

Azwain (*Trachyspermum Copticum*) Seed Extract as a Corrosion Inhibitor for Aluminum in Trichloroacetic acid

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Abstract: *The present work investigates the corrosion of aluminum in Trichloroacetic acid containing leaves extract by mass loss measurement and electrochemical techniques. The inhibitor efficiency of Azwain (*Trachyspermum Copticum*) seed extract was found to very with concentration was kept uniform for 24 hours and temperatures was kept uniform for 2 hours. Experimental results revealed that inhibition efficiency (I.E %) increased with increasing inhibitor concentration. As temperatures increased, percentage of inhibition decreases. The value of free energy of adsorption (ΔG^0_{ads}), energy of activation (E_a), enthalpy of adsorption (ΔH^0_{ads}) and entropy of adsorption (ΔS^0_{ads}) were calculated. The result also showed that, adsorption of inhibitor molecules on the surface of aluminum followed Temkin, Freundlich and Langmuir adsorption isotherm model. Potentiodynamic study and Electrochemical Impedance Spectroscopy (EIS) implies that film developed on aluminum using the both of Trichloroacetic acid exhibits good corrosion resistance.*

Keywords: Azwain (*Trachyspermum Copticum*), Aluminum, Trichloroacetic acid (TCA), Corrosion, Inhibitor

1. Introduction

Corrosion is defined as destruction of metals or deterioration of its physical properties due to chemical or electrochemical reaction with its surrounding atmosphere. Aluminum and its alloy show high resistivity towards a wide variety of corrosive environments. This is may be due to the formation as protective and at times invisible oxide film on the metal surface. The film is generally stable in solution of pH 4.5-8^[1].

Aluminum is the second most used metal after iron, it is used in a large number of application by itself and wide range of alloy of the standard electrode potential. Aluminum potentially attract as an anode material for power sources with high thermal, electrical conductivity and densities. Thus, inhibitor are one of the most convenient method for protection against corrosion, particularly in acid solution to prevent unexpected metal dissolution and acid consumption.

Aluminum and its alloy are widely used in many industries such as reaction vessels, pipes, machinery, automobile, aviation, household appliances, containers and chemical batteries. Aluminum is an important metal in many industries owing to it is good electrical and thermal conductivities, low density, high conductivity, low cost and availability for the fabrication and construction industries.

This study reports the inhibition effect of the Azwain seed extract which is commonly known as Azwain in India. Inhibition effect of Azwain on the corrosion of aluminum in TCA solution by mass loss method.

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 inhibitor.

The present study is based on the fact that some Nitrogen and Sulphur containing natural products like Hibiscus Sabdariffa^[2], Ananassativum^[3], Opuntia^[4,5], Argemone Mexicana^[6], Aloe-vera^[7], Cannabis^[8], Sansevieria Trifasciata^[9], Newbouldialeavis^[10], Dendrocalamus Brandisii^[11] etc. have been tested as corrosion inhibitors for metal. Synthetic dyes^[12], Synthetic drugs^[13], and heterocyclic^[14] compounds are widely used as corrosion inhibitors.

The aim of this study was to investigate the inhibition effect of TC as cheap, raw and nontoxic corrosion inhibitor on aluminum corrosion in TCA.

2. Material and Method

The Aluminum plate, which was used for the experiment having elemental composition: Al = 98.2%; Si = 0.316%; Fe = 0.71%; Cu = 0.292%; Mn = 0.102%; Mg = 0.014%; Cr = 0.022%; Ni = 0.0097%; Zn = 0.244%; Ti = 0.013%; Pb = 0.013%; Sn = 0.0088%. Specimens were prepared polished aluminum sheet by cutting into rectangular shaped pieces having dimension of 5.05cm × 0.255cm × 0.144cm with a small hole of 2mm diameter near the upper edge, were used for the determination of the corrosion rate.

Stock solution prepared by extraction of TC by refluxing 100 gm of dry material in 500 ml distilled water for 5 hours. The refluxed solution was filtered to remove any contamination. The concentration of the stock solution was calculated in terms of mM.

3. Result and Discussion

The results are presented in Table 1 to 3 and Figure 1 to 8. To assess the effect of corrosion of aluminum in TCA, TC were used as inhibitors.

The value of percentage inhibition efficiency (I.E %) and corrosion rate (C.R) obtained from mass loss method at 0.025 M, 0.050 M and 0.075 M concentration.

The inhibition efficiency was determined using the below given relationship.

