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Solanum trilobatum as a green inhibitor for aluminium corrosion in alkaline medium

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ABSTRACT

The inhibitive effect of Solanum trilobatum leaves extract on the corrosion of aluminium in 1M NaOH solution was studied using weight loss, hydrogen evolution, polarisation and electrochemical impedance spectroscopy methods. The extract acts as an excellent corrosion inhibitor with 94% efficiency at the highest concentration in the alkaline environment and the inhibition efficiency increased with increasing concentration of the extract. Polarisation studies revealed the fact that the leaves extract acted as a mixed type inhibitor. These results were supported by kinetic and thermodynamic parameters for corrosion and adsorption processes calculated from the experimental data at the various temperatures studied.

Key words: Aluminium, Weight loss, Hydrogen evolution, Polarisation, Electrochemical impedance spectroscopy, Adsorption.

INTRODUCTION

Aluminium possesses attractive properties like high energy density, high negative potential and low cost and hence it is used as an electrochemical fuel for the production of electrical charge. The electrochemical behaviour of aluminium in alkaline solutions has been studied for the development of aluminium as anode in metal/air batteries. It has been reported that the wastage of aluminium by self-corrosion, while functioning as a galvanic anode in sodium hydroxide solution, can be substantially reduced by employing corrosion inhibitors [1-5]. Some investigations in recent time have been made into the corrosion inhibiting properties of natural products of plant origin, which showed good inhibition efficiencies. This area of research is important because in addition to being inexpensive, natural products are readily available, eco- friendly and renewable sources of materials.

Natural products such as gum arabic [6], damsissa [7], gossipium hirsutum [8], phyllanthus amarus [9], vigna unguiculata [10], ipomoea involcrata [11], bacopa monnieri [12] were reported as corrosion inhibitors for aluminium in alkaline solutions. Plant products contain alkaloids, flavonoids, carbohydrates, proteins, steroids and terpenoids. These organic compounds contain π-electron centres and functional groups such as –C=C, -OR, -NR_2 and/or –SR. The inhibiting action of natural products is attributed to the presence of these organic compounds as phytochemical constituents.

The aim of the present work is to investigate the inhibition efficiency of *Solanum trilobatum* for the corrosion of aluminium in alkaline medium by chemical and electrochemical techniques. It is also aimed to study the effect of temperature on the corrosion rate of aluminium. Kinetic and thermodynamic studies for the adsorption of inhibitor on aluminium metal surface were also carried out and discussed.

EXPERIMENTAL SECTION

2.1 Material preparation

Aluminium specimens of dimensions 5 x1 x 0.15cm were used for weight loss measurements and hydrogen evolution studies. The specimens were mechanically polished and degreased with acetone before use. A cylindrical aluminum rod embedded in a Teflon holder with an exposed area of 0.282 cm^2 was used for electrochemical studies. Before being used, the aluminium rod was polished with a series of silicon carbide abrasive papers of different grades (800-1500), washed thoroughly with distilled water and degreased with acetone.

2.2 Corrosive medium

Inhibitors are usually added to aluminium-alkaline solution systems, which find applications in industrial processes such as alkaline cleaning, pickling, etching and to improve efficiency of devices such as aluminium/alkaline battery. Therefore 1M NaOH (pH≈12) aqueous solution was used as a corrosive media in the present work. Double distilled water and Analar grade sample were used for the preparation of 1M NaOH solution [13].

2.3 Preparation of extract

The leaves of *Solanum trilobatum* are collected and dried in shade for 1 week. The dried leaves were ground well into powder. From this 10g of the sample was taken and refluxed in 100mL distilled water for 1 hour. The refluxed solution was filtered carefully and the filtrate was heated on a water bath to evaporate fully the moisture content in order to get the dried compound. The inhibitor solutions of 0.3, 0.6, 0.9, 1.2, and 1.5g/L concentrations were prepared from the dried compound using 1M NaOH solution [14].

2.4 Weight loss determination

The procedure for weight loss determination was similar to that described elsewhere [15-20]. The specimens were weighed and their initial weight recorded before immersion in 100 mL of 1M NaOH solution (in open beakers) without and with different concentrations of *Solanum trilobatum* leaves extract at 30 °C for a total period of 1h immersion. After 1h the specimens were taken out, washed with distilled water, dried and reweighed. The experimental readings were recorded to the nearest 0.0001 g on a Mettler digital analytical balance. Duplicate experiments were set up for each of the concentration. The corrosion rate and the inhibition efficiency were calculated using the following equations [15].

$$\text{Corrosion rate (mmpy)} = \frac{kW}{ATD} \qquad (1)$$

where
k = 8.76 X10^4(constant)
W = Weight loss in grams
A = Area in square cm
T = Time in hours and
D = Density in gm/cu.cm (2.70)

$$\text{Inhibition efficiency (\%)} = \frac{W_B - W_I}{W_B} \text{ X } 100 \qquad (2)$$

where, W_B and W_I are weight loss per unit time in the absence and presence of inhibitor.

