Melia azedarach L as eco- friendly corrosion inhibitor for Aluminum in 2M HCl

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Abstract

The inhibitive action of aqueous extract of *Melia azedarach L* leaves on corrosion of aluminium in 2M HCl solution was investigated through potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and weight loss measurement. The inhibition efficiency was found to increase with increasing concentration of the extract. The effect of temperature on the corrosion behavior of aluminum was studied. In addition, the thermodynamic parameters of the corrosion process were calculated. The adsorption of the extract of *Melia azedarach* leaves on aluminum was found to follow the Langmuir adsorption isotherm

1. Introduction

Aluminum and its alloys are widely used in engineering applications because of their low density, favorable mechanical properties, good surface finish and relatively good corrosion resistance. The resistance of aluminum against corrosion in aqueous media can be attributed to a rapidly formed a compact, strongly adherent and continuous oxide film [1,2]. Therefore, aluminum and its alloys are widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries. Hydrochloric acid solutions are used for pickling, chemical and electrochemical etching of aluminum [3]. Because of the general aggressively of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials. Most of the corrosion inhibitors are synthetic chemicals which are toxic, expensive and non-biodegradable; hence, they have been limited because of the environmental threat. Therefore, it is desirable to source for environmentally safe inhibitors [4–10]. Plant extracts have become important because they are environmentally acceptable, readily available and renewable source for a wide range of needed inhibitors. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. Natural products were previously used as corrosion inhibitors for different metals in various environments [11–22] and their optimum concentrations were reported. The obtained data showed that plant extracts could serve as effective corrosion inhibitors. Corrosion inhibitors are widely used in industry to reduce the corrosion rate of metals and alloys in contact with aggressive environment. Inhibitors function by adsorption of ions or molecules onto metal surface. They reduce the corrosion rate by,

• Increasing or decreasing the anodic and/or cathodic reaction
• Decreasing the diffusion rate for reactants to the surface of the metal
• Decreasing the electrical resistance of the metal surface

In the present study, the effect of aqueous extract of leaves of *Melia azedarach L* on both the corrosion and kinetics of corrosion process of aluminum in 2 M hydrochloric acid solution have been investigated using weight loss, potentiodynamic polarization, EIS techniques .

2. Experimental

2.1 Materials
The specimens used in this investigation were taken from aluminum with purity of 99.99% provided by Aluminum Company of Egypt, Nagh Ammady.

The fresh *leaves Melia azedarach* were washed by distilled water. It was then extracted with distilled water for 6hrs, and then filtered. The filtrate was evaporated and the sludge residue was dried at $50^{o}C$. Stock solution was prepared from the collected residue and used for preparation the desired concentrations.

A solution of 2M HCl was prepared by diluting concentrated acid (37% Merck) by distilled water and used as the corrosive media.

2.2 Experimental methods
2.2.1 Gravimetric measurements

Gravimetric measurements were carried out in 50 ml 2M HCl solution with and without addition of the leave's extract. Rectangular aluminum specimens having a total surface area of $5.65cm^2$ were used. The sheets were abraded successively with fine emery papers (600 – 1200 grit), rinsed with distilled water, degreased with acetone, dried before being weighed, and then hanged in the corrosive medium. The duration time of immersion was extended up to 200 min at 303K in naturally aerated solutions. At the end of each experiment, the specimens were carefully washed by distilled water, dried between two filter papers and weighed. The corrosion rate was calculated in milligrams per square centimeter per min ($mg.cm^{-2}.min^{-1}$). The surface coverage (θ) and inhibition efficiency, *IE*, were determined according to the following equation:

$$\theta = 1 - (\frac{w_i}{w_o}) \tag{1}$$

$$IE = [1 - (\frac{w_i}{w_o})] x100 \tag{2}$$

Where w_i and w_o are the corrosion rates ($mg.cm^{-2}.min^{-1}$) of aluminum specimen in presence and absence of the leaves of *Melia azedarach* L extract.

2.2.2 Electrochemical measurements

Potentiostatic polarization studies were carried out using Meinsberger potentiostat/ Galvanostat with software zum ps6 remote for calculating the electrochemical parameters. EIS were carried out using the PARSTAT 4000 teamed with the VersaStudio software package. The PARSTAT 4000 is a potentiostat/galvanostat with frequency response analyzer (FRA) contained in a single unit. Polarization experiments were carried out in a conventional three electrode cell with a platinum counter electrode and a reference saturated calomel electrode (SCE). A cylindrical electrode of the aluminum with a bottom surface area of $0.5 \ cm^2$ was used as a working electrode. The electrode was abraded successively with fine emery papers (600 – 1200 grit), rinsed with distilled water, degreased with acetone before insert in the test solution. Before the start of each experiment, the working electrode was immersed for 10 minutes in the test solution in order to attain its steady state potential.