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

Where W_0 = Mass loss without inhibitor

W_1 = Mass loss with inhibitor

Degree of surface coverage (θ) was calculated using the relation.

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

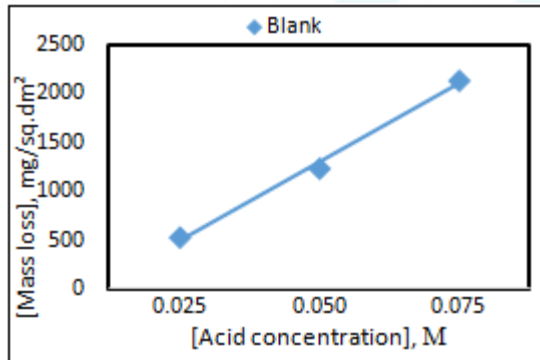


Figure 1: Effect of Mass loss of different Acid Concentration for 24 h at 301 K

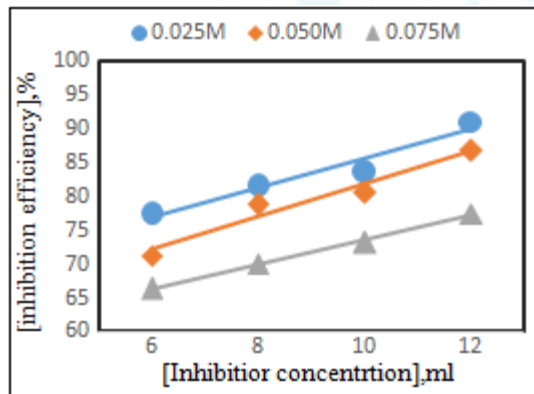


Figure 2: Effect of inhibition efficiency of TC for aluminum at different acid and inhibitor concentration for 24 h at 301 K

The inhibition efficiency decreases with the increase in 0.025, 0.050 and 0.075 M TCA. Maximum inhibition efficiency of 12 ml TC inhibitor is 91.10, 86.84 and 77.53% with respect to

0.025, 0.050 and 0.075 M TCA after 24 hours exposure time. For example 0.050 M TCA the inhibition efficiency was found to be 71.34, 78.95, 80.70 and 86.84% with respect to 6, 8, 10 and 12 ml inhibitor concentration.

The study the effect of temperature on corrosion rate, the specimen were immersed in 230 ml of 0.025 M TCA solution with TC inhibitor. Corrosion rate was measured in 0.025 M TCA containing temperature of 313, 323 and 333 K at 6, 8, 10 and 12 ml inhibitor concentration for 2 hours exposure time. The effect of temperature was used thermostat assembly with an accuracy of ± 0.5 .

The effect of change in temperature on corrosion rate of aluminum in 0.025M TCA. Previous investigators showed that the corrosion rate increase with increase in temperature. Effect of 313, 323 and 333K temperature of inhibition efficiency of TC extract for aluminum at 0.025M TCA and 6, 8, 10 and 12 ml inhibitor concentration.(Figure- 3)

Adsorption isotherm is usually used to describe the adsorption process. The most frequently used adsorption isotherms are Langmuir and Temkin. An assumption of Langmuir isotherm is the independence and equivalence of the adsorption site.

The Temkin isotherm is represented as:

$$\theta = C + K \quad (3)$$

C = Inhibitor concentration

K = Constant

θ = Degree of surface coverage

The Langmuir isotherm is represented as:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (4)$$

C = Inhibitor concentration

K = Constant

θ = Degree of surface coverage

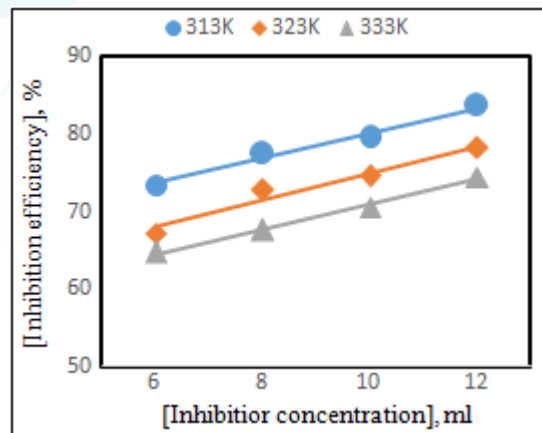


Figure 3: Effect of inhibition concentration of TC for aluminum in 0.025 M TCA at different temperature for 2 h

Table 1: Mass loss (mg/sq.m²) and inhibition efficiency (I.E %) for Aluminum in TCA containing with given inhibitor addition of TC.

