CASSIA ACUTIFOLIA EXTRACT AS CORROSION INHIBITOR FOR AL CU ALLOY IN NAOH SOLUTION.

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Abstract

Corrosion inhibition of Al-Cu alloy in 1.5 M NaOH by extract of Cassia acutifolia (CA) plant was studied using chemical and electrochemical measurements. The inhibition efficiency was found to increase with increasing concentration of CA extract. The adsorption behaviour followed Flory – Huggins and thermodynamic – Kinetic isotherms. The effects of temperature range (25-65°C) on the corrosion behaviour indicate that the inhibition efficiency of extract decreases with rise of temperature leads to physical adsorption. Thermodynamic parameters were calculated from Arrheinius transition state equation. Polarization curves showed that extract act as cathodic inhibitor. Tafel slopes are more or less constant indicating that the action of extract has no effect on the mechanism of corrosion process. The results obtained show that the CA extract could serve as an effective inhibitor of the corrosion of Al-Cu alloy in NaOH solution.

Keywords: Corrosion inhibition, chemical, electrochemical methods.

Introduction:

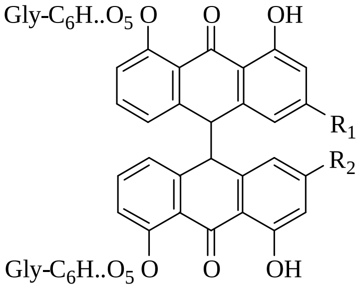
The use of inhibitors for the control of corrosion of metals and alloys which are in contact with aggressive environment is an accepted practice. Large numbers of organic compounds were studied(1-10), all these with N , S and O showed significant inhibition efficiency. But, unfortunately most of these organic compounds not only expensive but also toxic to living species. Plant extracts have become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors. Few of natural products(11-14) were previously used as corrosion inhibitors for aluminium and its alloys in NaOH solution.

There are no reports in the literature on the use of Cassia acutifolia (CA) therefore; the aim of the present work is to elucidate the effect of the plant extract of CA as corrosion inhibitor for Al-Cu alloy in NaOH solution, using chemical and electrochemical techniques.

Experimental:

Materials and electrolytes:

Corrosion tests were performed on Al-Cu alloy, of chemical composition (w%): 94.750 Al, 3.980 Cu, 0.725 Fe and 0.550 Mn using EDAX. Al alloy sheets with dimension of 3.0 x 1.0 x 0.2 cm were used for weight loss and thermometric measurements. For polarization and impedance measurements, a cylindrical rod mounted into glass tube by epoxy resin, with surface area of 1.68 cm^2. Before each experiment, the electrode surface was mechanically polished using successive grades of emery papers down to 4/0, and degreased with ethanol and then washed several times with bidistilled water and dried. The electrolytic solution of NaOH was prepared using Analar grade reagent, and bidistilled water. Preparation of plant extract, CA Fig.(1) is carried out by boiling weighed amounts of powder of the crused seeds of plant. After filtration the liquid was evaporated in an oven at 50°C for 48 hours. Crystalline precipitate is formed. The concentrations are expressed as w/v.



R_1 = COOH , R_2 = CHOH

Figure (1): The main chemical structure of Cassia acutifolia (Sennoside)(15)

Chemical measurements:

Weight loss measurement was recorded by the usual procedure (16) in temperature range 25-65°C with and without of different concentrations of plant extract. Triplicate samples were used to check reproducibility of results. Corrosion rates were expressed in g/cm^2.min, and the percentage inhibition efficiency(17) (IE%) was calculated from the following relationship :

$$IE\% = \left[1 - \left(\frac{R_{inh}}{R_{free}}\right)\right] \times 100$$

(1)

Where R_{free} and R_{inh} are corrosion rate of alloy sheet in free and inhibited solutions, respectively.

