Corrosion Inhibition of Aluminium in HCl by *Cuminum cyminum* (Jeera) Seeds Extract: Adsorption , Kinetic and Thermodynamic Study

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ABSTRACT: *Inhibition of the corrosion of aluminium in hydrochloric acid solution by Cuminum cyminum (Cumin) seeds extract has been studied using weight loss, temperature effect and kinetic study methods. Corrosion rate increases with the increase in acid concentration and temperature. As inhibitor concentration increases corrosion rate decreases while percentage of inhibition efficiency (I.E.) increases. The value of free energy of adsorption (ΔG^0_{ads}), heat of adsorption (Q_{ads}), energy of activation (E_a), enthalpy of adsorption (ΔH^0_{ads}) and entropy of adsorption (ΔS^0_{ads}) are calculated. The inhibition effect is discussed in view of Cuminum cyminum molecules adsorbed on the metal surface and obeys Langmuir adsorption isotherm. Maximum I.E. of Cuminum cyminum seeds extract was found up to 88.39 % at 1.2 g/L inhibitor concentration in 1.0 M HCl solution.*

Key Words: *Aluminium, HCl, Cuminum cyminum, Corrosion, Inhibition, Adsorption.*

Introduction

Any process of deterioration (or destruction) and consequent loss of a metallic material, through an unwanted (or unintentional) chemical or electrochemical attack by its environment, starting at its surface is called corrosion (Jain et al. 1997). The study of aluminium corrosion in different acidic and alkaline environments has attracted considerable attention in view of important application of the metal. Aluminium is a hard, strong and white metal. It is highly electropositive and resistance to corrosion because of hard, tough film of oxide it forms on the surface (Cotton et al. 1972). Hydrochloric acid is commonly used for pickling and etching purposes due to its low cost as compared to other acids. The corrosion rate of metals can be reduced with the application of inhibitors in aggressive environment (Eduok et al. 2012) (Tao et al. 2013). 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, vegetable peels, seeds etc., as a corrosion inhibitor. 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. In India, cumin seeds have been used for thousands of years as a traditional ingredient of innumerable dishes including kormas and soups and also form an ingredient of several other spice blends. Beside food use, it has also many applications in traditional medicine. In the Ayurvedic system of medicine in India, cumin seeds have immense medicinal value, particularly for digestive disorders. It is used in chronic diarrhea and dyspepsia (Singh et al. 2012) have studied theoretical and electrochemical studies of *Cuminum cyminum* (Jeera) extract as green corrosion inhibitor for mild steel in hydrochloric acid solution and found that complex formation between the inhibitor and the mild steel surface (Sribharathy and Rajendran 2013) have investigated *Cuminum cyminum* extract as eco-friendly corrosion inhibitor for mild steel in seawater (Idouhli et al. 2016) studied C*uminum cyminum* extract- A green corrosion inhibitor of S300 Steel in 1 M HCl (Li and Jian 2004) has studied chemical composition of essential oil of C*uminum cyminum*.The present work is to examine the aqueous *Cuminum cyminum* seed extract as an inhibitor for corrosion of Aluminium in 1.0 and 1.25 M HCl.

Experimental

Preparation of sample and solution

The aluminium specimens with a chemical composition of 99.54 % Al, 0.090 % Si, 0.320 % Fe, 0.0012 % Cu, 0.0034 % Mn, 0.0014 % Mg, 0.0042 % Cr, 0.0046 % Ni, 0.0020 % Zn, 0.0079 % Ti, 0.0005 % Pb, and 0.0026 % Sn are used in the present study. The metal sheet, test specimens of size 5.0 x 2.50 x 0.198 cm having an effective area of 0.2797 dm^2 are used. The specimens are cleaned by washing with distilled water, degreased by acetone, washed once more with doubled distilled water and finally dried and weighted by using electronic balance. Hydrochloric acid was used as corrosive solution having concentration of 1.0 and 1.25 M prepared by diluting analytical grade of HCl purchased from Merck using double distilled water.

Preparation of *Cuminum cyminum* seeds extract

The Cumin seeds are crushed into fine powder. The solution of Cumin are prepared by refluxing 10 gm of Cumin powder with 100 ml of distilled water for about 2 h and kept for 24 h, filtering and test solutions are prepared using stock solution with different concentration from 0.6, 0.8, 1.0 and 1.2 g/L by diluting in 1.0 and 1.25 M HCl.

