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Leaves Extract of Lawsonia Inermis (Heena) As a Corrosion Inhibitor for Copper in Trichloroacetic Acid

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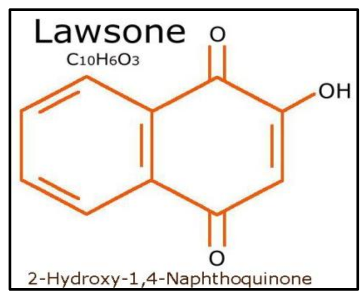
ABSTRACT

Lawsonia inermis (LI) leaves extract by mass loss measurement and electrochemical techniques. The inhibitor efficiency of LI extract was found to very with concentration was kept uniform for 24 h and temperatures was kept uniform for 2 h. Experimental results revealed that inhibition efficiency (I.E %) increased with increasing inhibitor concentration. As temperatures increased, percentage of inhibition decreases. The result also showed that, adsorption of inhibitor molecules on the surface of Copper followed Temkin, Freundlich and Langmuir adsorption isotherm model. The value of free energy of adsorption (ΔG^{θ}_{ads})*, heat of adsorption* (Q_{ads})*, energy of activation* (E_a)*, enthalpy of adsorption* (ΔH^{θ}_{ads}) *and entropy of adsorption* (ΔS^{θ}_{ads}) *were calculated Potentiodynamic study and Electrochemical Impedance Spectroscopy (EIS) implies that film developed on Copper using the both of TCA exhibits good corrosion resistance. The LI leaves extract is environmental friendly, biodegradable, nontoxic, cheap and easily available material which is used as corrosion inhibitor for Copper metal in TCA.*



Keywords: Lawsonia Inermis *(LI)* leaves, Copper, Trichloroacetic acid (TCA).

INTRODUCTION

Corrosion of metal and its alloys can be defined as the deterioration of materials due to their reaction with the environment. Copper is a metal having a wide range of application due to its good properties. Copper corrosion in TCA solution induced a great deal of research. Previous study where the aqueous extract of the leaves of *LI* was tested as corrosion inhibitors of carbon steel, nickel and zinc in acidic, neutral and alkaline [1].

The present study is based on the fact that some Sulphur, Nitrogen and Oxygen containing natural products like Azadirachta indica [2,3], Synthetic dyes [4,5], Organic compound [6], Tannin [7], Inorganic compound [8] etc compound is a widely used as corrosion inhibitor.

The importance of the study lies in the fact that naturally occurring plant products are non-polluting, eco-friendly, less toxic, biodegradable, less expensive and easily available. Due to the toxicity of some corrosion inhibitors, there has been increasing search for green corrosion inhibitors. *LI* has anti-inflammatory, antipyretic, anti-corrosive and analgesic effect [9].

Copper is broadly used in various industrial applications in heating and cooling system for its high electrical, good resistance, mechanical workability, and electronics for production of wire, sheet and tube. Inhibitive action of *LI* extract is the main constituent is Lowsone (2-hydoxy-1, 4-naphthoquinone) resin, Gallic acid, a-D-Glucose and tannic acid.

The present work carried out to investigation the inhibition efficiency of an extract of *LI* for controlling corrosion of Copper in TCA solution by Mass loss, Temperatures, Potentiodynamic polarization and Electrochemical impedance spectroscopic (EIS) method.

MATERIALS AND METHODS

Metal specimen and surface pretreatment: The Copper plate, which was used for the experiment having elemental composition- 99.99%Cu and 0.01%P. Specimens were prepared polished Copper sheet by cutting into rectangular shaped pieces having dimension of 5.10cm × 2.55cm × 0.529cm with a small hole of 2 mm diameter near the upper edge, were used for the determination of the corrosion rate. The specimens were used in the 'as cut' condition to determine inhibition efficiency, without further polishing; each sample was washed with double distilled water, degreased in ethanol and dried with AR grade acetone, weighed and stored in a moisture free desiccator before its use. The method gave mirror like finish.

