Research Article

Inhibition study of *Caesalpinia crista* on corrosion of mild steel in hydrochloric acid

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ABSTRACT

In this study, we report inhibition effect of *Caesalpinia crista* fruit on corrosion of mild steel in hydrochloric acid using weight loss measurements and electrochemical techniques. The inhibition efficiency of *Caesalpinia crista* was found to vary with concentration, temperature and immersion time. Good inhibition efficiency I.E.% was recorded in acid solution. The inhibition efficiency was found to be more than 90% in 1 M HCl solution of 5 mM inhibitor concentration. The adsorption study of these compounds on mild steel surface found to obey Temkin's adsorption isotherm. The activation energy values and values of free energy of adsorption indicated physical adsorption on mild steel surface. The potentiodynamic polarization results showed that the compound studied was mixed type inhibitor.

Keywords: Mild steel, *Caesalpinia crista*, corrosion, inhibition effect, hydrochloric acid, adsorption.

1. INTRODUCTION

Metals undergo corrosion in presence of oxygen and moisture and involve two electrochemical reactions. Oxidation occurs at anodic site and reduction occurs at cathodic site. In acidic medium hydrogen evolution reaction predominates. Corrosion inhibitors reduce or prevent these reactions, they are adsorbed on the metal surface and act by forming barrier to oxygen, moisture and some of the inhibitors facilitate formation of passive film on the metal surface.

Acid inhibitors are usually used in several industrial processes to control the corrosion of metals. They find wide applications as components in pretreatment composition, in cleaning solutions for industrial equipments. Inorganic substances such as phosphates, chromates, dichromates, silicates, borates, tungstates, molybdates and arsenates have been found effective as inhibitors of metal corrosion. Anti-corrosive coatings have major disadvantage as toxicity and comes under severe criticism [1-6].

Corrosion control of metals is of technical, economical, environmental and aesthetical importance. The use of inhibitors is one of the best options for protecting metals and alloys against corrosion. The environmental toxicity of organic corrosion inhibitors have prompted the search for green corrosion inhibitors as they are biodegradable, do not contain heavy metals or other toxic compounds[7-10]. As in addition to being environmental friendly and ecologically acceptable, plant products are inexpensive, readily available

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and renewable [13-16]. One of the green inhibitors, photochemical plant, *Caesalpinia crista* has been used for the study.

2. MATERIALS AND METHODS

Many papers have been reported about the investigation of corrosion inhibition process. There are two methods to determine the corrosion rate, (1) weight loss, (2) galvanostatic polarization. The effects of temperature and concentration of the inhibitors were also studied. The thermodynamic parameters for the process were computed and discussed. In this article both methods, weight loss and galvanostatic polarization, were employed.

2.1. Weight Loss

Weight loss method is simple, cheap and widely used method. It gives a quantitative data. It is a valid measure of corrosion only if corrosion is perfectly uniform. The corrosion rate was expressed in mdd (milligram per square decimeter per day) or mpy (mili inches per year).

Rectangular specimens of the size 5.5 × 2.5 × 0.20 cm having an area of 0.3074 sq. dm. with weight 10.207 gm of commercial grade iron (98.5% Fe, Pb-0.03% max. Cd-0.02%) with a small hole of about 2 mm diameter near the upper edge, were used for the determination of the corrosion rate. The specimens were polished with a linen buffing wheel to obtain a mirror like finish. The specimens were degreased by immersing in AR grade acetone and dried in warm air using air dryer and preserved in desiccator till use. The test specimens were immersed in 1.0, 1.5 and 2.0 M Hydrochloric acid solution with and without inhibitor.

At any instant a fraction 'θ' of the metal surface is covered by the inhibitor molecules and uncovered fraction (1-θ) reacts with acid as it does in the absence of the inhibitor. The nature of the inhibitor interaction with the corroding surface has been deduced from the adsorption characteristics of the inhibitor. Surface coverage values are very useful in explaining the adsorption characteristics. The inhibition efficiency (η%) and degree of surface coverage (θ) at each concentration of inhibitors was calculated by comparing the corrosion loss in the absence (W_u) and presence of inhibitor (W_i) using the relationships:

$$\eta\% = \frac{W_u - W_i}{W_i} \times 100 \quad (1)$$

$$\theta = \frac{W_u - W_i}{W_i} \quad (2)$$

2.2. Effect of Temperature

The study of the effect of variation in temperature and concentration on the protective effect of corrosion inhibitors is important in the understanding of the mechanism and kinetics of their action and ultimately in the proper selection of inhibitor for particular situation.

