

# Adsorption and inhibitive properties of ethanol extracts of *Acacia Nilotica* as a green corrosion inhibitor for mild steel in acidic media

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## ABSTRACT

The use of inhibitors for the control of corrosion of metals associated alloys that area unit contact with aggressive surroundings is an accepted practice. Huge number of organic were studied and being studied to research the corrosion inhibition potential. Plant extracts have become vital as an environmentally acceptable, readily available and renewable resource for wide range of inhibitors. They are the wealthy source of ingredients that have terribly very high inhibition efficiency. The inhibitive impact of ethanol extract of *Acacia Nilotica* (EEAN) on mild steel corrosion in 1N H<sub>2</sub>SO<sub>4</sub> and 1N HCl solutions has been studied by using weight loss method and polarization techniques between 303 K and 333K. The inhibition potency enhanced with increase in concentration of plant extract. The corrosion rate enhanced with increase in temperature and minimized with increase in concentration of inhibitor compared to blank. The adsorption of inhibitor on mild steel surface has been found to adapt Langmuir and Frumkin adsorption isotherms. Potentiodynamic polarization and impedance studies results concealed that *Acacia Nilotica* extract acts as mixed type inhibitor.

**KEY WORDS:** *Acacia nilotica*, mild steel, Langmuir and Frumkin adsorption isotherms, Potentiodynamic, polarization, electrochemical impedance, corrosion inhibition.

## 1. INTRODUCTION

Corrosion of metals is a serious environmental downside that has been given adequate attention within the oil and gas industries. Throughout industrial processes like acid improvement and etching of metal surfaces area unit typically created to come back in reality with acidic medium indicates the requirement of substance usages. Acid solutions areas are unit wide used for removal of undesirable scale and rust in several industrial processes. The utilization of inhibitors is one among the simplest choice for safeguarding metals surface against corrosion.

The inhibitors that area unit in use either synthesized from inorganic compounds and organic compounds having hetero atoms in their aromatic or long chain carbon system. These organic compounds will absorb on metal sheet and shows sensible anti-corrosive activity however these synthesized compounds area unit extremely cytotoxic and cause severe hazards to each persons and also the atmosphere. In industrial sectors the protection and environmental problems with corrosion inhibitors continually being in world concern. Since plants area unit perishable, promptly out there, non-cytotoxic and atmospheric friendly they are wide used as corrosion inhibitors for defense of metal in acid and alkalescent environment. Thus, recent analysis is focuses on natural product as corrosion substance.

Green corrosion inhibitors area unit perishable and do not contain serious metals or alternative cytotoxic compounds. The biodegradability, renewable and eco friendliness, the trend of victimization less non-toxic compounds area unit increasing a day. There is a good thought in literatures are studied the inhibition studies in natural compounds and extracts of the many present materials like alkaloids, eucalyptus leaves, tea leaves, pomegranate juice and peels. This study seeks to research the inhibitive properties of the fermentation alcohol extract of tree *Nilotica* (EEAN) on steel corrosion by weight loss technique.

## 2. MATERIALS AND METHODS

**2.1. Extraction of plant material:** A sample of *Acacia Nilotica* was collected from and around Karpagam University at Coimbatore. The samples were dried, grounded and soaked in a solution of ethanol for 48 hrs. After 48 hrs the filtrates were further subjected to evaporation at 352 K in order to leave the sample free of the ethanol. The stock solutions of the extract was used in preparing different concentrations of the extract by dissolving appropriate weight of the extract in water (0.5% v/v, 1% v/v, 1.5% v/v & 2% v/v).

**2.2. Material preparation:** The materials used for this study were mild steel rod of composition (wt %) C (0.050), Mn (0.3), S (0.025), P (0.030), Si (0.069) and the rest Fe. The dimension of the rod was 2.5 x 5 Cm<sup>2</sup>. Each rod was degreased by washing with ethanol, dried in acetone and conserved in desiccators. All reagents used for the study were of analytical grade and double distilled water was used for their preparation.

