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Investigation of Cumin (Cuminum Cyminum) extract as an eco-friendly green corrosion inhibitor for pure Aluminium in Acid medium

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Abstract

The inhibitive effect of cumin extract as corrosion inhibitor for pure Aluminium in 1N HCl has been investigated by using Weight loss, Galvanostatic polarization and Electrochemical impedance spectroscopy (EIS) techniques. The results obtained reveal that inhibition efficiency increases with increase in concentration of inhibitors but decreases with increase in temperature. The value of apparent activation energy shows that the cumin extract acts as a good inhibitor for pure Aluminium in acid medium. The values of free energy of adsorption and heat of adsorption show that the adsorption of cumin extract on Aluminium obeys mixed adsorption and exothermic in nature. Thermodynamic consideration shows that adsorption of cumin extract follows Langmuir Adsorption isotherm. The Galvanostatic polarization measurement indicates that the inhibitor is of mixed type. Electrochemical impedance study results are in good agreement with weight loss and Galvanostatic polarization studies.

Keywords: Pure Aluminium, Green corrosion inhibitor, Cuminum cyminum, Adsorption, Electrochemical methods, Acid.

Introduction

Aluminium has a remarkable industrial importance due to its light weight and low cost. It is used in electronics, for production of wires, sheets, tubes and also to form alloys. Aluminium and its alloys are exposed to the action of acid in industrial processes where acid play an important role such as oil well acidizing, acid pickling, acid cleaning and descaling. This can lead to substantial metal loss due to corrosion [1].

The use of inhibitors is one of the most practical options to protect metal from corrosion. Generally, organic and inorganic compounds are usually added to HCl as corrosion inhibitors. Since most of these compounds are toxic, non biodegradable and costly to synthesize, there is a growing demand to find the environmentally safe inhibitors. In attempt to find the eco friendly corrosion inhibitors, there is a growing trend to use natural products such as plants, spices, vegetable peels, seeds etc, as a corrosion inhibitors. This is because these natural products serve as a rich source of naturally synthesized chemical compounds which are environmentally acceptable, inexpensive, readily available and renewable source of materials. [1-21]

Extracts of some plants such as Henna leaves [22], fenugreek seeds [23], mentha spicata [24], musa peels [25] have been reported to inhibit corrosion of steel in acid medium. Extract of aningeria robusta [26], Combretum bracteosum [27], capparis decidua [28], red onion skin [29] have been reported for inhibition of Aluminium and Aluminium Alloy in acid medium.

The present work is another trial to find the environmentally safe corrosion inhibitor for Aluminium in acid medium, where the methanol extract of cumin (cuminum cyminum) at different concentrations were tested. [30]. Dried cumin contains 2-3% essential oil, 22% fatty oil, 18% protein, 14 free amino acids, flavonoid glycosides, tannins, resins, and gum. The main constituents of cumin which may be responsible for corrosion inhibition of Aluminium in 1N HCl is cuminaldehyde. Structure of the compound is given below:

Our research is undertaken

- To evaluate the efficiency of cumin extract as green inhibitor by using Weight loss, Galvanostatic polarization and Electrochemical impedance techniques for protecting the pure Aluminium from corrosion in 1N HCl.
- To propose a suitable mechanism for corrosion inhibition of pure Aluminium by cumin extract.

1. Material and Methods

1.1 Preparation of Aluminium specimen

Pure Aluminium specimen of dimension 3.0 × 6.0 × 0.05 cm were polished to mirror finish, by using jeweler's rouge, so as to eliminate the Aluminium oxide layer from its surface. They were however degreased with carbon tetrachloride, dried, weighed and finally stored in desiccators prior to use for weight loss measurements.

For Galvanostatic polarization and Electrochemical impedance measurements, metal coupons of circular design, diameter 2.802 cm with a handle of 3.0 cm long and 0.5 cm wide and thickness 0.087 cm with a small hole of about 2.0 mm just near the upper end of the specimen. The handle as well as the back of the metal coupon and the platinum electrode was coated with perspex leaving only the circular portion of specimen of apparent surface area 6.156 cm^2 exposed to the solution.