Potentiostatic polarization measurements were carried out by scanning the electrode potential from -1800 to 100mV with a scan rate of polarization was 10mV/sec. The corrosion parameters were determined by extrapolation of the cathodic and anodic Tafel lines to the corrosion potential. The inhibition efficiency (IE) and the fraction of surface coverage (θ) were calculated according to following equations:

$$\theta = 1 - (\frac{i_{corr(i)}}{i_{corr(o)}}) \tag{3}$$

$$IE\% = [1 - (\frac{i_{corr(i)}}{i_{corr(o)}})] x100 \tag{4}$$

where $i_{corr(i)}$ and $i_{corr(o)}$ are the corrosion current density of aluminum specimen (mA/cm^2) in presence and absence of the *Melia azedarach L* extract, respectively.

Electrochemical impedance spectroscopy study were carried out at potential amplitude of 10mV, peak-to-peak (AC signal) in E_{corr}, with 10 points per decade and the frequency ranging from 100 kHz to 0.1 Hz under potentiodynamic conditions.

The impedance diagrams were plotted in the Nyquist representation. The inhibition efficiency IE% was calculated using the following equation:

$$IE\% = 1 - (\frac{R_{ct(o)}}{R_{ct(i)}}) \tag{5}$$

where $R_{ct(o)}$ and $R_{ct(i)}$ are charge transfer resistance of aluminum in the absence and presence of inhibitor, respectively.
All the experiments were performed in naturally aerated solutions at $30^{o}C$.

3. Results and discussion.

3.1 Gravimetric measurements

3.1.1 Effect of immersion time

Weight loss of aluminum, in mg.cm^{-2} was determined at various time intervals in absence and presence of different concentrations of the *Melia azedarach L* extract. Figure.1 represents the relation between time and weight losses of aluminum coupons in solutions of 2M HCl devoid of and containing different concentrations of leaf of *Melia azedarach L* extract. Inspection of the figure reveals that the weight loss increases linearly with increasing time in all tested solutions. However, the slopes of the obtained lines, which represent the rates of weight loss, are affected by addition of extract. The presence of the extract causes a sharp decrease in the rate of weight loss. This means that the addition of *Melia azedarach L* extract retards the corrosion of aluminum in 2M HCl.
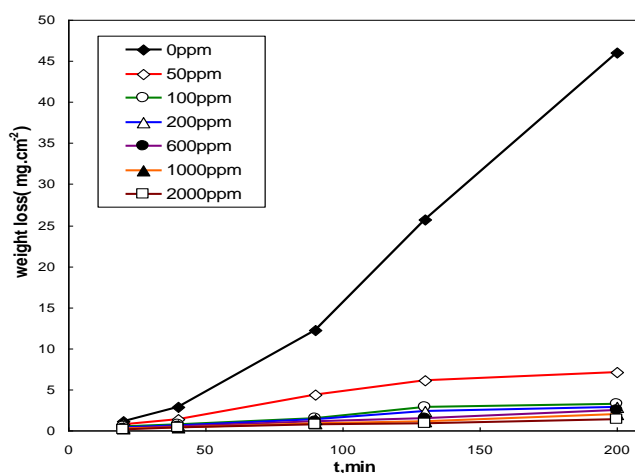

Figure1: Weight loss-time curves for aluminum in 2M HCl in absence and presence of *Melia Azedarach-L.*

3.1.2 Effect of inhibitor concentration

Figure.2 represents the relation between the extract concentration and inhibition efficiency (IE %) toward aluminum corrosion in 2M HCl solution. Inspection of the figure reveals that the inhibition efficiency (IE %) increases with increasing the concentration of the investigated extract at all experimental time.
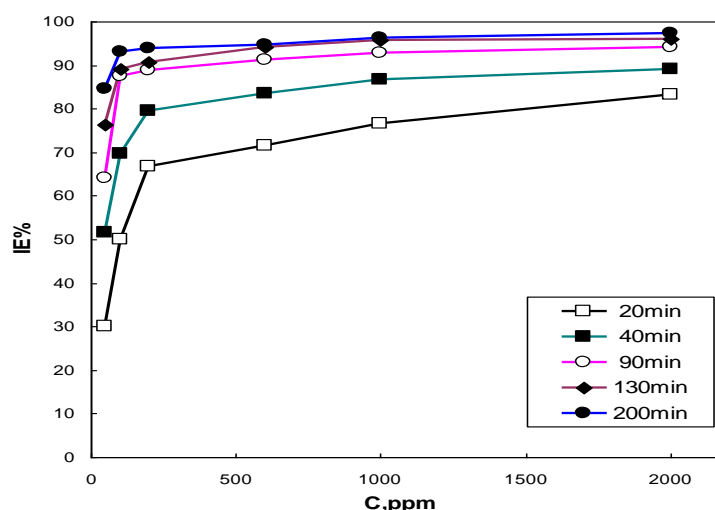

Figure2: Inhibition efficiency-concentration curves for Al in HCl in absence and presence of *Melia Azedarach-L* extract.

