18]. These compounds have been known for their medicinal characteristics like antibacterial, antioxidant anti-hypertensive, diuretic and most likely responsible for inhibiting corrosion. In Ayurvedic medicine, *Tribulus Terrestris* is referred to as Gokshura or Chhota Gokshura for the treatment of lower back pain, sciatica and inflammation of the pelvic and sacral region, dry cough and respiratory disorders [19, 20].

Experimental

For the study of corrosion inhibition efficiency of *Tribulus Terrestris*, mass loss method has been employed.

Specimen preparation - For the mass loss determination, rectangular specimen of mild steel of size 25 mm X 15 mm X 0.25 mm were so cut from a sheet having chemical composition as carbon (0.0889%), manganese (0.162%), sulphur (0.0128%), chromium (0.0128%) and rest iron steel was analysed by Optical Emission Spectroscopy at MNIT Jaipur.To clean the specimens were abraded with various grades of wax coated emery paper (1/0,2/0,3/0,4/0) and successively washed with benzene and soap and distilled water and finally with acetone then dried and weight. The metal coupons were then suspended with the help of glass hooks in borosil beakers containing 50 ml of corrosive electrolyte for complete immersion test.

Test solution preparation - The solution of 0.75 N H_2SO_4 were prepared using doubly distilled water. The Senegal extract was obtained by dried the parts of plants, then finely powdered and extracted with boiling methanol in a soxhlet.

To observe the influence of various parameters like inhibitor concentration, and temperature the inhibition efficiency (IE%), degree of surface coverage (θ) and corrosion rate (CR) were calculated by mass loss method.

The inhibitor efficiency (IE%) and the degree of surface coverage (θ) can be calculated [21] as.

$$IE\% = 100x\ (\Delta W_0 - \Delta W_i) / \Delta W_0 \qquad (1)$$

$$\theta = (\Delta W_0 - \Delta W_i) / \Delta W_0 \qquad (2)$$

Where, ΔW_0 is mass loss of metal in uninhibited acid and ΔW_i is mass loss of metal in inhibited solution

The corrosion rate (CR) in mille meter per year (mmpy) can be obtained by the following equation [22].

$$CR = \frac{\text{mass loss x } 8.76x10^4}{\text{Area x time x density}} \qquad (3)$$

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Where, mass loss is in gram, Area is in cm^2, time is expressed in hrs. and metal density is expressed in $gram/cm^3$.

Adsorption Isotherm

Langmuir Adsorption Isotherm equation shown as

$$\log(C/\theta) = \log C - \log K_{ads} \quad (4)$$

Where, C is concentration of inhibitor, θ is surface coverage and K_{ads} is adsorption equilibrium constant.According to Langmuir Adsorption Isotherm straight line should be obtained when a graph is plotted between log(C/θ) versus logC with gradient equal to one and intercept equal to $-\log K_{ads}$ for the extract.

Results and Discussion

Corrosion behaviour of mild steel in 0.75 N concentration of sulphuric acid with and without different inhibitor has been studied and the results are depicted in the Table -1.

Table 1. Comparative mass loss data for mild steel in 0.75 N H_2SO_4 with alcoholic extracts of plant *Tribulus Terrestris* 303 ± 1 K

Effective area of specimen - 7.50cm^2

Immersion Time – 24 hrs

Inhibitor Conc. (%)	ΔW (mg)	CR (mmpy)	θ	IE%
Blank	**293**	**18.142**		
Fruit extract				
0.12	81	5.015	0.7249	72.49
0.24	56	3.467	0.8098	80.98
0.36	37	2.291	0.8723	87.23
0.48	20	1.238	0.9301	93.01
0.60	14	0.867	0.9518	95.18
Leaf extract				
0.12	93	5.758	0.6825	68.25
0.24	59	3.653	0.7980	79.80
0.36	45	2.786	0.8460	84.60
0.48	26	1.61	0.9125	91.25
0.60	21	1.3	0.9274	92.74
Stem extract				
0.12	113	6.997	0.6138	61.38
0.24	72	4.458	0.7552	75.52
0.36	53	3.282	0.8179	81.79
0.48	43	2.662	0.8526	85.26
0.60	32	1.981	0.8901	89.01

It is found that the inhibition efficiency increases with increases of inhibitor concentration for different plant extracts from 0.12% to 0.60% from the mass loss data as shown in Fig-1.