To study the effect of temperature on corrosion rate, the specimens was immersed in 230 mL of 1.0M, 1.5M, 2.0M concentration of acid, with (5 mM concentration) and without inhibitor at solution temperatures of 313, 323 and 333 K for a period of 3 hours. Form the results, Inhibition efficiency (I.E.) (η%) and thermodynamic parameters such as energy of activation (Ea), heat of adsorption (Q_{ads}) free energy of adsorption (ΔG^0_{ads}), enthalpy of adsorption (ΔH^0_{ads}) and entropy of adsorption (ΔS^0_{ads}) were calculated using following equations:

Energy of activation (Ea) was calculated from the slopes of log ρ versus 1/T (ρ = corrosion rate, T = absolute temperature) and also with the help of Arrhenius equation.

$$\log \frac{\rho_2}{\rho_1} = \frac{Ea}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (3)$$

Where ρ_1 and ρ_2 are the corrosion rate at temperature T_1 and T_2 respectively. The enthalpy of adsorption (ΔH^0_{ads}) and entropy of adsorption (ΔS^0_{ads}) will be calculated using the following equations (4) and (5).

$$\Delta H^0_{ads} = Ea - RT \quad (4)$$

$$\Delta S^0_{ads} = \frac{\Delta H^0_{ads} - \Delta G^0_{ads}}{T} \quad (5)$$

The values of the free energy of adsorption (ΔG^0_{ads}) were calculated with slope of the following equation.

$$\log C = \log\left(\frac{\theta}{1-\theta}\right) - \log B \quad (6)$$

Where $\log B = -1.74 - \left(\frac{\Delta G^0_{ads}}{2.303RT}\right)$ and C is the inhibitor concentration. The values of heat of adsorption (Q_{ads}) calculated by the following equation (7).

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{T_1T_2}{T_2 - T_1} \quad (7)$$

2.3. Corrosion Potential Measurements

Metal specimen having an area of 0.0675 dm^2 was immersed in acid solutions with and without inhibitor at 1.0M, 1.5M, 2.0M concentrations and the potential was measured with reference electrode till a constant potential was attained.

For open circuit potential measurements, rectangular metal coupons were used and potential measured with an accuracy of ±5 mV with a pH meter against Ag/AgCl reference electrode. Immediately after the immersion of the specimen, the initial potential value (E_{inh}) was recorded. The value of (E_{corr}) were carefully and continuously recorded after each intervals of 5 min. till the potential attained the constant value (E_{const}).

2.4. Polarization Measurements

The electrochemical theory of corrosion had its origins of course, in more than one source. The first report on electrochemical nature of corrosion was made by August de Ia Rive [11]. The development of mix potential theory of Wagnar and Traud ultimately found its application in the measurement of corrosion rate by polarization resistance technique and was developed by Stern and Geary [12].

When electrochemical corrosion occurs, the current that flows between anode and cathode causes a change in the electrode potential, this change is termed as polarization. For polarization study, Metal specimens of circular design, having an area of 0.077 dm^2 exposed to corrosive solutions. The volume of corrosive media was 100 mL. Auxiliary platinum electrode was placed in a corrosive media through which external current was supplied from a regulated power supply. A silver-silver chloride reference electrode was placed in a saturated KCl solution which remains in contact with the corrosive solution via salt bridge. The change in potential was measured by Potentiostat/Galvanostat (Model-273) against the reference electrode.

2.5. Tafel Plot

This technique is used to measure the corrosion current (i_{corr}) so that the corrosion rate can be calculated. A Tafel plot can yield i_{corr} directly or it can yield the Tafel constants (βa and βc). The Tafel constants can then be used with the Rp value to calculate i_{corr}.

The values of corrosion current densities in the presence and absence of inhibitor were obtained from the graph while percentage efficiency (η %) was calculated using the equation (8).

$$\eta(\%) = \left[\frac{i_{corr}(u) - i_{corr}(i)}{i_{corr}(u)}\right] \times 100 \quad (8)$$

3. RESULTS AND DISCUSSION

3.1. Weight loss studies

The values of inhibition efficiency (I.E %) and the corrosion rate (CR) obtained from the weight loss method at different concentrations of HCl given in Table 1. The effect of acid concentration and exposure time on the corrosion loss of mild steel in HCl showed increase in corrosion with time and more in higher acid concentration.

The corrosion loss of mild steel increased with increase in concentration of HCl. It was also observed that corrosion rate decreased in presence of inhibitor 5 mM concentration as given in Table 1. The increased inhibition efficiency and decreased corrosion rate might be due to the increased adsorption and increased surface coverage θ of inhibitor on mild steel surface with increase in concentration.