1.2 Preparation of Cumin Extract

Cumin seeds were crushed into fine powder. The solution of cumin was prepared by refluxing 5.0 g of cumin powder with 100 ml of methanol for about 90 minutes and kept for 24 hours, filtered and stored. Test solutions were prepared using cumin stock solution with varying concentration from 0.04%-0.43% (v/v %) by diluting the extract in 1N HCl **[31, 32].**

2. Weight-loss Measurements

Weight loss measurements were carried out for Aluminium specimen in 250 ml beaker containing 230 ml of 1N HCl in presence and absence of inhibitor at different concentrations (0.04 % - 0.43 %), for the exposure period of 60 and 30 minutes respectively at 308 K. One specimen was suspended by a glass hook in each beaker containing test solution which was open to the air at 308K to the same depth of about 1.5 cm below the surface of the test solution. The temperature effect was also studied at 308 K, 318 K, 328 K, and 338 K for the exposure period of 60 and 30 minutes. The specimens were washed thoroughly with distilled water, dried and weight by using Metler balance – M5 type. The accuracy of the balance is .0001g. The mean of weight loss values of three identical experiments was used to calculate the inhibition efficiency of the inhibitor. The inhibition efficiency and surface coverage was calculated by Equation 1 and 2 respectively:

$$\text{Inhibition efficiency (\%IE)} = \frac{W_u - W_i}{W_u} \text{ X } 100 \qquad \text{….. (1)}$$

$$\text{Surface coverage } (\theta) = \frac{W_u - W_i}{W_u} \qquad \text{….. (2)}$$

Where W_u is the weight loss of Aluminum without inhibitor and W_i is the weight loss with inhibitor **[33, 34].**

3. Electrochemical Measurements

Electrochemical studies were carried out using standard three electrode cell where Calomel electrode act as a reference electrode, Platinum electrode as counter electrode and Aluminium electrode as working electrode. All the tests were performed under unstirred conditions without deaeration

(a) The potential is measured against a saturated calomel electrode in polarization study. The corrosion parameters such as; corrosion potential (E_{corr}), corrosion current density (I_{corr}) and Tafel slope (b_a and b_c) were measured by Galvanostatic polarization method. In this study current density was varied in the range from 2×10^{-4} to 3.25×10^{-2} A/cm^2 and potential was calculated. After that the graph is plotted between log of current density (log I in A/cm^2) and Potential (E in mV). From the graph, tafel slopes, E_{corr} and I_{corr} values were determined. The inhibition efficiency was calculated by Equation 3:

$$Inhibition\ efficiency\ (\%IE) = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}}\ X\ 100 \qquad \text{... (3)}$$

where $I^0_{corr}$and I_{corr} are uninhibited and inhibited corrosion current density.

(b) Electrochemical impedance measurements were carried out in the frequency range of 10 kHz-1Hz. The open circuit potential was measured after 30 minutes of immersion of electrode in test solution by applying amplitude of 5 mV sine wave ac signal (AUTOLAB). EIS data were analyzed using frequency response analyzer (FRA) electrochemical setup. The charge transfer resistance (R_t), was obtained from the diameter of the semicircle of the Nyquist plot. The interfacial double layer capacitance (Cdl) values were obtained by determining the frequencies at which the imaginary component of the impedance is maximum f (-Z"max) using Equation 4:

$$C_{dl} = 1/2\Pi.f\,(-Z''max)\,R_t \qquad \ldots(4)$$

The % of inhibitor efficiency was calculated by using Equation 5:

$$\text{Inhibition Efficiency (\%IE)} = \frac{R_t - R^o{}_t}{R_t} \text{ X } 100 \qquad \ldots(5)$$

Where, R_t and $R°_t$ are the value of charge transfer resistance in 1N HCl in presence and absence of cumin extract, respectively.

4. Results and Discussions

4.1 Weight loss method

4.1.1 Effect of inhibitor concentration

Weight loss data and corresponding value of inhibition efficiency of Cumin extract for pure Aluminium are given in Table 1.

Table 1: Corrosion parameters for pure Aluminium in presence and absence of cumin extract at 308 K for exposure period of 60 and 30 minutes

Inhibitor	*Inhibitor concentration (C) (v/v%)*	*Weight loss mgdm^{-2} for 60 minutes*	*Surface coverage (θ) for 60 minutes*	Inhibition efficiency I.E.% for 60 minutes	Weight loss mgdm^{-2} for 30 minutes	Surface coverage (θ) for 30 minutes	Inhibition efficiency I.E.% for 30 minutes
Blank	-	2368.5	-	-	379.4	-	-
	0.04	487.8	0.793	79.3	64	.83	83
	0.08	368.5	0.841	84.1	55.55	.853	85.3
	0.13	226.2	0.902	90.2	24.39	.934	93.4
	0.21	27.1	0.988	98.8	8.13	.978	97.8
	0.30	18.9	0.991	99.1	5.42	.985	99.1
	0.43	8.31	0.996	99.6	2.71	.993	99.3

From the results, it is observed that inhibition efficiency increases with increase in inhibitor concentration. This is due to the higher degree of surface coverage with increase in the concentration of inhibitor. The result reveals that there is not much difference in the values of inhibition efficiency for 60 minutes and 30 minutes. The maximum efficiency (99.6%) has been observed at highest concentration of inhibitor (0.43%) at 308 K for exposure period of 60 minutes. This is due to the time required by the inhibitor to form stable adsorption layer over the metal surface requires at least 60 minutes.

