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Acid Extracts of *Ervatamia coronaria* Leaves for Corrosion Inhibition of Mild Steel

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Corrosion inhibitors for acid cleaning processes are used to restrict dissolution of the base metal and decrease acid consumption and hydrogen gas evolution. Because of the toxic nature and high cost of some chemicals currently in use, it is necessary to develop environmentally acceptable and less expensive inhibitors. Natural products can be considered as a good source for this purpose. An evaluation of the effective performance of extract of *Ervatamia coronaria* leaves on the corrosion inhibition of mild steel in 1 M HCl and 0.5 M H_2SO_4 at ambient temperature has been made. Conventional weight loss and electrochemical measurements were used for the evaluation. Electrochemical studies reveal that the plant extracts act as mixed type inhibitors. The *Ervatamia coronaria* (Nandhiyavatai) leaves extracts yielded a maximum of 98 % in acid medium. Surface coverage values were tested graphically for suitable adsorption isotherm.

Key Words: Corrosion, Inhibition, Natural products.

INTRODUCTION

The mammoth increase in industrial activities has led to the use of H_2SO_4 and HCl in acid cleaning/pickling and descaling. Mild steel-a structural material of choice-encounters severe attack of these acids resulting in aweful degradation. Since it is impossible to eliminate corrosion, controlling, rather than preventing it, is the only remedy. Application of the acid corrosion inhibitors is one such corrosion control measures.

Numerous naturally occurring substances are evaluated as corrosion inhibitors, mainly due to their biodegradability and ecofriendliness[1]. Corrosion studies were carried out using the extracts of *Andrographis paniculata*[2], *Argel herb*[3], *Mangifera indica*[4], *Artemesia oil*[5], *Datura metel*[6], *Mentha pulegium*[7], *Datura stramonium*[8] and *Phaseolus aureus*[9], *etc*. The present study has been focused on reducing the corrosion rate of mild steel in acid medium using leaves extract of *Ervatamia coronaria*.

In order to contribute to the current research for green low cost inhibitors to replace the synthetic ones, the present study reports on the corrosion inhibition and adsorption behaviour of *Ervatamia coronaria* leaves extract on mild steel in 1 M HCl and 0.5 M H_2SO_4.

EXPERIMENTAL

Ervatamia coronaria leaves were collected in the nearby locality. Solutions of the inhibitor were prepared by extracting 25 g of the dried and crushed leaves of *Ervatamia coronaria* with *ca.* 500 mL of 0.1 M HCl and 0.5 M H_2SO_4, respectively. The cooled extract was filtered and made up to 500 mL (5 % extract).

The weight loss measurements were carried out with metal specimens of cold-rolled mild steel of area 5 $cm^2 \times 1$ cm^2. The experiments were conducted at room temperature (30 °C) as well as at higher temperatures (40, 50, 60 and 65 °C). The concentrate of the inhibitor was varied from 0.05-0.5 % and the time variation was from 0.5-24.0 h.

Electrochemical studies were carried out using conventional three electrode cell with larger area platinum foil as counter electrode, mild steel as working electrode and saturated calomel electrode (SCE) as reference electrode. Solatron electrochemical analyser model (1284 Z) inter-faced with an IBM computer and Zplot and Corrware softwares were used for data acquisition and analysis.

Potentiodynamic polarization curves and Nyquist plots were recorded for various concentrations of *Ervatamia coronaria* extract in 1 M HCl and 0.5 M H_2SO_4.

RESULTS AND DISCUSSION

The results pertaining to the present investigation of leaves extract of *Ervatamia coronaria* are tabulated and discussed according to the different parameters studied.

Effect of concentration of the inhibitors: Table-1 shows the variation of inhibition efficiency with increase in concentration of the inhibitor. It can be seen from the table that the maximum inhibition efficiency was 98 % for HCl (0.5 % extract) and 95 % for H_2SO_4 (0.5 % extract). This fact can be attributed to the increased coverage of the inhibitor on the mild steel surface.

Impact of immersion time: The results evaluated for the variation of weight loss with exposure time for the mild steel specimen immersed in 1 M HCl and 0.5 M H_2SO_4 are given in Table-1. From the Table, it can be seen that a maximum inhibition efficiency of 98 % was maintained till 3 h and thereafter for longer periods of immersion it was in the range of 94-96 %. Results can prove the consistency of the inhibitor for longer periods of immersion[10].