IE% α Inhibitor concentration

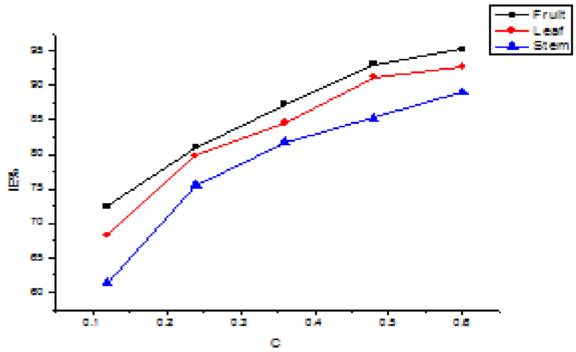

Fig 1. Variation of Inhibiton efficiency with extracts concentration for mild steel in 0.75 N H_2SO_4 containing different parts of plant (24hrs).

It is concluded that the plant extracts act as a good inhibitor for mild steel in acid solutions. Table-1 show that the fruit extract of *Tribulus Terrestris* has maximum inhibition efficiency. Inhibition efficiency of different parts of plant is observed as

Fruit > Leaf > Stem

It is also found that the inhibition efficiency decreases with increases in temperature for extracts from 0.12% to 0.60% from the mass loss data as shown in Fig-2. Here it is studied for leaf extract.

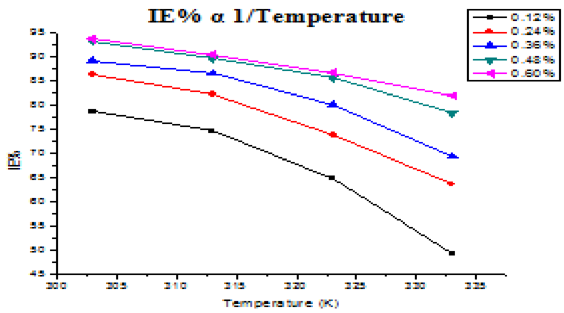

Fig 2. Variation of Inhibiton efficiency with change in temperature for mild steel in 0.75N H_2SO_4 with Leaf extracts of plant.

Table 2. Corrosion parameters for mild steel in solution of 0.75N H_2SO_4 in absence and presence of Leaf extracts of *Tribulus Terrestris* at different temperature Effective area of specimen – 7.50 cm^2 Immersion Time – 06 hrs.

Temperature(k)	Inhibitor concentration(%)	Δw(mg)	CR(mmpy)	θ	%IE
303	Blank	101	25.01		
	0.12	22	5.45	0.7859	78.59
	0.24	14	3.47	0.8610	86.10
	0.36	11	2.72	0.8911	89.11
	0.48	7	1.73	0.9319	93.19
	0.60	6	1.49	0.9358	93.58
313	Blank	197	48.79		
	0.12	50	12.38	0.7459	74.59
	0.24	35	8.67	0.8206	82.06
	0.36	27	6.69	0.8649	86.49
	0.48	21	5.20	0.8954	89.54
	0.60	19	4.71	0.9038	90.38
323	Blank	317	78.51		
	0.12	112	27.74	0.6470	64.70
	0.24	83	20.56	0.7369	73.69
	0.36	63	15.60	0.7998	79.98
	0.48	46	11.39	0.8553	85.53
	0.60	42	10.40	0.8666	86.66
333	Blank	584	144.64		
	0.12	296	73.31	0.4927	49.27
	0.24	213	52.75	0.6356	63.56
	0.36	179	44.33	0.6928	69.28
	0.48	126	31.21	0.7835	78.35
	0.60	107	26.50	0.8176	81.76

Langmuir Adsorption Isotherm - The adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions [23]. The experimental data obtained were best fitted with the Langmuir adsorption isotherm which is described by the equation (4). The Langmuir Adsorption Isotherm curve are plotted between log(C/θ) versus logC shown in Fig-3.

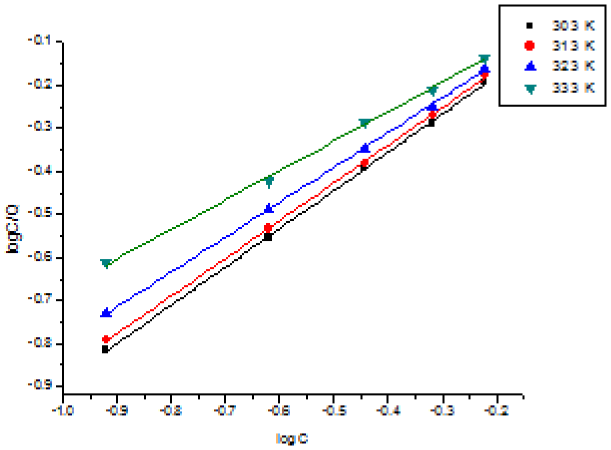

Fig 3. Langmuir Adsorption Isotherm for mild steel in 0.75N H_2SO_4 with Leaf extract of plant at different temperature (6 hrs).

