



iJRASET

International Journal For Research in
Applied Science and Engineering Technology



INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 7 Issue: I Month of publication: January 2019

DOI: <http://doi.org/10.22214/ijraset.2019.1055>

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Corrosion Prevention of Lagenaria Siceraria Peel on Carbon Steel in 1.0N HCl Acid Environment

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Abstract: *The Inhibitive nature of Lagenaria Siceraria Peel extract on Carbon Steel in 1.0N Hydrochloric acid has been investigated using various concentrations of inhibitor as well as temperature by mass loss measurements. The observed result reveals that the percentage of inhibition efficiency increased with increase of inhibitor concentration and temperature. Thermodynamic parameters (E_a , Q_{ads} , ΔG_{ads} , ΔH_{ads} , ΔE and ΔS) suggests that the adsorption of LSP extract is endothermic, spontaneous and chemisorptions process. It follows the Langmuir adsorption isotherm.*

Keywords: Carbon Steel, Mass Loss, LSP, 1.0N HCl.

I. INTRODUCTION

The protection of various metals against corrosion is a major industrial problem in the world wide. Most of the scientist is attempted for their research work in this corrosion field. The heavy loss of metal whenever it contact with acid and other environment can be minimized to a great extent by the use of corrosion inhibitors. Mild steel is widely used for mechanical and structural engineering purpose, boiler, plates, steam engine parts and automobile etc. For this reason, the corrosion behaviour of these metals has attracted more awareness of several investigators. Iron and steel is the most corrosion vulnerable metal. Thus, much attention is given for its protection from the hostile environments.

The heavy loss of metals is a result of its contact with the pollution environment can be minimized to a great extent by the use of corrosion inhibitors, inorganic compounds like chromates, phosphates, molybdates etc. and a variety of organic compounds containing heteroatom like nitrogen, sulphur oxygen and olefins are being investigated as corrosion inhibitor. Pure synthetic chemicals are costly, but some of them are easily biodegradable and their disposal creates pollution problems. Plant extracts are environmentally friendly, bio-degradable, non-toxic, plenty and potentially low cost. Recently, a few investigators studied the plant extracts and the derived organic species become more important as an environmentally benign, readily available, renewable and acceptable source for a wide range of inhibitors. Several efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors.

The plant extract are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as "Green Inhibitors". These inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Recent studies using plants containing heteroatom such as oxygen, nitrogen and sulphur like Tamarind tea leaves, Beet root1-2, Saponin3, Terminalia bellerica4, Oxandra asbeckii5, Argemone mexicana6, Betanin7, Henna8, Wheat9, Ginger10, Marraya koeningii11, Garlic extract12, Ananas sativum13, Artemisia Mesatlantica essential oil14, spirogyraalgae15, Tragacanth gum16, Prunus Persic17, Lemon Gross18, Secang heartwood extract (Caesalpinia sappan I)19, Dried marjoram leaves20.

In continuous of our research work, the present investigation is the Lagenaria siceraria Peel extract used as corrosion inhibitor on Carbon Steel in 1.0N Hydrochloric acid have been investigated with various periods of contact and temperature using the mass loss measurements.

II. MATERIALS AND METHODS

A. *Lagenaria Siceraria Peel Used As A Corrosion Inhibitor*

B. *Stock solution of Lagenaria Siceraria Peel Extract*

Lagenaria Siceraria Peel (LSP) was collected from the source and dried under shadow for about 10 days, grained well, then soaked in a solution of ethyl alcohol for about 48 hrs, Then it is filtered followed by evaporation in order to remove the alcohol solvent completely and the pure plant extract was collected. From this extract, different concentration of 10 to 1000ppm stock solution was prepared using double distilled water and used throughout our present investigation.

C. Specimen Preparation

Rectangular specimen of Carbon steel was mechanically pressed cut to form different coupons, each of dimension exactly 20cm² (5x2x2cm) with emery wheel of 80 and 120 and degreased with trichloroethylene, washed with distilled water, cleaned and dried, then stored in desiccators for our present study.

