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Mirabilis Jalapa flowers extract as corrosion inhibitor for the mild steel corrosion in 1M HCl

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Abstract: *The corrosion inhibition efficiency of the acid extract of mirabilis jalapa flowers for the dissolution of mild steel in 1M HCl was studied at different concentrations of the extract, various immersion periods and at certain elevated temperatures. Data were fit into Langmuir and Temkin isotherms. Activation energy (E_a), Entropy change (ΔS), Enthalpy change (ΔH) and Heat of adsorption (Q_{ads}) were obtained from the Arrhenius plot. Nyquist and Bode plots were obtained to discuss the mode of inhibition and the inhibition efficiency was calculated from the electrochemical kinetic parameters.*

Keywords: *Mirabilis jalapa, polarization and impedance, corrosion inhibition*

I. Introduction

Natural resources are depleted and have become scarce. So the material resources have to be protected for the future generation. One of the steps for the protection of materials is minimizing or completely eradicating corrosion. The study has been focused on mitigating the corrosion of metals and alloys, specifically mild steel, which is most commonly used. Successful and effective mitigation of mild steel corrosion in the highly corrosive mineral acids is one of the needs for the industrial development. Earlier researchers have proved that certain parts of plant origin containing various organic components such as acids, alkaloids, tannins and pigments have corrosion inhibitive action [1-15].

The objective of the study is to identify the inhibition efficiency of Mirabilis jalapa flowers (MJF) as corrosion inhibitor for mild steel in 1M HCl. There are no reports in the literature on the use of this plant as corrosion inhibitor for mild steel. The study was extended to investigate the effect of temperature on the corrosion process and evaluation of some thermodynamic parameters using weight loss method, polarization and impedance techniques.

II. Materials and Methods

2.1. Metal Coupon preparation

The CR mild steel sheets were procured from the market and machined into coupons of dimension 50 x 10 x 2 mm. Holes were drilled on the center of one end of all the coupons for suspension. These coupons were degreased, cleaned with emery paper and washed with double distilled water. The coupons were stored in desiccators in the absence of moisture before their use for the investigation.

Hydrochloric acid is widely used for pickling. Hence HCl medium was selected for the study. The chemicals used in the study were of analytical grade and distilled water is used for preparing them.

2.2. Extract preparation

The flowers were collected, shade dried and ground into powder. The extract was prepared by refluxing 50 grams of the powdered flowers in 1000 ml of 1M HCl for 3 hours; kept overnight, filtered and made up to 1000 ml with the same acid. From this stock solution, different concentrations of the inhibitor were prepared.

2.3. Weight Loss Method

Accurately weighed samples were fully immersed in 100 ml of 1M HCl in triplicate in the absence and presence of the extract. At the end of the test, the coupons were soaked in sodium bicarbonate, washed with distilled water, dried, dessicated for half an hour and then reweighed. The loss in weight was calculated from the difference between the before and end of the experiment weights. The average of the triplicate values were used for inhibition efficiency (IE) calculation. The weight loss method was adopted for various concentrations of the extract, different time intervals of immersion and at some elevated temperatures.

2.4. Electrochemical Method

Electrochemical experiments were carried out in a glass cell. A platinum electrode and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode respectively. The working electrode (WE) was mild steel coupon used for weight loss method but lacquered as to expose an area of 1 cm^2. Potentiodynamic polarization was conducted using a Solartran Electrochemical measurement unit (1280 B) with a software package of Corrware, Corrview, Z-plot and Z-view. The a.c impedance measurements were performed at corrosion potentials (E_{corr}) over a frequency range of 10 KHz to 20 MHz, with a signal amplitude perturbation of 10mv. Nyquist plots were obtained from the results of these experiments.

III. Results and Discussion

3.1. Weight loss method

3.1.1. Inhibitory behavior of MJF extract

The inhibition efficiency of the MJF extract was studied at different immersion periods and various concentrations of the extract. The calculated IE is provided in table 1.

Table 1: Variation of inhibition efficiency of the extract with concentration and immersion period for mild steel corrosion in 1M HCl

Conc. of the extract (%v/v)	Immersion period(in hours) / % IE				
	1	**3**	**7**	**12**	**24**
0.05	43	45	45	81	90
0.50	58	59	63	89	94
1.00	60	62	73	91	96
3.00	68	71	79	93	97
5.00	75	77	83	95	98

The percentage IE improved with increase in the concentration of the extract as well as the immersion period. The increase in inhibitive action with increase in concentration of the extract can be ascribed to the increase in blocking of active sites on the mild steel surface by the inhibitor molecules forming a protective layer on the surface of mild steel.