**2.3. Corrosion weight loss tests:** Weight loss measurements were performed on iron specimens of size 1 x 0.5mm. After polishing sequentially by different grades of emery paper (400-1200), the samples were immersed for 2 hours in 60ml of 1M H<sub>2</sub>SO<sub>4</sub> and HCl solution with and without addition of the plant extract at room temperature in the air without bubbling. Afterwards, the samples were distant from the test solution and washed with distilled water to

remove the corrosion products. The corrosion rate, inhibition efficiency (%), and degree of surface coverage ( $\theta$ ), were calculated using equations 1, 2 and 3 respectively.

$$\text{Corrosion rate (g h}^{-1} \text{Cm}^{-2}) = \frac{W}{A \times T} \quad (1)$$

$$\text{Inhibition efficiency (\%)} = \frac{(W_0 - W_e)}{W_0} \times 100 \quad (2)$$

$$\text{Degree of surface coverage (\theta)} = \frac{\text{IE}}{100} \quad (3)$$

Where  $W$  is the weight loss in mg,  $A$  is the total surface area of exposure in  $\text{cm}^2$ ,  $T$  is the immersion time in hours,  $W_0$  and  $W_e$  were the weight loss without and with inhibitors.

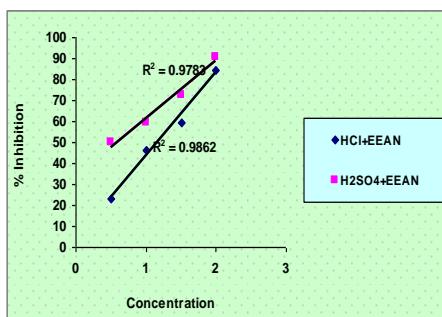
### 3. RESULTS AND DISCUSSION

**3.1. Effect of acid concentration:** The discrepancy of inhibition efficiency with acid concentration from 0.5N to 2.0N in HCl and  $\text{H}_2\text{SO}_4$  at room temperature is given in the Table 1. It reveals that inhibition competence of extract decreases with increasing acid concentration of both acids. It also examine that the extracts of *Acacia nilotica* leaves inhibits the corrosion of mild steel in both 1N HCl and 1N  $\text{H}_2\text{SO}_4$  but, the efficiency is slightly better in 1N  $\text{H}_2\text{SO}_4$ .

**3.2. Effect of inhibitor concentration:** Corrosion rate of the metal and inhibitor efficiency of the extract obtained by weight loss method for different concentrations at various periods of immersion in 1N HCl and 1N  $\text{H}_2\text{SO}_4$  are depicted in fig 1. Inhibition efficiency of the inhibitor increases with increase in inhibitor concentration. It shows that the efficiency is slightly better in 1N  $\text{H}_2\text{SO}_4$  solution than in 1N HCl. This behaviour may be attributed to the increase of the surface area covered by the adsorbed molecules of *Acacia Nilotica* with the increase of concentration.

**Table 1. Inhibition efficiency of EEAN on mild steel in HCl and  $\text{H}_2\text{SO}_4$**

Acid Concentration (N)	0.5	1.0	1.5	2.0
Inhibition efficiency of (EEAN) (%) in HCl	65.77	54.54	48.31	37.82
Inhibition efficiency of (EEAN) (%) in $\text{H}_2\text{SO}_4$	77.34	69.83	60.21	56.43



**Fig.1. Variation of inhibition efficiency with concentration**

**3.3. Effect of Immersion Time:** The variation of inhibition efficiency with immersion time in 1N HCl and 1N  $\text{H}_2\text{SO}_4$  is shown in Table 2. It is found that at all concentrations, inhibition efficiency increased with respect to immersion time. As based on this the efficiency is slightly better in 1N  $\text{H}_2\text{SO}_4$  solution which indicates the stability of adsorbed layer on the metal surface.

**Table 2. Inhibition efficiency of EEAN on mild steel in HCl and  $\text{H}_2\text{SO}_4$**

Immersion Time (hr)	1	2	3	4
Inhibition efficiency of EEAN(%) in HCl	14.28	45.45	53.33	62.85
Inhibition efficiency of EEAN(%) in $\text{H}_2\text{SO}_4$	66.22	72.15	76.66	90.78

**3.4. Effect of Temperature:** The calculated values of corrosion rate (mpy) for mild steel corrosion in 1N HCl and 1N  $\text{H}_2\text{SO}_4$  at 30-50°C from the weight loss measurements are shown in Table 3.

