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Research Article

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Inhibitive effect of *Morinda citrifolia L.* leaves extract on aluminium corrosion in HCl medium

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ABSTRACT

The corrosion inhibition of aluminium in 1 M HCl solution by Morinda citrifolia L. (M. citrifolia L.) using chemical (weight loss, gasometry) and electrochemical (ac impedance and polarisation) techniques. All the methods employed are in quite good agreement. The inhibition efficiency increased as M. citrifolia L. concentration increased. It was found that adsorption for M. citrifolia L. on aluminium obeys with Langmuir adsorption isotherm in all studied temperature. Thermodynamic parameters (ΔG_{ads}, ΔH_{ads} and ΔS_{ads}) for M. citrifolia L. adsorption on aluminium were found out and discussed at each temperature.

Key words: Aluminium; corrosion inhibition; acid medium; Morinda citrifolia L, Electrochemical impedance spectroscopy.

INTRODUCTION

Aluminium and its alloys are used in many industrial applications such as automobiles, house-hold appliances, electronic devices and aviation [0-0]. It forms protective oxide film in air on aluminium surface. Its surface film is amphoteric and dissolve substantially when metal is exposed to high concentration of acids and bases [0, 0]. Hydrochloric acid is used for pickling, chemical and electrochemical etching of aluminium. This solution dissolves the passive film. Many research work have also been using chemical compounds as inhibitors to reduce corrosion [6]. The organic inhibitors usually chemical inhibitors are expensive, toxic and hazardous to human beings and to the environment. To prevail over this problem, investigation are established to search on the usage of natural products which are eco-friendly, environmentally acceptable, readily available, renewable source and non-toxic inhibitors be found. Plant inhibitors are incredibly rich sources of natural chemical compounds (e.g. amino and organic acids, glucosinolates, alkaloids, polyphenols, tannins) and all are known for inhibitive action. The extracts from leaves, barks, seeds, fruits and roots contain a mixture of organic compounds containing nitrogen, sulphur or oxygen atoms and some have been reported to function as effective inhibitors for metal in aggressive media [7-0]. The plant products are good corrosion inhibitors for Al metal have been reported by several authors [0-31]. Inhibitive action of *Morinda citrifolia L.* (*M. citrifolia* L.) leaves on corrosion of aluminium in 1M HCl solution was investigated through weight loss, hydrogen evolution and electrochemical polarisation measurements. The effect of temperature was also studied.

EXPERIMENTAL SECTION

2.1. Materials

2.1.1. Preparations of plant extract

Morinda citrifolia L. commonly known as noni, is a shrub or small tree belongs to a family Rubiaceae, is a native to Southeast Asia and Australia but has been extensively spread by man throughout India and into the Pacific islands. It contains high level of peptide Val-Tyr-Val was found in leaves extract (15.856 ppm). The M.citrifolia contains various alkaloids present in the leaves. It also contains anthraquinones, organic acids, xeronine, several vitamins (such as beta-carotene, niacin, riboflavin, thiamine), some minerals, iron and calcium are responsible for inhibition [32].

The fresh leaves of *M. citrifolia* L. were washed under running water, shade dried and powdered. Leaves extract was extracted by refluxing of 20g of the dry materials in 200ml double distilled water for one hour in a round bottom flask fitted with Leibig condenser. The solution was filtered and evaporated over water bath until to get residue [33]. The residue is ground well and stored in desiccator for further study.

2.1.2. Preparation of the specimens

Commercial aluminium specimens of dimension $5\times 1 \times 0.15\text{cm}$ and cylindrical rod is embedded with Teflon holder and with exposed surface area 0.2826cm^2 were used for weight loss, hydrogen evolution and electrochemical study.

2.1.3. Electrolyte

An appropriate concentration of acid (1M) was prepared using double distilled water and AR grade hydrochloric acid. It is used to prepare the concentration range from 0.3 g/L to 1.5 g/L.

