International Journal of Scientific Engineering and Research (IJSER)
ISSN (Online): 2347-3878
Index Copernicus Value (2015): 62.86 | Impact Factor (2015): 3.791

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

Jetal J. Patel[1], K. N. Patel[2]

Department of chemistry, Shri U.P. Arts, Smt. M. G. Panchal Science and Shri V. L. Shah Commerce College-Pilvai-382850, Gujrat, India

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 (TrachyspermumCopticum), Aluminum, Trichloroacetic acid (TCA), Corrosion, Inhibitor

1. 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 Hibiscus Sabdariffa[2], Ananassativum[3],Opuntia[4,5], Argenmone 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 contaimination. The concentration of the stock solution was calucated 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.

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

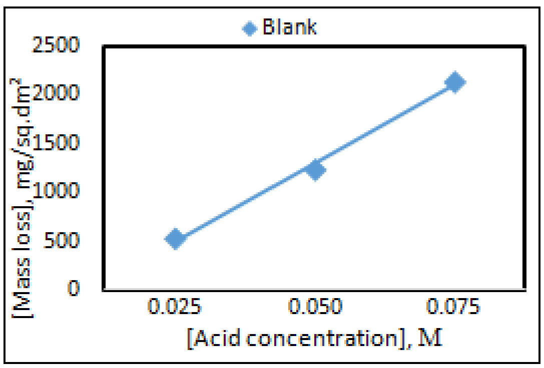

Figure 1: Effect of Mass loss of different Acid Concentration for 24 h at 301 K

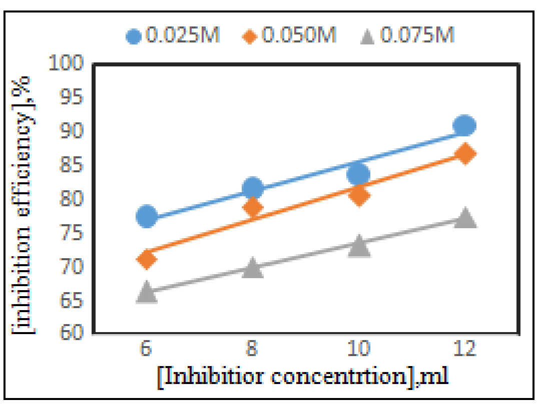

Figure 2: Effect of inhibition efficiency of *TC* for aluminum at different acid and inhibitor concentration for 24 h at 301 K

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 ofLangmuir 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

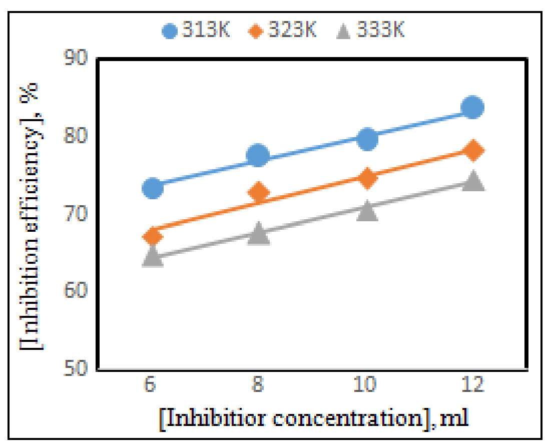

Figure 3: Effect of inhibition concentration of *TC* for aluminum in 0.025 M TCA at different temperature for 2 h

Table 1: Mass loss (mg/sq.m^2) 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.m^2

Inhibitors	Inhibitor Conc. (mM)	Acid concentration					
		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.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	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 polt of surfacecoverage [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-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 polt of [log θ] versus [Cinh], 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 R^2 = 0.9963 and R^2 = 0.9846 at 313K.