The results shown in the table 3 exposed that corrosion rate increases with increasing temperature. This is due to increased rate of dissolution process of mild steel and partial desorption of the inhibitor from the metal surface. This may be attributed to the higher dissolution rates of mild steel at elevated temperature and a possible desorption of adsorbed inhibitor due to increase solution agitation resulting from higher corrosion rates, which may also reduce the ability of inhibitor to be adsorbed on the metal surface. Such behavior is observed in this study, suggests that physical adsorption of the EEAN on the corroding mild steel surface.

**3.5. Adsorption isotherms:** In generally it is accepted that the organic molecules inhibit corrosion by adsorption at the metal/solution interface and that the degree of adsorption depends on the molecules chemical structure, chemical composition of the solution, the nature of metal surface, the temperature and the electrochemical potential at the metal/solution interface. The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metal has been deduced in terms of adsorption characteristics of the inhibitor. The surface coverage ( $\theta$ ) values are very useful while discussing the adsorption characteristics. The surface coverage of the inhibitor at a given concentration is calculated by using equation,

$$\theta = \frac{\text{IE}}{100} \quad (\text{Equation.3})$$

**Table.3.Inhibition efficiency of EEAN on mild steel in 1N HCl & 1N H<sub>2</sub>SO<sub>4</sub> for an Immersion time 2 hours**

Acid	Inhibitor	Temp K	Weight loss(mg)	Inhibition Efficiency (%)	Degree Coverage( $\theta$ )	C/ $\theta$	Corrosion rate (g h <sup>-1</sup> Cm <sup>-2</sup> ) $\times 10^{-5}$
HCl	EEAN	303	0.022	-	-	-	4.0036
		313	0.431	-	-	-	78.4349
		323	0.506	-	-	-	92.0837
		333	0.631	-	-	-	114.83
HCl	EEAN	303	0.012	45.45	0.4545	2.2002	2.1838
		313	0.286	33.64	0.3364	2.9726	38.7625
		323	0.286	33.64	0.3364	2.9726	52.0473
		333	0.409	35.18	0.3518	2.8425	74.4313
H <sub>2</sub> SO <sub>4</sub>	EEAN	303	0.013	-	-	-	2.3657
		313	0.614	-	-	-	111.73
		323	0.713	-	-	-	129.75
		333	0.784	-	-	-	142.67
H <sub>2</sub> SO <sub>4</sub>	EEAN	303	0.007	46.15	0.4615	2.1668	1.2738
		313	0.314	48.85	0.4885	2.0470	57.1428
		323	0.482	38.52	0.3852	2.5960	87.7161
		333	0.557	21.87	0.2187	4.5724	101.36

**3.6. Langmuir adsorption Isotherm:** Langmuir adsorption Isotherm was tested for its fit to the experimental data.

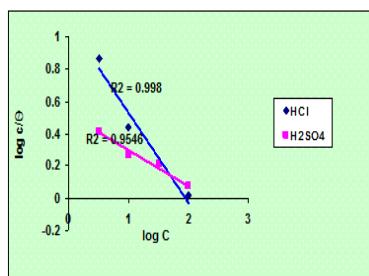
$$\theta = KC / (1+KC) \quad (\text{Equation.4})$$

Where K is equilibrium constant & C is the concentration.

The above equation may be modified as

$$C / \theta = (1 / K) + C \quad (\text{Equation.5})$$

A plot of  $\log C / \theta$  Vs  $\log C$  was a straight line it follows Langmuir adsorption Isotherm. Fig (2) indicating that the *Acacia Nilotica* under investigation obey Langmuir adsorption isotherm. The K values are tabulated. The high K value indicates that the inhibitor is strongly adsorbed on the mild steel in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> Medium. The K value is maximum at two hours immersion time on mild steel. The K value also follows the trend of inhibition efficiency with various temperatures.

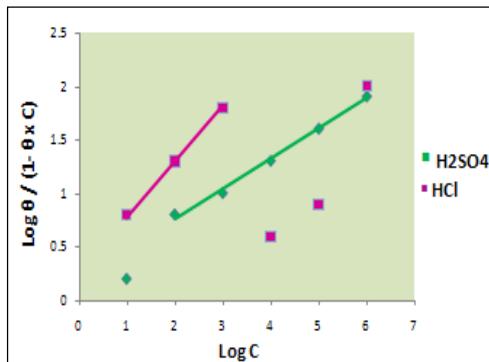


**Fig.2.Langmuir adsorption isotherm for the inhibition of EEAN on mild steel in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub>**