Preparation of test solution: All the chemicals and reagents used were of analytical grade and used as such without further purification. The aggressive media were, respectively, 0.5M, 1M, and 2M TCA with and without inhibitor solution. *LI* leaves extract was used as inhibitor in 6, 8, 10, 12 mM concentration. Only one specimen was suspended by a V shaped glass hook, in each beaker containing 230ml of the test solution and was open to air at room temperature for 24 h duration.

Preparation of inhibitor: Stock solution of *LI* leaves extract was extracted by refluxing of 50 g of dry material in 500mL distilled water for 2 h. The refluxed solution was filtered to remove any contamination. The concentration of the stock solution was calculated in terms of mM.

RESULTS AND DISCUSSION

Mass loss measurements: The value of percentage inhibition efficiency (I.E. %) and corrosion rate (C.R) obtained from mass loss method at different concentration.
The inhibition efficiency was determined using the below given relationship.

$$\text{Inhibition efficiency(I.E\%)} = \frac{W_0 - W_1}{W_0} \times 100 \qquad (1)$$

The results of inhibition efficiency (I.E. %) were calculated and are presented in Table1.

The inhibition efficiency decreases with the increase in 0.5, 1 and 2 M TCA. Maximum inhibition efficiency of 12 ml *LI* inhibitor is 83.03, 75.98 and 66.94 % with respect to 0.5, 1 and 2 M TCA after 24 h exposure time. For example 1 M TCA the inhibition efficiency was found to be 52.36, 61.42, 70.47 and 75.98 % with respect to 6, 8, 10 and 12 mL inhibitor concentration (Figure 2). Mass loss Vs Acid concentration of Copper of TCA is shown in Figure 1.

Degree of Surface coverage (θ) Vs different concentrations of the inhibitor in acidic media have been evaluated from mass loss experiments using this relation (Table 2).

$$\theta = \left(\frac{W_0 - W_1}{W_1}\right) \quad (2)$$

Table 1. Mass loss (mg/sq.m^2) and inhibition efficiency (I.E. %) for Copper in TCA containing with given inhibitor addition of *LI*.

Temperature 301±1K Immersion period: 24h Effective specimen area: 0.2962 sq.m^2

Inhibitors	Inhibitor Conc. (mM)	Acid concentration 0.5 M Mass loss (mg/sq.m^2)	0.5 M I.E. (%)	1 M Mass loss (mg/sq.m^2)	1 M I.E. (%)	2 M Mass loss (mg/sq.m^2)	2 M I.E. (%)
Blank	-	537.81	-	827.90	-	1173.04	-
Lawsonia Inermis	6mL	215.12	60.00	394.39	52.36	677.97	42.25
	8mL	166.23	69.09	319.42	61.42	556.85	52.54
	10mL	117.34	78.18	244.46	70.47	469.36	60.00
	12mL	91.26	83.03	198.83	75.98	387.87	66.94

Table 2. Corrosion rate (Log □) of copper in 0.5 M TCA in absence and presence of*LI* for an immersion period of 24 h**.**

Inhibitor Conc. (mM)	C.R (ρ)	Log ρ	I.E (%)	Surface coverage (θ)	1-θ	Log (θ/1–θ)
Blank	537.81	2.7306	-	-	-	-
6mL	215.12	2.3327	60.00	0.6000	0.4000	0.1761
8mL	166.23	2.2207	69.09	0.6909	0.3091	0.3493
10mL	117.34	2.0694	78.18	0.7818	0.2182	0.5542
12mL	91.26	1.9603	83.03	0.8303	0.1697	0.6896

