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A new pharmaceutically expired drug acts as corrosion inhibitor for mild steel in acid medium

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ABSTRACT

Expired drug (non-toxic characteristics) was used as corrosion inhibitors for mild steel in 1 M HCl medium was studied by weight loss and electrochemical methods. Effect of temperature was investigated at temperature range (303-343 K). The obtained results reveals that, the inhibition efficiency increases with increases of concentration of the inhibitor. Polarization curves indicated that they are mixed – type of inhibitor. The data collected from Thermodynamic studied are in good agreement to confirm the ability of using expired LF drug acts as corrosion inhibitors for mild steel in hydrochloric acid corrosive medium.

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Introduction

The use of corrosion inhibitors has become an answer to the corrosion attack of mild steel which always lead to damage and total replacement of these mild steel. Most studies on corrosion inhibitors reported that a large number of inhibitors are organic compounds with O, N and S hetero atoms; they have higher basic properties with electron density, making them the reaction centers [1-7]. These compounds are adsorbed on the metallic surface and block the active corrosion sites; most of them are highly toxic to the human beings and the environment. Hence, a large number of scientific studies have been devoted to the subject of corrosion inhibitor for mild steel in acidic media [8-14].

Most of commercial inhibitors are toxic in nature; therefore replacement by environmentally benign inhibitors is necessary. Few non-toxic compounds have been investigated as corrosion inhibitors by some researchers [15-18]. The use of pharmaceutical compounds offers interesting possibilities for corrosion inhibition due to the presence of its hetero atoms in their structure, and they are of particular interest because of their safe use, high solubility in water and high molecular structure size. Some of the azosulpha and anti malarial drugs have been reported as good corrosion inhibitors [19-24].

In this study, the expired LF drug have been selected to study anticorrosion on mild steel in 1M hydrochloric acid medium using weight loss, Potentiodynamic polarization and electrochemical impedance spectroscopy techniques. It reveals that the LF is a non-toxic pharmaceutical compound used as a mucolytic agent prescribed in respiratory infection like bronchitis and bronchial asthma. The inhibitor is available in the brand name of Lupicof. Hence, attempts are made to utilize the acid solution of expired LF acts as anticorrosion agent on mild steel in hydrochloric acid medium.

Materials and Method

Experimental Procedure

Mild steel strips were mechanically cut into strips of size 5 cm x 1 cm x 0.2cm containing the composition of 0.03% C, 0.259 % Mn, 0.027 % Si, 0.004 % P and the remainder Fe and

provided with a hole (2mm) of uniform diameter at one end of the coupons for easy hooking. For electro chemical studies, mild steel strips of the same composition were fabricated by fixing the mild steel of size 1 cm² to a mild steel rod of 1mm diameter using araldite. Each specimen was polished with different grades of emery paper, degreased with acetone and used. Accurate weight of the samples was taken using electronic balance. Analar grade HCL and double distilled water were used to prepare all solutions. Expired LF drug obtained from the medical shop and used for this study without any further purification.

Weight loss method

The pretreated specimen's initial weights were noted and were immersed in the experimental solution with the help of glass hooks at 303K temperature for the period of 0.5, 2, 4, 6, 8 and 24 hours. The influence of temperature on the corrosion of mild steel has also been studied at five different temperatures ranging from 303K to 343K in absence and presence of the inhibitors at different concentrations (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 and 1.1%) for 30 minutes. From the weight loss, the inhibition efficiency (IE %), surface coverage (θ) and corrosion rate (mpy) were calculated using the following formula.

$$IE (\%) = \frac{W_U - W_I}{W_U} \times 100 \quad \dots\dots(1)$$

Where, W_U and W_I are the weight losses in absence and Presence of inhibitor respectively.

$$\text{Corrosion rate (mmpy)} = \frac{87.6 \times \text{weight loss (mg)}}{\text{density (gm/cc)} \times \text{area (cm}^2\text{)} \times \text{time (hours)}} \quad \dots\dots(2)$$

Electrochemical Method

Potentiodynamic Polarization method

Potentiodynamic polarization measurements were carried out using electrochemical analyzer. The polarization measurements were made to evaluate the corrosion current, corrosion potential and Tafel slopes. Experiments were carried out in a conventional three electrode cell assembly with working electrode as mild steel specimen with exposed area of 1 cm² and

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the rest being covered with insulation tape, a rectangular Pt foil was used as the counter electrode and the reference electrodes as SCE. A time interval of 10-30 minutes was given for each experiment to attain the steady state open circuit potential. The polarization was carried from a cathodic potential of -700mV (vs SCE) to an anodic potential of -200mV (vs. SCE) at a sweep rate of 10mV per second. From the polarization curves Tafel slopes, corrosion potential and corrosion rate were calculated. The inhibitor efficiency was calculated using the formula.

$$\text{Inhibition efficiency} = \frac{I_{\text{corr}} - I_{\text{corr}(i)}}{I_{\text{corr}}} \times 100 \quad \dots(3)$$

Where I_{corr} is the corrosion current in the absence of inhibitor and $I_{\text{corr}(i)}$ is the corrosion current in presence of inhibitor.