**3.7. Frumkin adsorption Isotherm:** Frumkin adsorption Isotherm is expressed as

$$Bc = (\theta / 1 - \theta)^{e-2a\theta} \quad (\text{Equation.6.})$$

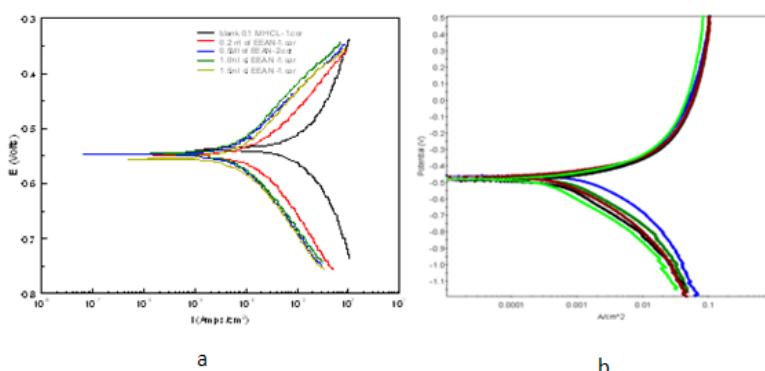
The observation has been found it gives the best fit to the weight loss results of the three tested inhibitors are shown in fig (3). Straight line obtained by plotting  $\log c$  Vs  $\log \theta / (1 - \theta \times C)$ , it revealed that the adsorption of *Acacia Nilotica* could be fitted with Frumkin adsorption isotherm also. The experimental datas are fitted with both Langmuir and Frumkin adsorption isotherms.



**Fig.3.Frumkin adsorption isotherm for the inhibition of EEAN on mild steel in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub>**

### 3.8. Electrochemical Measurements:

**3.8.1. Potentiodynamic polarization studies:** The effect of plant extract concentration on the anodic and cathodic polarization behavior of mild steel in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> solution has been studied by polarization measurements and the recorded Tafel plots are shown in Fig 4(a) and (b).



**Fig.4.(a) & (b) Comparison of Tafel plots of mild steel in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> with or without EEAN at 30°C**

The respective kinetic parameters derived from the plots are given in Table 4 and 5. It reveals that both anodic metal dissolution of iron and cathodic hydrogen evolution reaction were inhibited after the addition of EEAN to 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> solution. The inhibition of these reactions was more pronounced on increasing EEAN concentration.

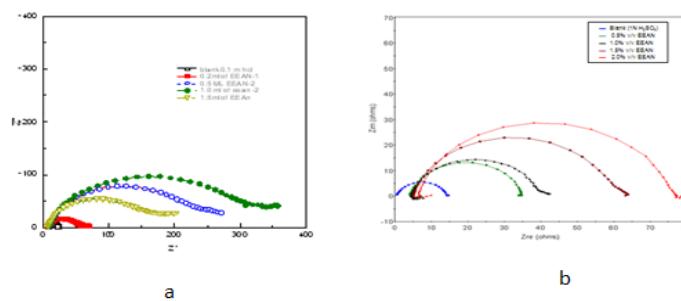
**Table 4. Kinetic parameters derived from Tafel plots of mild steel immersed in 1N HCl containing EEAN at 30°C**

Parameter	Blank	0.5%v/v EEAN	1.0%v/v EEAN	1.5%v/v EEAN	2.0%v/v EEAN
E <sub>corr</sub> (mV)	-359.692	-387.80	-412.64	-442.06	-460.2
I <sub>corr</sub> ( $\mu$ A)	$2.807 \times 10^3$	$2.478 \times 10^3$	$2.245 \times 10^3$	$1.614 \times 10^3$	$1.006 \times 10^3$
$\beta_c$ (mV)	234.345	245.204	267.020	311.856	342.113
B <sub>a</sub> (mV)	63.453	72.981	88.624	94.042	107.121
Corrosion rate (mpy)	$3.805 \times 10^3$	$2.243 \times 10^3$	$1.190 \times 10^3$	$1.048 \times 10^3$	$0.084 \times 10^3$

**Table 5: Kinetic parameters derived from Tafel plots of mild steel immersed in 1N H<sub>2</sub>SO<sub>4</sub> containing EEAN at 30°C**