3.1.2. Temperature effect

Acid pickling of steel is usually carried out at elevated temperatures up to 60^0C in HCl and up to 90^0C in Sulphuric acid [16]. The chemically stable inhibitors are expected to provide high protection efficiency under these conditions. This is considered in the practical aspects of the present investigation. The study was carried out at 303, 313, 323, 333 and 343K for an exposure time of 1h.

Table 2: Impact of temperature on the inhibition efficiency of MJF extract for mild steel corrosion in 1M HCl

Conc. of the extract (%v/v)	Solution Temperature in Kelvin/ % IE				
	303	**313**	**323**	**333**	**343**
0.05	43	53	61	52	17
0.50	58	69	80	75	41
1.00	60	74	85	82	62
3.00	68	80	88	88	71
5.00	75	85	91	91	81

The IE increased with increase in temperature till 323 K and then decreased with further increase in temperature. The decrease in efficiency at 333K and 343K may be due to desorption of the molecules of the extract from the surface of mild steel after adsorption till 323 K. In all the different temperatures at which the study has been carried out, the efficiency increased with concentration of the extract. The optimum temperature was found to be 323K.

3.1.3. Adsorption Isotherms

Inhibitors protect metals from corrosion by adsorbing onto the surface by forming a thin adsorption layer. The efficiency of an inhibitor is largely dependent on the extent of adsorption of the inhibitor molecules on the metal surface. The nature of corrosion inhibitor has been deduced in terms of the adsorption characteristics of the inhibitor. The adsorption characteristic of the extract is evaluated by plotting surface coverage against inhibitor concentration using the common adsorption isotherms namely Langmuir, Freundlich and Temkin isotherms.

All these isotherms are of the general form

$f(\theta,x)\exp(-2a\ \theta)=kC$

The data were fit into Langmuir and Temkin Isotherms. Fig. 1a shows the Langmuir isotherm and Fig. 1b shows the Temkin adsorption isotherms for inhibition of mild steel corrosion in 1M HCl by MJF extracts.

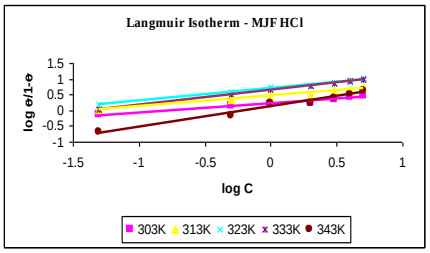

Figure 1a: Langmuir adsorption isotherms for Inhibition of mild steel corrosion in 1M HCl by MJF extracts

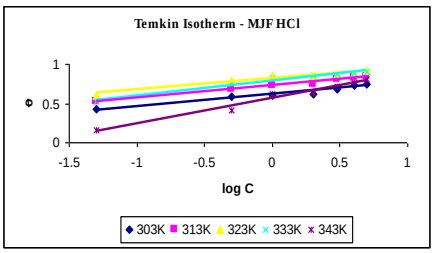

Figure 1b: Temkin adsorption isotherms for Inhibition of mild steel corrosion in 1M HCl by MJF extracts

Table 3: Change in Free energy of Adsorption ΔG, a and log k obtained from Temkin Isotherm

Temp. (K)	a	log k	ΔG kJ/mole
303	14.88	3.98	33.23
313	14.88	4.71	35.05
323	15.87	5.63	45.61
333	11.95	4.1	37.29
343	7.17	1.76	23.03

A straight line was obtained for θ Vs log C suggesting that the adsorption of components of MJF follows Temkin adsorption isotherm (Fig 1b). The values of 'a' depend on the intermolecular interaction in the adsorption layer and on the heterogeneity of the surface. The high and positive values of 'a' shows the attractive force and a high degree of surface coverage providing better inhibitive property of the extract. K denotes the strength between adsorbate and adsorbent. Larger values of k obtained imply that adsorption is more efficient. ΔG values obtained at 303 to 333 K ranged from 33 kJ/mol to 46 kJ/mol which states that the adsorption tends to chemisorption at this temperature range.