3.2. Effect of temperature

The effect of temperature was studied in 1.0 M HCl containing 5mM of inhibitor concentration at 313, 323 and 333 K temperature. The results showed corrosion loss increased with increase in temperature. Inhibition efficiency of inhibitors decreased with the rise in temperature. In 1.0 M HCl at 5mM inhibitor concentration, the inhibition efficiency for *Caesalpinia crista* was 99.6%, 99%, 97% at 313, 323 and 333 K respectively.

Activation energy calculated from the slopes of plots of log ρ vs 1/T (ρ=corrosion rate and T=absolute temperature) and also using the Arrhenius equation. The Ea values are given in Table 3 shows that the energy of activation for the corrosion of mild steel in 1.0 M HCl decreases in acid containing inhibitor. The higher values of Ea indicate physical adsorption of the inhibitors of metal surface. The Ea calculated from the slopes of Arrhenius plot and by using equation (8) are almost similar.

The values of heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG^0_a) were calculated from the equation (7). From Table 4 it is evident that in all the cases, the Q values are negative. The negative Q values show that the adsorption and hence the inhibitive efficiency decreases with rise in temperature. The values of ΔG_{ads} are given in Table 4. In all the cases mean ΔG_{ads} values are negative.

3.3. Potential measurement

In 1.0 M HCl the potential shifted to the negative direction from its initial value (-0.529 mV) and settled at about (-0.532 mV) within 3 minutes. On addition of 5mM of the inhibitor *Caesalpinia crista* in 1.0 M HCl the initial value of the OCP (open circuit potential) increased (become less negative) (-0.491 mV) and settled at about (-0.510 mV) within 15 minutes.

3.4. Polarization Measurements

Anodic and cathodic polarization curves for mild steel in 1 M HCl at 5 mM inhibitor concentration in the presence of inhibitors are shown in Figure 1. The value of the corrosion potential with inhibitors were found more positive than without inhibitors as shown in Figure 2. Polarization study reveals that the inhibitor functions as little anodic, but significant cathodic inhibitor, inhibitor functions as a mixed inhibitor. It is evident from the figure that cathodic Tafel slopes (β_c) remain almost unchanged with increasing inhibitor concentration. This indicates that hydrogen evolution is active controlled and the addition of inhibitor did not change the mechanism of cathodic hydrogen evolution reaction. It is observed from Figure 3 that the electrochemical impedance diagram is almost semicircular in appearance, but not perfect semicircle. The difference has been attributed to frequency dispersion. The semicircular nature of the plots indicates that the corrosion of mild steel is mainly controlled by charge transfer process.

Table 1. Effect of various concentrations of HCl on corrosion loss (CL) and inhibition efficiency (I.E.) of mild steel containing *Caesalpinia crista* as inhibitor

Hours	Acid Concentration	Corrosion loss				I.E.%
		CL (gm)		CL (mg/dm^2)		
		Blank	With inhibitor	Blank	With inhibitor	
24 hrs	1.0 M	0.690	0.0028	3828.65	15.3146	99.6
	1.5 M	0.789	0.0134	4377.98	74.4257	98.3
	2.0 M	0.903	0.0280	5010.54	155.3268	96.9
48 hrs	1.0 M	0.802	0.0209	4450.12	115.7030	97.4
	1.5 M	0.909	0.0273	5043.83	151.3151	97.0
	2.0 M	1.020	0.0388	5659.74	215.0705	96.2
72 hrs	1.0 M	0.901	0.0360	4999.45	199.9778	96.0
	1.5 M	1.340	0.0670	7435.36	371.7678	95.0
	2.0 M	1.600	0.1040	8878.04	577.0725	93.5
96 hrs	1.0 M	1.100	0.0869	6103.65	482.1884	92.1
	1.5 M	1.488	0.1815	8034.62	1007.3022	87.8
	2.0 M	1.884	0.2581	10453.89	1432.1829	86.3

Table 2. Corrosion loss (CL) of mild steel in HCl and effect of inhibitor *Caesalpinia crista*