Parameter	Blank	0.5%v/v EEAN	1.0%v/v EEAN	1.5%v/v EEAN	2.0%v/v EEAN
E <sub>corr</sub> (mV)	-459.692	-463.87	-475.6	-482.97	-490.5
I <sub>corr</sub> ( $\mu$ A)	$1.837 \times 10^3$	$1.202 \times 10^3$	$0.175 \times 10^3$	$0.814 \times 10^3$	$0.297 \times 10^3$
$\beta_c$ (mV)	305.238	305.306	319.020	331.968	389.246
B <sub>a</sub> (mV)	82.553	99.991	108.684	154.541	157.301
Corrosion rate (mpy)	$2.995 \times 10^3$	$1.960 \times 10^3$	$1.170 \times 10^3$	$0.848 \times 10^3$	$0.005 \times 10^3$

**3.8.2. Electrochemical Impedance studies:** EIS experiments were also conducted for mild steel immersed in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> with and without EEAN at 30°C and are shown in Fig 5 (a) & (b). The respective kinetic parameters are given in Table 6 and 7. The EIS plots of mild steel in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> with or without EEAN at 30°C showed a depressed capacitive loop at high frequency region (HF) and an inductive loop in low frequency region (LF) indicating occurrence of a faradic process on free electrode sites. A capacitive loop arises from the time constant of electric double layer and charge transfer resistance and an inductive loop originates from the adsorption relaxation of intermediates controlling the anodic process resulting from the iron dissolution and adsorption of hydrogen.



**Fig.5(a) & (b).Comparison of Impedance plots of mild steel in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> with or without EEAN at 30°C**

**Table.6.Kinetic parameters derived from EIS plots of mild steel immersed in 1N HCl containing EEAN at 30°C**

Parameter	Blank	0.5%v/v EEAN	1.0%v/v EEAN	1.5%v/v EEAN	2.0%v/v EEAN
R <sub>s</sub>	0.786	1.840	2.345	2.446	2.679
C <sub>dl</sub> (F)	1.954 x 10 <sup>-5</sup>	1.48 x 10 <sup>-5</sup>	1.225 x 10 <sup>-5</sup>	1.039 x 10 <sup>-5</sup>	0.994 x 10 <sup>-5</sup>
R <sub>ct</sub> (ohm Cm <sup>2</sup> )	12.87	24.6	32.68	54.1	66.63

**Table.7.Kinetic parameters derived from EIS plots of mild steel immersed in 1N H<sub>2</sub>SO<sub>4</sub> containing EEAN at 30°C**

Parameter	Blank	0.5%v/v EEAN	1.0%v/v EEAN	1.5%v/v EEAN	2.0%v/v EEAN
R <sub>s</sub>	0.865	1.026	1.845	2.046	2.967
C <sub>dl</sub> (F)	2.534 x 10 <sup>-5</sup>	1.657 x 10 <sup>-5</sup>	1.426 x 10 <sup>-5</sup>	1.112 x 10 <sup>-5</sup>	0.875 x 10 <sup>-5</sup>
R <sub>ct</sub> (ohmCm <sup>2</sup> )	16.56	29.64	36.43	45.17	56.63

As the concentration of EEAN increased, the R<sub>ct</sub> values increased indicating decrease in the formation of anodic process controlling intermediates from metal dissolution and subsequently inhibition of corrosion. The adsorption of EEAN concentrations may be attributed to the formation of a protective layer at electrode surface. The maximum R<sub>ct</sub> values were achieved for 2% v/v EEAN at 30°C. The above results showed that this plant extract act as inhibitor in the temperature range at 30°C.

#### 4. CONCLUSION

The data obtained from the present study reveals the presence of various green corrosion Inhibitors EEAN exhibits maximum efficiency towards inhibition of corrosion on mild steel in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> media. The inhibition efficiency increases with increase in concentration of inhibitor; this implies that decrease in corrosion rate. Thus EEAN act as a good inhibitor. The adsorption of Inhibitor EEAN on mild steel in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> obeys Langmuir adsorption isotherm and Frumkin adsorption isotherm at all studied temperature. Polarization curves obtained in the presence of the *Acacia Nilotica* extract indicating that it behaved as a mixed type inhibitor. Biodegradable green Inhibitor *Acacia Nilotica* can be securely used without hydrogen damage poisonous effects and pollution problems. The EEAN acts as strong inhibitor for corrosion of mild steel in both 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> medium.

#### 5. ACKNOWLEDGEMENT

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