

Calotropis Procera as Potential Corrosion Inhibitor for Commercial Aluminium in HCl Medium

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ABSTRACT

Corrosion inhibition of commercial aluminium in 1M HCl by leaves extract was investigated using weight loss method, hydrogen evolution method, potentiodynamic polarisation method and impedance spectroscopy method. The results indicate that Calotropis procera leave extract was a good corrosion inhibitor for aluminium in hydrochloric acid medium. Hydrogen evolution study shows that inhibition efficiency depends on the concentration of the inhibitor. Potentiodynamic polarisation curves shows that the leaves extract act as mixed type inhibitor. EIS indicates that the charge transfer control the corrosion process. Adsorption of inhibitor on the aluminium surface follows Langmuir adsorption isotherm. The mechanism of physical adsorption is proposed from the inhibitory action of calotropis procera leaves extract and is satisfactorily explained by thermodynamic and kinetic parameters such as ΔH^0 , ΔS^0 , ΔG^0 and E_a are calculated. All the experiments show good agreements.

Key words: corrosion inhibitor, aluminium, acid, Calotropis procera leaves extract, adsorption.

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INTRODUCTION

Aluminium and its alloys are used in automotive, ship building, aerospace and industrial application due to its low cost and light weight in nature [1-3]. In industries HCl is used in pickling, chemical and electrochemical etching for aluminium foil [4,5]. Aluminium form protective oxide form on the surface of the metal and is stable between the pH range 4 to 8.5. The 1M HCl cause the passive film crash at certain spots on the metal surface. Several inhibitors have used to control the corrosion of aluminium. Inhibitors generally reduce the aggressiveness of the environment towards the metal and may provide an insoluble precipitate. The most important method is the use of sulphur, oxygen or nitrogen containing organic compounds as corrosion inhibitors to delay the corrosion reaction and thus decrease the corrosion rate [6,7]. The hazardous effect of organic inhibitors and the need to develop cheap, non-toxic and biodegradable nature have attracted the researcher to focus on the use of naturally occurring plant products. Plants extracts contain different organic compounds (e.g. tannins, alkaloids, pigments, saponins, carbohydrates, proteins, organic and amino acids), some of which have been reported to possess corrosion inhibition abilities [8-11]. There have been many research reports on the natural products as corrosion inhibitor in aggressive solutions [12,13] but no published information is available on Calotropis procera leaves extract as corrosion inhibitor for aluminium in 1M HCl solution.

Calotropis procera (Ait) R. Br. (Sodom Apple) belongs to the family Asclepiadaceae. It occurs in most parts of the tropical world, in dry sandy and alkaline soils, in waste land and grows abundantly as a weed. It is a shrub. The results of phytochemical screening of water shows that Tannins, Flavonoids, Saponins, Alkaloids, Saponins Glycosides, Cardiac Glycosides, Steroids, Balsams, Volatile Oils, Glycosides [14]. The present study investigates the efficiency of *Calotropis procera* leaves extract as corrosion inhibitor for aluminium in HCl solution using weight loss method, hydrogen evolution method, potentiodynamic polarisation method and impedance spectroscopy method.

MATERIALS AND METHODS

The aluminium pieces are mechanically cut into 5cm X 1cm X 0.15 cm thickness. Each specimen was perforated with a hole of about 0.02 cm at one end to allow the passage of thread. Each specimen was degreased in alcohol, washed with double distilled water and dried with acetone and it was used for weight loss method and hydrogen evolution method. Aluminium cylindrical rod is embedded using teflon holder with flat surface was the only exposed area at the bottom of the rod is 0.2826 cm^2 was used for electrochemical study. The leaves were shade dried for few days and then the dry leaves were ground well and made in to fine powder. 20 g of the leaves powder was dissolved in 200ml of double distilled water and refluxed in 250ml R.B. flask for one hour. The refluxed solution was filtered off carefully and the filtrate is evaporated over the water bath until solid mass was obtained. The solid mass was ground well and preserved for future study. Inhibitor test solution was prepared in the concentration range of 0.3, 0.6, 0.9, 1.2 and 1.5 g/L using 1M hydrochloric acid as medium at 303 to 333K using water bath.