In present investigation, the plots are linear but gradient is not equal to unity. The deviation from unity behaviour can be explained on the basis of interaction of the adsorbed molecule on the metal surface. According to Langmuir, the adsorbed layer is unimolecular i.e. there is no interaction between adsorbed molecules themselves and between adsorbate and adsorbent molecules. Only then the gradient is unity but in actual practise, it is not possible. There may be an interaction between adsorbed molecules themselves and between adsorbate and adsorbent molecules, that's why the gradient is not unity. The values of adsorption equilibrium constant (K_{ads}) and Gibbs free energy (ΔG^0_{ads}) are given in Table 3. K_{ads} is calculated from intercept of Langmuir Adsorption Isotherm and ΔG^0_{ads} is calculated by following equation [24].

$$\Delta G^0_{ads} = -RT\ln(55.5\ K_{ads}) \quad (5)$$

Where, ΔG^0_{ads} is change in Gibbs free energy; K_{ads} is adsorption equilibrium constant ; R is universal gas constant (8.314 JK^{-1} mol^{-1}); T is absolute temp and 55.5 is concentration of water (mol/litre).

Table 3 . Change in K_{ads} and ΔG^o_{ads} at various temperatures for mild steel in 0.75 N H_2SO_4 with Leaf extract; Immersion Time – 6hrs.

Temperature (K)	K_{ads}	(ΔG^0_{ads}) ($kJmol^{-1}$)
303	1.0012	-10.12
313	0.9742	-10.38
323	0.9680	-10.70
333	0.9727	-11.04

The negative values of $\Delta G°_{ads}$ ensure the spontaneity of adsorption process and stability of the adsorbed layer on the mild steel surface. Generally, the values of $\Delta G°_{ads}$ around -20 kJ/mol or lower are consistent with physiosorption, while those around -40 kJ/mol or higher involve chemisorption [25, 26]. Results obtained indicate that the values of $\Delta G°_{ads}$ are negative in all cases and are less than 20 kJ/mol. This is consistent with literature survey and therefore endorses physical adsorption. This implies that the plant extracts adheres on the surface of the corroding system and so gives a very strong inhibitor.

Thermodynamic Study

Determination of Activation Energy- The values of activation energy (E_a) is listed in Table-4 is calculated from the slope of Arrhenius equation [27] shown in Fig-4

$$\ln CR = \ln A - \frac{E_a}{RT} \quad (6)$$

Where, CR is corrosion rate at temperature T, E_a is apparent activation energy, R is molar gas constant and A is frequency factor.

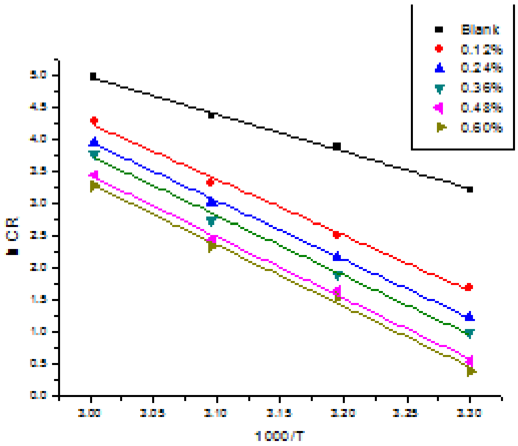

Fig 4. Arrhenius plot for mild steel in 0.75N H2SO4 with Leaf extracts of plant at different temperature (6 hrs).

The higher value of activation energy E_a in presence of inhibitor indicating that the presence of inhibitor creates energy barrier for the corrosion interaction. On the basis of the experimentally determined activation energy value of E_a < 80 kJ/mol in this study, we propose that the additive is physically adsorbed on the coupons [28]. Therefore, it is plausible that a multilayer protective coverage on the entire mild steel surface was obtained.