Thermometric measurements were described by Mylius(18). Each experiment was carried out with 15 ml of test solution. The initial temperature in all experiments was 25°C. The reaction number (RN) is defined as

$$R.N = \frac{T_m - T_i}{t} \; {}^{o}\mathrm{C/min} \qquad (2)$$

Where T_m and T_i are the maximum and initial temperatures respectively, and t is the time in minutes taken to reach T_m.

Electrochemical Measurements:

The potentiodynamic polarization (PDP) and the electrochemical impedance spectroscopy (EIS) measurements are carried out in a conventional three-compartment cell with a cylindrical rod of Al-Cu alloy as working electrode. A saturated calomel electrode (SCE) used as reference and Platinum wire as counter electrode.

PDP and EIS measurement were achieved using ACM Gill AC connected to a Samsung computer. The frequency range for EIS of 100 kHZ – 10 mHZ with applied signal amplitude of 30mV around the rest potential. Before the measurements the working electrode was introduced into the test solution and left for 10 min at open circuit potential. Polarization curves were obtatied at scan rate of 5 mV/min starting from cathodic potential going to anodic direction. All the measurements were done at 25 ± 1°C in aerated NaOH solution and under unstirred conditions.

Results and discussion:

Weight loss measurements:

Al-Cu samples were immersed in aerated solution of NaOH of different concentrations range (0.5- 2.5 M) along a period of 60 min. The calculated corrosion rate with the concentration, are 1.69e-6, 2.13e-6, 2.89e-6, 3.64e-6 and 4.50e-6 indicates that R_{corr} of Al-Cu alloy is a function of concentration. Fig.(2) represents the relation between weight loss (g/cm^2) and the immersion time for Al-Cu alloy in 1.5 M NaOH solution in absence and presence of different concentrations (0.4 to 8.0 g/L) of Cassia acutifolia (CA) extract . As can be seen from the curves, there is a remarkable decrease in weight loss comparing with blank solutions. The linearity with time indicates that the absence of insoluble surface film during corrosion, and the inhibitor was adsorbed onto the metal surface and thereafter, inhibits the corrosion process$^{(19)}$

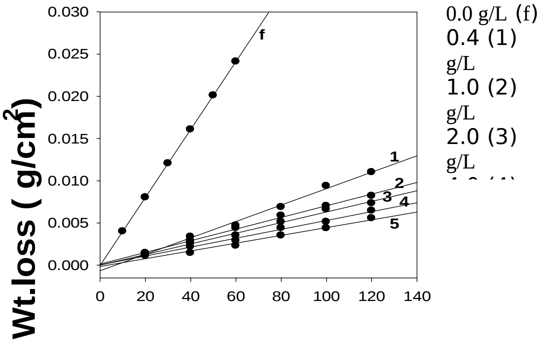


Figure (2): Weight loss-time curves for Al-Cu alloy in 1.5 M NaOH solution in absence and presence of different concentrations of CA extract at 25ºC.

The inhibition efficiency percent, IE% and the degree of the surface coverage Θ which represents the part of the metal surface covered by inhibitors molecules were calculated using the following equation$^{(17)}$.

$$\theta = 1 - \left(\frac{R_{inh}}{R_{free}}\right) \qquad (3)$$

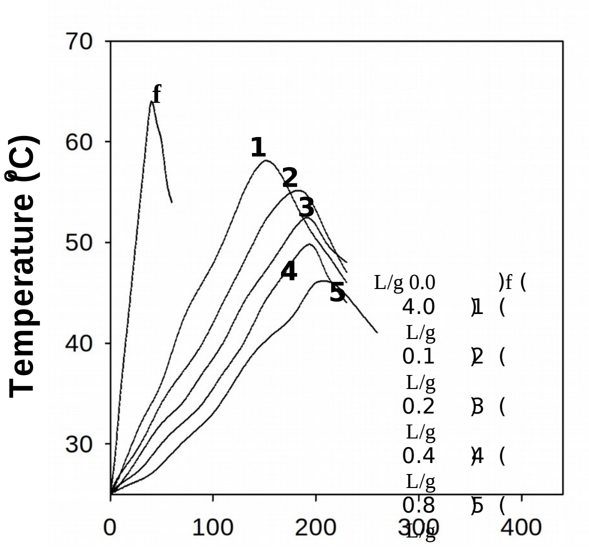
The values of R_{corr} , IE% and ϴ at different concentrations of CA extract in 1.5 M NaOH solution are listed in Table (1) . Inspection of these Table, the data revealed that as CA extract concentration is increased, R_{corr} decreases while the IE% and ϴ increases. The increase of ϴ may be due to the increase of the number of adsorbed molecules of CA extract at Al-Cu alloy surface. A good inhibition efficiency percent observed at 8.0 g/L, with 88.56% .