Fig. 2 shows the Arrhenius plot obtained for the mild steel dissolution in 1M HCl in the absence and in the presence of various concentrations of MJF extract at different temperatures. The values of E_a (activation energy), ΔS (Entropy change), ΔH (Enthalpy change) and Q_{ads} (Heat of adsorption) obtained from the plot is presented in table 4.

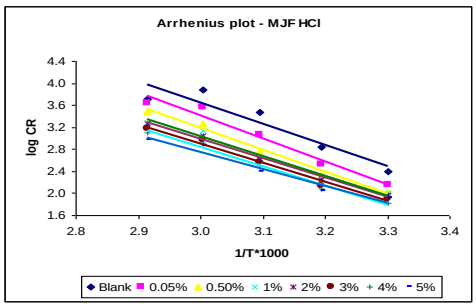

Figure 2: Arrhenius plot for the mild steel dissolution in 1M HCl in the absence and in the presence of various concentrations of MJF extract at different temperatures

Table 4: Activation parameters for the dissolution of mild steel in 1M HCl in the absence and presence of various concentration of MJF extract

Conc. of the extract % v/v	$-E_a$ kJ/mol	ΔS_{ads} J/K mol	$-\Delta H_{ads}$ kJ/mol	Q_{ads}
0.00	73.76	62.83	169.63	
0.05	79.85	62.77	192.26	21.66
0.5	76.88	62.80	186.14	7.96
1.0	68.57	62.88	162.3	-7.07
3.0	67.11	62.90	160.10	-8.36
5.0	58.85	62.98	136.17	-12.23

The values of E_a in the absence and in presence of the extract are indicative of the physical adsorption of extract molecules on the surface of mild steel. The increase in E_a in the presence of the extract, when compared to that in the absence is suggests the formation of adsorption film of physical nature.

The negative values of enthalpy change and heat of adsorption indicates that the adsorption process is exothermic in nature. The Q_{ads} values < 80 kJ/mol confirms physical adsorption mechanism [17]. The large and positive values of ΔS_{ads} suggest that the rate of spontaneous adsorption of the components of the inhibitors on the mild steel surface is most likely to be controlled by the activation complex.

3.2. Electrochemical method

The polarization characteristics of a sample are measured by plotting the current response as a function of the applied potential. Since the current response varies over several orders of magnitude, the plot of logarithm of current against potential on a semi-log paper known as potentiodynamic polarization curve is obtained. Potentials positive to E_{corr} give anodic currents and potentials negative to E_{corr} give cathodic currents [18].

Table 5: Electrochemical kinetic parameters for the dissolution of mild steel in 1M HCl in the absence and in the presence of various concentrations of MJF extract

Conc. of the extract (%v/v)	$-E_{corr}$ mV	b_a mV/decade	b_c mV/decade	I_{corr} mA/cm^2	R_p Ω/cm^2	IE %	
						I_{corr}	R_p
0.00	518	246.73	247.78	14.48	4.17		
0.05	506	185.87	209.66	5.08	9.44	65	56
1	493	140.46	160.26	1.71	21.50	88	81
3	483	129.50	157.98	1.33	25.53	91	84
5	486	126.59	154.31	1.13	29.46	92	86

From the electrochemical kinetic parameters presented in table 5, it is noted that, as the concentration of the extract increased, there is a marginal shift in E_{corr} and a decrease in I_{corr}. A low I_{corr} value in the presence of the extracts implies that the rate of electrochemical reaction were reduced due to the formation of a barrier layer over the surface of mild steel by the components of the extract. The adsorbed inhibitor may not cover the entire metal surface, but occupies sites which are electrochemically active and thereby reduces the extent of anodic or cathodic reaction or both.

It is noted that R_p increases with the increase in concentration of the extract, indicating the formation of an insulated adsorption layer. The extracts are effective at 5% v/v concentration providing a maximum efficiency of 86%.

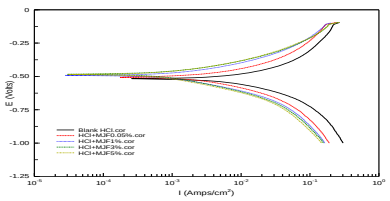

Figure 3: Potentiodynamic polarization curves for mild steel in 1M HCl for various concentrations of MJF extract

The addition of the extract to the acid medium shifts the anodic polarization to more positive and the cathodic polarization to more negative values (fig. 3). The increase in concentration increases the polarization shifts. From the curves it is noted that the increase in concentration of the extracts gives rise to a consistent decrease in anodic and cathodic current densities indicating that both anodic and cathodic reactions are controlled. Hence the inhibitor is of mixed type.