Weight loss method

The aluminium specimens were weighed before experiment using Mettler Toledo electronic balance with the accuracy of ± 0.0001 . Pre-weighed specimens were immersed for 1h, 2h and 3h in 100 ml of inhibitor solution after which the specimens were withdrawn and rinsed under running tap. The specimens rinsed in acetone, air dried and then reweighed. From the difference between the initial and the final weight, the weight loss was calculated. Duplicate experiments were also conducted. The percentage inhibition efficiency was calculated using equation

$$\text{Corrosion rate (CR)} = \frac{K \times W}{\text{DAT}} \quad \text{mmpy} \quad (1)$$

Where, mmpy - millimetre per year, K- constant, W -Weight loss in g, D-Density in g / cm^3 (2.7 g / cm^3 for aluminium) and A-Area in cm^2 and T- immersion time in h

$$\text{Inhibition efficiency (\%IE)} = \frac{\text{CR}_{\text{inh}} - \text{CR}_{\text{uninh}}}{\text{CR}_{\text{uninh}}} \times 100 \quad (2)$$

Where CR_{inh} - Corrosion rate of aluminium in the presence of inhibitor and CR_{uninh} - Corrosion rate of aluminium in the absence of inhibitor

Gasometry method

This technique gives a rapid and sensitive means for gauging any interruption by an inhibitor with regards to gas evolution at the metal-corrodent interphase. The corrosion rates of aluminium in the absence and presence of leaves extract was assessed by monitoring the volume of gas evolved at fixed time interval of 3 minutes.

$$\% \text{ IE} = \frac{V_H - V_{HI}}{V_H} \times 100 \quad (3)$$

Where, V_H is the volume of H_2 evolved without inhibitor and V_{HI} is the volume of hydrogen evolved with inhibitor.

Electrochemical methods

Electrochemical experiments such as potentiodynamic polarisation and impedance spectroscopy method were carried out by CH electrochemical workstation (model 608, USA). It consist of three electrode cell with the platinum counter electrode (CE), a saturated calomel electrode (SCE) used as reference electrode and Al as working electrode(WE) in order to avoid ohmic resistance, the Luggin capillary was placed close to the working electrode. The working electrode were polished with emery papers in the range (300-2000) grit, rinsed with double distilled water, degreased with acetone and air dried. The working electrode was immersed in the test solution before 30 minutes to attain the steady state open circuit potential. The potentiodynamic current-potential curves record the data after the electrode potential was changed from -200mV to +200mV with the scanning rate 1mVs^{-1} . For EIS measurements the test solution was conducted by ac signal of impedance measurements.

RESULTS AND DISCUSSION

Weight loss method

The corrosion rate (CR), surface coverage (Θ) and percentage inhibition efficiency (%IE) of aluminium specimens exposed to 1M HCl solution at 303K with out and with different concentration of leaves extract are shown in Table 1.

Table 1. The value of corrosion rate, surface coverage and inhibition efficiency for Al in 1M HCl solution without and with different concentration of the Calotropis procera leaves extract at 303K.

Concentration of CP extract (gL^{-1})	Weight loss (g/cm^2)	Corrosion Rate (mmpy)	Inhibitor Efficiency (%)	Surface coverage (Θ)
Blank	0.0101	437	-	-
0.3	0.0025	156	75.3	0.753
0.6	0.0016	69	84.2	0.842
0.9	0.0012	52	88.1	0.881
1.2	0.0010	43	90.1	0.901
1.5	0.0009	39	91.1	0.911

Table 1. shows that the corrosion rate of aluminium decreased on increasing concentration of the Calotropis procera leaves extract. The decrease in the weight loss and corrosion rate in presence of Calotropis procera leaves extract in 1M HCl solution shows inhibition of aluminium corrosion. Inspection of the chemical structure of the components reveals that these compounds can be adsorbed on the metal surface inside oxide layer via the lone pairs of electrons present on the oxygen atoms. The adsorption of compounds on aluminium surface reduce the surface area that is available for the attack of the aggressive chloride ions from the aggressive solution. The surface coverage could be used to represent the fraction of surface occupied by the adsorbed molecules. The inhibition efficiency increases with increase in concentration of the Calotropis procera leaves extract.