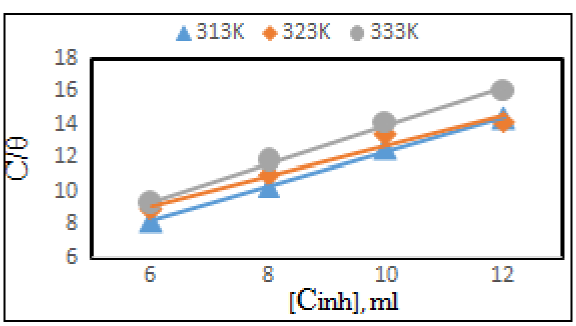

Figure 4: Effect of [C/θ] versus [Cinh] for *TC* at different temperature at 0.025M TCA at different inhibitor concentration.

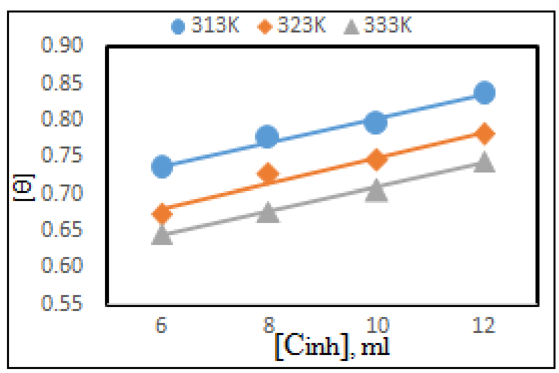

Figure 5: Effect of [θ] versus [Cinh] for *TC* at different temperature at 0.025 M TCA at different inhibitor concentration

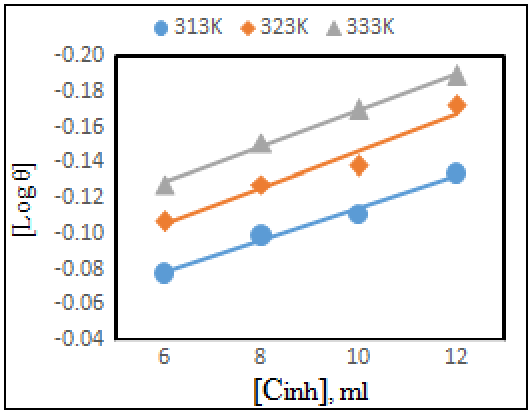

Figure 6: Effect of [log θ] versus [Cinh] for *TC* at different temperature at 0.025 M TCA at different inhibitor concentration.

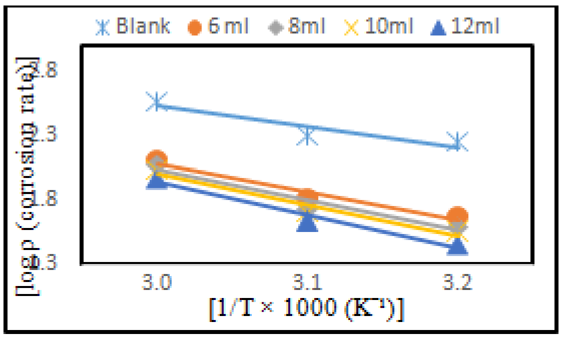

Figure 7: Effect of Arrhenius for aluminum in 0.025M in absence and presence of the different concentration of *TC*extract.

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

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

where, $\rho_1$andρ_2 are the corrosion rate at temperature T_1 and T_2 respectively.

Mean 'Ea' 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 Ea 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 Ea calculated from 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 potentiostatGamry 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.

$$\eta\,\% = \frac{\text{icorr} - \text{icorr (inh)}}{\text{icorr}} \times 100 \quad (6)$$