Table (1): Effect of CA extract concentration on R_{corr} , IE% and ϴ for Al-Cu alloy in 1.5 M NaOH solution at 25ºC.

C_{inh} (g/L)	**$R_{corr.}$**	**IE%**	**ϴ**
0.4	9.72e-5	75.82	0.758
1.0	6.91e-5	82.81	0.828
2.0	6.30e-5	84.33	0.843
4.0	5.25e-5	86.94	0.869
8.0	4.60e-5	88.56	0.886

Thermometric measurements:

In this method the temperature change of the system involving Al-Cu alloy in 1.5 M NaOH solution, was followed in absence and presence of different concentrations (0.4 – 8.0 g/L) of CA extract Fig.(3). The maximum temperature T_m measured in free NaOH is 64ºC and attained after 40 min, corresponds to the reaction number (RN) of 0.97 ºC/min. Upon increasing concentrations of CA extract, T_m decrease and the time required to reach T_m increases, both factors cause a large decrease in RN of system. This indicates that CA extract act as inhibitor and adsorb on both anodic and cathodic sites of the sample surface.



Time(min)

Figure (3): Thermometric curves for Al-Cu alloy in 1.5 M NaOH solution in absence and presence of different concentrations of CA extract at 25ºC .

$$IE\% = \left[1 - \left(\frac{R.N_{inh}}{R.N_{free}} \right) \right] \times 100 \qquad (4)$$

The values of R.N and IE% of different concentrations of CA are given in Table (2). These values show that the CA extract is a good inhibitor of Al-Cu alloy in NaOH solution, and this agreement to that obtained from weight loss method.

Table (2): Effect of CA extract concentrations on RN and IE% for Al-Cu alloy in 1.5 M NaOH solution at 25ºC.

C_{inh} (g/L)	RN	IE%
0.4	0.219	77.54
1.0	0.157	83.90
2.0	0.143	85.33
4.0	0.128	86.87
8.0	0.105	89.23

Adsorption isotherm:

The adsorption of organic adsorbate on the surface of metal is regarded as substitutional adsorption process between the organic compound in the aqueous phase $(Org)_{aq}$ and the water molecules adsorbed on the metal surface $(H_2O)_{ads}$(20) .

$$Org_{sol} + x(H_2O)_{ads} \Leftrightarrow Org_{ads} + x(H_2O)_{sol} \qquad (5)$$

Where x is the number of water molecules replaced by one organic molecule. The variation of surface coverage Θ with concentration of CA extract in NaOH solusion is shown in Fig.(4).

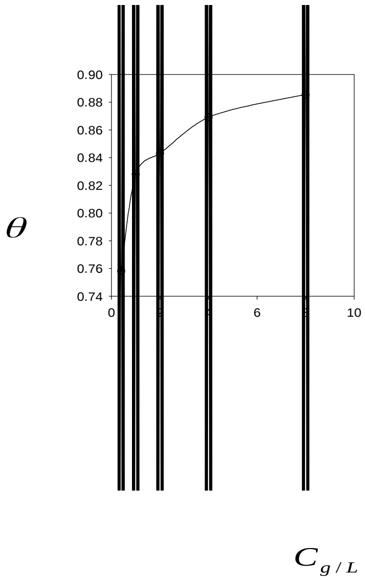


Figure (4): Variation in surface coverage with concentration of CA extract in 1.5 M NaOH solution at 25ºC.