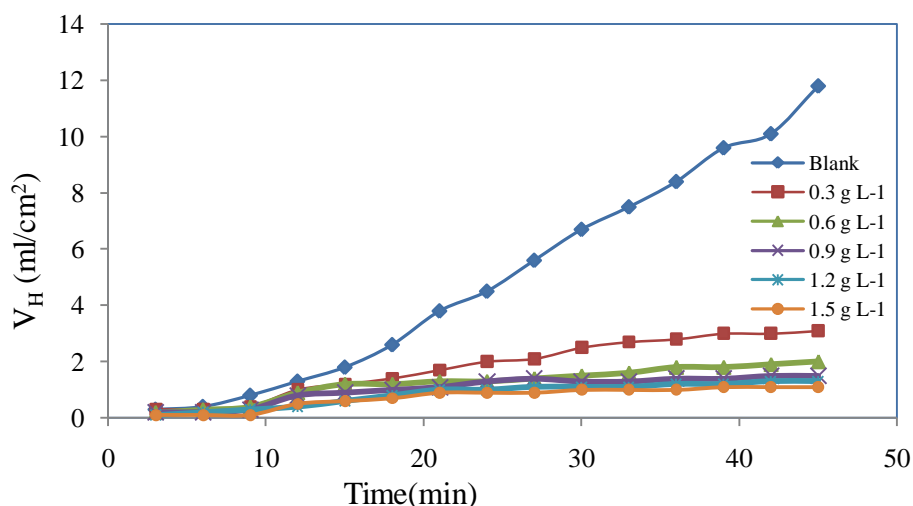


Fig 1. variation of volume of H₂ evolved with time (min) for aluminium corrosion in 1M HCl in the absence and presence of Calotropis procera leaves extract at 303K

Inspection of the Figure 1. reveals that the volume of hydrogen evolved was low in presence of inhibitor when compared to blank solution. Further decrease in the volume of hydrogen evolved when the concentration of inhibitor increased. The decrease in the volume of hydrogen evolved in the presence of inhibitor suggesting that the inhibiting action was concentration dependent.

Electrochemical methods

Potentiodynamic polarisation curves for aluminium in 1M HCl solution without and with various concentration of Calotropis procera leaves extract at 303K. Table 2. shows that the presence of Calotropis procera leaves extract causes a prominent decrease in the corrosion rate i.e. it shift the anodic and cathodic Tafel constants β_a and β_c changed in presence of the extract. This confirms the mixed mode of inhibition of the extract. The Tafel regions further indicate that the electrode reactions are activation controlled. It is also shown that corrosion current (i_{corr}) decreases markedly in the presence of extract and the magnitude of change increases with increasing extract concentration. With increase in Calotropis procera leaves extract concentration, the corrosion potential (E_{corr}) is not varying much.

Table 2. Potentiodynamic polarisation parameters for aluminium in 1M HCl in the presence of Calotropis procera leaves extract

Concentration CP of extract (g L ⁻¹)	-E _{corr} (mV)	i _{corr} (mA/cm ²)	Tafel slope (mV/decade)		Corrosion rate mmpy	Inhibition efficiency(%)
			β_a	β_c		
Blank	744	14.77	199	247	569	-
0.3	749	3.7	178	216	144	75
0.6	751	2.2	185	268	86	85
0.9	754	1.8	223	237	68	88
1.2	754	1.4	167	142	65	91
1.5	763	1.0	206	215	41	93

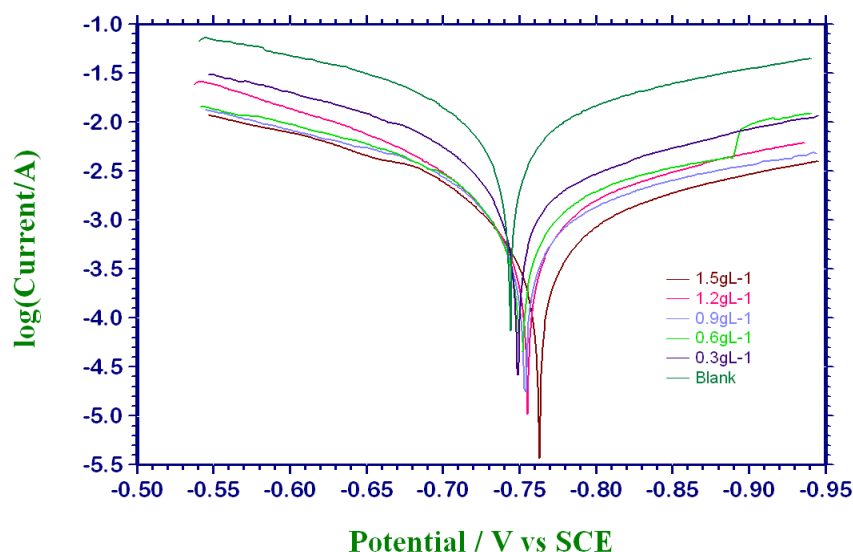


Fig 2: potentiodynamic polarisation curves for aluminium in 1M HCl without and with different concentration of Calotropis procera leaves extract at 303K.