4.1.2 Adsorption behavior

Adsorption isotherm is usually used to describe the adsorption process. It was found that the cumin extract obeys Langmuir adsorption isotherm for corrosion inhibition of pure Aluminium in 1N HCl, for exposure period of 30 and 60 minutes, as can be seen from correlation coefficient value, R^2 = .9994 and .9997 respectively, in Figure 1(a) and (b) respectively.

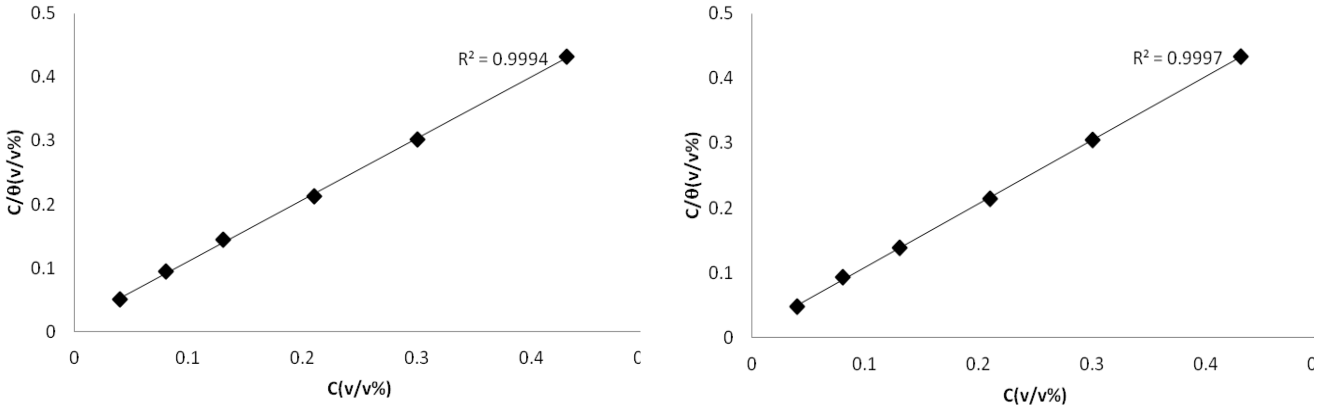
These results suggest that:

- The metal surface contains the fixed number of adsorption sites and each site hold one adsorbate.
- The adsorbates do not interact with each other **[35].**

Langmuir isotherm is given by Equation 6:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad \ldots(6)$$

where θ is the degree of surface coverage, c is the v/v% of inhibitor concentration in solution; K_{ads} is the equilibrium constant for adsorption process.



(a) (b)

Figure 1: Langmuir adsorption isotherm plot for cumin extract at 308 K for 60 (a) and 30 (b) minutes

Free energy of adsorption (ΔG_{ads}) can be calculated by using Equation 7:

$$K_{ads} = 1/55.5 \exp(-\Delta G_{ads}/RT) \qquad \ldots (7)$$

Where R is the universal gas constant and T is the absolute temperature. The value 55.55 in the above equation is the concentration of water in solution in mol L^{-1}. But due to the presence of various compounds in the inhibitor, it is not possible to determine the exact molecular weight of the inhibitor. As a result, value of free energy of adsorption (ΔG_{ads}) is not possible to determine. **[36]**

4.1.3 Effect of Temperature

The effect of temperature on inhibition efficiency was studied at various temperatures ranging from 308 K -338 K for 60 and 30 minutes in presence and absence of 0.43% of cumin extract by weight loss technique which is shown in Figure 2 (a) and (b) respectively. The results from Table 2(a) and Table 2(b) show that corrosion rate increases with increase in temperature. It is observed that at 338K, for exposure period of 60 minutes, the inhibition efficiency at once decreases to 51.6% from 96.9% at 328 K. This observation proves that the inhibitor layer decays at a faster rate in 338 K for 60 minutes but for 30 minutes the layer is intact on the surface of Aluminium showing inhibition efficiency of 96.7%. These results suggest that there is an increase in rate of metal dissolution leading to decrease in surface coverage degree.