Table 6 provides the impedance parameters for the corrosion of mild steel in 1M HCl in the absence and presence of different concentrations of MJF extract.

Table 6: Impedance parameters for the corrosion of mild steel in 1M HCl in the absence and presence of different concentrations of MJF extract

Conc. of the extract (%v/v)	R_{ct} Ω	% IE	C_{dl} μF/cm^2	% IE
0.00	27.34		642	
0.05	42.50	35.67	296	54
1	72.25	62.16	222	75
3	84.78	67.75	162	65
5	156.58	82.54	159	76

The increase in concentration of the extract enhanced the charge transfer resistance (R_{ct}) values and reduced the double layer capacitance (C_{dl}) values. The decrease in C_{dl} may be due to the adsorption of the components in the extract to form a film on the surface of mild steel and the corrosion process involved is an activation controlled reaction [19].

The decrease in C_{dl} value is attributed to the increase in thickness of the double layer. The decreasing C_{dl} values also suggest a decrease in local dielectric constant between the mild steel and electrolyte induced by the adsorption of the inhibitor at the metal solution interface [20].

Nyquist plots for mild steel in 1M HCl in the absence and presence of various concentrations of MJF extract is presented as fig. 4

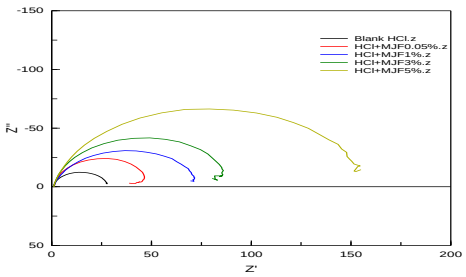

Figure 4: Nyquist plots for mild steel in 1M HCl in the absence and presence of various concentrations of MJF extract

From fig. 4, it is observed that the diameter of the Nyquist plots increases on increasing the concentration of the extract as observed from the figure. This suggested that the formed inhibitive film is strengthened by the addition of the extract. The Nyquist plots with no loops suggest that the mild steel – inhibitor system is under charge transfer resistance control and that the inhibitor is selectively adsorbed in specific places on the surface of mild steel [21].

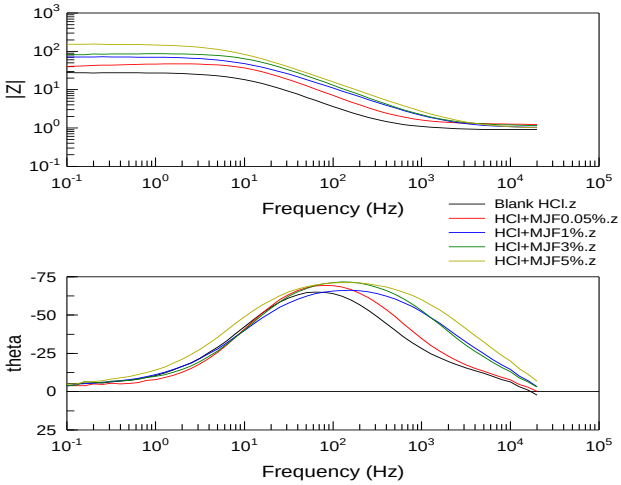

Figure 5: Bode plots for mild steel in 1M HCl for various concentrations of MJF extract

From the Bode plots (fig. 5), it is interpreted that the adsorption of the extract molecules by the displacement of water takes place by a single step mechanism. Bode plots show only one time constant indicating the predominance of an activation phenomenon in the electrochemical process [22].

IV. Conclusion

- Mirabilis jalapa flowers acted as an efficient corrosion inhibitor for mild steel in 1M HCl.
- The inhibition efficiency of the extract was maximum at 5% v/v concentration of the stock and at 323 K.
- The inhibition process followed Langmuir and Temkin adsorption isotherms suggesting monolayer and physical adsorption.

- Electrochemical studies suggested the inhibitor as mixed type and inhibition occurs by activation controlled mechanism.

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