The maximum inhibition efficiency was observed to be 97.30% at 2000ppm. Further increase in the extract concentration did not cause any significant change in the performance of the extract. The corrosion inhibition can be attributed to adsorption of phytochemicals molecules present in the plant on the surface of the metal. The phytochemical screening was carried on the leaves extracts of *Melia azedarach,* revealed the presence of some active ingredients such as alkaloids, tannins, phenols, glycosides, steroids, terpenoids and flavonoids [23, 24]. High performance liquid chromatography (HPLC) was used to elucidate components present in water leaf

extracts of *Melia azedarach L.* The analysis revealed the presence of 34 polyphenolic compounds, 7 chlorogenic acid, quercetin, quercetin-3-*O*-β-D-glucoside, 3 p-coumaric acid and kaemferol-conjugated compounds, kaempferol-3-*O*-β-rutinoside in addition to rutin. Water leaf extracts shows minor differences between undefatted and defatted extracts. Owing to the complex chemical composition of the *Melia Azadarach*, it is quite difficult to assign the inhibitive effect to a particular constituent. The adsorption of these compounds on the aluminium surface reduces the surface area available for corrosion.

3.2 Electrochemical measurements
3.2.1 Potentiostatic Polarization
3.2.1.1 Effect of extract concentration on Corrosion process
Figure.3 shows the anodic and cathodic polarization curves of aluminum in 2M HCl; both free and containing different concentrations of *Melia azedarach L* extract.
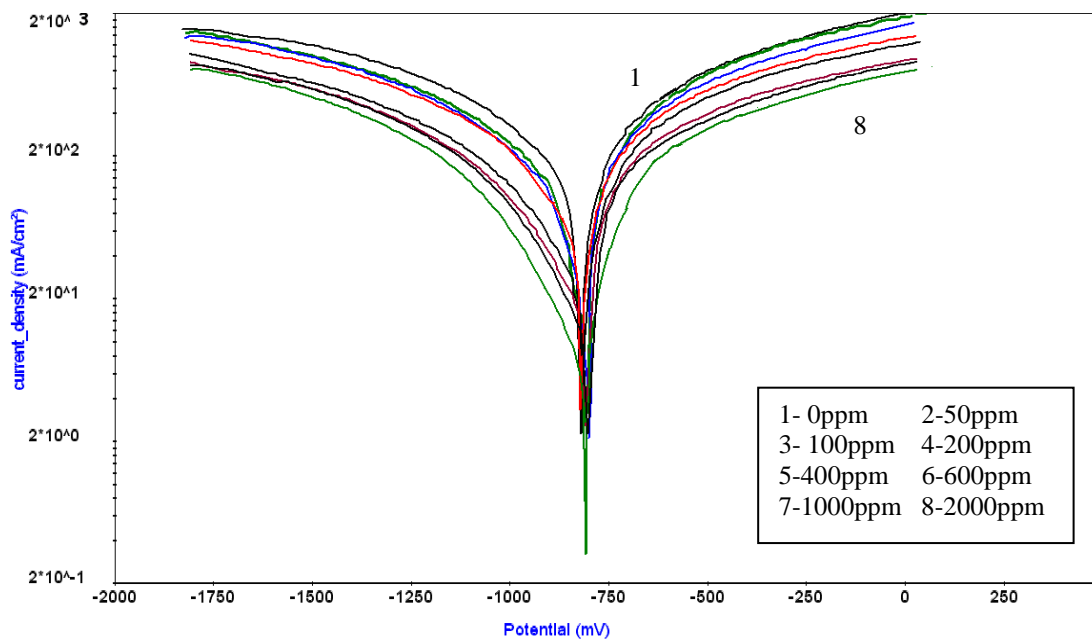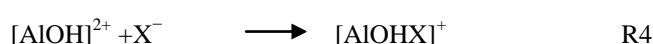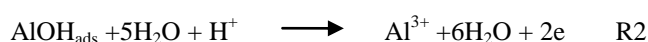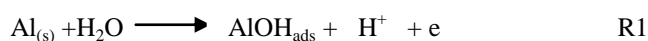

Figure 3: Potentiostatic polarization curves of aluminum in 2M HCl containing different concentrations of *Melia azedarach L* extract at 10mV/Sec.