Weight loss measurement

For weight-loss measurement, the aluminium specimen having an area of 0.2797 dm^2 are each completely suspended in 230 ml of 1.0 and 1.25 M HCl solution with and without different *Cuminum cyminum* seeds extract concentrations using glass hooks at 301± 1 K for 24 h. The coupons are retrieved after 24 h washed with distilled water, dried well and reweighed. From the weight loss data, corrosion rate (CR) are calculated.

Temperature effect

To study the effect of temperature on corrosion rate, aluminium coupons are completely immersed in 230 ml of 1.0 M HCl solution without and with different concentrations of *Cuminum cyminum* seeds extract at 313, 323 and 333 K for 2 h. From the data corrosion rate, inhibition efficiency (I.E.), activation energy (E_a) and heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG^0_{ads}) are calculated.

Results and Discussion

Weight loss experiments

The weight loss experiments was carried out in 1.0 and 1.25 M HCl solution containing 0.6, 0.8, 1.0 and 1.2 g/L concentration of *Cuminum cyminum* seeds extract at 301±1 K for a exposure period of 24 h was investigated. Corrosion rate (C.R.) was calculated using following equation:

$$\text{C.R. } (mg/dm^2 d) = \text{Weight loss (gm.) x 1000 / Area in } dm^2 \text{ x day} \quad \ldots\ (1)$$

Inhibition efficiency (I.E.) was calculated by using following equation:

$$\text{I.E. } (\%) = \left\{\frac{(W_u - W_i)}{W_u}\right\} \times 100 \quad \ldots\ (2)$$

where, W_u= Weight loss in absence of inhibitor, W_i = Weight loss in presence of inhibitor.

The degree of Surface coverage (θ) of the aluminium specimen for different concentration of HCl solution have been evaluated by weight loss experiments using the following equation:

$$\theta = \frac{(W_u - W_i)}{W_i} \quad \ldots\ (3)$$

Effect of Inhibitor concentration

At constant acid concentration, as the inhibitor concentration increases corrosion rate decreases while I.E. increases. e.g. in case of *Cuminum cyminum* in 1.0 M HCl the I.E. was found to be 65.19, 72.15, 79.11 and 88.39 % correspond to 0.6, 0.8, 1.0 and 1.2 g/L inhibitor concentration respectively (Table-1). At constant acid concentration, as the inhibitor concentration increases corrosion rate decreases while I.E. increases (Fig.-1).

Temperature effect

To investigate the influence of temperature on corrosion of aluminium, the weight loss experiments are carried out at 313, 323 and 333K in 1.0 M HCl in absence and presence of *Cuminum cyminum* seeds extract for an immersion period of 2h. The results given in Table-2 shows that corrosion rate increases with rise in temperature (Table-2). The value of energy of activation (E_a) has been calculated with the help of Arrhenius equation (Bruker et al. 1979).

$$\log\frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \ldots\ (4)$$

where ρ_1 and ρ_2 are the corrosion rate at temperature T_1 and T_2 respectively.

Results given in Table-2, indicates that the values of E_a are higher in inhibited acid ranging from 33.20 to 41.81 kJ mol^{-1} than E_a value for uninhibited acid (23.39 kJ mol^{-1}) which indicates physical adsorption of the inhibitor on metal surface and the adsorption of inhibitor causes an increase in the E_a value of the process (Lebrini et al. 2010). Results of Table-2 indicates that as temperature increases, rate of corrosion increase while percentage of I.E. decreases. The value of E_a are also calculated from the slope of the Arrhenius plot of log ρ versus 1/T x 1000 (Fig.-2) shows good agreement with the calculated values.

The values of heat of adsorption (Q_{ads}) were calculated by using the following equation (Thomson 1971).

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right]\left[\frac{T_1 T_2}{T_2 - T_1}\right] \quad \ldots..(5)$$

where θ_1 and θ_2 are the fraction of the metal surface covered by the inhibitor at temperature T_1 and T_2 respectively. It is evident that in all cases, the value of Q_{ads} were negative and ranging from -14.44 to -35.18 kJ mol^{-1}. The negative values show that the adsorption and hence the I.E. decreases with rise in temperature (Martinez et al. 2003). The surface coverage 'θ' value was calculated by using equation-3. A plot of inhibitor concentration C_{inh} versus C_{inh}/θ was presented in Fig. 3 which gives straight line with slope values equal to unity indicates that the system follows Langmuir adsorption isotherm (Mu et al. 2005). This isotherm can be represented as

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

where, K_{ads} is the equilibrium constant and C_{inh} is the inhibitor concentration.