Temperature 301±1K Immersion period: 24h Effective specimen area: 0.27761 sq.m²

		Acid concentration					
Inhibitors	Inhibitor Conc. (mM)	0.025 M		0.05 M		0.075 M	
		Mass loss (mg/sq.m ²)	I.E. (%)	Mass loss (mg/sq.m ²)	I.E. (%)	Mass loss (mg/sq.m ²)	I.E. (%)
Blank	-	525.91	-	1231.94	-	2132.48	-
TC	6 ml	118.87	77.40	353.03	71.34	713.26	66.52
	8 ml	97.26	81.51	259.37	78.95	637.61	70.10
	10 ml	86.45	83.56	237.75	80.70	569.16	73.30
	12 ml	46.82	91.10	162.10	86.84	479.11	77.53

Table 2: Corrosion rate (Log ρ) of aluminum in 0.025 M TCA in absence and presence of TC 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	525.91	2.7209	-	-	-	-
6ml	118.87	2.0751	77.40	0.7740	0.2260	0.5346
8ml	97.26	1.9879	81.51	0.8151	0.1849	0.6442
10ml	86.45	1.9368	83.56	0.8356	0.1644	0.7061
12ml	46.82	1.6704	91.10	0.9110	0.0890	1.0101

Table 3: Effect of temperature on corrosion rate (C.R) inhibition efficiency (I.E. %) and activation energy (Ea) for aluminum in TCA containing with give inhibitor addition of TC.

Immersion period: 24h Effective specimen area: 0.27761 sq.m²

Inhibitor Concentration	Temperature K						Mean(Ea) from equation(4) (kJ/Mol)
	313K		323K		333K		
	C.R mg/sq.m ²	I.E. %	C.R mg/sq.m ²	I.E. %	C.R mg/sq.m ²	I.E. %	
Blank	176.51	-	198.13	-	367.44	-	32.4758
6 ml	46.83	73.47	64.84	67.27	129.68	64.71	44.6704
8 ml	39.63	77.55	54.03	72.73	118.88	67.65	48.2953
10 ml	36.02	79.59	50.43	74.55	108.07	70.59	48.2338
12 ml	28.82	83.67	43.23	78.18	93.66	74.51	51.6220

The plot of surface coverage [θ] versus [C_{inh}], ml show straight line (Figure-5). When the fraction of surface covered is determined as function of the concentration at constant temperature adsorption isotherm could be evaluated at equilibrium condition. The plot of [C/θ] versus [C_{inh}], ml show straight line (Figure-4). The inhibition action appears to be the adsorption and inhibitors cover both anodic and cathodic region through general adsorption following Langmuir isotherm and also obey Freundlich adsorption isotherm. The plot of [log θ] versus [C_{inh}], ml show straight line. (Figure-6). Langmuir, Temkin and Freundlich adsorption isotherm for corrosion inhibition of aluminum in 0.025M TCA as can be seen from correlation coefficient value of R² = 0.9963 and R² = 0.9846 at 313K.

Figure 4: Effect of [C/θ] versus [C_{inh}] for TC at different temperature at 0.025M TCA at different inhibitor concentration.

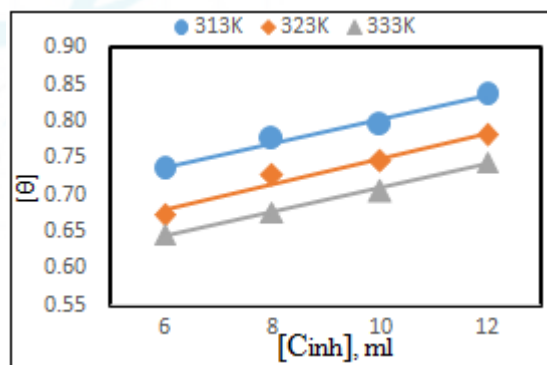
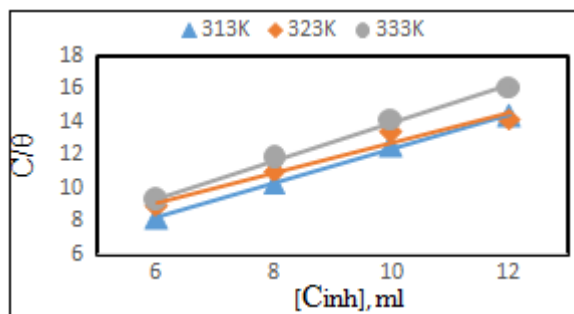