 Inspection of Figure.3 reveals that, the addition of extract shifts both anodic and cathodic curves toward less current density. This indicates that the extract decreases the acid attack of the aluminum surface. The corrosion parameters drawn from the polarization curves are listed in Table (1). Regarding to this table, we can see that the current density (i_{corr}) decreased with increasing the extract concentrations. This means that the inhibition efficiency increased with increasing the concentration of extract. This may be attributed to adsorption of the extract molecules on aluminum surface and blocked the active sites. It was reported that [25], an inhibitor can be classified as cathodic or anodic type if the displacement in corrosion potential is more than 85 mV with respect to corrosion potential of the blank. The presence of the extract shifts the corrosion potential (E_{Corr}) of aluminum 37mV anodically compared to the blank. This result indicates that the extract acts as mixed type inhibitors, reduces anodic dissolution and retards the cathodic hydrogen evolution reaction. Again, inspection of Table (1), we can see that, both cathodic and anodic Tafel slopes of aluminum in 2M HCl medium decreased with increasing concentrations of the extract. This confirms that *Melia azedarach L* extract acts as mixed-type inhibitor with predominant anodic effectiveness. Corrosion of aluminum in aqueous solution depends on the concentration of anions in solution [26]. A general mechanism for the dissolution of aluminum as follows:

$$Al_{(s)} + H_2O \longrightarrow AlOH_{ads} + H^+ + e \qquad R1$$

$$AlOH_{ads} + 5H_2O + H^+ \longrightarrow Al^{3+} + 6H_2O + 2e \qquad R2$$

$$Al^{3+} + H_2O \longrightarrow [AlOH]^{2+} + H^+ \qquad R3$$

$$[AlOH]^{2+} + X^- \longrightarrow [AlOHX]^+ \qquad R4$$

The controlling step in the metal dissolution is the complexation reaction between the hydrated cation and the anion, (R4). In the presence of chloride ions the reaction will correspond to:

$$[AlOH]^{2+} + Cl^{-} \longrightarrow [AlOHCl]^{+} \qquad \text{R5}$$

Thus soluble complex ion formed leads to the dissolution of the metal. The adsorption of the inhibitor molecule is often a displacement reaction involving removal of adsorbed water molecules from the metal surface [27].

$$\text{Inhibitor}_{(sol)} + XH_2O_{(ads)} \longleftrightarrow \text{Inhibitor}_{(ads)} + XH_2O_{(sol)} \qquad \text{R6}$$
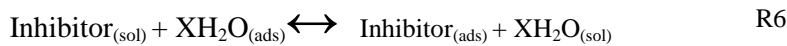
This displacement blocks the formation of $AlOH_{ads}$ (R1). Thus both the oxidation reaction of $AlOH_{ads}$ to Al^{3+} as shown by step (R2) and the complexation reaction between the hydrated cation $[AlOH]^{2+}$ species which are formed in step (R3) and chloride ions can be prevented in step (R5).

The complex chemical compositions in *Melia azedarach L* extract make it rather difficult to attribute the inhibiting action to a particular constituent or group of constituents.

Table 1: Corrosion parameters of Al/2M HCl without and with different concentrations of *Melia azedarachL.*

C, ppm	β_a (mV/decade)	β_C (mV/decade)	E_{Corr} (mV)	I_{Corr} (mA/cm^2)	IE (%)	θ
0	376	- 370	- 848	41.12	------	-----
50	218	-363	-830	34.00	17.32	0.173
100	198	-324	-821	25.30	38.47	0.385
200	180	-280	-823	23.00	44.1	0.441
400	178	-273	-834	15.20	63.04	0.630
600	156	-253	-817	13.12	68.09	0.681
1000	148	-271	-811	10.00	75.68	0.757
2000	91	-240	-811	5.75	86.02	0.860

From the polarization results, it is evident that the precence of polyphenolic compounds inhibit the corrosion by controlling both the anodic and cathodic reactions. This may be attributed to, in acidic solutions the extract compounds may exist as protenated species. These protonated species compete with the hydrogen ions, therefore going to reduce hydrogen evolution on the cathodic sites of aluminum. Adsorption on the anodic sites occurs through the π electrons of aromatic rings and the lone pair electrons of oxygen atoms, which decrease anodic dissolution of aluminum. For example, quercetin is the major constituent in the extract and a strong hydroxyl antioxidant. Hydroxy- and oxogroups present in the quercetin structure have the ability to form complexes with various metal ions. The main chelating sites occurring in quercetin are, respectively: the 3- hydroxy-4-keto, the 5-hydroxy-4-keto and orthodihydroxyl (catechol) groups. It was found that [28] for aluminum in acidic solution, the 3-hydroxy-4-keto group has the strongest chelating power with molar ratio 1:1 at the λ_{max} of complex at 425nm whereas catechol site do not never coordinate to aluminium ion. These results confirm the inhibition efficiency of *Melia azedarach* extract on corrosion of aluminum in hydrochloric acid.