2.5 Gasometric method

The corrosion rate of aluminium in an alkaline medium was monitored by hydrogen gas evolution in a gasometric assembly [21, 22].

The inhibition efficiency was calculated from the gasometry plots using the relationship.

$$IE\ (\%) = \frac{V_o - V}{V_o} \text{X}100$$

Where V_0 and V are the volume of hydrogen gas evolved in the absence and presence of inhibitor.

2.6 Electrochemical Methods

Polarization and electrochemical impedance measurements were carried out in a three electrode cell connected to CHI 608 electrochemical workstation. A saturated calomel electrode equipped with a Luggin capillary and a platinum foil were used as reference and counter electrodes respectively. Aluminium rod was used as the working electrode. From the polarisation curves, Tafel slopes, corrosion potential and corrosion current were calculated. The inhibitor efficiency was calculated using the formula;

$$\text{I E (\%)} = \frac{i_{corr} - i^{*}_{corr}}{i_{corr}} \text{x100}$$

Where I_{corr} and I_{corr}^{*} are corrosion current in the absence and presence of *Solanum trilobatum* leaves extract. Impedance experiments were carried out at the open circuit potential in the frequency range of 100 kHz to 10 mHz and a plot of real part (Z') vs imaginary part (Z") was made. The charge transfer resistance (R_{ct}) and double layer capacitance values were calculated. The inhibitor efficiency was calculated using the formula:

$$\text{\% I.E} = \frac{R^{*}_{ct} - R_{ct}}{R^{*}_{ct}} \text{x100}$$

where R^{*}_{ct} and R_{ct} are the charge transfer resistance in the presence and absence of *Solanum trilobatum* extract.

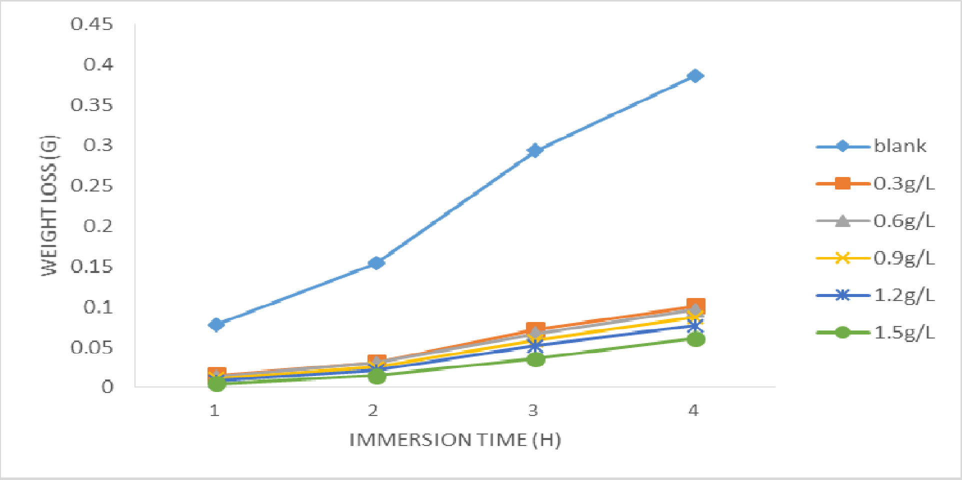
RESULTS AND DISCUSSION

3.1 Corrosion rates and inhibition efficiency

The material loss as corrosion rate (mm/year) of the aluminium specimen for different concentrations of the extract in 1M NaOH solution monitored at 30°C is summarized in Table1. The results revealed that inhibition efficiency increases with increasing inhibitor concentration in 1M NaOH medium. This trend may result from the fact that adsorption process enhances with increase in inhibitor concentration. As concentration increases more inhibitor molecules are adsorbed on the metal surface, thus resulting larger surface coverage. It denotes that the dissolution of aluminium decreases with increase in concentration of extract.

The inhibition efficiency increases with increase in extract concentration and reaches a maximum value of 94% with 1.5g/L extract concentration. Several factors could contribute to this, which includes the presence of a mixture of organic and resinous matter in the extract composition.