Impedance spectroscopy method

The corrosion behaviour of aluminium in 1M HCl in absence and presence of Calotropis procera leaves extracts were investigated by EIS after immersion for 30 min at $303 \pm 1\text{K}$. Nyquist plots are not perfect semicircles as expected from the theory of AC impedance technique. The increasing diameter of capacitive loop obtained in 1M HCl in presence of leaves extract indicates the inhibition of aluminium corrosion. The deviation of a Nyquist plot from a semicircle was attributed to frequency dispersion. In a corrosion system, formation of a double layer at the metal/solution interface occurs. The high frequency capacitive loop may be attributed to the charge transfer reaction. The presence of low frequency inductive loop may be attributed to the relaxation process obtained by adsorption species like Cl^-_{ads} and H^+_{ads} on the electrode surface [15,16].

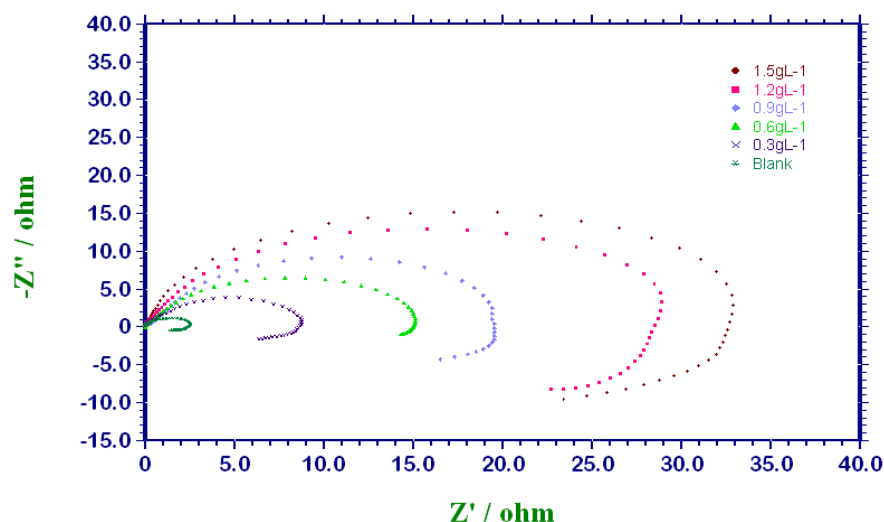


Fig 3: Nyquist plots obtained for the aluminium in 1M HCl in the absence and presence of different concentration of Calotropis procera leaves extract at $303 \pm 1\text{K}$

Table 3. Corrosion kinetic parameters derived from EIS measurements and inhibition efficiencies in presence of Calotropis procera leaves extract at $303 \pm 1\text{K}$

Concentration of CP extract (gL^{-1})	R_{ct} $\Omega \text{ cm}^2$	C_{dl} ($\mu\text{F}/\text{cm}^2$)	Inhibition efficiency (%)
Blank	2.0	12.74	-
0.3	8	8.407	75
0.6	14	7.470	86
0.9	18	6.859	88
1.2	23	1.617	91
1.5	30	1.602	93

It is apparent from Table 3 that the impedance of the inhibited system increased with increasing the inhibitor concentration and the C_{dl} values decreased with increasing inhibitor concentration. This decrease in C_{dl} results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggested that inhibitor molecules inhibit the aluminium corrosion by adsorption at the metal/acid interface [17].

The depression in Nyquist semicircles is a feature for solid electrodes and often referred to as frequency dispersion and attributed to the roughness and other inhomogeneities of the solid electrode [18].

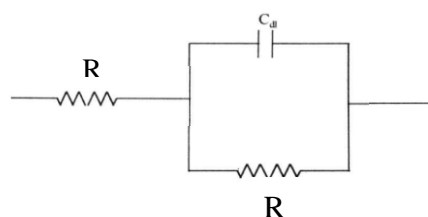


Fig 4: Equivalent Randle's circuit for a simple electrochemical cell.