2.2. Methods

Two different techniques have been employed for studying the inhibition of corrosion of aluminium by the leaves extract, are: chemical technique (weight loss and hydrogen evolution method) and electrochemical techniques (potentiodynamic polarisation and AC impedance technique).

2.2. Chemical techniques

2.2.1. Weight loss measurements

The aluminium specimens of 5cm x1cm x 0.15cm sizes were used for weight loss measurements and were abraded with emery sheets (grade 400-2000) and degreased with acetone, rinsed in double distilled water and dried in the air and weighed accurately. The cleaned aluminium specimens were immersed in 100ml of 1M HCl with and without addition of different concentration of *M. citrifolia* L. leaves extract. After 1hour immersion, the aluminium specimens were carefully washed in double distilled water, dried and re-weighed.

2.2.2. Gasometry

The volume of hydrogen gas evolved from the corrosion reaction was monitored by volume changes in the level of paraffin oil in the graduated burette at fixed time intervals [34] at 303K. The test solution was kept at 100ml. The inhibitor efficiency was then determined using the technique by the following equation.

$$\%\ \text{IE} = \frac{V_H - V_{HI}}{V_H} \times 100 \qquad (1)$$

2.3. Potentiodynamic polarisation and EIS measurements

Potentiodynamic polarisation and EIS measurements were carried out in a conventional three electrode using potentiostat (model: CHI 608, electrochemical workstation, USA), a saturated calomel electrode equipped with Luggin capillary used as reference electrode and the counter electrode was platinium. The working electrode which was polished with emery sheets from 400 to 1200, degreased with acetone, rinsed in double distilled water, dried in acetone and finally dipped in to the electrolytic cell. The corrosion medium was 1M HCl solution prepared from analytical grade HCl (Merck). Before measurement, the working electrode was immersed in test solution for approximately 30 minutes until a steady open-circuit potential (OCP) was reached. EIS measurement was carried out in the 100kHz -10 mHZ frequency range at OCP. The polarisation curves were carried out from cathodic potential of -0.2V to +0.2 V with respect to the open circuit potential at a sweep rate of 1mVs^{-1}. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential (E_{corr}) to obtain the corrosion current densities (i_{corr}). Several runs were performed to obtain reproducible data.

RESULTS AND DISCUSSION

3.1. Weight loss measurements

The corrosion of aluminium in 1M HCl in the absence and presence of different concentrations of *M. citrifolia* L. in the room temperature was studied using weight loss technique.

The percentage of inhibition efficiency (% IE) was calculated using the following equation

$$\text{Inhibition efficiency (\%IE)} = \frac{CR_{inh} - CR_{uninh}}{CR_{uninh}} \times 100 \qquad (2)$$

Where CR_{inh} and CR_{uninh} are corrosion rate of aluminium in the presence and absence of inhibitor.

The degree of surface coverage (θ) for different concentrations of the inhibitor has been evaluated by using the expression

$$\text{Surface coverage } (\theta) = \frac{CR_{inh} - CR_{uninh}}{CR_{uninh}} \qquad (3)$$

Where θ is the surface coverage

Table I Corrosion rate, inhibitor efficiency and surface coverage of inhibitor at various concentration of 1M HCl at room 303K

Concentration of MC extract(gL^{-1})	Weight loss (g)	Corrosion Rate (mmpy)	Inhibitor Efficiency (%)	Surface coverage (Θ)
Blank	0.0103	446	-	-
0.3	0.0021	91	80	0.80
0.6	0.0020	87	81	0.81
0.9	0.0014	61	86	0.86
1.2	0.0013	56	87	0.87
1.5	0.0010	43	90	0.90

The calculated values of corrosion rate (mmpy), inhibition efficiency (%IE) and surface coverage for aluminium corrosion in 1M HCl in the presence of different concentration of the leaves extract from the weight loss measurements are shown in Table 1. Results presented in the table indicates that corrosion rate of aluminium in the acid medium was reduced in the presence of *M. citrifolia* L. extract which is compared to the blank solution. This indicates that the leaves extract inhibited the acid induced corrosion of Al. Inhibition efficiency values were found to increase with increase in concentration of *M. citrifolia* L. extract. Maximum inhibition efficiency of 90% was obtained with extract concentration 1.5 g/L at 30^{0}C.