The curve has S-shaped adsorption isotherm, indicating a physical adsorption. To clarify the nature of adsorption of CA extract on the Al-Cu alloy surface, the theoretical fitting of Flory- Huggins and the kinetic thermodynamic models were investigated in 1.5 M NaOH solution.

Folry – Huggins isotherm is given by$^{(21)}$

$$\theta / \left[x(1-\theta)^{x} \right] = K\left[C\right] \qquad (6)$$

where x is the number of adsorbed water molecules substituted by a given inhibitor molecules.

The kinetic – thermodynamic model is given by (22)

$$\log\left[\theta/(1-\theta)\right] = \log k + y\log C \qquad (7)$$

where y is the number of inhibitor molecules occupying one active site. Value of y>1, imply the formation of multilayer of inhibitor molecules on the metal surface, and when y<1 indicate that the given inhibitor will occupy more than one active site. The binding constant K is given from the intercept of equation(7). The relation between the binding constant of the adsorption (K) and the standard free energy of adsorption ΔG°_{ads} is given by the following equation:

$$K = \left(\frac{1}{C_{H_2O}}\right)\exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \qquad (8)$$

where C_{H_2O} is the concentration of water molecules (g/L) at electrode/electrolyte interface at 25C°, R is the gas constant (8.314 J/mol/degree) and T is the absolute temperature.

$$\log\left(\frac{\theta}{1-\theta}\right)$$

The parameters of K, y, 1/y, x and ΔG°_{ads} are given in Table (3). It is clear that the values of x, 1/y indicating that, more than one water molecule displacing from the surface, and CA molecules will occupy more than one active site , K values is large, this means that the stronger interaction between CA extract and Al-Cu alloy surface.

The calculated values of ΔG°_{ads} are low suggesting that the nature of the inhibitor adsorption is mainly physical adsorption and negative sign meaning spontaneous interaction of inhibitor molecule with corroding metal surface(23).

Tabel (3): Linear fitting parameters and the standerd free energy of CA extract for Al-Cu alloy in 1.5 M NaOH solution at 25°C.

Kinetic-thermodynamic				Flory-Huggins		
Y	**Y/1**	**K (g^{-1} *l*)**	**-ΔG°$_{ads}$(kJ/mol)**	**X**	**K (g^{-1} *l*)**	**-ΔG°$_{ads}$(kJ/g^{-1}L)**
0.29	3.45	163.50	29.75	3.81	129.83	29.18

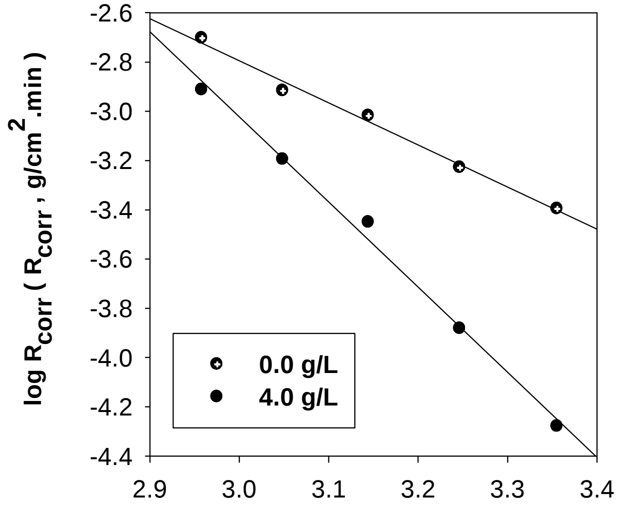
Activation energy calculation:

The effect of temperature range (25-65°C) on R_{corr} and IE% of Al-Cu alloy in 1.5 M NaOH solution in absence and presence of 4.0 g/L of CA extract, using weight loss method. Table (4) indicates that R_{corr} in absence and presence of CA extract increased with rise in temperature, indicating that CA extract was adsorbed on alloy surface at all temperatures. Also IE% decreases with increasing temperature, and the high IE% at 25°C. This result suggests a physical adsorption of CA extract on Al-Cu alloy surface.