III. RESULTS AND DISCUSSION

A. Effect Of Time Variation

The dissolution behavior of Carbon steel in 1.0N HCl containing the presence and absence of LSP extract with various exposure times (24hrs to 360 hrs) are shown in Table-1. The observed values clearly indicate that the presence of LSP extract, the corrosion rate moderately decreased from 2.7205 to 0.2473 mmpy for 24 hrs and 0.1133 to 0.0082 mmpy after 360 hrs with increase of inhibitor concentration (0 to 1000 ppm). The maximum of 95.34 % of inhibition efficiency is achieved after 240 hrs exposure time, suggests that the adsorption process occurs mainly due to the presence of active phytochemical constituents present in the inhibitor molecule especially oxygen containing species and the metal ion from the surface of the metal.

Table-1: The corrosion parameters of Carbon steel in 1.0N HCl containing different concentration (0 to 1000ppm) of LSP extract after 24 to 360 hours exposure time

Conc. of inhibitors (ppm)	24 hrs		72 hrs		120 hrs		240 hrs		360 hrs	
	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E
0	2.7205	-	0.9274	-	0.3957	-	0.1978	-	0.1133	-
10	2.2259	18.18	0.8450	8.88	0.3153	20.31	0.1854	6.26	0.0865	23.65
50	0.6801	75.00	0.7831	15.55	0.2658	32.82	0.1576	20.32	0.0845	25.41
100	0.6492	76.13	0.4431	52.22	0.1854	53.14	0.1298	34.68	0.0721	36.36
500	0.5564	79.54	0.3194	65.55	0.0741	81.27	0.0618	68.75	0.0247	78.19
1000	0.2473	90.90	0.1648	82.22	0.0247	93.75	0.0092	95.34	0.0082	92.49

B. Effect of Temperature

Dissolution behavior of Carbon Steel in 1.0N HCl containing various concentration of LSP extract at 303 to 333K and the observed values are listed in Table-2. The observed results reveal that the corrosion rate decreased with increase of inhibitor concentrations and increased with rise in Temperature from 303 to 333K. The maximum of 77.46% inhibition efficiency is achieved at 333K. However the value of inhibition efficiency is increased with rise in Temperature may suggest and support the facts that the process of adsorption follows chemisorption.

Table-2: The corrosion parameters of Carbon Steel in 1.0N HCl containing different concentration of LSP extract at 313 to 333 K after one hour exposure time.

Conc. of inhibitor (ppm)	303 K		313 K		333 K	
	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E
0	92.7463	-	96.4561	-	105.3598	-
10	89.0364	4.00	90.5203	6.15	102.3919	2.81
50	85.3266	7.99	83.1006	13.84	77.1649	26.76
100	71.9711	22.40	55.6477	42.30	70.4871	33.09
500	60.8415	34.40	52.6799	45.38	50.4539	52.11
1000	46.7441	49.60	44.5182	53.84	23.7430	77.46

C. Activation Energy

The activation energy (E_a) for the corrosion of Carbon steel in the presence and absence of LSP extract is calculated using the following Arrhenius equation (4) and its derived form equation (5).

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

$$\log(CR_2/CR_1) = E_a/2.303 R (1/T_1 - 1/T_2) \quad \text{----- (5)}$$

(Where CR_1 and CR_2 are the corrosion rate at the temperature T_1 and T_2 respectively, E_a is the activation energy and R is the universal gas constant).

The value of activation energy (E_a) for the blank (3.5662 kJ/mol) is higher than in the presence of inhibitors (Table-3). This observation clearly indicates that the adsorption process also is chemisorption.

D. Heat Of Adsorption

The heat of adsorption on the surface of various metals in the presence of plant extract in 1.0N HCl environment is calculated by the equation (6).

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

(Where R is the gas constant, θ_1 and θ_2 are the degree of surface coverage at temperatures T_1 and T_2 respectively).