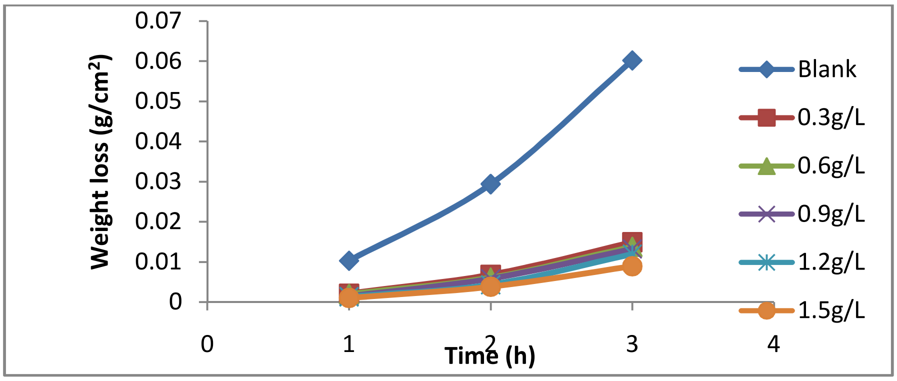
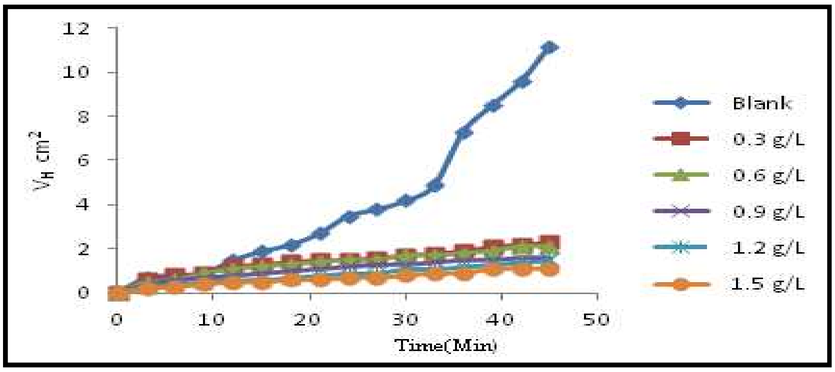


Figure 1. Weight loss versus immersion time for Al with different concentrations of leaves extract

Fig. 1 shows plots of weight loss against immersion time for Al corrosion in the blank and in the presence of different concentrations of *M. citrifolia* L. extract. From the plot, it is seen that at a room temperature the weight loss of Al increases as the period of immersion increased in the presence of inhibitor indicating that the rate of corrosion of Al increases with time.



3.2. Hydrogen evolution technique

Figure 2. is a plot showing the variation of volume of H_2 gas evolved with time for 1M HCl in absence and presence of different concentration of the leaves extract.

The plot indicate that slow rates of hydrogen evolution at the start of the reaction and after sometime, the volume of gas evolved H_2 gas varies linearly with reaction time. On introduction of the leaves extract the volume of hydrogen evolved was decreased, and further decreases as the concentration of the extract increases.

3.2. Potentiodynamic polarisation method

Potentiodynamic polarisation curve for aluminium in 1M HCl solution with various concentration of *M. citrifolia* L. leaves extract at 303K are shown in Table II, Fig. 2. The presence of leaves extract causes a remarkable decrease in current density values because of the formation of a barrier film on aluminium surface while inhibition efficiency values increase with leaves extract and maximum is up to 88% for addition of 1.5g/L of leaves extract. The E_{corr} values shifted towards more negative direction, and these results suggest that the hydrogen evolution reaction is retarded. The large changes in cathodic Tafel slope in presence of inhibitors that the inhibitors affect the cathodic reactions. Therefore, leaves extract could be classified as cathodic inhibitor [0].