Effect of temperature

The effect of temperature on the corrosion behaviour of aluminium in uninhibited and inhibited solutions containing Calotropis procera leaves extract was investigated at $303-333 \pm 1\text{ K}$.

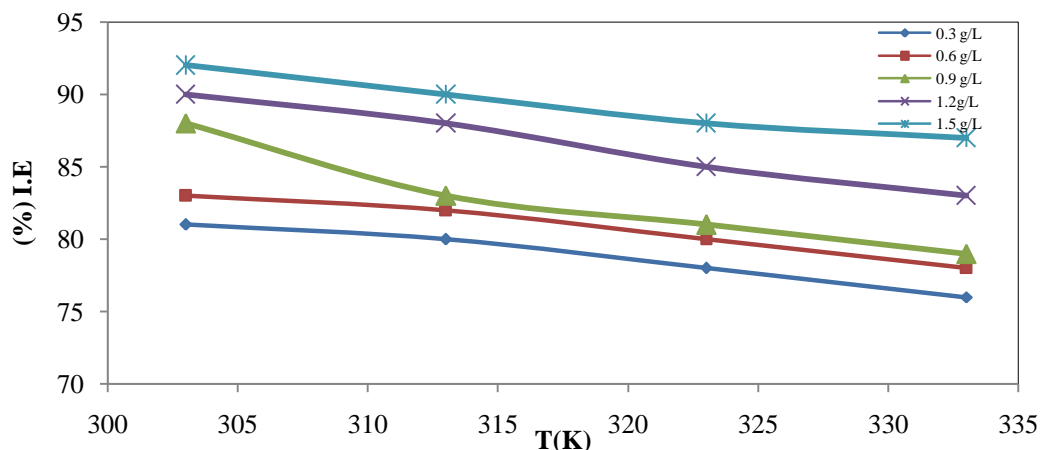


Fig 5: A plot of inhibition efficiency versus temperature in presence of different concentration of the Calotropis procera leaves extract

Inhibition efficiency is observed from Figure 5 increase with rise in temperature in 1M HCl for the *Calotropis procera* leaves extract. Adsorption of an organic inhibitor can affect the corrosion rate by either decreasing the available reaction area (geometric blocking effect) or by modifying the activation energy of the anodic or cathodic reactions occurring in the inhibitor-free surface in the course of the inhibited corrosion process. Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies in absence and presence of inhibitor gives some insight into the possible mechanism of inhibitor adsorption. A decrease in inhibition efficiency with rise in temperature, with corresponding increase in corrosion activation energy in the presence of inhibitor compared to its absence, is frequently interpreted as being suggestive of physical adsorption. The dependence of corrosion rate on temperature can be expressed by Arrhenius equation.

$$\text{Corrosion rate (log CR)} = \frac{-E_a}{2.303RT} + \log A \quad (4)$$

$$CR = \frac{RT}{Nh} \left(e^{\frac{\Delta S^*}{R}} e^{\frac{-\Delta H^*}{RT}} \right) \quad (5)$$

Where, R is the universal gas constant, N is the Avogadro's number (6.022×10^{23} molecule mol^{-1}), ΔH^0 the change in enthalpy of activation, ΔS^0 the change in entropy of activation, T is absolute temperature, h is the Planck's constant (6.626×10^{-34} Js mol^{-1}). The values of enthalpy and entropy of activation for Al corrosion in 1.0M HCl in absence and presence of inhibitors can be evaluated from the slope and intercept of the curve of $\log \frac{CR}{T}$ versus $\frac{1}{T}$ give a straight line. From the graph, slope of $\left(\frac{-\Delta H^0}{2.303R} \right)$ and an intercept of $\left(\log \frac{R}{Nh} + \frac{\Delta S^0}{2.303R} \right)$ from which the values of ΔH^0 and ΔS^0 were calculated.

