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 Azwain (Trachyspermum copticum) seed extract by mass loss measurement and electrochemical techniques. The inhibitor efficiency of Azwain 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 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. The Azwain seed extract is environmental friendly, biodegradable, nontoxic, cheap and easily available material which is used as corrosion inhibitor for aluminum metal in trichloroacetic acid (TCA).

Keywords: Azwain (Trachyspermum copticum) seed, Corrosion, Aluminum, Trichloroacetic acid.

Introduction:

Corrosion is defined as destruction of metals or deteriotion of its physical properties due to chemical or electrochemical reaction with its surrounding atmosphere. Aluminum and it´s 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 it´s 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 Murry koenigii [2], Ananas sativum [3], Neem leaf [4,5], Piper guineense [6], Carica papaya [7], Fenugreek seed [8], Marigold [9], Oxandra askeckii[10], Achyranthes aspera L [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 Azwain as cheap, raw and non-toxic corrosion inhibitor on aluminum corrosion in TCA.

Experimental procedure

Metal specimen and surface pretreatment

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.

Azwain (Trachyspermum copticum) seed

Preparation of inhibitor

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

Result and discussion

Mass loss measurements

The results are presented in Table 1 to 3 and Figure 1 to 8. To assess the effect of corrosion of Aluminum in TCA, of Azwain was 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.

$$\text{Inhibition efficiency (I.E\%)} = \frac{W_0 - W_1}{W_0} \times 100$$ Where W_0 = Mass loss without inhibitor

W_1 = Mass loss with inhibitor

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

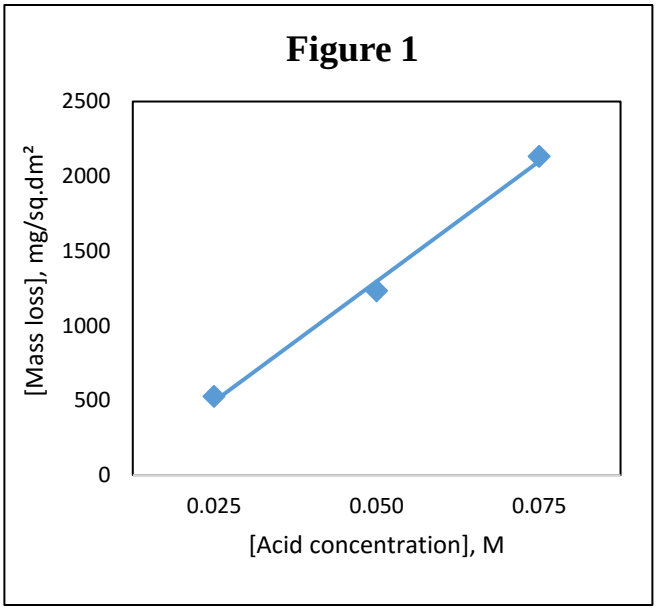
$$\theta = \left(\frac{W_0 - W_1}{W_1}\right)$$

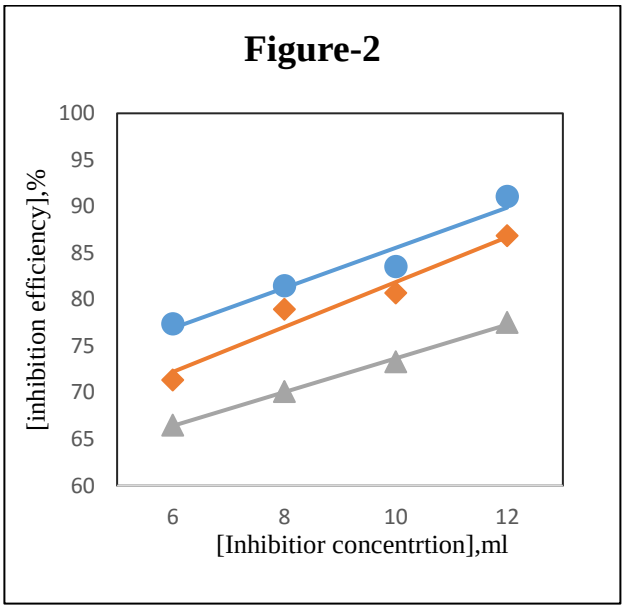
TABLE-1

Mass loss (mg/sq.m^2) and inhibition efficiency (I.E %) for Aluminum in TCA containing with given inhibitor addition of Azwain.