Table II Corrosion parameters of aluminium in 1M HCl in the presence and absence of different concentrations of *M. citrifolia* L. obtained from polarisation measurements.

Concentration of MC extract (gL^{-1})	$-E_{corr}$ (mV)	I_{corr} (mA/cm^2)	Tafelslope (mV/decade)		Corrosion rate (mmpy)	Inhibition efficiency (%)
			β_a	β_c		
Blank	744	14.8	199	247	569	-
0.3	747	2.9	172	219	112	80
0.6	747	2.8	183	226	107	81
0.9	754	2.1	205	205	80	86
1.2	755	1,9	144	211	74	87
1.5	757	1.8	142	191	74	88

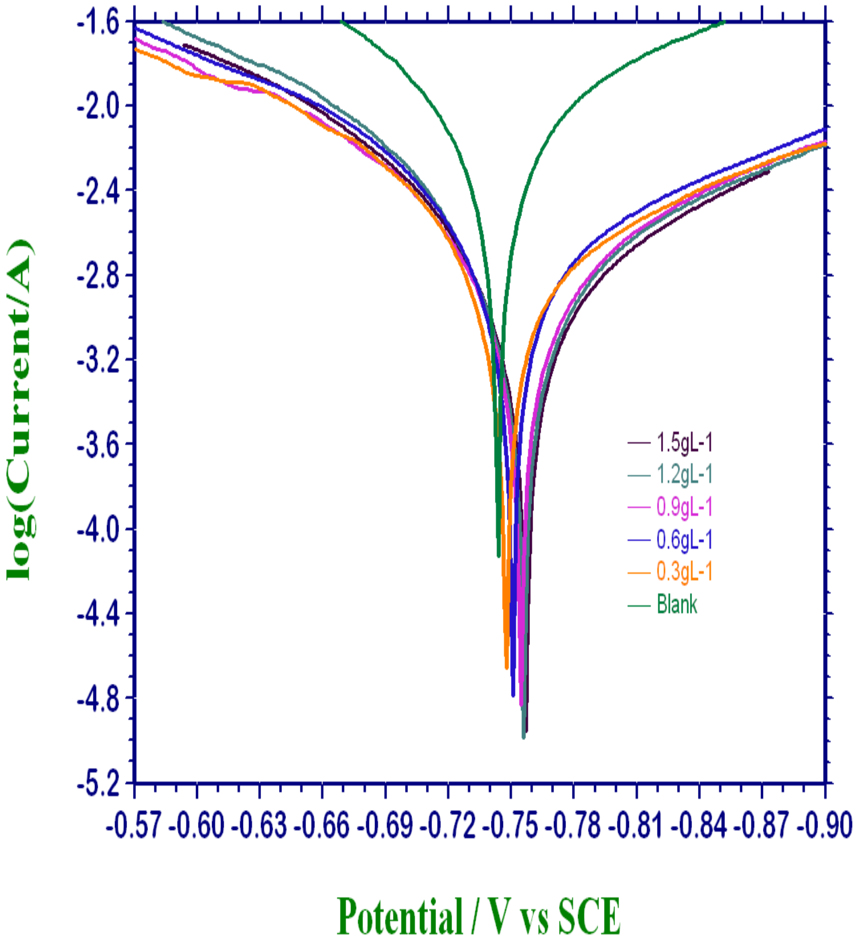


Figure 2 Effect of various concentrations of *M. citrifolia* L. in 1M HCl on aluminium polarisation curves

3.3. Electrochemical impedance spectroscopy

The effect of different concentrations of leaves extract on the impedance behaviour of aluminium in 1M HCl solution at 303K studied and corresponding Nyquist plots are shown in Figure 3. From Figure 3, the impedance spectra consist of a large capacitive loop at higher frequencies followed by a large inductive loop at low frequencies up to the concentration of 0.9 g/L of *M. citrifolia* L. and at higher than 0.9 g/L the inductive loop in the Nyquist plots completely disappears, which indicates prevention of local corrosion [0].