Temperature effect: The samples were exposed to acidic media at specific temperatures (303, 313, 323, 333 and 338 K) for duration of 0.5 h. Table-2 illustrates the maximum inhibition efficiency is 98.8 % (for room temperature) and 93.42 % (388 K) in 1 M HCl and as can be seen, there is significant difference between the two, which proves that the inhibitor is temperature dependent.

Experiments performed with 0.5 M H_2SO_4 at higher temperatures revealed that the maximum inhibition efficiency at room temperature is 95.19 % whereas at 338 K it was found to be at 84.4 %. The results indicate that the protective film starts to break down with increasing temperature. This can be attributed to the fact that most probably the desorption of inhibitor molecules from the metal surface occurs at a faster pace at higher temperature.

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TABLE-1
INFLUENCE OF *Eravatamia coronaria* LEAVES ON THE INHIBITION EFFICIENCY (1 M HCl AND 0.5 M H_2SO_4)

Conc. (%)	Inhibitor efficiency (%)											
	0.5 h		1 h		3 h		6 h		12 h		24 h	
	HCl	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4
0.05	86	88	80	83	79	64	78	72	70	87	69	68
0.10	87	89	83	85	80	75	79	81	76	92	74	78
0.15	94	91	88	85	84	78	81	83	80	93	78	84
0.20	94	91	88	86	85	84	84	85	83	94	80	88
0.25	96	92	89	87	86	81	85	87	84	95	83	90
0.30	96	92	90	88	88	85	87	87	85	95	84	91
0.35	96	93	92	89	90	87	88	88	86	97	85	91
0.40	97	94	93	91	92	90	91	91	90	97	89	92
0.45	98	94	95	92	94	91	93	94	92	97	90	92
0.50	98	95	98	94	98	94	97	96	95	97	94	97

TABLE-2
INFLUENCE OF TEMPERATURE ON THE INHIBITION EFFICIENCY ON THE EXTRACT OF *Eravatamia coronaria* IN 1 M HCl AND 0.5 M H_2SO_4

Conc. (%)	Inhibitor efficiency (%)									
	303 K		313 K		323 K		333 K		338 K	
	HCl	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4
0.05	86.26	88.73	84.8	94.56	84.04	61.04	73.20	60.820	72.60	59.92
0.10	87.50	89.45	86.7	96.28	85.80	70.60	83.53	70.060	82.40	64.29
0.15	94.20	91.50	92.8	90.24	91.90	70.96	89.45	74.540	88.15	65.60
0.20	94.96	91.99	93.6	90.10	92.80	76.13	90.20	80.215	88.90	70.78
0.25	96.40	92.25	95.5	91.34	94.60	75.85	92.06	81.730	90.60	75.21
0.30	96.60	92.95	95.7	94.07	94.80	78.70	92.27	83.720	90.86	79.85
0.35	96.80	93.36	96.0	94.90	95.09	79.33	92.47	84.620	91.05	81.90
0.40	97.03	94.18	96.4	94.67	95.40	79.63	92.80	85.960	91.40	82.29
0.45	98.50	94.73	97.3	94.80	97.10	82.64	94.40	86.380	92.90	83.50
0.50	98.80	95.19	98.5	94.44	97.60	90.35	94.95	88.480	93.42	84.40

Adsorption kinetics: Since what is *hitherto* discussed leads always to adsorption phenomenon, the inhibition data are used for the construction of experimental adsorption isotherms.

It is assumed that the inhibition efficiency is comparable to the degree of coverage (θ) of the inhibitor on the metal surface. When the surface of the iron metal is ideally homogenous and there is no interaction among adsorbed species, the adsorption will follow Langmuir isotherm. It is clear from the linear plot (Fig. 1) that the inhibitors follow Langmuir adsorption isotherm. Deviation from unity, as in the present case reveals that there is heterogeneity of the surface and further examination of the data obtained (Fig. 2) confirms that the adsorption isotherm follows Temkin isotherm, thereby indicating that the behaviour of adsorption is affected by the heterogeneity of the electrode surface[11].