The calculated Q_{ads} values (Table-3) are ranged from -10.2327 to 34.9678 kJ/mol. This negative value indicate and suggests that the adsorption of LSP extract on the Carbon steel surface is endothermic.

Table -3: Calculated values of Activation energy (E_a) and heat of adsorption (Q_{ads}) of LSP extract on Carbon Steel in 1.0N HCl environment.

S.No	Conc. of inhibitor(ppm)	% of I.E		E_a (KJmol ⁻¹)	Q_{ads} (KJmol ⁻¹)
		30°	60°		
1.	0	-	-	3.5662	--
2.	10	4.00	2.81	3.9087	-10.2327
3.	50	7.99	26.76	-2.8118	40.1840
4.	100	22.40	33.09	-0.5827	15.0625
5.	500	34.40	52.11	-5.2358	20.4075
6.	1000	49.60	77.46	-18.9451	34.9678

E. Adsorption Studies

Process of adsorption are very important phenomenon to determine the corrosion rate of reaction mechanism. The most frequently use of isotherms are viz: Langmuir, Temkin, Frumkin, Flory- Huggins, Freundlich, Bockris-Swinkles, Hill-de Boer, Parson's and the El-Amady, thermodynamic-kinetic model.

1) *Frumkin, El-Awady and Temkin Adsorption Isotherm*: The Langmuir adsorption isotherm of LSP extract on Carbon steel surface proceeded according to the following equation (7).

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

(Where θ is the degree of surface coverage, C is the concentration of the inhibitor solution and K is the equilibrium constant of adsorption of inhibitor on the metal surface).

By plotting the values of $\log(C/\theta)$ Vs $\log C$, linear plots are generated (fig-3). Inspection of this figure reveals that the experimental data fitted with the Langmuir adsorption isotherm, means that there is no interaction between the adsorbed species.

The Figs 2(a-c) shows Frumkin and El-Awady, Temkin isotherm model respectively. The values of K , R^2 and ΔG_{ads} are derived from these adsorption isotherm at different temperature ranges from 303K to 333K are given in Table -4. Frumkin adsorption isotherm model fit the corrosion rate data of LSP inhibitor on mild steel strongly and clearly indicates that the average value of Regression co-efficients $R^2=0.9741$ is almost unity. The other adsorption isotherm values viz, El-Awady ($R^2=0.9514$), Temkin (0.9575) are also move to near unity. we also attempt the Florry-Huggins ($R^2=0.8370$), Langmuir ($R^2=0.7730$) and Fruendlich ($R^2=0.9399$) adsorption isotherm models of LSP extract. This observed values relatively far from unity as compared with the values obtained with Frumkin adsorption isotherm which is clearly indicate that the weak correlation between the two variables (i.e surface coverage, inhibitor concentration). It is concluded that the inhibitor obeys Frumkin adsorption isotherm.