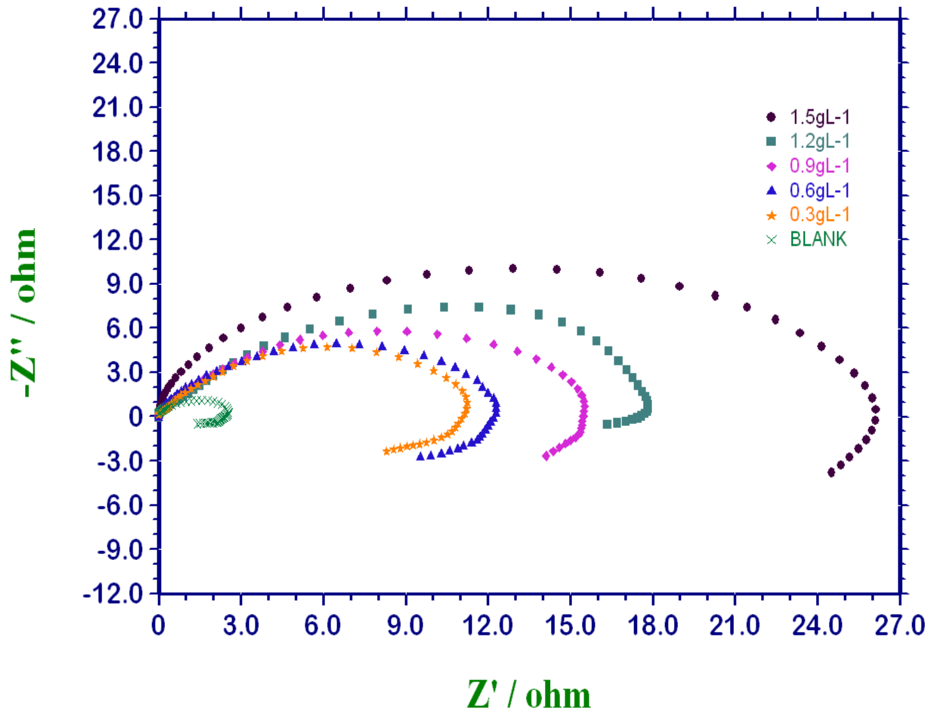


Figure 3 Impedance plots obtained in 1M HCl in various concentration of *M. citrifolia* L. at 303K

The impedance parameters were calculated from the analysis of these diagrams is given in Table III. Values of charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) were calculated from the Randle equivalent circuit model.

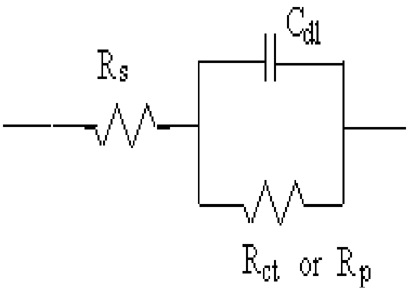


Figure 3 is a Randle circuit generally used to describe the aluminium acid interface model [0]

Table III Fitting impedance data of aluminium in 1M HCl in absence and presence of different concentration of *M. citrifolia* L. at 303K

Concentration of extract (gL^{-1})	R_{ct} Ω cm^2	C_{dl} ($\mu F/cm^2$)	Inhibition efficiency (%)
Blank	2	12.74	-
0.3	10	7.584	80
0.6	11	6.231	82
0.9	14	5.359	86
1.2	17	3.603	88
1.5	23	2.691	91

Table III shows that the (R_{ct}) value increases and (C_{dl}) value decreases with increase in inhibitor concentration, due to the adsorption of the inhibitor on the electrode surface [38].