Figure 5: Effect of [θ] versus [C_{inh}] for TC at different temperature at 0.025 M TCA at different inhibitor concentration



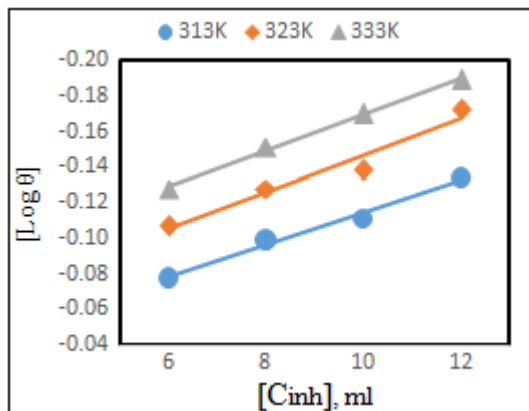


Figure 6: Effect of $[\log \theta]$ versus $[C_{inh}]$ for TC at different temperature at 0.025 M TCA at different inhibitor concentration.

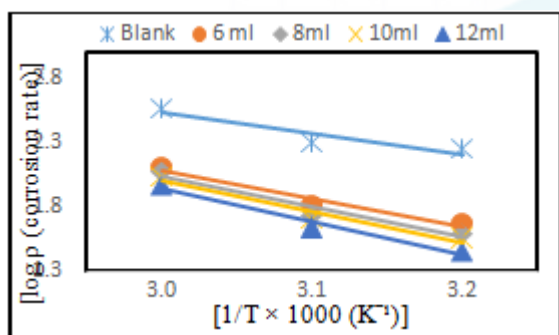


Figure 7: Effect of Arrhenius for aluminum in 0.025M in absence and presence of the different concentration of TC extract.

Energy of activation (E_a) was calculated from the slope of $\log p$ versus $1/T \times 1000$ (P = corrosion rate, T =absolute temperature) and using Arrhenius equation.

$$\log \frac{P_1}{P_2} = \frac{E_a}{2.303R} \left[\left(\frac{1}{T_1} \right) - \left(\frac{1}{T_2} \right) \right] \quad (5)$$

where, p_1 and p_2 are the corrosion rate at temperature T_1 and T_2 respectively.

Mean ' E_a ' value was calculated by using equation (5) for aluminum in 0.025M TCA is 32.48 kJ/mol. While in acid containing inhibitor the mean E_a value are found to be higher than that of an uninhibited system (Table -3). which indicate that the inhibitor induces energy barrier for the corrosion reaction and the inhibitor was strongly adsorbed on metal surface.

From the data of Table-2 and Figure-3 as temperature increase, rate of corrosion increase while percentage of inhibition efficiency decrease. The value of E_a calculated from

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

System	E_{corr} (mV)	I_{corr} (μA)	Tafel Slope			Inhibition efficiency (I.E %)	
			Anodic $+\beta_a$	Cathodic $-\beta_c$	β (mV)	By Polarization Method	By Mass Loss Method
Blank	-707	536	177.3	1	0.4323	-	-
TC	-657	2.46	35.6	291	13.7911	91.1	99.54

Electrochemical Impedance spectroscopy measurement (EIS)

the slop of an Arrhenius plot (Figure-7) are almost similar, show good agreement with the calculated values.

Potentiodynamic study

Corrosion behavior of anodized aluminum sample were study as per standards in 12 ml inhibitor and 0.025M TCA solution using potentiostat Gamry reference 600. Corrosion cell which consists of calomel electrode as reference electrode graphite rod as counter electrode and test sample as working electrode. The important corrosion potential (E_{corr}), cathodic and anodic Tafel slop (β_a and β_c) value were obtained by extrapolating the Tafel straight line on the Tafel plot.

$$\eta \% = \frac{i_{corr} - i_{corr}(inh)}{i_{corr}} \times 100 \quad (6)$$

Potentiodynamic curve of TC extract in 0.025 M solution with 12 ml of TC extract are shown. (Figure-8). In anodic value of β_a decreases with presence of TC extract. The inhibition efficiency (η %) increased with TC extract concentration reaching a maximum value 99.54 % at 12 ml.