Table 2(a): Temperature effect on the weight loss for pure Aluminium in 1N HCl for 60 minutes

Inhibitor	Concentration (C) (v/v%)	Weight loss mgdm^{-2} For 60 minutes			
		308	318	328	338
Blank	-	2368.5	4436	5303	5808
Cumin extract	0.43%	8.13 (99.6%)	81.3(98.1%)	160 (96.9%)	2807(51.6%)

Table 2(b): Temperature effect on the weight loss for pure Aluminium in 1N HCl for 30 minutes

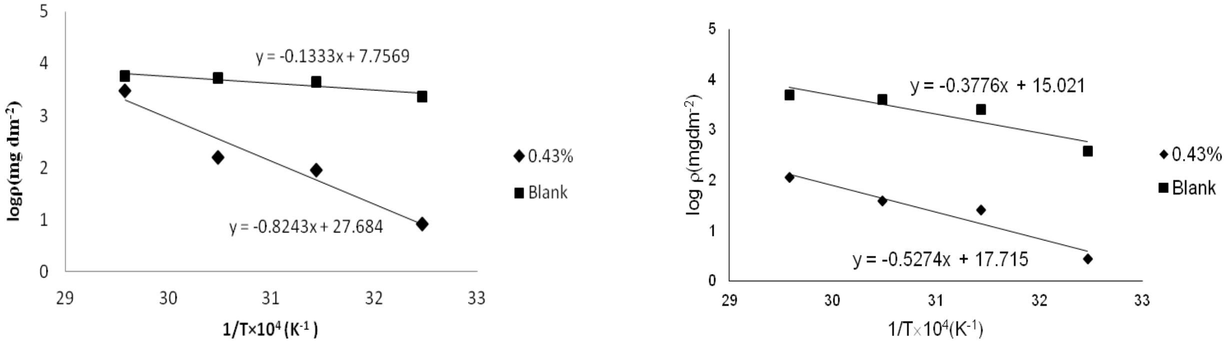
Inhibitor	Concentration (C)	Weight loss mgdm^{-2} For 30 minutes			
		308	318	328	338
Blank	-	379	2699	4043	4617
Cumin extract	0.43%	2.71 (99.3%)	27.1 (98.9%)	40.6 (98.9%)	168 (96.7%)

4.1.4 Kinetic Parameter

In acidic solution the corrosion rate is related to temperature by Arrhenius Equation 8:

$$\rho = K \exp(-E_a/RT) \qquad \ldots (8)$$

Where ‘ρ’ is the corrosion rate, ‘E_a’ is the apparent activation energy, ‘R’ is molar gas constant and ‘T’ is the absolute temperature.



(a) (b)

Figure 2: logρ vs 1/T×10^4 to calculate the activation energy of corrosion process for exposure period of 60 (a) and 30 (b) minutes in absence and presence of cumin extract

The apparent activation energy for exposure period of 60 and 30 minutes is determined from the slope of log ρ versus 1/T×10^4 graph depicted in Figure 2. The calculated apparent activation energy is reported in Table 3 and it can be observed that the apparent activation energy of inhibited solution in both the time periods (60 and 30 minutes) is greater than the uninhibited one, indicating that the inhibition efficiency decreases with increase in temperature [37, 38].

Table 3: Apparent Activation energy and Thermodynamic parameters for adsorption of cumin extract inhibitor on pure Aluminium in 1N HCl for exposure period of 60 and 30 minutes

Inhibitor	*E_a (KJ/mol) For 60 minutes*	*Ea (KJ/mol) For 30 minutes*
Blank	25.5	72.2
Cumin extract	157.8	100.9

4.1.5 Effect of Time

The inhibition efficiency of 0.43% of cumin extract was studied at 308 K with a variation of time from 60 and 30 minutes to 240 minutes. It can be seen from Figure 3 that as the time increases from 60 and 30 minutes to 120 minutes, inhibition increases from 99.3% to 99.6% and then decreases to 98.8% for 240 minutes. This may be due to the time required by the inhibitor to form protective film over pure Aluminium to inhibit corrosion is around 60 and 30 minutes **[39]**. Therefore, the optimum concentration of inhibitor is 0.43%, for obtaining maximum inhibition efficiency at 308 K for the exposure period of 60 minutes. The adsorption layer remains strongly bounded over Aluminium till 120 minutes. After 120 minutes inhibitive layer starts decaying.