3.5. Adsorption isotherm

The nature of processes between inhibitor and metal surface can be provided by the adsorption isotherm [0]. Several adsorption isotherms are attempted to fit the surface coverage, θ including Freundlich, Temkin and Langmuir isotherms. It was found that the experimental data obtained from weight loss measurements could fit the Langmuir adsorption isotherm. According to this isotherm, the surface coverage (θ) is related to inhibitor concentration.

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (4)$$

Where K_{ads} is the equilibrium constant for the adsorption process and C_{inh} is the leaves extract concentration. Straight line are obtained when $\frac{C_{inh}}{\theta}$ is plotted verses C_{inh} with a slope is obtained (R^2 = 0.99) as seen in Figure 4

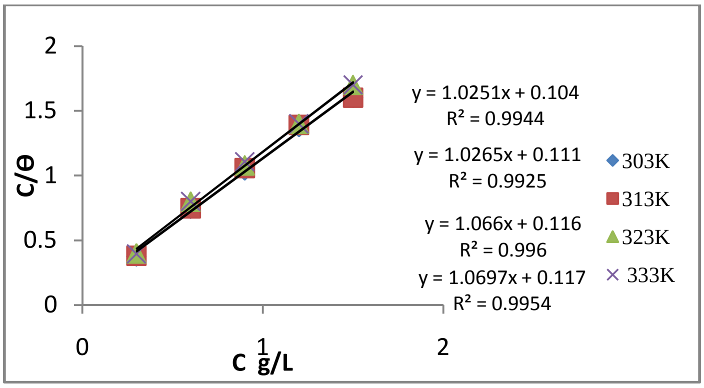


Figure 4 Langmuir adsorption isotherm in presence of leaves extract in 1M HCl

Table IV Equilibrium constant, K and the free energy of adsorption ΔG°_{ads} of leaves extract for Al in 1M HCl solution at 303K

Temperature (K)	K_{ads}	$-\Delta G^{o}$(kJ mol^{-1})
303	9.62	15.82
313	9.00	16.17
323	8.62	16.57
333	8.55	17.06

The value of K_{ads} can be calculated from the intercepts of the straight lines from Figure 4. K_{ads} is related to the standard free energy of reaction ΔG°_{ads} with the following equation [40]

$$\Delta G^{\circ}_{ads} = -RT \ln (55.5\ K_{ads}) \qquad (5)$$

Where 55.5 is the concentration of water in the solution in mol/L, R is the universal gas constant

The calculated values of the standard free energy of reaction ΔG°_{ads} varys between 15.82 to 17.06 kJ/mol. This indicates that the adsorption mechanism of leaves extract in 1M HCl solution is through physisorption.

3.6. Thermodynamic and kinetic parameters

Activation energy can be obtained by modified Arrhenius equation as follows

$$\log CR = \left(\frac{-Ea}{2.303R}\right)\left(\frac{1}{T}\right) + \log A \qquad (6)$$

weight loss measurement were utilised to obtain the corrosion rate values of Al in the absence and presence of 1M HCl of leaves extract at different temperature of 30- 60^{0}C. These values were plotted as shown in Figure 5. The values of activation energy of corrosion were determined from the slope of log C versus 1/ T plots. It is clearly seen from the results obtained that the values of Ea is higher in the presence of leaves extract. This may be attributed to an appreciable decrease in adsorption process of the leaves extract on the metal surface with rise in temperature [41] and also physically adsorbed on the metal surface. A transition state complex is decays to products after forming the high energy [42]. The mathematical form of transition state theory is shown as below

$$CR = \left(\frac{RT}{Nh}\right) e\left(\frac{-\Delta H^{\circ}}{RT}\right) e\left(\frac{\Delta S^{\circ}}{R}\right) \qquad (7)$$