Determination of Enthalpy and Entropy-Other thermodynamic parameters such as enthalpy (ΔH) and entropy (ΔS) of activation of corrosion process may be calculated from the effect of temperature. The enthalpy (ΔH^0_{ads}) and entropy (ΔS^0_{ads}) of activation of corrosion process was evaluated from the transition state equation:

$$\ln\frac{CR}{T} = \left(\ln\left\{\frac{R}{Nh}\right\} + \frac{\Delta S^0_{ads}}{R}\right) - \frac{\Delta H^0_{ads}}{RT} \quad (7)$$

Table 4. Thermodynamic parameters for mild steel in 0.75 N H_2SO_4 with Leaf extract Immersion Time – 6hrs.

Inhibitor Conceration (%)	Corrosion Rate at Temperature(mmpy)				Activation Energy (E_a) (kJ/mol)	Enthalpy (ΔH^0_{ads}) (kJ/mol)	Entropy (ΔS^0_{ads}) (kJ/mol/k)
	303K	313K	323K	333K			
Blank	25.01	48.79	78.51	144.64	48.22	45.56	-0.225
0.12	5.45	12.38	27.74	73.31	72.17	69.51	-0.159
0.24	3.47	8.67	20.56	52.75	75.74	73.08	-0.151
0.36	2.72	6.69	15.60	44.33	77.24	74.66	-0.148
0.48	1.73	5.20	11.39	31.21	79.40	76.74	-0.144
0.60	1.49	4.71	10.40	26.50	79.32	76.66	-0.146

Where CR is the Corrosion Rate at Temperature T, R is the molar gas constant, N is Avogadro's constant, and h is the Planck's constant. A plot of of ln (CR/T) vs 1/T is a straight line graph (Fig. 5) with a slope of ($-\Delta H^0_{ads}/R$) and an intercept of [ln (R/Nh) + ($\Delta S^0_{ads}/R$)] from which the values of (ΔH^0_{ads}) and (ΔS^0_{ads}) were calculated [29]. As indicated in Table 4 that the enthalpy of activation values are all positive for *Tribulus Terrestris* which reflects the endothermic nature of the mild steel dissolution process. Also, the entropies of activation energy were large and negative. Indicating that the activated complex in the rate determining step represents association steps rather than dissociation, indicating that a decrease in disorder takes place, in going from reactant to the activated complex [30] and that the reaction was spontaneous and feasible.

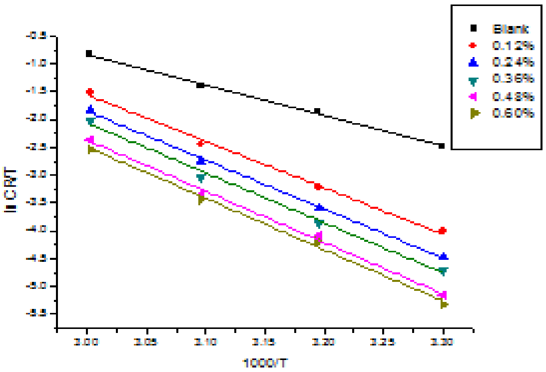

Fig 5. Transition state plot for mild steel in 0.75N H2SO4 with Leaf extracts of plant at different temperature (6 hrs.)

Conclusion

- It is concluded that the extract of plant *Tribulus Terrestris* is a good corrosion inhibitor for mild steel in H_2SO_4 solutions.
- Inhibition Efficiency (IE%) increases with inhibitor concentration and maximum IE% was observed for the fruit extract 95.18% at the concentration of 0.60% at 303K.
- Inhibition efficiency decreases and corrosion rate increases with increases in temperature.
- The adsorption of different concentrations of the plant extract on the surface of the mild steel in 0.75N H_2SO_4 solution follows Langmuir adsorption isotherm.
- The negative sign of the ΔG^o_{ads} indicates that the adsorption of the inhibitors on the mild steel surface was a spontaneous process and was found to be physisorption.
- E_a was found to be 48.22kJmol^{-1} for 0.75N H_2SO_4 and increases to 79.32kJmol^{-1} in the presence of leaf extract of plant at 0.60% w/v which shows that the adsorbed organic matter has provided a physical barrier to change and mass transfer, leading to reduction in the rate of corrosion.
- Thermodynamic parameters E_a, $\Delta H°_{ads,}$ $\Delta S°_{ads}$ revealed that the adsorption process is spontaneous.
- This type of inhibitor are eco-friendly, biodegradable and less toxic therefore these type of inhibitors can be used to replace toxic chemicals.

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