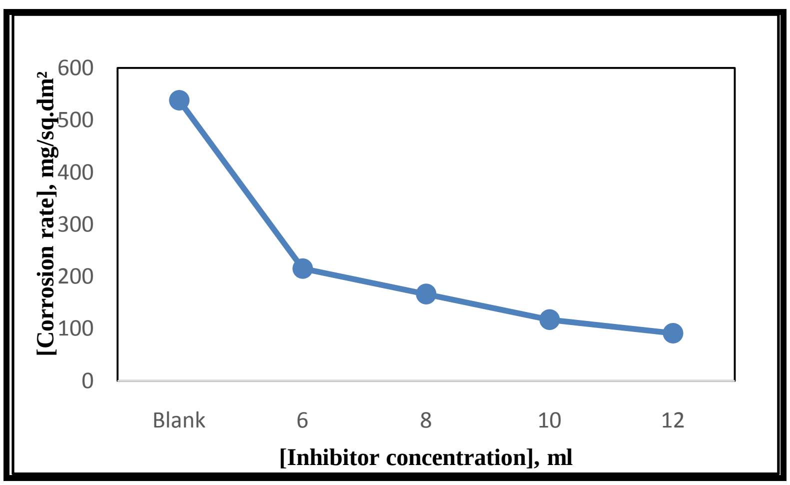


Figure 1

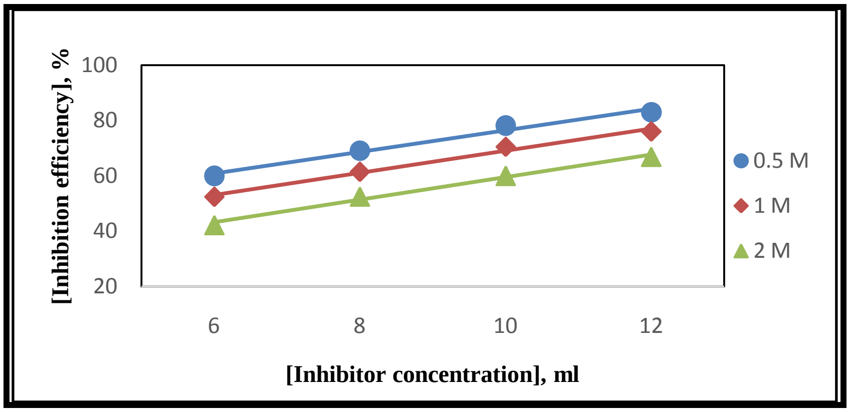


Figure 2

Figures: Corrosion rate 0.5 M TCA and I.E (%) of copper in presence of different concentration of *LI* extract for an immersion period of 24 h.

The plot of C_{inh} versus Cinh/θ (inhibitor concentration) shows straight line Figure-4, which indicates that the inhibition action appears to be the chemisorption and inhibitors cover both anodic and cathodic region through general adsorption following Langmuir isotherm.

$$\frac{\text{Cinh}}{\theta} = \frac{1}{Kads} + \text{Cinh} \quad (3)$$

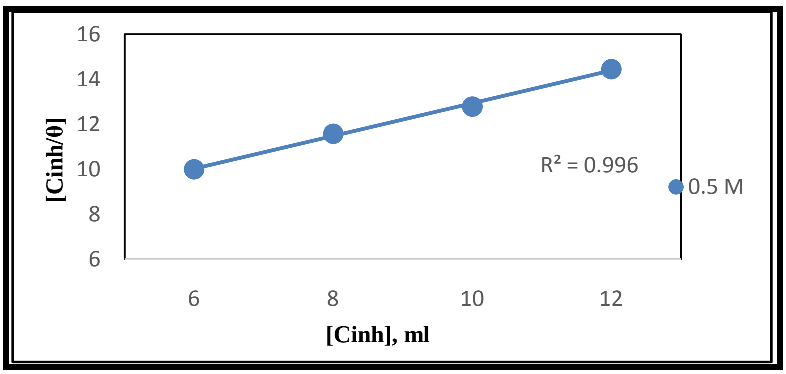


Figure 3: Langmuir adsorption isotherm for corrosion of copper in 0.5M TCA Solution containing different concentration of *LI* extract for an immersion period of 24 h.

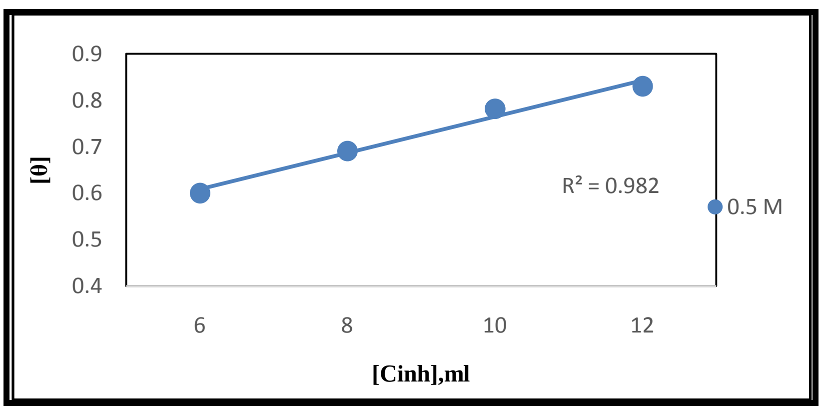


Figure 4: Temkin adsorption isotherm for corrosion of copper in 0.5 M TCA Solution containing different concentration of *LI* extract for an immersion period of 24 h.