Temp.	Acid Concentration	CL mg/dm^2 Blank	CL mg/dm^2 With inhibitor(ρ)	log ρ	I.E %	Surface coverge (θ)	1-θ	log (θ/1-θ)
313 K	1.0 M	1564.75	5.55	0.7443	99.6%	0.9964	0.0036	2.4421
	1.5 M	2075.24	33.29	1.5223	98.0%	0.9839	0.0161	1.7861
	2.0 M	2707.80	61.04	1.7856	97.7%	0.9775	0.0225	1.6379
323 K	1.0 M	1753.41	11.09	1.0449	99.0%	0.9937	0.0063	2.1979
	1.5 M	2341.58	72.13	1.8581	97.0%	0.9692	0.0308	1.4979
	2.0 M	2985.24	160.91	2.2066	95.0%	0.9461	0.0539	1.2443
333 K	1.0 M	1969.81	55.48	1.7441	97.0%	0.9718	0.0282	1.5373
	1.5 M	2824.32	138.71	2.1421	95.0%	0.9509	0.0491	1.2871
	2.0 M	3406.94	205.30	2.3124	94.0%	0.9397	0.0603	1.1927

Table 3. Effect of temperature on Corrosion Loss (CL), Energy of Activation (Ea) for the corrosion of mild steel in HCl in presence of inhibitor *Caesalpinia crista* concentration

Acid Conc	Temperature									Activation Energy (Ea) KJ/mol			Ea from Arrhe-nius Plot
	313 K			323 K			333 K						
	CL mg/dm^2		I.E	CL mg/dm^2		I.E	CL mg/dm^2		I.E	313K	323K	Mean	
	Blan	With	%	Blan	With	%	Blan	With	%	-	-		
1.0	1564.	5.55	100	1753.	11.09	99	1969.	55.48	97	58.20	144.00	101.10	99.30
1.5	2075.	33.29	98	2341.	72.13	97	2824.	138.71	95	65.00	58.49	61.74	61.86
2.0	2707.	61.04	98	2985.	160.91	95	3406.	205.3	94	81.49	21.79	51.64	52.86

Table 4: Effect of temperature on heat of adsorption Q_{ads} and free energy of adsorption (ΔG^0_a) of mild steel in HCl concentration in presence of inhibitor (kachako)

Acid (HCl) Conc.	Heat of adsorption Q_{ads} KJ/mol			Free Energy of Adsorption (ΔG^0_a) kJ/mol			
	313K - 323K	323K - 333K	Mean	313 K	323 K	333 K	Mean
1.0 M	-47.27	-136.05	-91.66	-38.9661	-38.7784	-36.32	-38.0204
1.5 M	-55.79	-43.41	-49.60	-35.3662	-35.0887	-35.26	-35.2378
2.0 M	-76.19	-62.85	-69.52	-34.6383	-34.094	-34.94	-34.5580

Table 5. Electrode potential (mv) of mild steel in 1 M HCl containing the inhibitor *Caesalpinia crista* at different exposure time

Time (in minutes)	Electrode Potential(mv)		Time (in minutes)	Electrode Potential(mv)	
	Blank	With inhibitor		Blank	With inhibitor
0	-0.529	-0.491	11	-0.532	-0.508
1	-0.53	-0.496	12	-0.532	-0.509
2	-0.531	-0.499	13	-0.532	-0.509
3	-0.532	-0.501	14	-0.532	-0.509
4	-0.532	-0.502	15	-0.532	-0.51
5	-0.532	-0.503	16	-0.532	-0.51
6	-0.532	-0.504	17	-0.532	-0.51
7	-0.532	-0.504	18	-0.532	-0.51
8	-0.532	-0.504	19	-0.532	-0.51
9	-0.532	-0.506	20	-0.532	-0.51
10	-0.532	-0.507	21	-0.532	-0.51

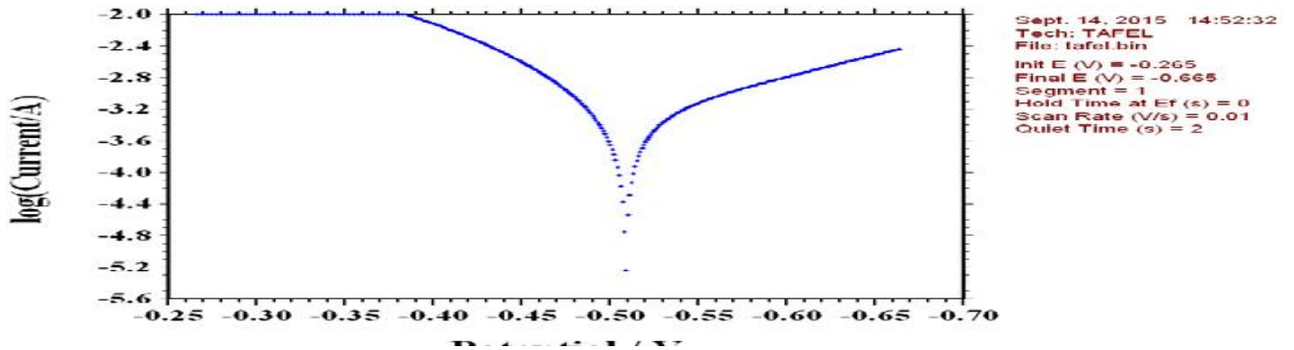

Figure 1. Polarization curve showing potential versus log current data for corrosion of mild steel in 1 M HCl containing 5 mM *Caesalpinia crista* inhibitor