3.2.1.2 Effect of temperature on Corrosion process

The current densities of Al corrosion, in the acidic medium in absence and presence of 2000 ppm of leaves extract *of Melia azedarach L* were determined in temperature range of $30^o – 70^oC$ K by polarization technique. It was found that the rates of aluminum corrosion, in both free and inhibited acid solutions, increase with increasing temperature. However, the corrosion rates in inhibited solutions are affected by the rise of temperature more than that in free acid solution. Consequently, the IE of the extract decreases with increasing temperature as shown in Figure 4. This behavior can be interpreted on the basis that the increases in temperature results in desorption of the inhibitors from the surface of aluminum. The plot of logarithm of the corrosion rate versus the reciprocal absolute temperature gives straight lines (Fig.5) according to Arrhenius equation which represented as [26]:

$$\ln r = A - (\frac{E_a}{RT}) \qquad (6)$$

where r is the corrosion rate (mA/cm^2), A is the frequency factor, E_a is the apparent activation energy and R is the molar gas constant.

The values of E_a^* for free and inhibited acid solutions were obtained from the slopes of the straight lines are given in Table (2). It is clear that, the corrosion process is inhibited via increasing the activation energy of the electrochemical reactions.
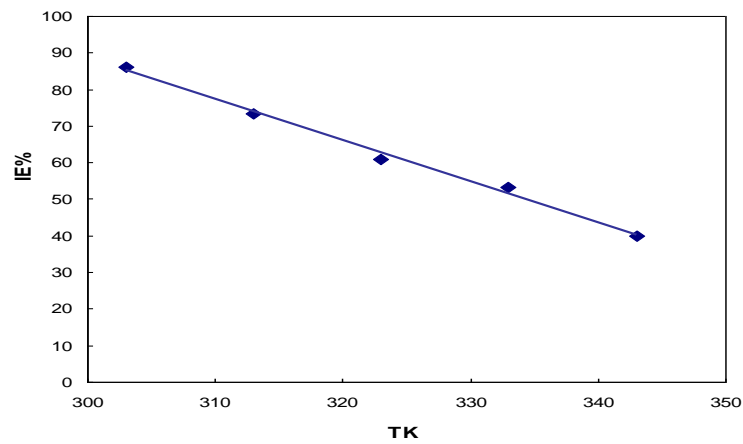

Figure 4: IE%-T(K) curve for aluminum in 2M HCl in presence of 2000 ppm of *Melia azedarach L* extract.
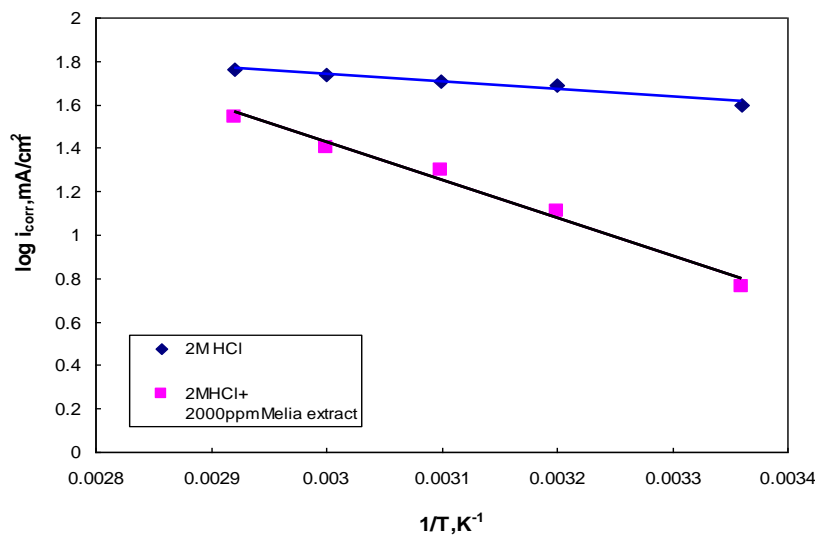

Figure 5: Log (corrosion rate mA/cm^2)-1/T curves for aluminum in 2M HCl in the absence and presence of 2000ppm of *Melia azedarach* L extract.

Table 2: Activation parameters of the dissolution of aluminum in 2M HCl in the absence and presence of 2000ppm *Melia azedarach* L extract.

Activation parameters	ΔE_a^* kJmol^{-1}	ΔH^* kJmol^{-1}	ΔS^* Jmol^{-1}K^{-1}
Free	11	4.3	-195.12
Inhibited	33.2	30.792	-126.17

The increase in activation energy is achieved via formation of an adsorbed film on the metal surface leading to retarding the energy and mass transfer. However, increasing temperature retards this effect by enhancing the desorption process and thus the inhibition efficiency of the *Melia azedarach L* is decreased.