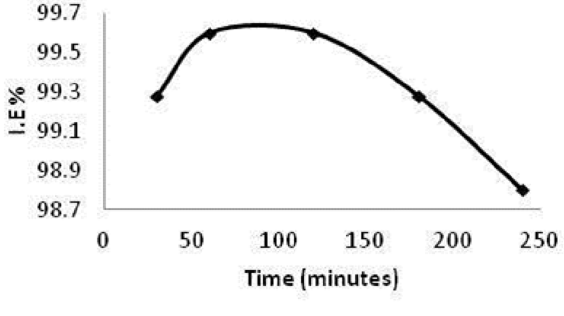


Figure 3: Variation of inhibition efficiency with exposure time for pure Al immersed in acid in presence of inhibitor

4.2 Galvanostatic Polarization

Galvanostatic polarization curves for pure Aluminium in 1N HCl in presence and absence of various concentration of inhibitor is shown in Figure 4. There is no observable change in corrosion potential on addition of inhibitor suggesting that the inhibitor is adsorbed on the metal surface, covers both cathodic as well as anodic sites. Therefore,

the inhibitor is of mixed type. Further, the addition of inhibitor reduces cathodic current significantly, indicating that it is predominantly cathodic inhibitor. It is further supported from the fact that the cathodic slope values (b_a) are always greater than anodic slope values (b_c) suggesting the predominance of cathodic inhibitor. **[40-42]**
The values of electrochemical parameters such as E_{corr}, cathodic tafel slope (b_c), anodic tafel slope (b_a) and corrosion current density, I_{corr} was obtained by extrapolation of tafel lines, are shown in Table 4.

Table 4: Electrochemical parameters of corrosion of pure Aluminium in presence of different concentration of cumin extract at 308 K and corresponding inhibition efficiencies obtained by polarization technique

Inhibitor	*Concentration*	E_{corr}	b_a *(mV/dec)*	b_c *(mV/dec)*	I_{corr} *for cathodic A/cm²*	%I.E
Blank	-	-820	153	200	7.70×10^{-3}	-
Cumin Extract	0.04	-824	123	195	1.66×10^{-3}	78.6
	0.30	-824	130	193	2.57×10^{-4}	96.6
	0.43	-825	166	187	1.23×10^{-4}	98.4

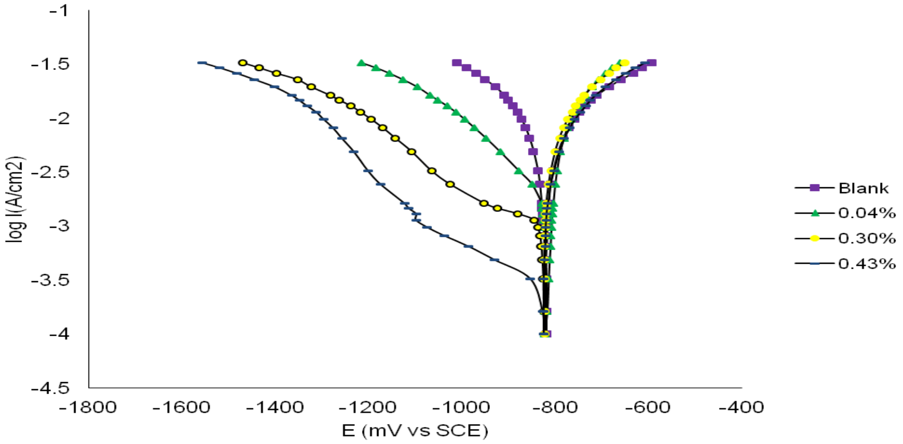


Figure 4: Anodic and cathodic polarization curves obtained from pure Aluminium at 308 K in 1N HCl in various concentration of cumin extract

4.3 *Electrochemical Impedance Spectroscopy (EIS) Measurements*

The Nyquist plot for corrosion of pure Aluminium in 1N HCl in absence and presence of various concentration of cumin extract is shown in Figure 5. The plots were investigated at open circuit potential conditions and were analyzed by fitting the experimental data to a circuit model $R_s(QR_t[R_LL])$ .The plots includes Q as double layer capacitance (C_{dl}), charge transfer element (R_t), solution resistance (R_s) and inductive elements (R_L, L). In the high frequency limit, the inductive contribution to the overall impedance is insignificant. Therefore, Nyquist plot of the impedance is a semicircle characteristic of the parallel arrangement of the double layer capacitance and charge-transfer resistance corresponding to the aluminum dissolution reaction. Contribution to the total impedance at intermediate frequencies comes mainly from the charge-transfer resistance and inductive component in parallel. The inductive loop may be attributed to the stabilization of layer by adsorbed intermediate products of the corrosion reaction on the electrode surface involving inhibitor molecules as well as reactive products. These values are depicted in Table 5.