Table (4): Effect of temperatures on R_{corr} and IE% for Al-Cu alloy in 1.5 M NaOH solution in absence and presence 4.0 g/L of CA extract.

	R_{corr} g/cm^2 .min		**IE%**	
$C_{inh.}$ (g/L)	**Free** 0.0	**inhibited** 4.0	0.0	4.0
25 °C	4.02e-4	5.25e-5	-	86.94
35 °C	5.90e-4	1.31e-4	-	77.80
45 °C	9.58e-4	3.54e-4	-	63.05
55 °C	1.21e-3	6.38e-4	-	47.27
65 °C	1.98e-3	1.22e-3	-	38.38

Arrhenius plot for R_{corr} (g cm^{-2} min^{-1}) vs 1/T (°K^{-1}) was found to be linear Fig.(5) . The energy of activation (E_a^*) is calculated from the slope of this plot.



$10^3 / T\ (^oK^{-1})$

Figure (5): Arrhenius plots of the corrosion rate for Al-Cu alloy in 1.5 M NaOH solution in absence and presence of CA extract

Activation thermodynamic parameters of Al-Cu alloy in test solution in absence and presence of CA extract is given by Arrhenius transition state equation(24).

$$R_{corr} = \left[\left(\frac{RT}{Nh} \right) \exp\left(\frac{\Delta S^*}{R} \right) \right] \exp\left(\frac{-\ \Delta H^*}{RT} \right) \qquad (9)$$

where h is plank's constant, N is Avogadro's number and ΔS^* , ΔH^* are the activation entropy and enthalpy, respectively. A plot of $\log \frac{R_{corr}}{T}$ vs $\frac{1}{T}$ gives straight line with slope of $\left[\frac{-\ \Delta H^*}{2.303R} \right]$ and an intercept of $\left[\log\left(\frac{R}{Nh} \right) + \left(\frac{\Delta S^*}{2.303R} \right) \right]$, represented in Fig.(6)

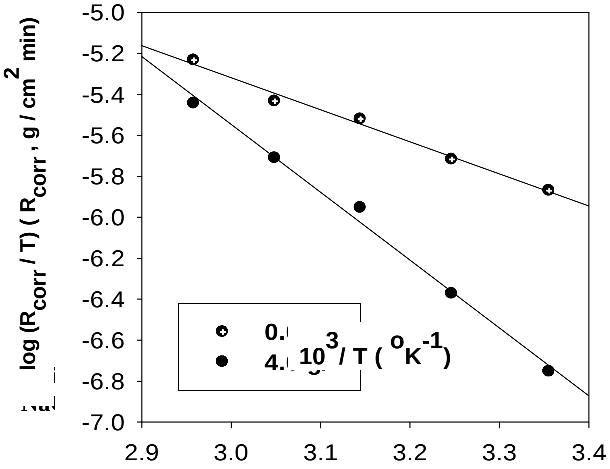


Figure (6): A oy in 1.5 M Na

The calculated values of activation parameters E_a^* , ΔH^* and ΔS^* for Al-Cu alloy in test solution in absence and presence of different CA extract are shown in Table (5). It is clear that, E_a^* increases in the presence CA extract, suggested that the corrosion inhibition of CA occured through physical adsorption. Also higher ΔH^* values indicate that, the degree of surface coverage decreased with rise in temperature, supporting the proposed physical adsorption mechanism. The entropy ΔS^* in absence and presence of CA extract is large and negative meaning that the increasing in ordering accompained the dissolution process.