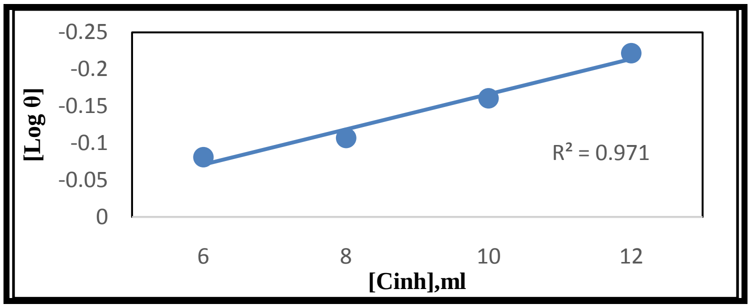


Figure 5: Freundlich adsorption isotherm for corrosion of copper in 0.5M TCA solution containing different inhibitor concentration of LI extract for an immersion period of 24 h**.**

Effect of temperature: The effect of temperature on corrosion rate and the specimen were immersed in 230 mL of 0.5 M TCA solution with *LI* inhibitor. Corrosion rate was measured in 0.5 M TCA containing temperature of 313, 323 and 333 K at 6, 8, 10 and 12 mL inhibitor concentration for 2 h exposure time. The effect of temperature was used thermostat assembly with an accuracy of ± 0.5.

$$\log\frac{P_1}{P_2} = \frac{Ea}{2.303R}\left[\left(\frac{1}{T_1}\right) - \left(\frac{1}{T_2}\right)\right] \qquad (4)$$

Where P_1 and P_2 are the corrosion rates at temperatures T_1 and T_2 respectively.

Table 3: Effect of temperature on corrosion rate (C.R) inhibition efficiency (I.E. %) and activation energy (Ea) for Copper in TCA containing with given inhibitor addition of *LI*.
Immersion period: 24h Effective specimen area: 0.2962 sq.m^2

Inhibitor Concentration	Temperature K						Mean (Ea) from eqation (4) (kJ/Mol)
	313K		323K		333K		
	C.R mg/sq.m²	I.E. %	C.R mg/sq.m²	I.E. %	C.R mg/sq.m²	I.E. %	
Blank	267.28	-	329.20	-	436.77	-	21.4038
6 ml	117.34	56.10	153.19	53.47	215.12	50.75	26.3958
8 ml	91.26	65.86	123.86	62.38	176.01	59.70	28.5469
10 ml	65.19	75.61	97.78	70.30	140.16	67.91	31.3649
12 ml	55.41	79.27	78.23	76.24	11408	73.88	33.1484

The change in temperature effect on corrosion rate of Copper is in 0.5 M TCA. Previous investigators showed that the corrosion rate increase with increase in temperature [10]. Effect of inhibition efficiency and activation energy (Ea) were calculated in (Table 3) of *LI* extract for Copper at 0.5 M acid and 6, 8, 10 and 12 mL inhibitor concentration. (Figures 6 and 7)