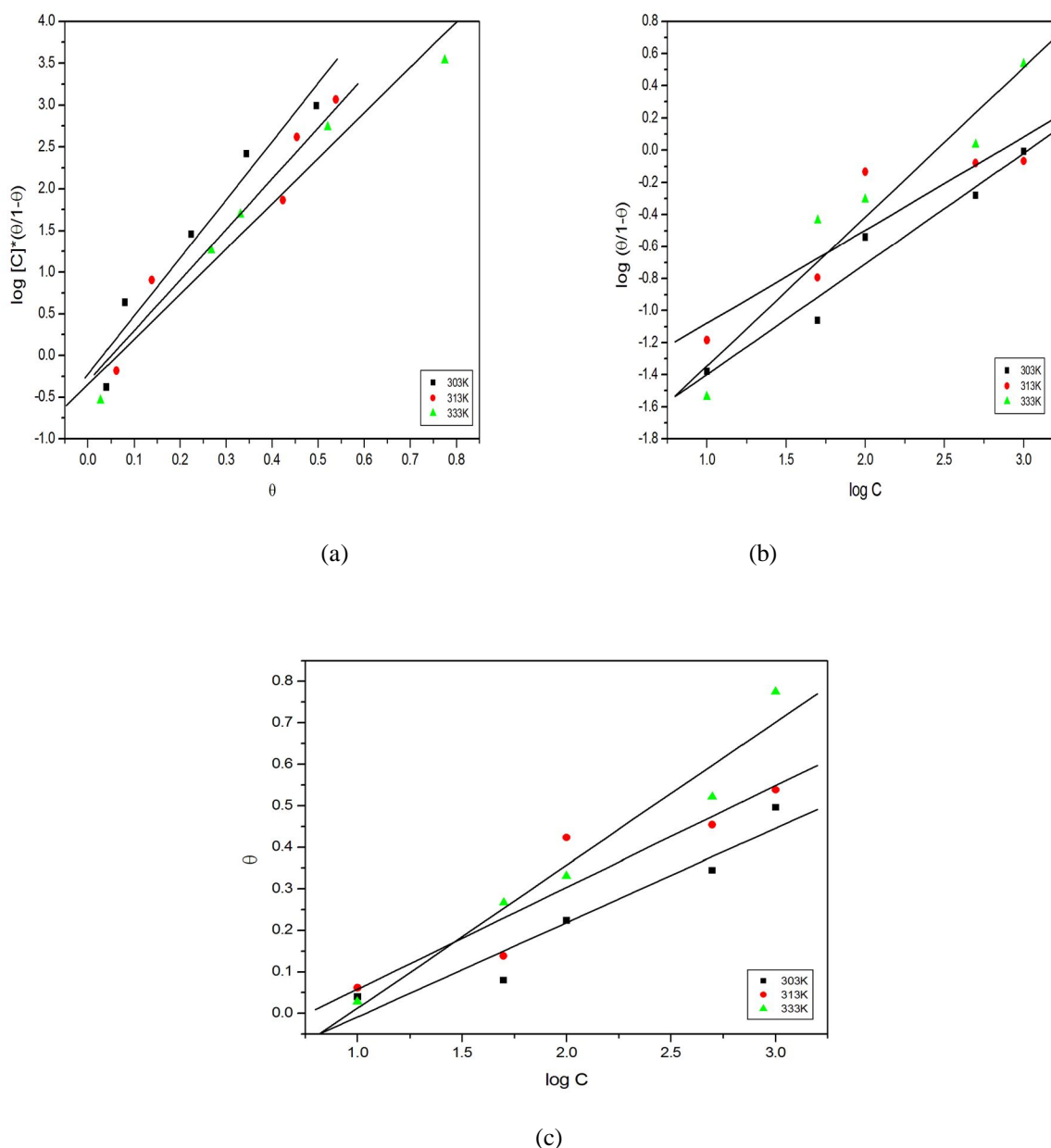


Fig. 2 (a)Frumkin (b) El-Awady, (c) Temkin isotherm for the adsorption of LSP inhibitor on Carbon steel in 1.0N HCl.

- 2) *Free Energy Of Adsorption*: The equilibrium constant of adsorption for various plant extract on the surface of Carbon steel is related to the free energy of adsorption ΔG_{ads} by equation (8).

$$\Delta G_{ads} = -2.303 RT \log (55.5 K) \quad \text{----- (8)}$$

(Where R is the gas constant, T is the temperature, K is the equilibrium constant of adsorption).

The values of intercept (K) obtained from Frumkin, El-Awady and Temkin adsorption isotherm is substituted in equation (8) and the calculated values of ΔG_{ads} are placed in Table-4. In El-Awady adsorption isotherm, the decrease of equilibrium constant (K_{ads}) values suggest that the process is physisorption phenomenon, which attributed to electrostatic interaction between the charged metal and active inhibitor molecules. Also the values of $1/y$ are less than unity, showing that there is a multilayer adsorption of the inhibitor molecule on the metal surface.[21-22]. In Langmuir adsorption, the negative values of ΔG_{ads} suggested that the adsorption of LSP extract onto Mild steel surface is a spontaneous process and the adsorbed layer is more stable one.