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

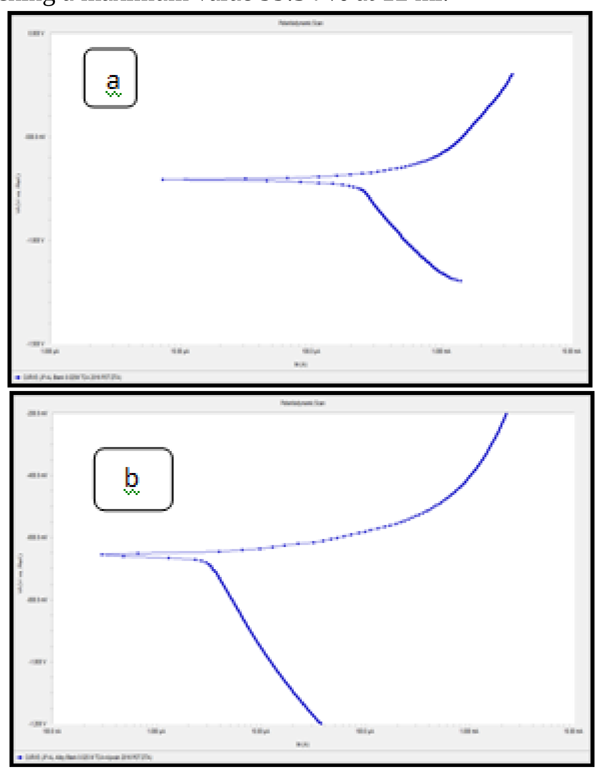

Figure 8: Effect of potentiodynamic curve for aluminum (a) in 0.025M TCA and (b) 0.025M TCAin presences of 12 ml *TC* extract.

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

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.

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

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

Followed by the reaction,
$H + H \rightarrow H_2$

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

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

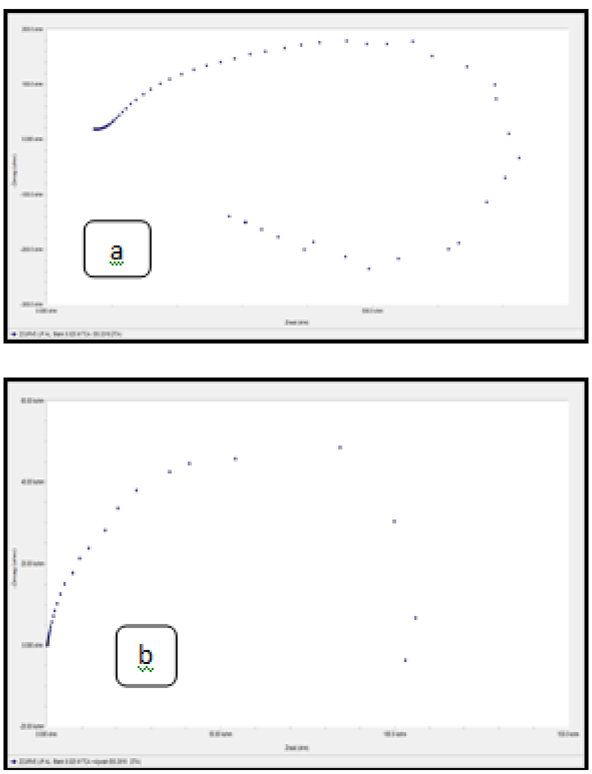

Figure 9: Effect of Nyquist curve for aluminum (a) in 0.025M TCA and (b) 0.025M TCAin presences of 12 ml *TC* extract

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.

Acknowledgment

Authors are thankful to Prof. J. J. Vora, Head of Chemistry Department, H. N. G. University Patan, Gujarat and Prof. S. S. Shah, Principal of Shri U. P .Arts, Smt. M. G. Panchal Science and Shri V. L. Commerce College, Pilvai, Gujarat for providing necessary facilities.