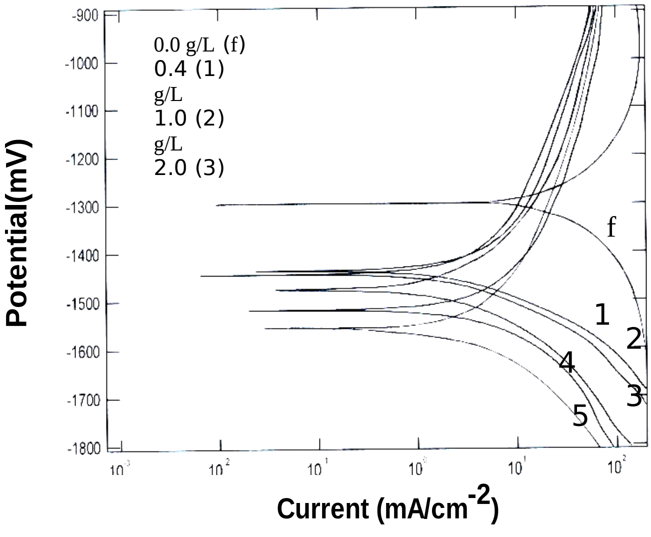
Table (5): The values of activation parameters E_a^* , ΔH^* and ΔS^* for Al-Cu alloy in 1.5 M NaOH solution in absence and presence of CA extract.

free solution			Inhibited solution		
E_a^* kJ/mol	ΔH^* kJ/mol	ΔS^* J/ °K/mol	E_a^* kJ/mol	ΔH^* kJ/mol	ΔS^* J/ °K/mol
32.71	30.07	-209.19	66.15	63.52	113.23-

Polarization measurements:

Fig.(7) shows the anodic and cathodic curves of Al-Cu alloy in aerated 1.5 M NaOH solution in absence and presence of different concentrations (0.4 – 8.0 g/L) of CA extract. The curves produces a little shift on the anodic region and a greater shift on the cathodic region.

Potential(mV)



Current (mA/cm^{-2})

H_2SO_4(c)

Figure (7): Potentiodynamic polarization curves for Al-Cu alloy in 1.5 M NaOH solution in absence and presence of different CA extract concentrations at 25ºC.

The electrochemical parameters E_{corr} i_{corr}, B_a, B_c and IE% are given in Table(6). The inhibition efficiencies are defined as:

$$IE\% = 100 \times \left(1 - \frac{i_{corr}}{i^{o}_{corr}}\right) \qquad (10)$$

where i_{corr} , i^{o}_{corr} refer to corrosion current densities of inhibited and uninhibited test solution , determined by extrapolation of Tafel lines to corrosion potential. Inspection of the Table reveals that E_{corr} shifted towards the cathodic direction, and the values of the corrosion current densities i_{corr} decreases with increasing the concentration of CA extract, indicating that the inhibitive property of the plant extract is concentration dependent. In alkaline medium**(25)** the plant extracts extend the pH stability range of the amphoteric oxide or hydroxide layers, as well as repairing the defective oxide or hydroxide films, decreasing the diffusion rate of reactant to the surface and removing corrosion products from the surface. Tafel slopes B_a , B_b are more or less constant suggesting that the inhibiting action of CA extract does not effect on the mechanism of the corrosion process. Also IE% increases with their concentration, and at 8.0 g/L it gives high efficiency 90.97% in 1.5M NaOH solution at 25ºC.

Table (6): Potentiodynamic parameters of Al-Cu alloy in 1.5 M NaOH solution in different concentrations of CA extract at 25 ºC.

$C_{inh.}$ (g/L)	**$-E_{corr.}$ mV**	**.i_{corr} mA/cm^2**	**β_a mV/dec**	**$-\beta_c$ mV/de**	**IE%**
0.0	1300	30.00	155.0	145.3	-
0.4	1442	8.06	134.0	89.46	73.13
1.0	1445	6.01	127.1	83.67	79.97
2.0	1478	4.77	147.0	94.86	84.10
4.0	1520	4.01	149.2	95.40	86.63
8.0	1550	2.71	144.9	88.87	90.97

Electrochemical impedance spectroscopy (EIS):

The Fig.(8) show the Nyquist plots for Al-Cu alloy in 1.5 M NaOH solution in absence and presence of various concentrations of CA extract at 25°C.