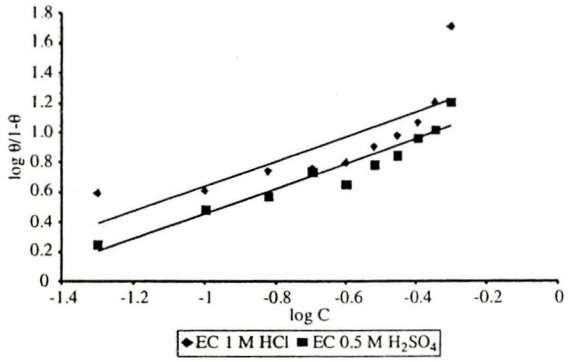


Fig. 1. Langmuir adsorption isotherm for *Ervatamia coronaria* in acidic media

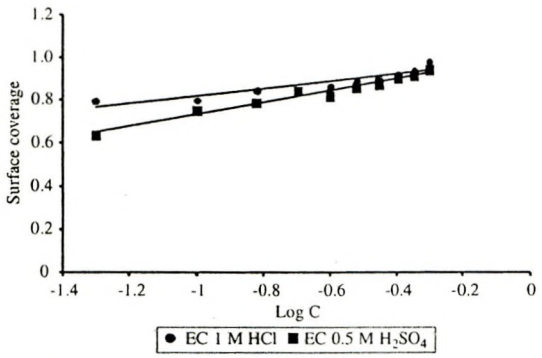


Fig. 2. Temkin adsorption isotherm for *Ervatamia coronaria* in acidic media

Polarization behaviour: Figs. 3 and 4 show typical potentiodynamic polarization curves for the mild steel electrodes obtained at 303 K in 1 M HCl and 0.5 M H_2SO_4, respectively.

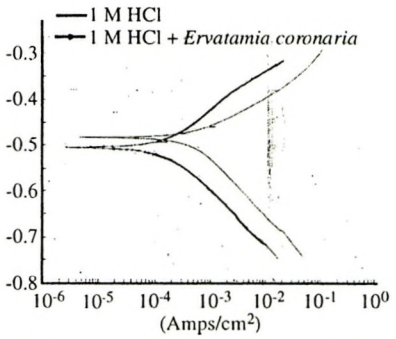


Fig. 3. Polarization plots of mild steel in HCl-effect of inhibitor (natural products)

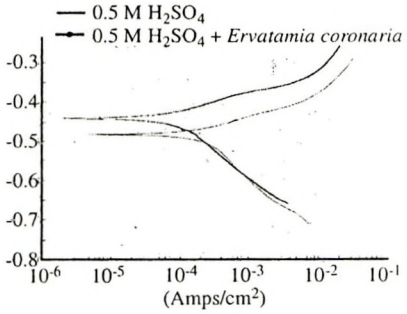


Fig. 4. Polarizatin plots of mild steel in 0.5 M H_2SO_4 effect of inhibitor (natural products)

The results indicate a considerable reduction in the i_{corr} values in the presence of inhibitors (Table-3). These high values of b_c can be correlated to the decrease of the cathodic transfer coefficient which can be ascribed to the thickening of the electrical double layer due to the adsorbed inhibitor molecules[12].

TABLE-3
ELECTROCHEMICAL CORROSION PARAMETERS FOR MILD STEEL IN 1 M HCl ACID AND 0.5 M H_2SO_4 IN THE PRESENCE OF VARIOUS INHIBITORS

System	E_{corr} (mV/ SCE)	I_{corr} (A/cm^2)	b_a (mV/ dec)	b_c (mV/ dec)	I.E. (%)	R_{ct} (ohm cm^2)	I.E. (%)	C_{dl} (μF cm^2)	θ
0.5 M H_2SO_4 (blank)	-480	3.25×10^{-4}	85	165	–	53.72	–	152.0	–
0.5 M H_2SO_4 + *Ervatamia coronaria*	-440	9.41×10^{-5}	60	145	71.04	100.40	47	81.6	0.46
1 M HCl (blank)	-482	5.3×10^{-3}	74	128	–	32.60	–	190.0	–
1 M HCl + *Ervatamia coronaria*	-502	5.1×10^{-5}	52	110	99	139.8	76	85.2	0.55

It is found that b_a and b_c values (Table-3) change with respect to blank thereby indicating that the leaves extract of *Ervatamia coronaria* reduce the dissolution of metal as well as hydrogen evolution and thus act as mixed type inhibitor.