Free energy of adsorption (ΔG^{o}_{ads}) was determined by the Langmuir isotherm was given by a plot of C/θ versus C (Fig.-3). From the intercept of the straight line on the C/θ axis, K_{ads} can be calculated which was related to ΔG^{o}_{ads} as given by the following equation (Obot et al. 2009 and Popova et al. 2003).

$$\Delta G^{o}_{ads} = -RT \ln (55.5\, K_{ads}) \quad \ldots..(7)$$

Where, R is the gas constant, T is the concentration of water in solution in Molar (Langmuir 1916), K_{ads} is the equilibrium constant of the adsorption/desorption process. The mean ΔG^{o}_{ads} value was negative (-11.35 kJ mol^{-1}) indicating that the adsorption mechanism of *Cuminum cyminum* on aluminium in 1.0 M HCl at the studied temperatures is physisorption with adsorptive layer having electrostatic character (Donahue and Nobe 1965). This is concluded on the fact that the values of ΔG^{o}_{ads} -20 kJ $mol^{-1}$are consistant with physisorption, while those around -40 kJ mol^{-1}or higher are associated with chemisorption (Ibrahim et al. 2012).

The enthalpy of adsorption (ΔH^{o}_{a}) and entropy of adsorption (ΔS^{o}_{a}) are calculated using the equations (8) and (9),

$$\Delta H^{o}_{a} = Ea - RT \quad \ldots..(8)$$

$$\Delta S^{o}_{a} = \Delta H^{o}_{a} - \Delta G^{o}_{a} / T \quad \ldots..(9)$$

Results indicates that values of ΔH^{o}_{a} are positive and increase in presence of inhibitor indicating a higher degree of surface coverage and higher protection efficiency attained due to raising the energy barrier for the aluminium corrosion reaction. The enthalpy change ΔH^{o}_{a} was positive and ranging between 80.75 to 177.38 kJ mol^{-1} indicating the endothermic nature of the reaction suggests that higher temperature favours the corrosion process (Yaro et al. 2011). Value of ΔS°_{a} are found positive and lie between 0.32 to 0.88 kJ mol^{-1} K indicates the affinity of the adsorbent for the inhibitor and the corrosion process is entropically favorable (Issa et al. 2002).

Kinetic parameters: Rate constant (k) and Half-life ($t_{1/2}$)

The values of half-life ($t_{1/2}$) were calculated by using the following equation (Ebenso 2004);

$$t_{1/2} = 0.693 / k \quad \ldots..(10)$$

where, 't' is time in hours and 'k' is rate constant.

The rate constant k decreases with increase in concentration of inhibitor whereas the half-life increases with concentration of inhibitor (Table-3). The results are in agreement with the result obtained by Talati and Modi (1986). The adsorption of the organic molecules can affect in several ways, the behaviour of the electrochemical reactions involved in the corrosion process. The action of organic inhibitors also depends on the type of interaction between the substance and the metallic surface. This interaction causes a change either in the electrochemical process mechanism or in the surface available to the process (Granese et al. 1992 and Damaskin 1971).

Mechanism of Inhibition

The extracts of plants contain different organic compounds. Most of these compounds contain N, S, and 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. Dried cumin contain 2-3 % essential oil, 22 % fatty oil, 18 % protein, 14 free amino acids, flavonoids, glycosides, tannins, resins and gum. The main constituents of cumin are Cuminaldehyde, p-cymene and terpenoid (Ladha et al. 2013). Structures of these compounds are given below in Fig. 4.

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

$$C_{10}H_{12}O + xH^{+} \longrightarrow (C_{10}H_{12}+xO)\ x^{+} \quad .....(11)$$

The protonated cuminaldehyde however, could be attached to the aluminium surface which by means of electrostatic interaction between Cl^- and protonated cuminaldehyde. When cuminaldehyde adsorbs on the aluminium 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 (Obot et al. 2009). It is not possible to consider a single adsorption mode between inhibitor and metal surface because of the complex nature of adsorption and inhibition of a given inhibitor. Our results are in good agreement with the results obtained by Idouhli et al. (2016) for S300 steel in 1 M HCl in their work on cumin extract as corrosion inhibitor.