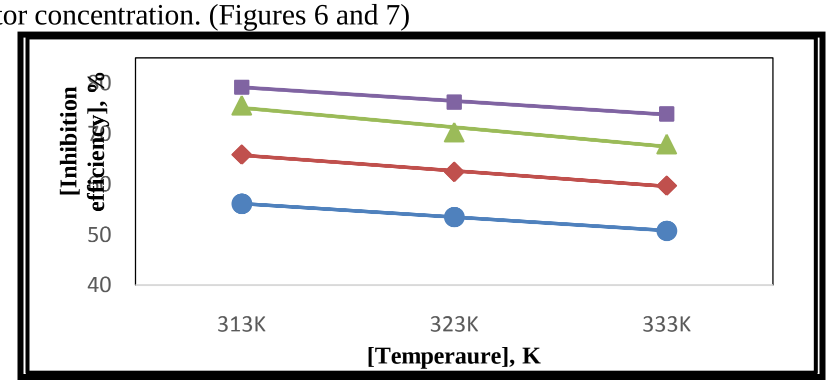


Figure 6: Effect of temperature on I.E (%) for Copper corrosion in 0.5 M TCA at different inhibitor concentrations of *LI* extract for immersion period of 2 h**.**

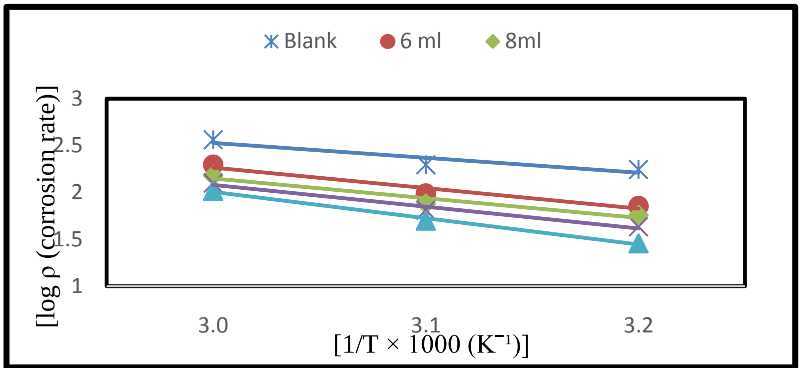


Figure 7: Effect of Arrhenius plots for copper in 0.5 M TCA in absence and presence of the different temperature of *LI* extract

Potentiodynamic study: Corrosion behavior of anodized Copper sample were study as per standards in 12 mL inhibitor and 0.5 M TCA solution using potentiostat Gamy reference 600. Corrosion cell consists of calomel electrode as reference electrode graphite rod as counter electrode and test sample as working electrode. The important corrosion potential (Ecorr), cathodic and anodic Tafel slop (βa and βc) value were obtained by extrapolating the Tafel straight line on the Tafel plot.

$$\eta\ \% = \frac{\text{icorr} - \text{icorr (inh)}}{\text{icorr}} \times 100 \qquad (5)$$

Potentiodynamic curve of *LI* extract in 0.5 M solution with 12 ml of *LI* extract are shown in figure-7. In anodic value of βa decreases with presence of *LI* extract. The inhibition efficiency (η %) increased with *LI* extract concentration reaching a maximum value 99.54 % at 12 mL.

Table 4. Potentiodynamic data and inhibition efficiency I.E (%) for copper in 0.5 M TCA at 12 ml *LI* inhibitor.

System	**Ecorr (mV)**	**Icorr (μA)**	**Tafel Slop**			**Inhibition efficiency (I.E %)**	
			Anodic +βa	**Cathodic -βc**	**β (mV)**	**By Polarization Method**	**By Mass Loss Method**
Blank	105.0	5.510	135.7	652.8	48.78	-	-
LI	76.40	0.340	99.60	264.8	31.43	93.83	83.03

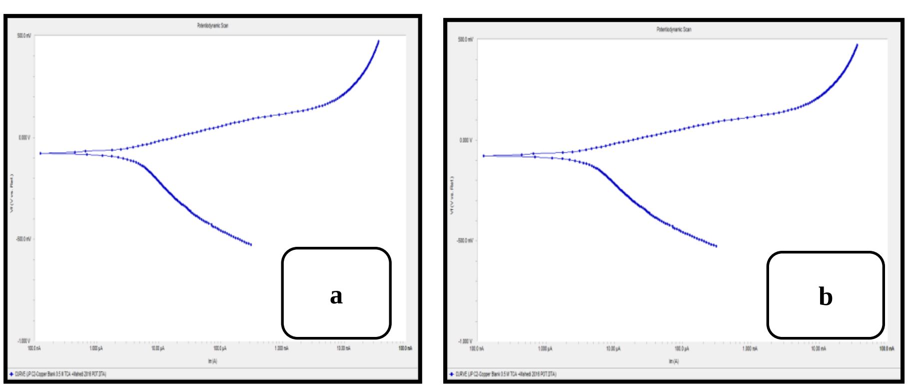


Figure 8: Potentiodynamic polarization curve for copper in (a) 0.5 M TCA and (b) 0.5 M TCA in the presence of 12 mL *LI* extract.