Where ΔH° and ΔS° are the enthalpy and the entropy of activation, N is Avogadro number (6.022 x 10^{23} molecule,mol^{-1}) and h is the Planck's constant (6.626 x 10^{-34} J s mol^{-1}) and Cr is the corrosion rate. The values of enthalpy and entropy of activation for Al corrosion in 1.0 M HCl in absence and presence of inhibitors can be evaluated from the slope and intercept of the curve of $\log\frac{CR}{T}$ versus $\frac{1}{T}$. It gives a straight line with a slope of $(\frac{-\Delta H^\circ}{2.303R})$ and an intercept of ($\log\frac{R}{Nh} + \frac{\Delta S^\circ}{2.303R}$) from which the activation parameters (kinetic parameters E_a, ΔH° and ΔS°) were calculated. Figure 6 shows the slopes and the intercepts give the values of ΔH° and ΔS° in the absence and presence of different concentrations of *M. citrifolia* L. (Table VI). It is clear from the Table VI. shows that ΔS° was negative because inhibitor molecules freely moving in the bulk solution were adsorbed in an orderly fashion onto the aluminium surface resulting in a decrease in entropy. The positive values of ΔH° reflect the endothermic nature of the aluminium dissolution process in the 1M HCl. Increase in the ΔH° with increasing concentration indicating more energy barrier for the reaction in the presence of the inhibitor.

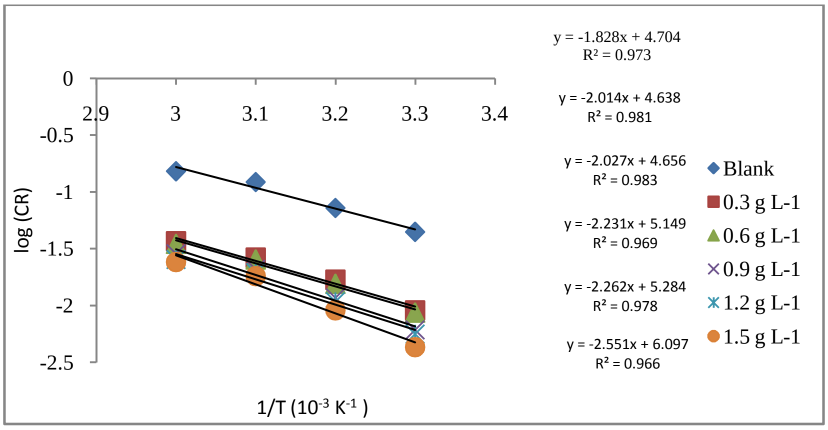


Figure 4 Arrhenius plot of the corrosion rate of the aluminium in 1M hydrochloric acid containing various concentrations of *M. citrifolia* L.

Table VI Kinetic and thermodynamics corrosion parameters for aluminium in 1M HCl in absence and presence of various concentrations of *M. citrifolia* L

Concentration of MC Extract (gL^{-1})	E_a(kJ mol^{-1})	ΔH°(kJ mol^{-1})	-ΔS°($JK^{-1}mol^{-1}$)
Blank	35.00	31.69	19.59
0.3	38.56	35.80	19.59
0.6	38.81	36.03	19.59
0.9	42.72	40.11	19.54
1.2	43.31	40.70	19.52
1.5	48.84	48.84	19.44

CONCLUSION

- The investigated leaves extract are efficient inhibitor for aluminium in 1M HCl.
- The inhibition efficiencies increase with increasing inhibitor concentration and with decreaing temperature.
- Tafel behaviour indicates that corrosion inhibition of aluminium in 1M HCl by the leaves extract is under cathode and anodic control.
- The increase in charge transfer resistance, Rct values of inhibitor with increase in leaves extract concentrations shows that inhibition abilities of the leaves extract depend on the degree of adsorption of the molecule on the metal surface.
- From the effect of temperature, the activation parameters for the corrosion process (Ea, ΔH° and ΔS°) were calculated and indicate that corrosion is much reduced in the presence of inhibitor.
- The adsorption of the leaves extract on the aluminium surface was found to obey Langmuir adsorption isotherm.

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