Thermodynamic parameters for corrosion of aluminum in 2M HCl devoid of and containing 2000ppm of the aqueous extract of *Melia azedarach* L extract are calculated from an alternative formula of the Arrhenius equation is the transition state equation.

$$R_{corr} = \frac{RT}{Nh} \exp(\frac{\Delta S^*}{R}) \exp(\frac{-\Delta H^*}{RT}) \qquad (7)$$

Where h is planck's constant, N is the Avogadro's number, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation. Plot of log (R_{corr}/T) vs. 1/T, Fig.6, give straight lines with slope equal (-ΔH^*/2.303R) and an intercept equal (log R/NH+ΔS^*/2.303R).
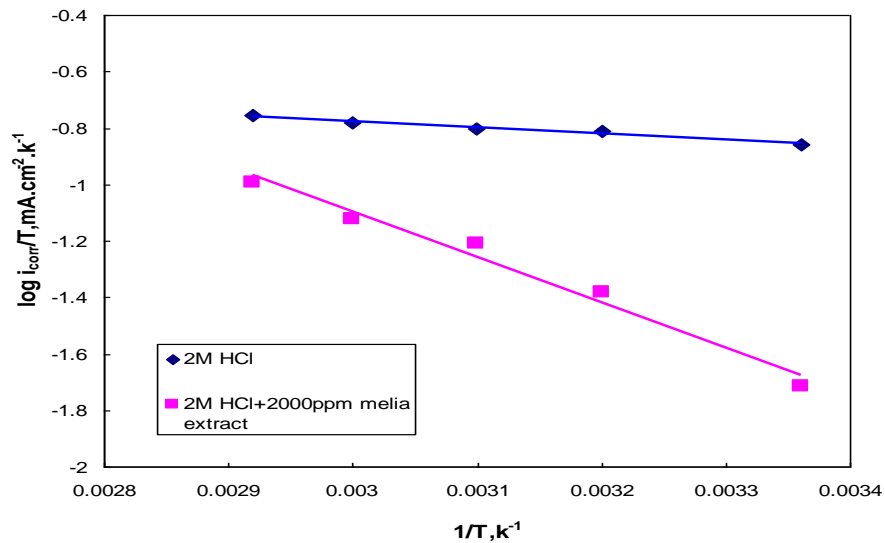

Figure 6: Log (corrosion rate mA/cm²/ T)-1/T curves for aluminum in 2M HCl in the absence and presence of 2000ppm *Melia azedarach* L extract.

The values of ΔS^* and ΔH^* were calculated and tabulated in Table (2).
The data of Table (2) show that the values of ΔE_a^* and ΔH^* are higher for the inhibited solutions than for the uninhibited solutions. This indicates that the inhibitive action of the extract is established by increasing the energy barrier for the corrosion process, emphasizing the electrostatic character of the inhibitor's adsorption on the aluminum surface. In addition, Positive sign of the enthalpies reflects the endothermic nature of the aluminum dissolution process. This result could be interpreted on the basis that aluminum metal always covered by a thin film of oxide. The dissolution of this aluminum oxide layer is endothermic reaction [29]. Small and negative values of entropies show that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [30, 31].

3.2.2 Electrochemical impedance spectroscopy study
Impedance spectra for aluminum in 2M HCl in absence and presence of different concentrations of leaves extract of *Melia azedarach* are shown in the form of Nyquist plots Figure 7. Analysis of the Nyquist plots showed a depressed capacitive loop which arise from the time constant of the electrical double layer and charge transfer resistance.
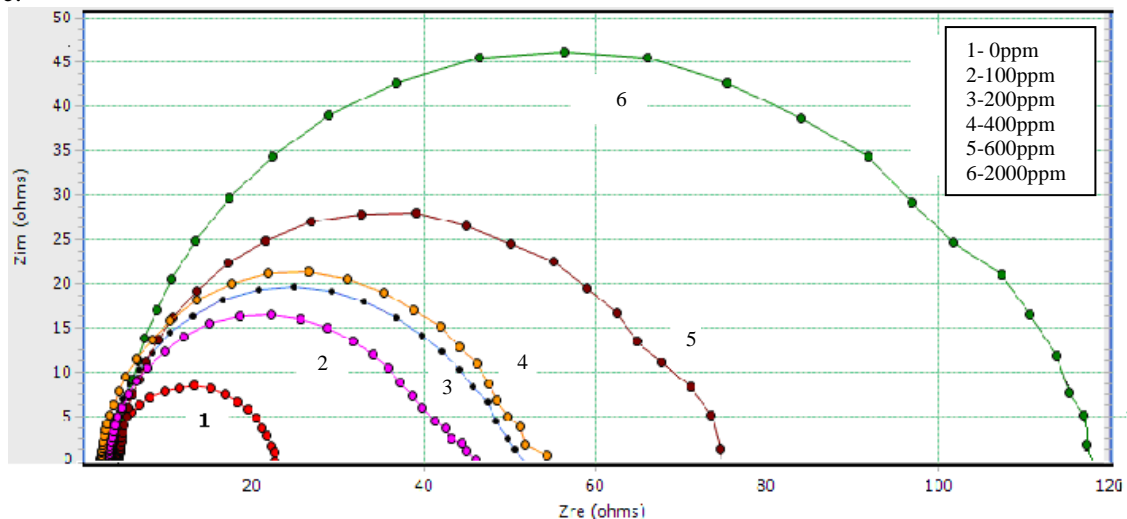