Electrochemical Impedance spectroscopy measurement (EIS): EIS were carried over the frequency range from 10 kHz to 0.01 Hz at open circuit potential. The capacitive semicircle at higher frequencies is attributed to the redox $Cu\text{-}Cu^+$ reaction since it was assumed to be the rate determining step in the charge transfer process [11]. Therefore, the resistance value obtained from intercept of the first capacitive semicircle with real axis corresponds to the $Cu\text{-}Cu^+$ charge transfer resistance.

Nyquist plots of Copper in 0.5 M TCA solution in the presence of 12 mL concentration of *LI* extract are given in (Figure-9) , where it can be observed that the diameter of the semicircles increase with increasing *LI* extract concentration. The increase capacitive semicircles, suggests that the inhibition action of these inhibitor is due to their adsorption on the metal surface with altering the corrosion mechanism.

$$I.E\% = \frac{Rct\,(inh) - Rct}{Rct\,(inh)} \times 100 \quad (6)$$

$$Cu \rightarrow Cu^{+2} + 2e^- \text{ (anode)}$$
$$H^+ + e^- \rightarrow H \text{ (cathode)}$$

Followed by the reaction,

$$H + H \rightarrow H_2$$

The following secondary reaction can also take place in TCA solution [12].

$$2M + 2H^+ \rightarrow H_2 + 2M^+ \text{ (anode)}$$
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \text{ (cathode)}$$

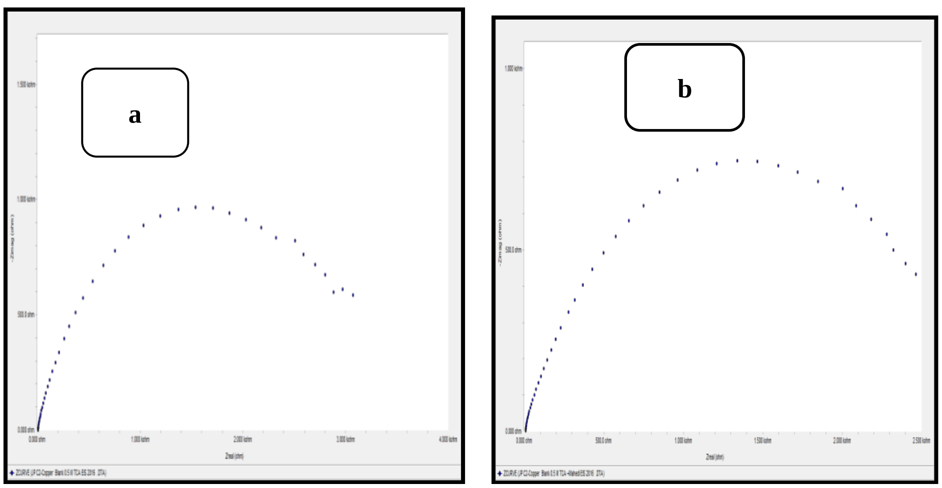


Figure 9: Nyquist plot for copper in (a) 0.5 M TCA and (b) 0.5 M TCA in presence of 12 ml *LI*.

APPLICATIONS

This study is useful for prevention of corrosion of copper by Lawsonia Inermis *(LI)* leaves extract as green inhibitor in TCA media. The corrosion of copper is mainly controlled by charge transfer process.

CONCLUSIONS

From the present study, it is concluded that *LI* extract can be used as an effective inhibitor for Copper corrosion in TCA medium. At all concentration of acid, as the inhibitor concentration increases inhibition efficiency increases and corrosion rate decreases. As the temperature increases corrosion rate increases in plain acid. It has also been found that the inhibitive action of *LI* extract is basically controlled by temperature and the concentration of the inhibitor.

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