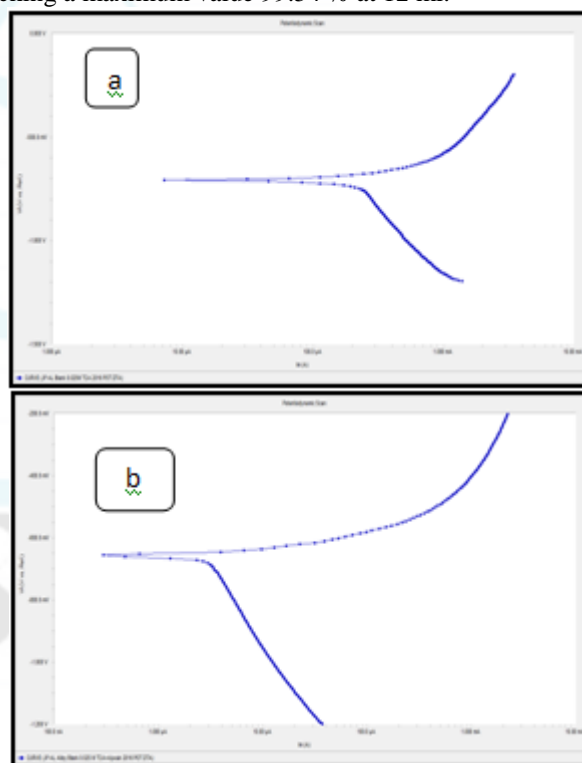
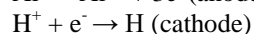
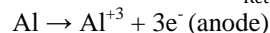


Figure 8: Effect of potentiodynamic curve for aluminum (a) in 0.025M TCA and (b) 0.025M TCA in presences of 12 ml TC extract.

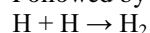
EIS were carried over the frequency range from 10 kHz to 0.01 Hz at open circuit potential. The capacitive semicircle at

higher frequencies is attributed to the redox Al-Al⁺³ reaction since it was assumed to be the rate determining step in the charge transfer process [12]. Therefore, the resistance value obtained from intercept of the first capacitive semicircle with real axis corresponds to the Al-Al⁺³ charge transfer resistance. Nyquist plots of aluminum in 0.025 M TCA solution in the presence of 12 ml concentration of TC extract are given in (Figure-9), where it can be observed that the diameter of the semicircles increase with increasing TC 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.

$$I.E\% = \frac{R_{ct}(inh) - R_{ct}}{R_{ct}(inh)} \times 100 \quad (7)$$



Followed by the reaction,



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

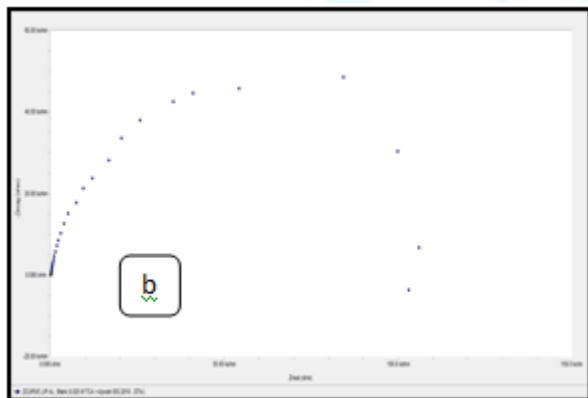
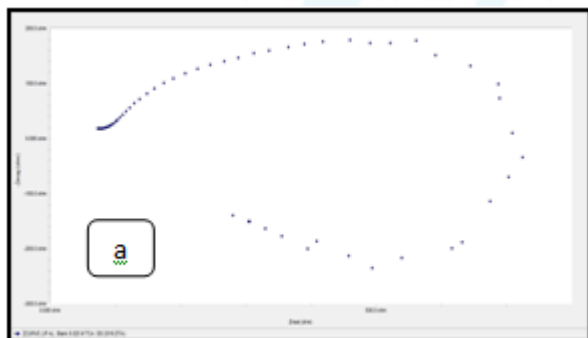
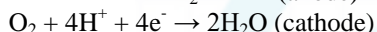
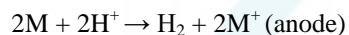


Figure 9: Effect of Nyquist curve for aluminum (a) in 0.025M TCA and (b) 0.025M TCA in presences of 12 ml TC extract

Conclusion

From the present study, it is concluded that *LI* extract can be used as an effective inhibitor for aluminum 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 TC extract is basically controlled by temperature and the concentration of the inhibitor.

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