Figure1. Plot of weight loss against time for aluminium corrosion in 1M NaOH at 30-60°C



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The adsorption of these compounds on the aluminium surface reduces the surface area available for the attack of the aggressive OH^{-} ions from the alkaline solution for corrosion. The degree of protection increases with increase in extract concentration due to a higher degree of surface coverage resulting from enhanced inhibitor adsorption. The presence of a mixture of organic and resinous matter in the extract composition, such as glycosides, proteins, aminoacids, flavanoids, alkaloids and tannins is attributed to the inhibitor action of the leaves extract.

Table.1 Corrosion parameters obtained from weight loss measurements for aluminium in 1M NaOH solution containing various concentrations of *Solanum trilobatum* leaves extract at 30°C

System / Concentrations (gL^{-1})	Corrosion rate (mm/year)	Inhibition efficiency (%I)	Surface coverage (θ)
1M NaOH	0.0782	-	-
0.3	0.0156	80.0	0.80
0.6	0.0135	82.7	0.82
0.9	0.0115	85.2	0.85
1.2	0.0082	89.4	0.89
1.5	0.0047	93.9	0.93

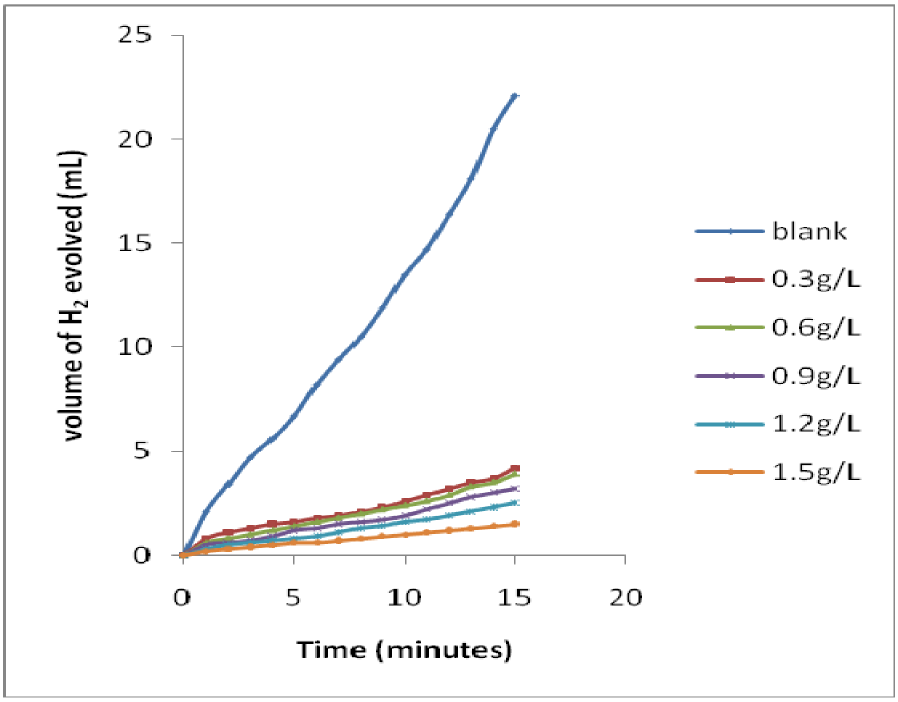
3.2 Gasometric technique

The inhibitor action with increasing concentration is closely observed by the changes in H_2 gas evolution using gasometric technique. Fig-2 shows the variation of the volume of hydrogen gas evolved as a function of time when an aluminium specimen reacts with 1M NaOH in presence of different concentrations of *Solanum trilobatum* leaves extract. The volume of the hydrogen gas evolved is characterized by a sharp rise and approximately linear increase. The rate of hydrogen evolution which is equivalent to the rate of aluminium dissolution and the inhibitor efficiency were calculated from the gasometry plots. The inhibition efficiency values obtained were 77.29%, 79.91%, 83.84%, 89.08% and 91.27% for increasing concentrations of *Solanum trilobatum* leaves extract.

Table 2 Variation of volume of hydrogen evolution with concentration (g/L) of *Solanum trilobatum* leaves extract for aluminium corrosion in 1M NaOH solution

Concentration of extract (gL^{-1})	Volume of hydrogen evolved (ml)	Inhibition efficiency (%)
Blank	22.1	--
0.3	4.2	80.9
0.6	3.9	82.3
0.9	3.2	85.5
1.2	2.5	88.6
1.5	1.5	93.2

Figure 2. Plot of volume of hydrogen evolution with time in minutes in 1M NaOH solution for aluminium in *Solanum trilobatum* leaves extract at room temperature



The study of aluminium corrosion rate by monitoring the H_2 gas evolution rate can provide information concerning the chemical nature of the surface film in situ at the metal corrodent interphase. Furthermore, this technique ensures rapid and more reliable results than the ex situ measurement, such as weight loss method.