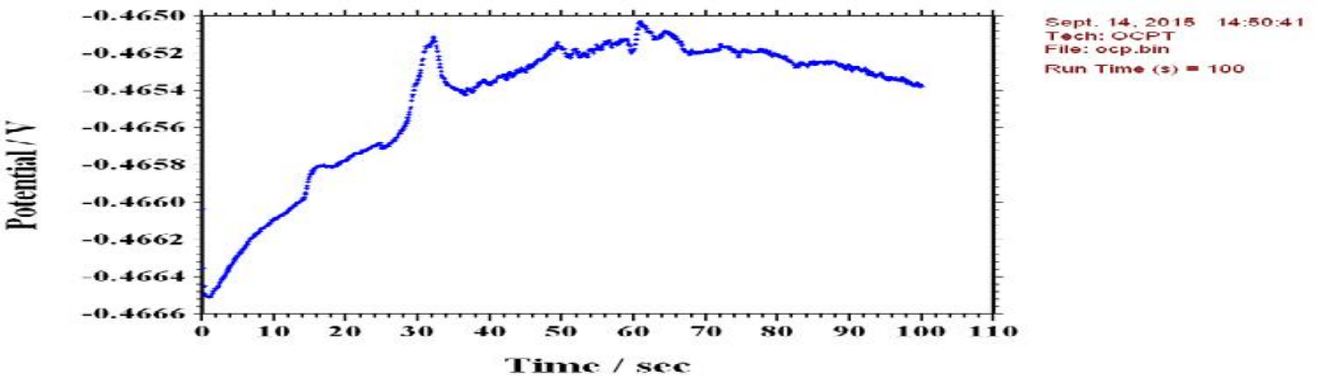

Figure 2. Polarization curve plotted between time and potential for corrosion of mild steel in 1 M HCl containing 5 mM *Caesalpinia crista* inhibitor

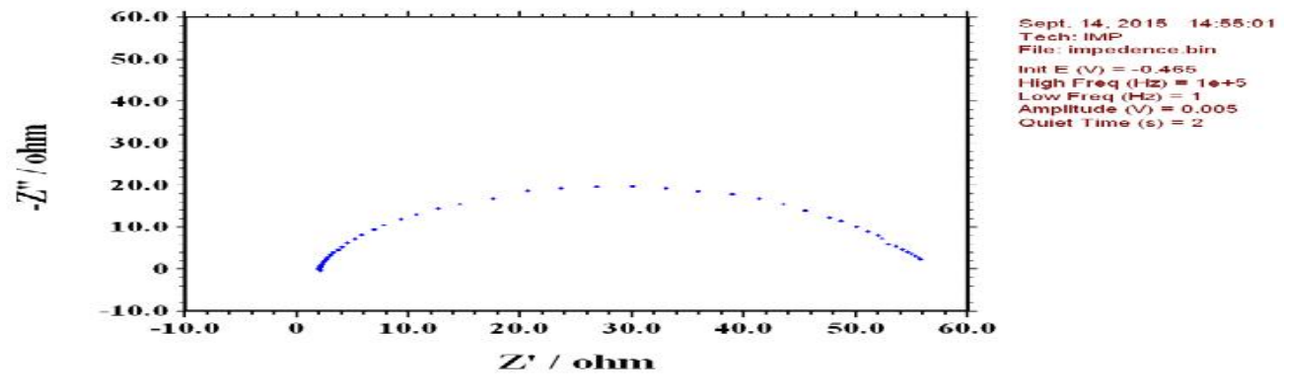

Figure 3. Electrochemical impedance diagram obtained for mild steel in 1 M HCl containing 5 mM *Caesalpinia crista* inhibitor

4. CONCLUSION

Caesalpinia crista was found as eco-friendly inhibitor for the corrosion control of mild steel in HCl solution. The inhibition efficiency increases with increase in C*aesalpinia crista* concentration. *Caesalpinia crista* adsorbed on metal surface follows Langmuir adsorption isotherm. Tafel plot indicates *Caesalpinia crista* acts as a mixed type inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. All techniques used in current study give almost identical values of inhibition efficiency for mild steel in HCl.

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