Electrochemical Impedance methods

For the measurements of impedance, the cell used was same as that used for potentiodynamic polarization. An AC potential of 50 mV was super imposed on the steady open circuit potential. The real part (Z') and the imaginary part (Z'') were measured at various frequencies in the range of 10 kHz to 10MHz. The real and imaginary parts of the impedance were plotted in Nyquist plots. The charge transfer resistance (R_{ct}) values were obtained from the plots of Z' vs. Z'' . The value of ($R_t + R_s$) corresponds to the point where the plot cuts z' and at higher frequency the difference between R_t and R_s gives the charge transfer resistance R_{ct} values. The double layer capacitance C_{dl} values were obtained from the equation (4),

$$C_{dl} = \frac{1}{2\pi f_{\text{max}} R_{ct}} \quad (4)$$

Where, C_{dl} - double layer capacitance
 R_{ct} - charge transfer resistance
 f_{max} -frequency at Z'' value maximum.

Besides, the above method, the inhibition efficiencies were obtained from $R_{p(i)}$ and R_p values as follows

$$\text{Inhibition efficiency} = \frac{R_{p(i)} - R_p}{R_{p(i)}} \times 100 \quad \dots(5)$$

Where, $R_{p(i)}$ and R_p are the charge transfer resistance in the presence and absence of inhibitor.

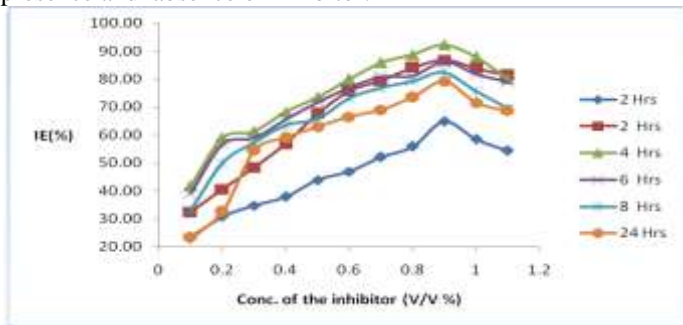


Fig 1. Variation of inhibition efficiency of LF inhibitor at different concentrations on mild steel in 1M HCl at room temperature

Result And Discussion

Weight loss studies

Using the weight loss data, corrosion rate (CR), inhibition efficiency (IE) and surface coverage (θ) and the optimum concentration of the inhibitor have been calculated. Corrosion parameters obtained from weight loss measurements are listed in Table 1. It reveals that, the inhibition efficiency increased with increase in the concentration of the inhibitor. Fig.1 illustrated that, the variation of inhibition efficiency of LF, at different

concentrations, on mild steel in 1M HCl, at different different temperature. The maximum inhibition efficiency of 92.28% was noticed at a concentration 0.9%. This result indicated that the non toxic inhibitor could acts as effective corrosion inhibitor for mild steel in 1M HCl medium

Thermodynamic Consideration

The calculated values of activation energy (E_a), free energy of adsorption (ΔG_{ads}), the enthalpy of adsorption (ΔH) and the entropy of adsorption (ΔS) for mild steel in 1M HCl with and without LF inhibitor showed in Table 2. The ΔG , ΔS and ΔH values do not show any gradual increase or decrease with respect inhibitor concentration. This shows that adsorption of the constituents is dependent not only on concentration but also on other factors like presence of other constituents, electronic and steric interaction of the inhibitor constituents among themselves as well as with the other constituents present in the corrosive media. The negative value of free energy of adsorption (ΔG_{ads}) indicates the spontaneous adsorption. Energy of activation (E_a) was calculated by Arrhenius equation

$$\text{Log} \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303 \times R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad \dots (5)$$

Where, ρ_1 - the corrosion rates at T_1 temperature, ρ_2 - the corrosion rates at T_2 temperature and 'R' is a gas constant.