3.3 Polarisation curves

Polarisation curves of aluminium in 1M NaOH solution without and with different concentrations of *Solanum trilobatum* extract are shown in Fig 3. It could be observed that both the anodic and cathodic reactions were suppressed by the addition of *Solanum trilobatum* extract. It suggests that the inhibitor exerted an efficient inhibitory activity both on anodic dissolution of metal and on cathodic hydrogen reduction reaction.

Electrochemical parameters such as E_{corr}, $I_{corr,}$ anodic and cathodic Tafel slopes ($\beta_{a,}$ and β_c) are obtained from polarization studies. From Table 3 it was clear that the corrosion potential was not shifted significantly in the presence of the extract. It indicates that *Solanum trilobatum* leaves extract controlled both anodic and cathodic reactions to inhibit the corrosion of aluminium by blocking active sites on the aluminium surface .This reveals that the inhibitor showed mixed type of action [23-26].

Figure 3. Polarisation curves for aluminium corrosion in 1M NaOH with and without *Solanum trilobatum* leaves extract

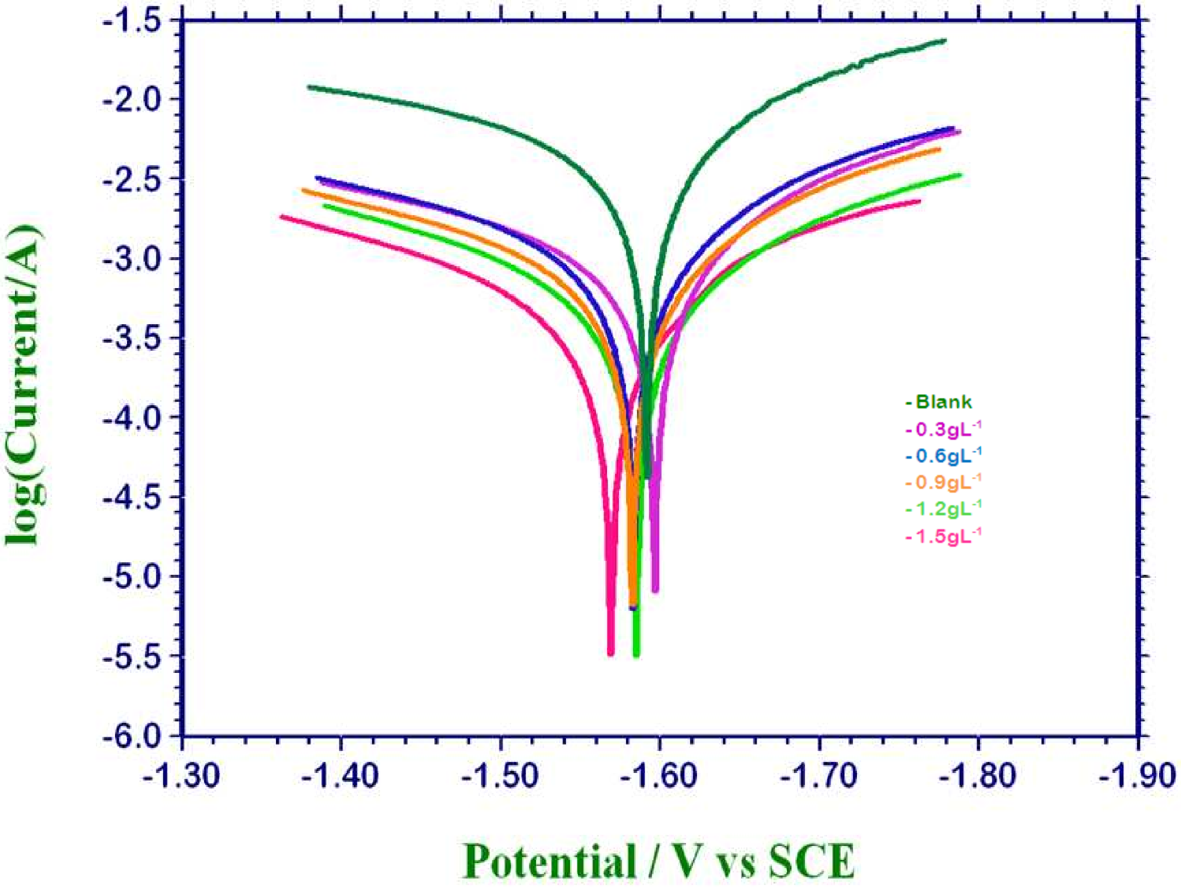


Table 3. Tafel polarisation parameters for the corrosion of aluminium in the presence and absence of inhibitor in 1M NaOH