Figure7: Nyquist plots for aluminum in 2M HCl in the presence and absence of *Melia azedarach L extract*.

This could attribute to different physical phenomena such as surface inhomogeneity, roughness, impurities, grain boundaries and distribution of active sites [32]. All the curves obtained are approximated by a single capacitive semicircle, showing that the corrosion process was mainly charge transfer controlled [33]. It is worthy noting that the similar profile of the Nyquist plots is observed in the absence and presence of the inhibitors, indicating that the addition of inhibitors do not change the mechanism for the dissolution of aluminum in HCl. The equivalent circuit model used to fit the experimental results is given in Figure 8 as previously reported [34].
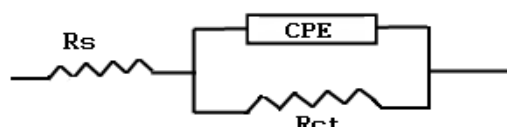

Figure 8: The electrical equivalent circuit for AC impedance measurement.

In this equivalent circuit, R_s is the solution resistance, CPE is a constant phase element and R_{ct} represents the inhibitors resistance to the charge transfer upon oxidation of the metal. All the impedance parameters are derived from Nyquist plots and the IE of all examined concentrations of the inhibitor are given in Table (3). Inspection of Table (3) showed that, the charge transfer resistance and the IE values increase with an increase in the concentration of inhibitor, while the values of capacity of the double layer (C_{dl}) decrease.

Table 3: Electochemical impedance parameters for aluminum in 2M HCl in absence and presence of different concentrations of *Melia azedarach*.

C, ppm	R_{ct}(ohm.cm^2)	C_{dl}(F/cm^2)	IE (%)
0	16.47	1.876×10^{-4}	------
100	42.8	7.660×10^{-5}	61.52
200	49.5	6.434×10^{-5}	66.73
400	54.2	5.970×10^{-5}	69.61
600	61.7	5.550×10^{-5}	73.31
2000	113.6	4.080×10^{-5}	85.50

The decrease in this capacity of the double layer with increase in inhibitors concentrations may be attributed to the formation of a protective layer on the electrode surface [35]. The thickness of this protective layer increases with increase in inhibitor concentration, since more inhibitors will electrostatically adsorb on the electrode surface, resulting in a noticeable decrease in C_{dl} and also leading to an increase in the IE with increasing inhibitor concentration. The results obtained from the EIS measurements are in good agreement with those obtained from the polarization method. It is concluded that the corrosion rate depends on the chemical nature of the electrolyte rather than the applied technique.

3.3 Adsorption isotherm
The adsorption of the extract compounds on the metal surface makes a barrier for mass and charge transfers. This situation leads to a protection of the metal surface from the attack of the acid. Determination of the adsorption mechanism can be explained according to the applied isotherm with respect to the surface coverage (θ). The values of the surface coverage (θ) were obtained, as a function of the inhibitor concentration from potentiostatic polarization technique. Attempts were made to find the best fit of θ values to various isotherms graphically. It was found that the adsorption of tested compound at experimental concentration range on the aluminum surface in 2M HCl follows Langmuir adsorption isotherm as shown in Figure 9. The Dependence of the fraction of the surface occupied by the adsorbed molecules (θ) on the inhibitor concentration is presented in Figure 9. A plot of C/θ versus C gives a straight line with approximately unit slope. This result suggests that the adsorption of inhibitor molecules on the aluminum surface follow Langmuir isotherm.