Temperature 301±1K Immersion period: 24h Effective specimen area: 0.27761 sq.m^2

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	-
Azwain	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





The inhibition efficiency decreases with the increase in 0.025, 0.050 and 0.075 M TCA. Maximum inhibition efficiency of 12 ml Azwain 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 exampal 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. (Figure-2). Mass loss Vs Acid concentration of Aluminum of TCA. (Figure-1).

Effect of temperature

The study the effect of temperature on corrosion rate, the specimen were immersed in 230 ml of 0.025 M TCA solution with Azwain 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.

TABLE - 2

Effect of temperature on corrosion rate (C. R) inhibition efficiency (I.E %) for Aluminum in 0.025 M TCA containing with given Azwain inhibitor.

Immersion period: 2 hours Effective specimen area: 0.27761 sq.m^2

	Inhibitor Concentration	**Temperature K**					
		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		176.51	-	198.13	-	367.44	-
Azwain	6 ml	46.83	73.47	64.84	67.27	129.68	64.71
	8 ml	39.63	77.55	54.03	72.73	118.88	67.65
	10 ml	36.02	79.59	50.43	74.55	108.07	70.59
	12 ml	28.82	83.67	43.23	78.18	93.66	74.51

Figure-3

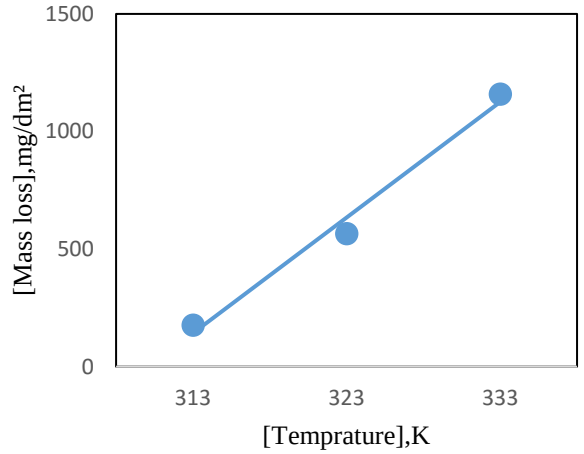
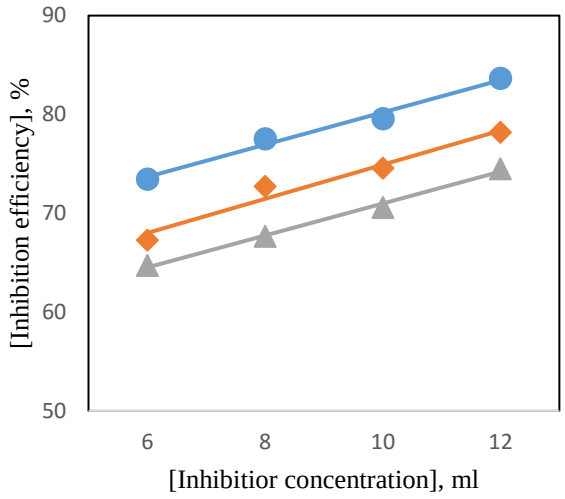


Figure-4



The effect of change in temperature on corrosion rate of Aluminum in 0.025 M TCA. Previous investigators showed that the corrosion rate increase with increase in temperature [15]. Effect of inhibition efficiency of Azwain extract for Aluminum at 0.025 M acid and 6, 8, 10 and 12 ml inhibitor concentration. (Figure-4)

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:

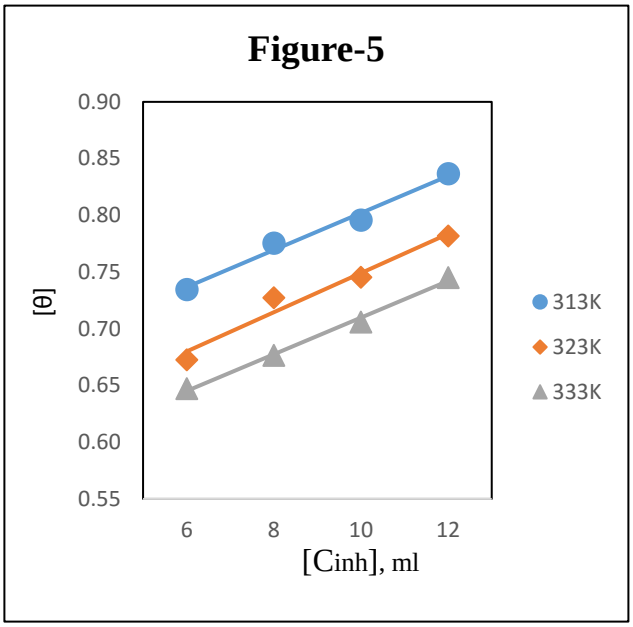
$\theta = C + K$ C = Inhibitor concentration K = Constant