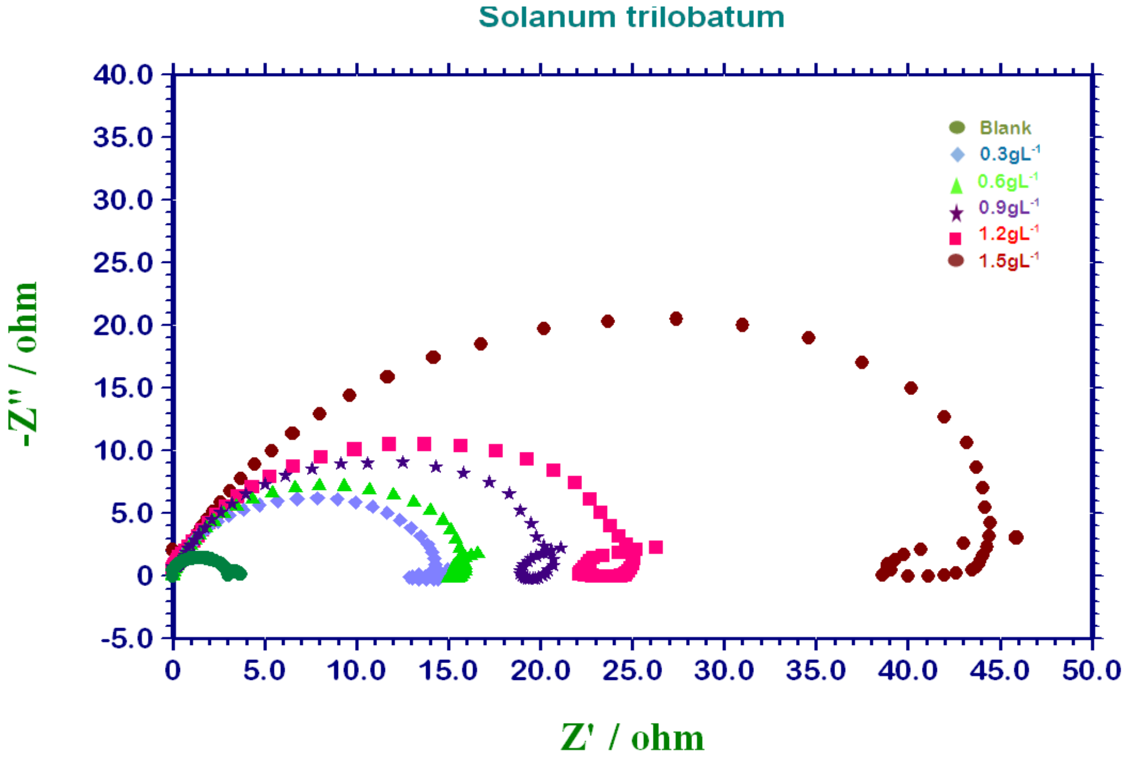
C g /L	$-E_{corr}$ (mV)	β_c ($mVdec^{-1}$)	β_a ($mVdec^{-1}$)	I_{corr} $mA.cm^{-2}$	R_{corr} mmpy	IE%
Blank	158.8	185	313	5.421	209.01	--
0.3	158.4	174	260	1.020	39.32	81.1
0.6	159.6	169	250	1.017	39.22	81.2
0.9	158.2	172	245	0.786	30.33	85.5
1.2	158.4	178	224	0.553	21.34	89.7
1.5	156.9	175	218	0.406	16.79	92.5

3.4 Electrochemical impedance studies

Impedance studies are carried out to understand the corrosion behaviour of aluminium in 1M NaOH in the absence and presence of *Solanum trilobatum* leaves extract. The charge transfer resistance (R_{ct}) and double layer capacitance

(C_{dl}) values are calculated. Fig 4 shows the Nyquist plots for aluminium in 1M NaOH in the absence and presence of different concentrations of leaves extract. The corresponding impedance parameters are given in Table 4.

Figure 4. Nyquist plots for aluminium corrosion in 1M NaOH with and without *Solanum trilobatum* leaves extract



The spectra show that the impedance changes according to the change in inhibitor concentration. It is known from the figure that the obtained Nyquist plots are almost semicircle in nature with a high frequency loop and an inductive loop at the low frequency region. The semicircular nature of the Nyquist plot is due to the charge transfer process which mainly controls the corrosion of aluminium. The low frequency inductive loop is due to the growth and dissolution of the surface oxide film. The presence of *Solanum trilobatum* leaves extract increased the value of R_{ct} in alkaline solution and the values of double layer capacitance are reduced to a large extent in the presence of inhibitor. The maximum R_{ct} value of was obtained at the concentration of 1.5 gL^{-1} of *Solanum trilobatum* extract [14, 27].