Thus, this result suggests that there are no interaction or repulsion forces between the adsorbed molecules. It is of interest to mention here that, the θ values obtained from the weight loss measurements obeys also the Langmuir adsorption isotherm. Langmuir adsorption isotherm could be represented using the following equations [36, 37]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{8}$$

and

$$K_{ads} = \frac{1}{55.5} e^{\frac{-\Delta G_{oads}}{RT}} \tag{9}$$

where ΔG^o_{ads} is the standard free energy of adsorption where one molecule of water is replaced by one molecule of inhibitor [37] and the numerical value (55.5) in the equation stands for the molarity of water. It is difficult to calculate the value of standard free energy of adsorption for extract because the extract contains various constituents, which may work together in synergism to decrease corrosion of aluminum by formation a protective film.
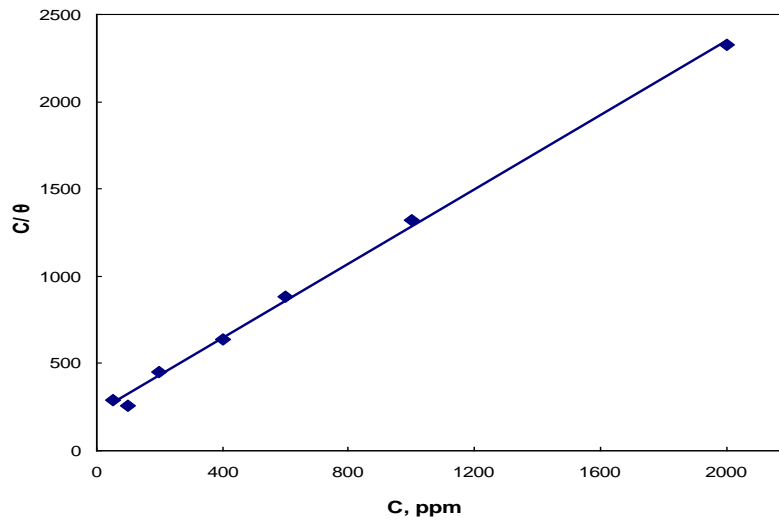

Figure 9: Langmuir adsorption isotherm for aluminum.

Figure 10 shows the plot of log $(\theta/1-\theta)$ versus $(1/T)$ curves for aluminum in 2M HCl in presence of 2000ppm of the extract, gives straight line According to the equation [39]:

$$\log(\frac{\theta}{1-\theta}) = \log A + \log C - (\frac{Q_{ads}}{2.303RT}) \tag{10}$$

where A is independent constant. The values of heat of adsorption Q_{ads} were obtained from the slope and its values are -41KJmol^{-1} of the extract. The negative values of heat of adsorption indicate that the degree of surface coverage decreased with rise in temperature, supporting the earlier proposed physical adsorption mechanism, and show the process of adsorption is exothermal.
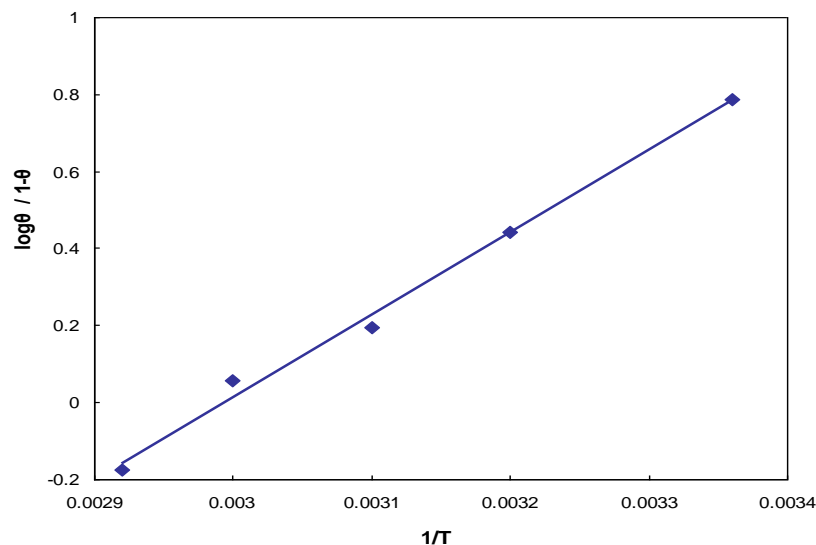

Figure 10: log $\theta/(1-\theta)$ -1/T curves for aluminum in 2M HCl in presence of 2000ppm of *Melia Azadarach* L.extract.

Conclusion

1. The aqueous leaves extract of *Melia Azadarach* L acts as a good corrosion inhibitor for aluminum in 2M HCl solution. The IE increases with increasing extract concentration.

2. The inhibition action is performed via adsorption of the extract compounds on aluminum surface. The adsorption process follows Langmuir adsorption isotherm.

3. The increase of temperature decreases the IE of the extract. The adsorption process may be physical in nature.

4. The presence of the leaf of *Melia Azadarach* L extract increases the activation energy of the corrosion reaction.

5. The negative value for the heat of adsorption indicate that the degree of surface coverage decreased with rise in temperature

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