References

[1] El Hosary A A, Saleh R M and Shams El Din A M. **(1972)**, "Corrosion inhibition by naturally occurring substance-I. The effect of Hibiscus Subdariffa (karkade) extract on the dissolution of Al", Corrosion Science. Vol.12, 897-904
[2] Molina-Ocampo L B, M G valladares-Cisneros and J G Gonzalez-Rodriguez. **(2014)**, "Using Hibiscus Sabdariffa as corrosion inhibitor for Al in 0.5M H_2SO_4"International Journal Electrochemical Science. Vol.10, 388-403
[3] Ating E I, S AUmoren, I IUdousoro, E EEbenso and A P Udoh. **(2010)**, "Leaves extract of AnanasSativum as green corrosion inhibitor for aluminum in HCL acid solution", Green Chemistry Letter and Review. Vol.3, 61-68
[4] El- Etre. **(2003)**, "Inhibition of aluminum corrosion using Opuntia extract", Corrosion Science. Vol.45, 2485-2495
[5] Sharma P, Chaturvedi A, Upadhyay R K and Parashar P. **(2008)**, "Study of corrosion inhibition efficiency of naturally occurring Argenmone Mexicana on aluminum in HCL solution", Journal of Technology Research Chemistry. Vol.15(1), 21
[6] Al-Turkustani A M, Arab S T and Aldahiri R H. **(2010)**, "Aloe plant extract as an environmentally friendly inhibitor on the corrosion of aluminum in HCL in absence and presence of Iodide ions", Journal of Modern Applied Science. Vol.4, 105-124
[7] James A O and Etela A O. **(2008)**, "Aloe-vera an inhibitor of aluminum corrosion in HCL", Journal of Pure and Applied Chemistry. Vol.3(3), 159-163
[8] Abdel-Gaber A, Abd-El-Nabey B and Saadaway M. **(2009)**, "Inhibitive action of Cannabis plant extract on the corrosion of copper in 0.5M H_2SO_4", Corrosion Science. Vol.51, 1038
[9] Oguzie E E. **(2007)**, "Corrosion inhibition of aluminum in acidic and alkaline media by SansevieriaTrifasciata extract", Corrosion Science. Vol.49, 1527-1539
[10] Nnanna L A, Obasi V U, Nwadiuko O C, Mejeh K I, Ekekwe N D, Udensi S C. **(2012)**, "Inhibition by Newbouldialeavis leaf extract of the corrosion of aluminum in HCL and H2SO4 solution", Archives of Applied Science Research. Vol. 4(1), 207-217
[11] Deng S and X Li. **(2012)**, "Inhibition effect of DendrocalamusBrandisii leaves extract on aluminum in HCL solution", Corrosion Science. Vol.65, 299-308

[12] Desai P S and Vashi R T. **(2010)**, "Inhibitive efficiency of Xylenol Orange as corrosion inhibitors for aluminum in TCA", Indian Journal of Chemical Technology. Vol.17, 50-55
[13] Desai P S and Kapopara S M. **(2014)**, "Inhibitory action of Xylenol Orange on aluminum corrosion in HCL solution", Indian Journal of Chemical Technology. Vol.21(2), 139-145
[14] Desai P S and Vashi R T. **(2011)**, "Inhibitive efficiency of Sulphathiazole for aluminum corrosion in TCA", Anti Corrrosion Methods and Materials. Vol.58(2), 70-75
[15] Qureshi Absar A and Eswarkumar K. (2010), "Phytochemical constituents and pharmacological activities of Trachyspermumammi", Plant Archives. Vol.10, 955-959
[16] Singh Ambrish and Quraishi M A. (2012), "Azwain (TrachyspermumCopticum) seed extract as an efficient corrosion inhibitor for aluminum in NaOH solution", Research Journal of Recent Science. Vol.1, 57-61
[17] Rajendran S, J Jeyansundari, P Usha, J A Selvi, B Narayansamy, A P P Regis and Rengan. (2009), "Corrosion behavior of aluminum in the presence of an aqueous extract of Hibiscus Rosa-Sinensis," Portugaliae Electrochemical Acta. Vol.27 (2), 153-164
[18] Obot I B, Obi-Egbedi N O, Umoren S A, Ebenso E E. (2010), "Synergistic and antagonistic effects of anions and Ipomoea Involcrata as green corrosion inhibitor for aluminum dissolution in acidic medium", International Journal Electrochemical Science. Vol.5, 994-1007