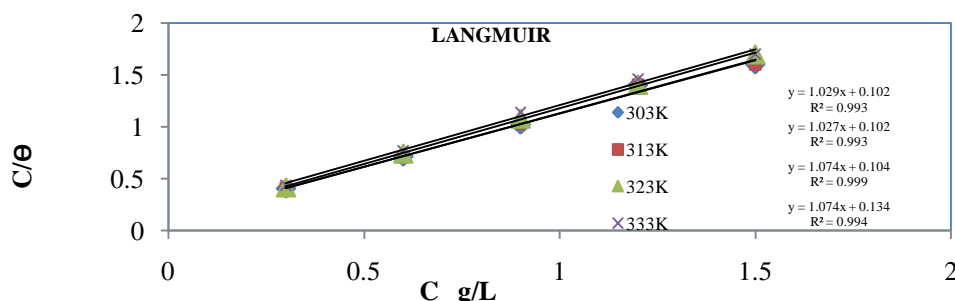


Fig 6: Langmuir adsorption plot for *Calotropis procera* at 303 – 333K

Table 4. Parameters obtained from Langmuir adsorption isotherm

Temp(K)	K_{ads}	$-\Delta G_{ads}$ kJ/mol
303	7.09	15.05
313	6.10	15.16
323	5.71	15.46
333	5.05	15.60

The change in free energy of adsorption (ΔG_{ads}^0) of the inhibitors on aluminium surface can be used the following equation.

$$\Delta G_{ads}^0 = -RT \ln (55.5K_{ads}) \quad (6)$$

Where R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature (K), and the value 55.5 in the above equation is the concentration of water in solution in M, K_{ads} is the equilibrium constant of the adsorption / desorption process. The negative values of ΔG_{ads} indicate spontaneous adsorption of the inhibitor molecule on the metal surface

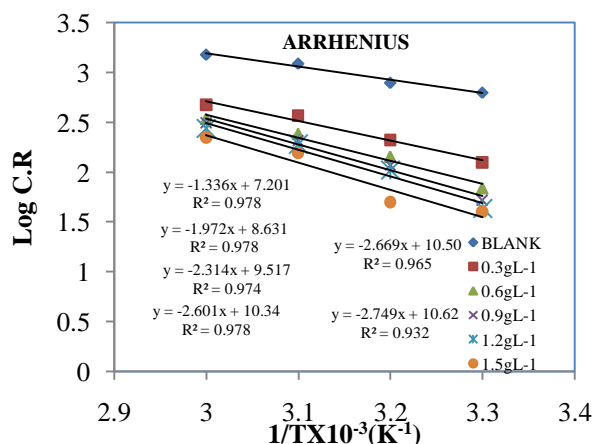


Fig 7: Arrhenius plot of log C.R. Versus $1/T$ for aluminium in 1M HCl in the absence and presence of Calotropis procera leaves extract.

Table 5 Thermodynamic adsorption parameters for Calotropis procera leaves extract on aluminium

Concentration Of CP extract(gL ⁻¹)	Ea kJ /mol	ΔH^0 kJ /mol	$-\Delta S^0$ J/mol/K
Blank	25.58	33.37	83.48
0.3	37.76	41.32	65.84
0.6	44.31	44.82	62.02
0.9	49.80	49.15	49.69
1.2	51.10	50.22	47.41
1.5	52.64	51.83	44.08

Table 5 indicates that the increase in activation energy in the presence of extract is often interpreted as physical adsorption with the formation of an adsorptive film with an electrostatic character. The positive values of ΔH^0 reflect that inhibitor adsorbs onto the aluminium surface through endothermic reaction. The negative value of ΔS^0 shows that the inhibitor molecules, freely moving in the bulk solution were adsorbed in an orderly fashion onto the aluminium surface resulting in a decrease in entropy.

CONCLUSIONS

1. Calotropis procera showed an inhibiting effect on aluminium corrosion in 1 M HCl solution, at the temperature range of 303-333K. The inhibition efficiency increased with the increase of inhibitor concentration.
2. Calotropis procera found to affect both the anodic and cathodic processes and act as mixed-type inhibitor.
3. EIS results indicate that as the additive concentration was increased the polarisation resistance increased whereas double-layer capacitance decreased.
4. Phytochemical constituents in the extract, adsorbed on the surface of the aluminium.
5. The adsorption of the studied inhibitor obeyed Langmuir's isotherm.

6. Thermodynamic adsorption parameters (ΔH^0 , ΔS^0 and ΔG^0) were calculated at each studied temperature. ΔG^0 values were found in negative which show that Calotropis procera adsorbed on aluminium surface by spontaneous process.
7. ΔS^0 values are getting smaller with increasing temperature, which indicates that orderliness caused by adsorption of inhibitor molecules
8. The inhibition efficiencies obtained by weight loss measurements, hydrogen evolution method, polarisation and EIS show good agreement.

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