The recorded impedance values are found to increase with increasing the inhibitor concentration indicating that the metal surface is more protected. It is important to develop the appropriate circuit model for the impedance which can be used to fit the experimental data and determine the parameters which characterize the corrosion process. The equivalent circuit model used to fit the experimental data is shown in Figure-5. In the electric circuit C_{dl} is double layer capacitance, R_{ct} is the interfacial charge transfer resistance and R_s is the solution resistance. The numerical values of R_{ct} and C_{dl} are determined by analysis of complex plane impedance plot and the equivalent circuit model by means of a computer program.

Figure-5 Equivalent electric circuit for a simple electrochemical cell

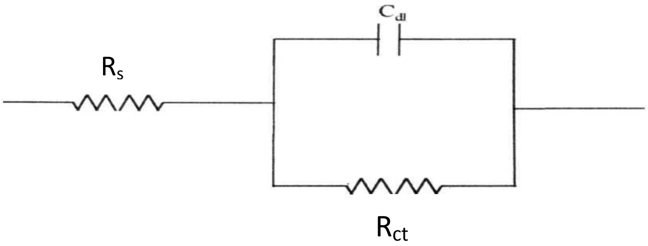


Table-5. Electrochemical impedance parameters and inhibition efficiencies for aluminium in 1 M NaOH solution in the absence and presence of different concentrations of *Solanum trilobatum* leaves extract

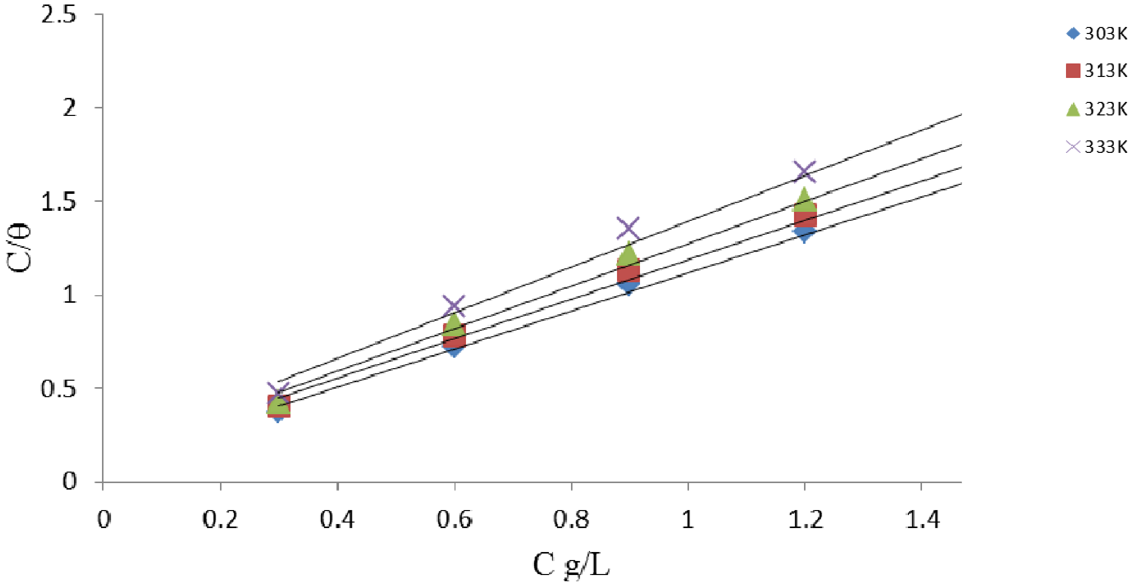
Concentration of *Solanum trilobatum* extract (gL^{-1})	R_{ct} $\Omega\ cm^2$	C_{dl} ($\mu F/cm^2$)	Inhibition efficiency (%)
Blank	3.09	88.76	----
0.3	13.95	10.61	77.82
0.6	14.75	9.61	79.03
0.9	19.06	8.40	83.77
1.2	22.85	6.55	86.46
1.5	40.45	5.26	92.35

3.5 Kinetic and thermodynamic studies

3.5.1 Adsorption isotherm

Basic information about the interaction between the inhibitor molecule and metal surface can be provided by adsorption isotherm. The degree of surface coverage values for various concentrations of *Solanum trilobatum* extract from the weight loss measurements obtained (θ = % I/100), has been adopted to determine the adsorption characteristics of *Solanum trilobatum* in 1M NaOH solution.