Conclusion

On the basis of the study the following conclusions can be drawn:

1. As acid concentration increases corrosion rate increases while I.E. decreases.
2. At constant acid concentration, as inhibitor concentration increases corrosion rate decreases while I.E. increases.
3. As temperature increase corrosion rate increases while I.E. decreases.
4. The leaves extract of *Cuminum cyminum* seeds showed maximum I.E. of 88.39 % at an optimum concentration of 1.2 g/L inhibitor concentration in 1.0 M HCl solution.
5. The values of E_a obtained in the presence of the extract were higher compared to the blank which indicates that inhibitor was more effective at lower temperature.
6. The values of ΔG^{o}_{ads} are negative, which reveals the spontaneous adsorption of inhibitor on the aluminium metal surface and was found to be physisorption.
7. Plot of C/θ versus C shows straight line with almost unit slope, which suggest that the inhibitor cover both anodic and cathodic regions through general adsorption following Langmuir isotherm.
8. It is concluded that the seeds extract of *Cuminum cyminum* is a good corrosion inhibitor for aluminium in HCl solutions and this inhibitor is eco-friendly, biodegradable and less toxic therefore, it can be used to replace toxic chemicals.

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TABLES

Table 1: Corrosion rate (C.R.), Inhibition efficiency (I.E.) and Surface coverage **(θ)** of *Cuminum cyminum* seeds extract on aluminium in 1.0 M HCl for an immersion period of 24h at 301±K.

Inhibitor	Inhibitor Concentration (g/L)	C.R. (ρ) (mg/dm²d)	log ρ	I.E. (%)	Surface coverage (θ)	C/θ
Blank	-	6163.74	3.789	-	-	-
***Cuminum cyminum* (Jeera)**	**0.6**	2145.15	3.331	65.19	0.651	921.0
	0.8	1716.12	3.234	72.15	0.721	109.1
	1.0	1287.09	3.109	79.11	0.791	264.1
	1.2	715.05	2.854	88.39	0.883	359.1

Table 2: Temperature effect on corrosion rate activation energy and heat of adsorption for aluminium in 1.0 M HCl in absence and presence of *Cuminum cyminum* seeds extract for an immersion period of 2 h.

Inhibitor concentr-ation (g/L)	Temperature						Mean (E_a) From Equation (4) (kJ mol⁻¹)	Q_{ads} (kJ mol⁻¹)	
	313 K		323 K		333 K				
	CR mg/dm²d	I. E. (%)	CR mg/dm²d	I. E. (%)	CR mg/dm²d	I. E. (%)		313-323 K	323-333 K
Blank	33421.44	-	45434.28	-	57447.26	-	23.39	-	-
0.6	17032.53	49.03	26127.99	42.49	36725.04	36.07	33.20	-22.33	-24.12
0.8	13728.99	58.92	21966.39	51.65	32134.32	44.06	36.76	-24.87	-27.36
1.0	11583.83	65.34	19606.72	56.84	27114.72	52.80	36.61	-30.15	-14.44
1.2	9052.55	72.91	16388.98	63.92	23896.92	58.40	41.81	-35.18	-20.78

Table 3: Kinetic parameter data for the corrosion of aluminium in various concentration of HCl containing *Cuminum cyminum* seeds extract.

Inhibitor	Inhibitor concentration (g/L)	Acid concentration			
		1.0 M		1.25 M	
		Rate const. ($k\times10^{-3}$)	Half life ($t_{1/2}$)	Rate const. ($k\times10^{-3}$)	Half life ($t_{1/2}$)
Balnk	**0.0**	307.53	2.25	439.41	1.57
***Cuminum cyminum* (Jeera)**	**0.6**	96.69	7.21	166.30	4.16
	0.8	76.75	9.11	127.50	5.43
	1.0	57.06	12.15	98.00	7.07
	1.2	31.30	22.35	79.70	8.69

FIGURES

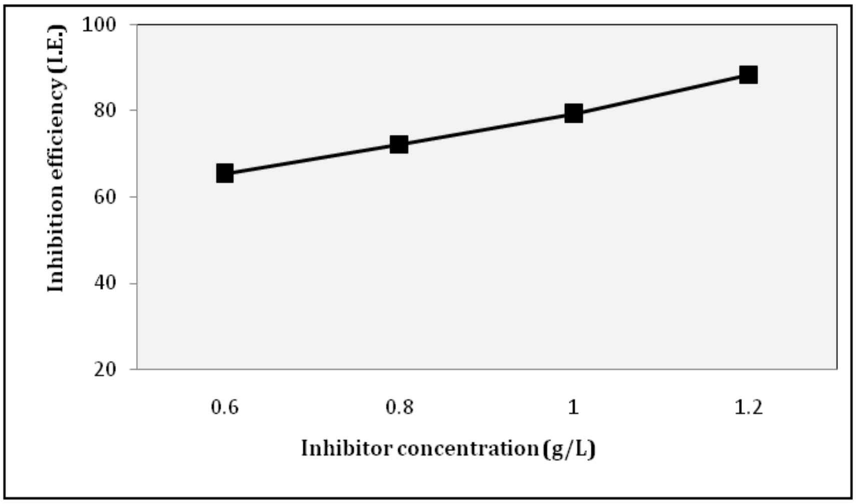

Figure 1: Inhibition efficiency of aluminium corrosion in 1.0 M HCl solution in presence of different concentration *Cuminum cyminum* (Jeera) seeds extract for an immersion period of 24 h.