The increase in inhibition efficiency for the inhibitors in HCl media might have been due to the synergistic effect of Cl^- ions (of HCl) adsorbed on the, mild steel surface that acted as a main force in the formation of electrostatic bond with the cationic species due to protonation by hydrogen ions of the acid species[13] of the extract which might have probably adsorbed perpendicular to the mild steel surface.

Impedance techniques: The impedance spectral curves of *Ervatamia coronaria* in 1 M HCl and 0.5 M H_2SO_4 are given in Figs. 5 and 6, respectively. From the

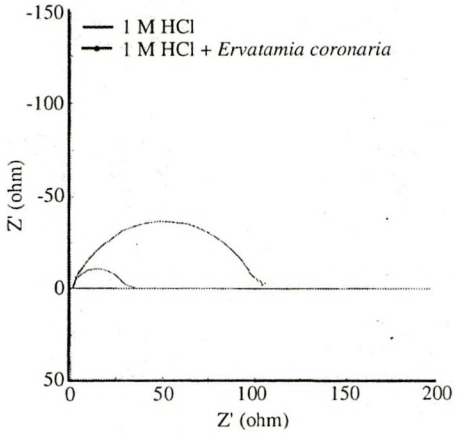


Fig. 5. Nyquist plots of mild steel in 1 M HCl effect of inhibitor (natural products)

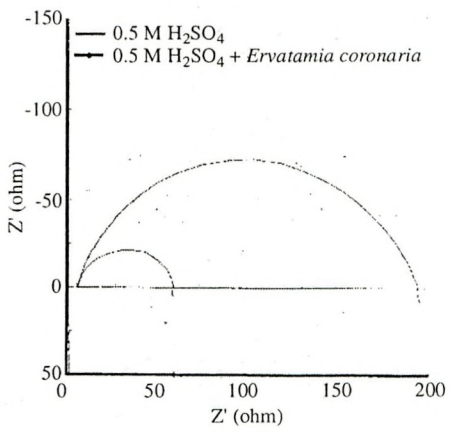
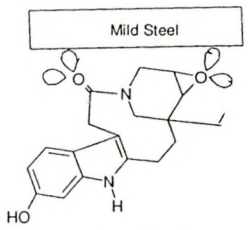


Fig. 6. Nyquist plots of mild steel in 0.5 M H_2SO_4 effect of inhibitor (natural products)

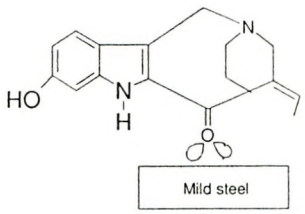
figures, it can be observed that they are not perfect semicircle in nature. This can be attributed to the presence of pores on the electrode surface or due to the adsorption of the inhibitor[14]. Values of R_{ct} and C_{dl} infer that increase in R_{ct} values and decrease in C_{dl} values in the presence of *Ervatamia coronaria* leaves extract (Table 3). This confirms the adsorption behaviour of leaves extract of *Ervatamia coronaria* on mild steel surface.

In present study, the leaves extract of *Ervatamia coronaria* works out to be a good inhibitor for mild steel corrosion. The leaves extract was found to be adsorbed on mild steel surface which was confirmed by Langmuir adsorption isotherm. Electrochemical measurements also confirm the mixed inhibitive nature. The phytochemical constituents present in the leaves extract of *Ervatamia coronaria* was found to contain indole alkaloids *viz.*, ervatinine and ervaticine. The indole alkaloids may be adsorbed on mild steel surface and reduce corrosion of mild steel in acid medium, due to the presence of active centres such as nitrogen and oxygen[15].

The skeletal representation of proposed adsorption model is as given below:



Ervatinine



Ervaticine

Conclusion

From the above findings, it can be concluded that leaves extract of *Ervatamia coronaria* acts as an effective inhibitor at different environmental condition, the effectiveness can be attributed to the presence of indole alkaloids ervaticine and ervatinine. The inhibitors used in the current study were found to follow Langmuir and Temkin adsorption isotherm which indicated the monolayer formation with heterogeneity in the surface of the electrode. From electrochemical measurements, it can be seen that the plant extracts under investigation behaved as mixed type inhibitors.

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