Figure 6. Plot of Langmuir adsorption isotherm for *Solanum trilobatum* extract in 1M NaOH solution for aluminium at different temperatures



The most important thermodynamic adsorption parameter is the free energy of adsorption (G_{ads}). The adsorption constant K_{ads} is related to the standard free energy of adsorption, ΔG_{ads} with the following equation [28].

$$\Delta G_{ads} = - RT \ln (55.5 \text{ X } K_{ads})$$

where 55.5 is the water concentration of the solution in mol^{-1}.

Table 6. Adsorption parameters for the Langmuir adsorption isotherm of *Solanum trilobatum* extracts in 1M NaOH on aluminium at different temperature

Medium	T^0c	K_{ads}	$-\Delta G°_{ads}$ KJ/mol
1M NaOH	30°C	9.93	15.90
	40°C	7.66	15.75
	50°C	7.49	16.19
	60°C	5.75	15.96

The negative values of ΔG^0_{ads} obtained indicate the spontaneous adsorption of the inhibitor and are usually characteristic of strong interaction with the metal surface. It was found that the ΔG^0_{ads} values are less than –40KJ/mole indicating that inhibitor molecules are physically adsorbed on the metal surface [29-32].

The maximum efficiency of 94% was observed in the case of 1.5 g/L extract concentration. The lower concentration of the inhibitor causes multilayer film formation which collapses and exposes the metal to the corrodent. Hence higher concentration of inhibitor is required for maximum adsorption in a single layer [33, 34].

3.5.2 Effect of temperature

Temperature study was carried out to get more information about the effectiveness of *Solanum trilobatum* at higher temperatures, the nature of adsorption and thereafter to evaluate the activation process. Weight loss measurements are done in the range of temperature 30 - 60°C, with and without inhibitor at different concentrations during 1 h immersion period. From the data given in Table7 it is clearly understood that the increase in temperature leads to an increase in the corrosion rate of aluminium with or without inhibitor.

Figure 7 showed that inhibition efficiency (% I) decreased with increasing temperature as a result of fast dissolution of aluminium at higher temperature. This may be attributed to the fact that a higher temperature could quench the inhibitor performance to a large extent and this suggests physical adsorption mechanism of *Solanum trilobatum* on aluminium surface.

Figure 7. Plot of inhibition efficiency (% I) against extract concentration for aluminium in 1M NaOH at 30-60°C

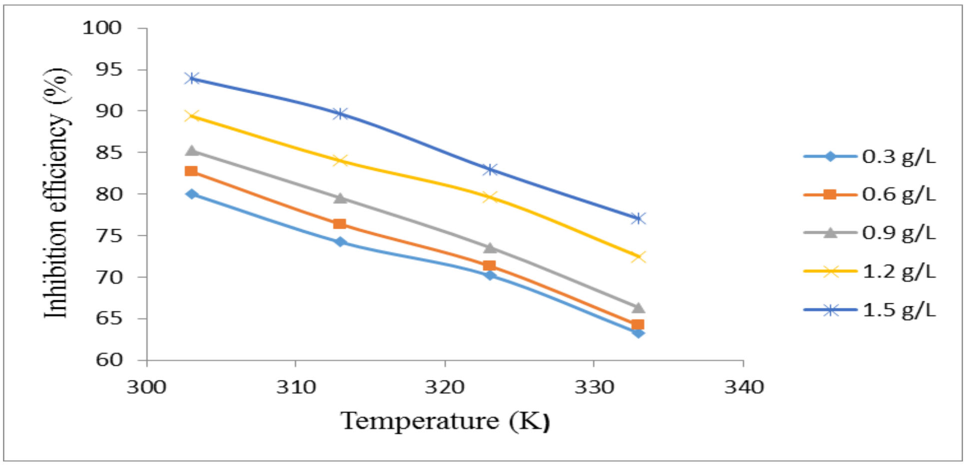


Table 7. Effect of temperature on inhibition efficiency of *Solanum trilobatum* leaves extract in 1M NaOH solution for aluminium corrosion