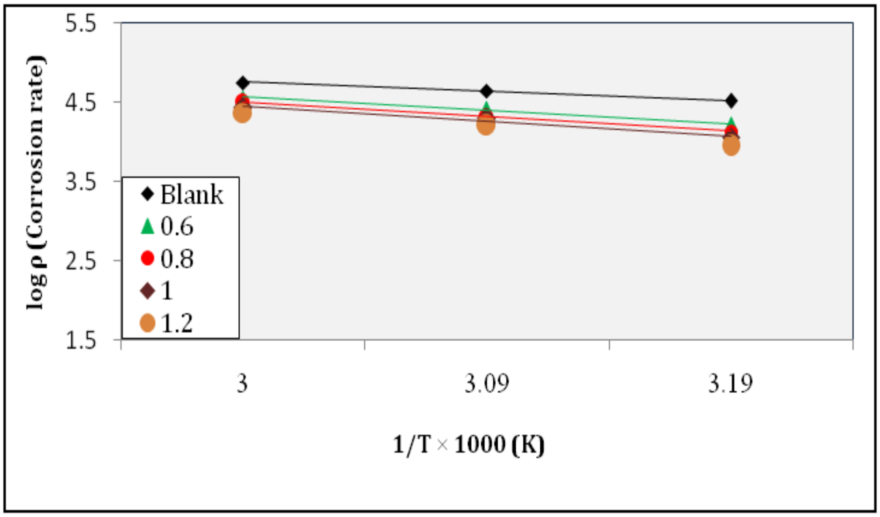

Figure 2: Arrhenius plots for aluminium in 1.0 M HCl in absence and presence of the different concentration of Cuminum cyminum seeds extract.

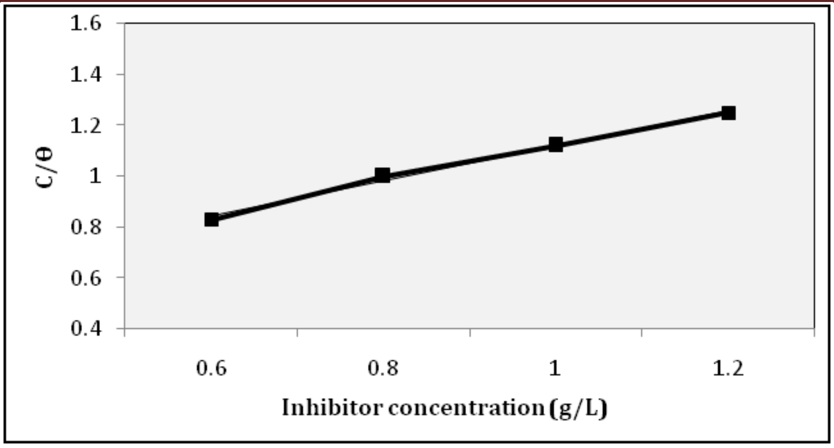

Figure 3: Langmuir adsorption isotherm plot for aluminium in 1.0 M HCl containing *Cuminum cyminum* as green inhibitor at 301 K.

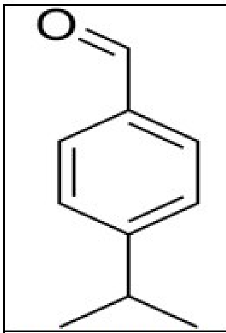	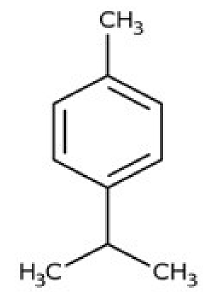	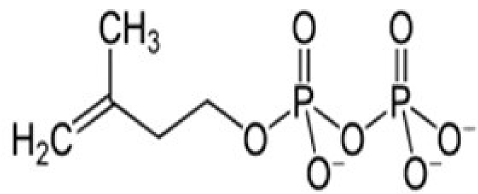
Cuminaldehyde	***p*-Cymene**	**Terpenoid**

Figure 4: Structure of main constituents of *Cuminum Cyminum* extract.