Table- 4 Frumkin, El-Awady and Temkin adsorption parameters for the adsorption of LSP inhibitor on Carbon steel in 1.0N HCl.

Temperature (Kelvin)	Adsorption Isotherms									
	Frumkin			El-Awady				Temkin		
	K	R ²	- ΔG _{ads} kJ/mol	K	1/y	R ²	-ΔG _{ads} kJ/mol	K	R ²	-ΔG _{ads} kJ/mol
303K	0.5957	0.9712	-8.81	0.0081	0.6896	0.9788	-2.01	0.5818	0.9606	-8.75
313K	0.4892	0.9708	-8.59	0.0219	0.5807	0.9092	-0.50	0.6513	0.9318	-9.33
333K	0.4467	0.9805	-8.89	0.0053	0.9296	0.9663	-2.98	0.4660	0.9801	-9.00

3) *Thermodynamics Parameters:* An alternative formula of the Arrhenius equation is the transition state equation

$$CR = RT/Nh \exp(\Delta S/R) \exp(-\Delta H/RT) \text{ ---- (9)}$$

(Where h is the Planck's constant, N the Avogadro's number, ΔS the entropy of activation, and ΔH the enthalpy of activation).

A plot of log (CR/T) Vs. 1000/T gives a straight line (Fig. 3) 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 out in Table-5. The negative value of enthalpy of activation clear that the exothermic nature of dissolution process is very difficult. The positive value of entropy (ΔS) is gradually increasing at the solid/liquid interface during the adsorption of the metal ions onto inhibitor molecules present in the extract.

Table 5: Thermodynamic parameters of Carbon Steel in 1.0N HCl obtained from weight loss measurements.

S.No	Concentration of LSP (ppm)	ΔH (kJ mol ^{−1})	ΔS (J k ^{−1} mol ^{−1})
1	0	0.4140	77.5758
2	10	0.6235	78.0796
3	50	-2.3919	68.0363
4	100	-0.8323	72.1775
5	500	-3.2449	63.8677
6	1000	-9.8138	41.6427

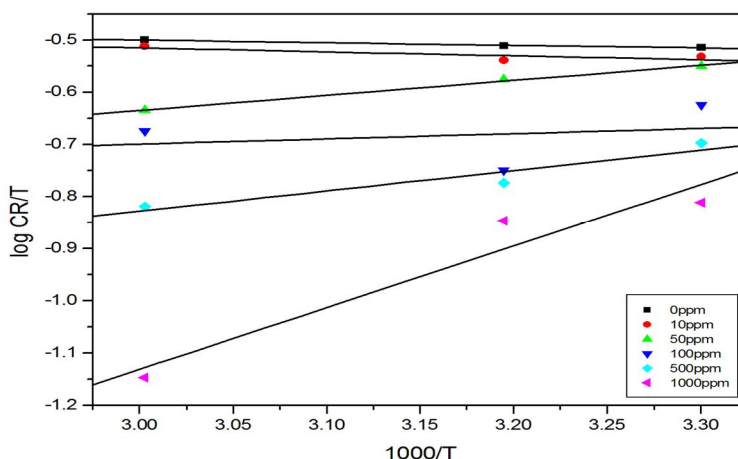


Figure- 3 The relation between log (CR/T) and 1000/T for different concentrations of LSP extract.

IV. CONCLUSIONS

Lagenaria Siceraria Peel has shown good inhibition performance for Carbon Steel in 1.0N HCl environment. The inhibition efficiency increased with the increase of inhibitor concentration. The maximum inhibition efficiency was achieved 95.34%. Also, the inhibition efficiency increased with the rise in temperature to 77.46% for 333K respectively. It follows chemical adsorption mechanism. The value of activation energy (E_a), enthalpy of adsorption (ΔH_{ads}) and free energy changes (ΔG_{ads}) indicates that the adsorption of inhibitor on metal surface follows chemisorption, endothermic and spontaneous process respectively. The close unity of R^2 values suggest that the inhibitor is found to obey Frumkin adsorption isotherms.

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