HCl(a)

Z"(ohm.cm^2)

'(ohm.cm^2)

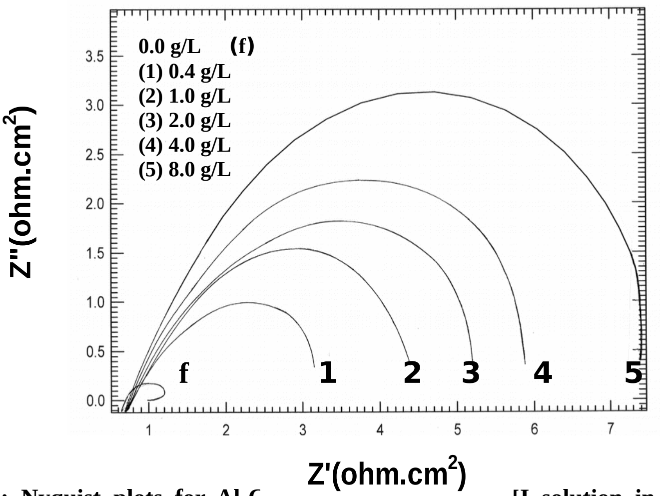


Figure (8): Nyquist plots for Al-C H solution in absence and presence of different CA extract concentrations at 25°C.

The presence of inhibitor led to change of the impedance plots in both shape and size. The plots exhibited depressed semicircles with center below the real axis. This phenomenon could be related to the surface heterogeneity due to the microscopic roughness of the electrode surface and distribution of active sites adsorption of inhibitor$^{(26)}$. Also the size of the capacitive loops are increased by increasing the concentration of CA extract. This indicated that CA increased the charge transfer resistance and then it had an inhibiting effect on Al-Cu alloy in alkali electrolyte solution. The inhibition efficiencies had the same trend of those obtained from the weight loss and potentiodynaic measurements. The inhibition efficiency IE% is calculated from the charge transfer R_{ct} , usingthe following equation :

$$IE\% = \left[1 - \left(\frac{R_{ct_{inh}}}{R_{ct_{corr}}}\right)\right] \times 100 \qquad (11)$$

Table (7) showed that, by increasing the CA extract concentration the charge transfer resistance, R_{ct} and IE% values increased. The higher R_{ct}, the lower corrosion rate and more efficient is the inhibitor.

Based upon the experimental results, the inhibition effect of CA extract can be related to a physical adsorption process it contains of organic compounds e.g. anthraquinone, glucoside flavonoid and alkaloid, these containing electrophilic substituents as N_2 and O_2 which decrease the electron density at an adsorption centers of plant extract molecules and facilitate the adsorption of molecules on a negatively charged sites and reduce corrosion.

Table (7): Impedance parameters of Al-Cu alloy in 1.5 M NaOH solution with different concentrations of CA extract at 25°C.

$C_{inh.}$ (g/L)	C_{dl} (µF / cm²)	R_{ct} (Ω . cm²)	IE%
0.0	2.88e-3	4.61e-1	-
0.4	1.17e-3	2.00	76.95
1.0	6.46e-4	2.96	84.43
2.0	1.81e-4	3.82	87.93
4.0	1.59e-4	4.34	89.38
8.0	1.32e-4	6.02	92.34

Also attractive lateral(1) interaction between the inhibitor molecules containing long hydrocarbon chains due to Vander Waals forces give rise to stronger adsorption and higher inhibition efficiency as in CA plant extract.

Therefore, it could be concluded that Cassia acutifolia extract acts as excellent corrosion inhibitor for Al-Cu alloy in 1.5 M NaOH solution.

Conclusion:

1)CA displayed higher inhibitive properties towards the corrosion of Al–Cu alloy in 1.5 M NaOH solution in temperature range 25 – 65°C

2)The physical adsorption behaviour of CA in agreement with the Flory – Huggins and thermodynamic/kinetic model, one molecule of inhibitor occuping more than one active site.