Table 5: Impedance parameters and corresponding inhibition efficiency for the corrosion inhibition of pure Aluminium by cumin extract at 308 K

Inhibitor	*C (v/v%)*	R_s *(Ω)*	R_t *(Ω)*	C_{dl} *(µF)*	% I.E.	R_L (Ω)	L(H)
Blank	-	1.533	1.58	154.6	-	1.609	.4228
Cumin extract	0.04%	1.509	7.24	151.5	78.2	7.27	.9820
	0.17%	1.559	19.26	136.7	91.7	25.56	2.097
	0.30%	1.682	39.6	124.9	96.0	37	9.627
	0.43%	1.696	58.2	114.9	97.2	53.1	11.3

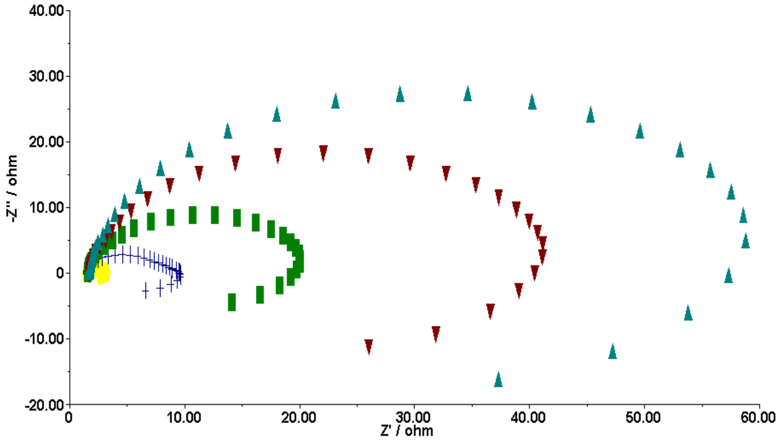


Figure 5: Impedance plot obtained at 308 K for corrosion inhibition of pure Aluminium by cumin extract at various concentrations

'R_t' value increases with increase in inhibitor concentration indicating the decrease in corrosion rate. 'C_{dl}' decreases with increase in inhibitor concentration indicating the reduction of charges accumulated in the double layer due to formation of adsorbed inhibitor layer **[43].**

5. Mechanism of Inhibition

The extracts of plants contain various organic compounds. Most of these compounds contain N, S, O atoms and an aromatic ring in their structure. These atoms or the π electrons of aromatic ring if present in the organic compound can coordinate with the empty orbital of corroding metal to protect it from corrosion.

The main constituent of cumin extract which contains heteroatom and an aromatic ring in its structure is cuminaldehyde. The active oxygen centre of cuminaldehyde may form complex with the metal cation to retard the dissolution of pure Aluminum in acid medium.

Cuminaldehyde can be protonated in an acid medium, predominantly affecting the oxygen atom present in it. Thus, it forms cations, existing in equilibrium with the corresponding molecular form as shown in Equation 9:

$$C_{10}H_{12}O + xH^+ \rightarrow (C_{10}H_{12+x}O)^{x+} \qquad \text{..... (9)}$$

The protonated cuminaldehyde however, could be attached to the Al surface which by means of electrostatic interaction between Cl^- and protonated cuminaldehyde. When cuminaldehyde adsorbs on the Al surface, electrostatic interaction takes place by partial transfer of electrons from the polar O-atom and the delocalized π electrons around the benzene ring to the metal surface **[44].**

6. Conclusion

Our present study leads to the following conclusions for controlling the corrosion of pure Aluminium by cumin extract in 1N HCl:

- The inhibition efficiency increase with increase in concentration of inhibitor and decreases with increase in temperature.
- The inhibitor obeys Langmuir adsorption isotherm.
- The value of apparent energy of activation proves that the cumin extract act as a good inhibitor for pure Aluminium in presence of 1N HCl.
- The cumin extract act as a mixed type inhibitor with predominance of cathodic inhibitor on pure Aluminium surface.
- Electrochemical impedance study shows that the charge transfer resistance increases and double layer capacitance decreases with increase in concentration of inhibitor.

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