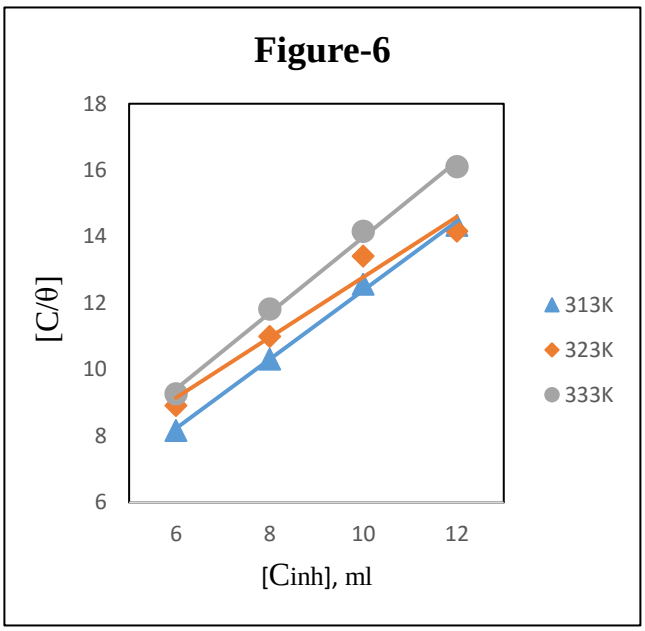
θ = Degree of surface coverage

The Langmuir isotherm is represented as:

$\frac{C}{\theta} = \frac{1}{K} + C$ C = Inhibitor concentration K = Constant

θ = Degree of surface coverage





The polt of surface coverage [θ] versus [Cinh], 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 polt of [C/θ] versus [Cinh], ml show straight line (Figure-6). The inhibition action appears to be the adsorption and inhibitors cover both anodic and cathodic region through general adsorption following Langmuir isotherm. Langmuir and Temkin adsorption isotherm for corrosion inhibition of Aluminum in 0.025 M TCA as can be seen from correlation coefficient value of R^2 = 0.9963 and R^2 = 0.9846 at 313 K.

Potentiodynamic study

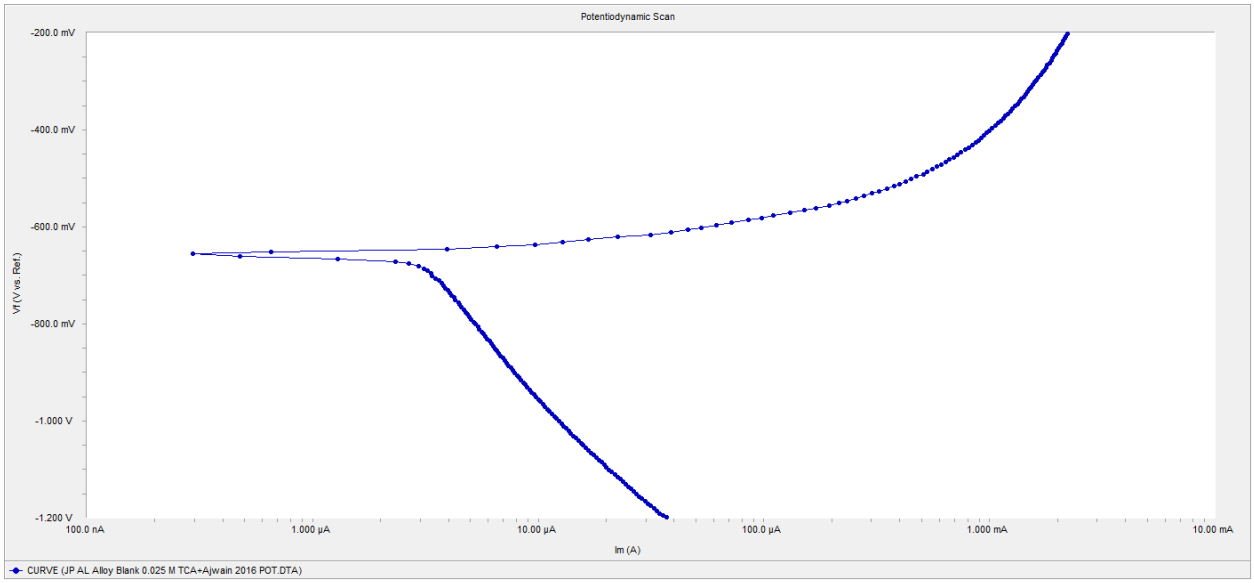
Corrosion behavior of anodized Aluminum sample were study as per standards in 12 ml inhibitor and 0.025 M TCA solution using potentiostat Gamry reference 600. Corrosion cell which consists of calomel electrode as reference electrode graphite rod as counter electrode and test sample as working electrode.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