3)Polarization studies show that CA extract acts as cathodic – type inhibitor.

4)The results of EIS indicate that values of R_{ct} and IE% increase with increasing the inhibitor concentration.

5)There is a great agreement between the results obtained by different techniques of measurements.

References:

1. SASTRI V. S.; Corrosion Inhibitors, Principle and Application", New York, John Wiley and Sons, P. 33 (1998).
2. ASHASSI-SORKHABI H. , GHASEMI Z. AND SEIFZADEH D. ; Appl. Surf. Sci. 249 (1-4) , 408 (2005).
3. OGUZIE E.E., OKOLUE B.N., EBENSO E.E., ONUOHA G.N. AND ONUCHUKWU A.I. ; Mater. Chem. Phys. 87 (2-3), 394 (2004).
4. METIKES-HUKOVIC M. , BABIC R. AND GRUBAC Z. ; J. Appl. Electrochem. 32 (1) , 35 (2002).
5. LOCHANI M. , JEYARAJ T. , RAJA C. AND RAMYA S. ; Electrochem. Sci. and Technol. 36 (3-4) (2001).
6. BACCARIA A.M. ; Corros. Sci. 41 , 885 (1999).
7. AHMED M.M. ; Portugalia Electrochimica Acta, 24 , 1 (2006).
8. OGURTSOV N.A. , PUD A.A. , KAMARCHIK P. AND SHAPOVAL G.S. ; Synthetic Metals, 143 (1) , 43 (2004).
9. ABD EL-REHIM S.S. , HASSAN H.H. AND AMIN M.A. ; Corros. Sci. 46 (9), 5 (2004).
10. AL-JUHAIMAN L. , AL-MAYOUF A. AND SUHAYBANY A. ; J. Saudi Chem. Soc. 8 (3) , 547 (2003).
11. SALEH R.M. , ISMAIL A.A. AND EL-HOSARY A.A. ; Corros. Sci. 23 (11) , 1239 (1983).
12. MULLER ; Corros. Sci. 44, 1583(2002)
13. OGUZIE E.E. , ONUOHA G.N. AND EJIKE E.N. ; Pigment and Resin Technology, 36 (1) , 44 (2007).
14. ABDEL-GABER A.M. , KHAMIS E. , ABO-ELDAHAB H. , ADEEL SH. ; Mat. Chem. and phys. 96 , 9 (2008).
15. TREASE AND EVANS ; Pharmacognosy, 15 Ed., New York, Toronto (2000).
16. SANYAL B. AND SRRIVASTAVA K. ; Br. Corros. J. 8,28, (1975).
17. SINGH R. N., VERME N. AND SINGH W. R. ; Corrosion, 45 , 222 (1989).
18. MYLIUS M ; Z Metallk, 14 , 233 (1922).
19. EL-MAHDY G. A. AND MAHMOUD S. S. ; Corros. Sci, 51 (6), 436 (1995).

20. BOCKRIS J. AND SWINKLS D.; J. Electrochem. Soc.111, 736 (1964).
21. FLORY P. J. ; J chem.phys. 10, 51 (1942).
22. KHAMIS E., AMEER M. A. , ALANDIS N. M. AND SENANI G. A. ; Corrosion, 56 (2), 127(2000).
23. BRACHER D. AND MERCER A. D.; Br. Corros. J. 3, 120 (1968).
24. VASHI R. T. AND CHAMPANERI V. A.; Ind. J. Chem. Technol. 4, 180, (1997).
25. MOORE W. M., CHEN C. T. AND SHIRN G. A. ; Corrosion–NACE, 40 (12), 644 (1984).
26. ASHASSI – SORKHABI H., GHALEBSAZ – JEDDLI N. , HASEM ZAHED F. , AND JAHANI H. ; Electrochim. Acta, 51, 3848, (2006).