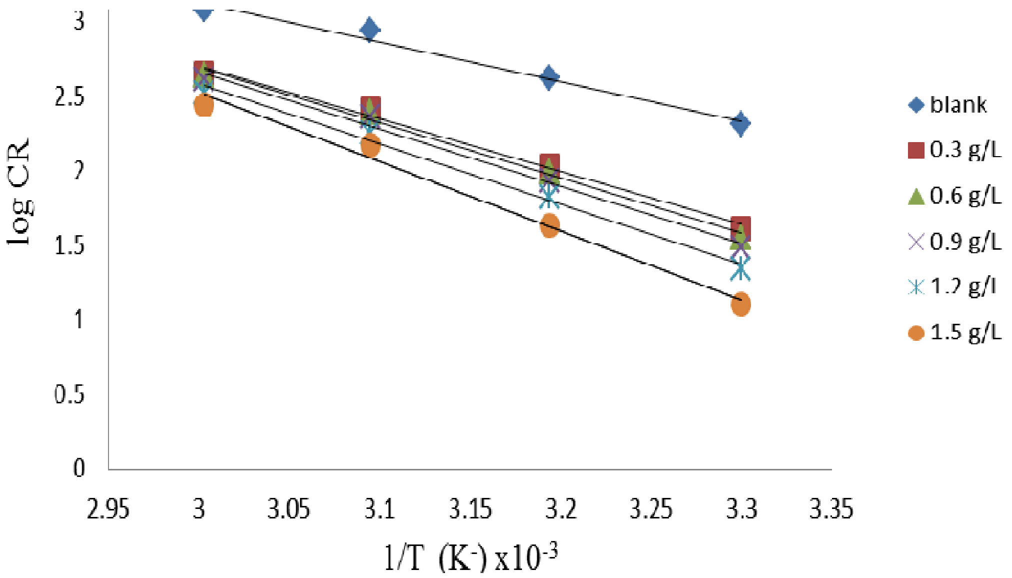
Concentration of extract (gL^{-1})	Inhibition Efficiency (%)			
	30°C	40°C	50°C	60°C
0.3	80.0	74.2	70.2	63.2
0.6	82.7	76.3	71.3	64.1
0.9	85.2	79.5	73.5	66.3
1.2	89.4	84.0	79.6	72.4
1.5	93.9	89.6	83.0	77.0

Activation energy, E_a is calculated with the help of the Arrhenius equation.

$$K = Ae^{-E_a/RT}$$

Where,
k = corrosion rate
A= Arrhenius frequency factor.
E_a = Activation energy for corrosion process.
R = Gas constant (8.314J/K mole)
T =Temperature in Kelvin

Figure 9 Arrhenius plot of log CR vs 1/T for aluminium corrosion in 1M NaOH in absence and presence of various concentrations of *Solanum trilobatum*. leaves extract



In order to have a better understanding about effect of temperature on adsorption of inhibitor molecule on aluminium surface in 1M NaOH solution, activation energy (E_a) is calculated from the slope of the straight line obtained the logarithm of the corrosion rate(k) against the reciprocal of the absolute temperature(1/T).

Higher E_a values in the presence of the inhibitor compound compared to that in the blank solution indicates that the inhibitor will be effective at ordinary temperature but the efficiency will be considerably diminished at higher temperatures.

Table.8 Activation parameters obtained for various concentration of *Solanum trilobatum* leaves extract.

Concentration of Extract (gL^{-1})	E_a(kJ mol^{-1})	ΔH^o(kJ mol^{-1})	ΔS^o($JK^{-1}mol^{-1}$)
Blank	50.78	48.14	41.47
0.3	67.38	64.74	-0.01
0.6	70.81	68.16	-10.18
0.9	73.71	71.07	-18.40
1.2	76.89	74.25	-26.26
1.5	88.56	85.91	-60.16

Enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) are calculated from the slope and intercept of the line obtained from log k/T versus 1/T. The values of Ea, ΔH^* and ΔS^* for aluminium corrosion in 1M NaOH in presence and absence of different concentration of *Solanum trilobatum* leaves extract are given in Table 8.

The results obtained revealed that E_a and ΔH^* values increase in presence of *Solanum trilobatum* leaves extract, indicating a higher degree of surface coverage and higher protection efficiency attained due to raising the energy barrier for the aluminium corrosion reaction. Furthermore, the entropy of activation in the presence and absence of the inhibitor is small and negative. This may be attributed to the fact that the adsorption process is rather slow and activated complex in the rate determining step represents association rather than dissociation step, which means that a decrease in disordering occurs on going from reactants to activated complex.

CONCLUSION

- *Solanum trilobatum* shows significant inhibitive effect on aluminium corrosion in alkaline environment.
- Inhibition efficiency increases with the increase of extract concentration and upto 94% inhibition efficiency was obtained for 1.5g/L.
- The inhibition efficiency of *Solanum trilobatum* extract is temperature dependent and its addition leads to a relative increase of apparent activation energy.
- Adsorption of inhibitor species on aluminium surface in 1M NaOH suggest physisorption mechanism and it is clear cut by following the trend of inhibitor adsorption with solution temperature.

- The adsorption of the extracts onto aluminium surface was found to obey Langmuir adsorption isotherm from the fit of the experimental data at all the concentrations and temperatures studied.

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