TABLE-3

Potentiodynamic data and inhibition efficiency I.E (%) for aluminum in 0.025M TCA at 12 ml Azwain inhibitor.

System	E_{corr} (mV)	I_{corr} (µA)	Tafel slope (mV/decade)		IE (%)	
			+βa	-βc	Mass loss method	Pot. Method
Blank	-707	536.0	177.3	1.000	-	-
Azwain	-657	2.460	35.60	291.0	91.10	99.54

Figure-7



Potentiodynamic curve of Al in 0.025 M solution with 12 ml of Azwain extract are shown. (Figure-7). In anodic value of βa decreases with presence of Azwain extract. The inhibition efficiency (η %) increased with Azwain extract concentration reaching a maximum value 99.54 % at 12 ml.

$$Al \rightarrow Al^{+3} + 3e^{-} \text{ (anode)}$$

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

Followed by the reaction,

$$H + H \rightarrow H_2$$

The following secondary reaction can alsso take place in TCA solution [16].

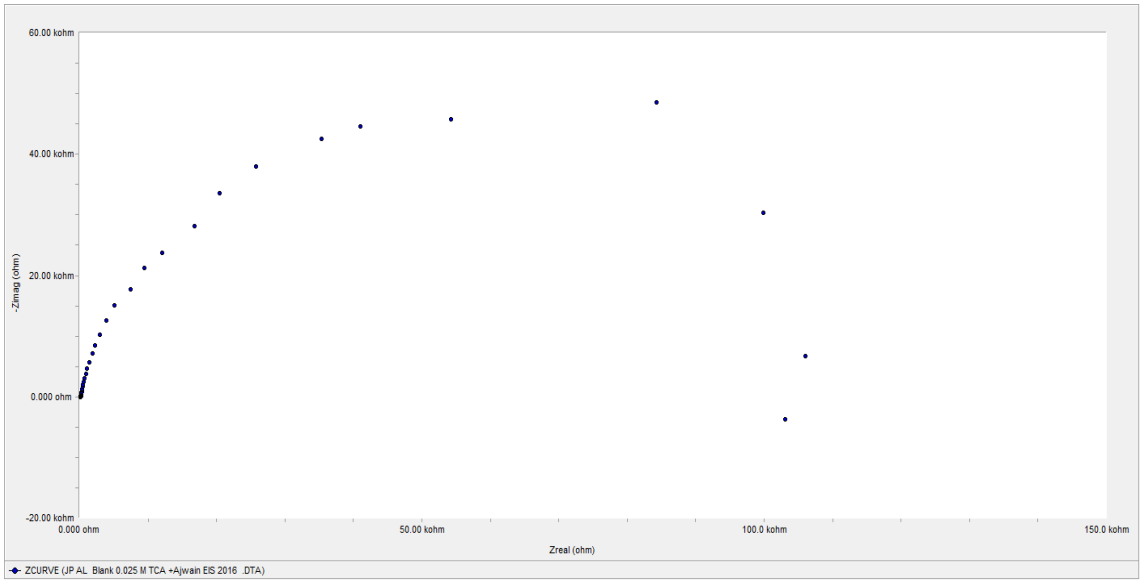
$$2M + 2H^{+} \rightarrow H_2 + 2M^{+} \text{ (anode)}$$

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

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 Al-Al^{+} reaction since it was assumed to be the rate determining step in the charge transfer process [17]. Therefore, the resistance value obtained from intercept of the first capacitive semicircle with real axis corresponds to the Al-Al^{+} charge transfer resistance.

Figure-8



Nyquist polts of Aluminum in 0.025 M TCA solution in the presence of 12 ml concentration of Azwain extract are given in (Figure-8) , where it can be observed that the diameter of the semicircles increase with increasing Azwain 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.

Conclusions

From the present study, it is concluded that Azwain 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 Azwain extract is basically controlled by temperature and the concentration of the inhibitor.

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