The change in free energy of adsorption for different higher temperatures in comparison with room temperature at various concentration of inhibitor was calculated using the equation (6),

$$\Delta G_{\text{ads}} = -2.303 \times 8.314 \times T \times \text{Log}(K \times 55.5) \quad \dots (6)$$

$$K = \frac{\theta}{(1 - \theta)C}$$

Where, θ - Surface coverage of the metal surface, C - Concentration of the inhibitor in percentage T - Temperature in Kelvin and K - Equilibrium constant

Activation energy (E_a) value for blank is 54.77 kJ/mol and 52.96 kJ/mol for 0.9% concentration of the inhibitor. Figure 2 illustrated the Arrhenius plot for the dissolution of mild steel in 1M HCl with and without inhibitor at various temperatures. The magnitude of E_a show that the chemical adsorption is involved Sankarapavinasam et al. [14]

Adsorption Consideration

The surface coverage (θ) values for different concentrations of the inhibitor in HCl medium have been evaluated from the weight loss data. The data were tested graphically to find a suitable adsorption isotherm. A plot of $\log(\theta / (1 - \theta))$ against $\log C$ (Fig 3) shows a straight line indicating that adsorption from the acid follows the Langmuir adsorption isotherm.

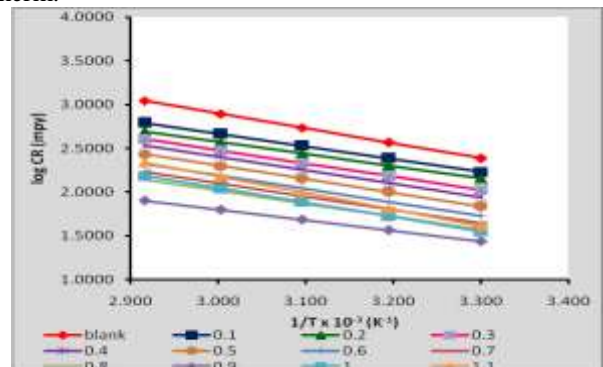


Fig. 2. Arrhenius plot for the dissolution of mild steel in 1M HCl with and without inhibitor at various temperatures

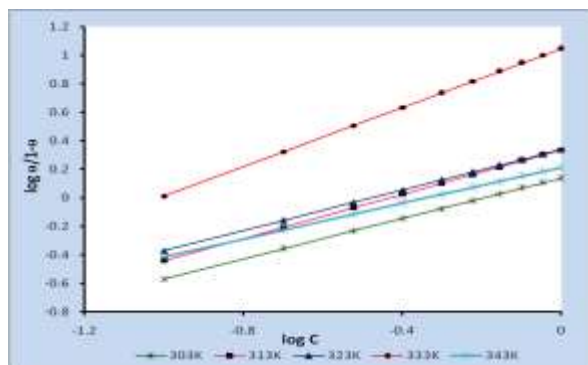


Fig 2 Langmuir isotherm plot for the adsorption of the inhibitor in 1 M HCl solution

It is observed that although the plot is linear, the gradients are never unity, contrary to what is expected for ideal Langmuir adsorption isotherm equation. Organic molecules having polar atoms or groups which are adsorbed on the metal surface may interact by mutual repulsion or attraction and this may be advocated as the reason for the departure of the slope values from unity. The number of active sites of the surface occupied by one molecule of the inhibitor is given by the value of (1/y). A straight line was obtained when the surface coverage (θ) was plotted against log C for the inhibitor. This shows that the adsorption obeys a Temkin adsorption isotherm, which is graphically represented in Fig 3.

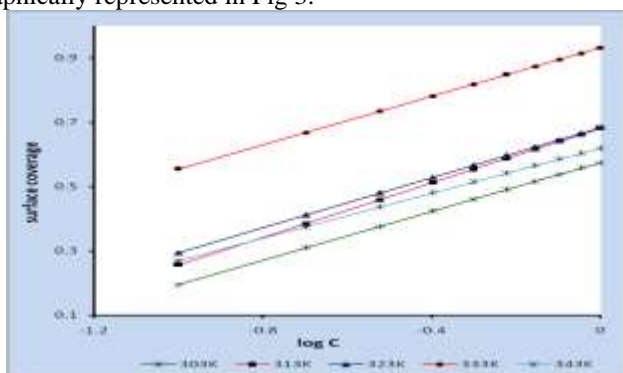


Fig 3 Temkin isotherm adsorption model for inhibitor in 1 m HCL on the surface of mild steel

The plot of log θ Vs log C is shown in Fig 4. The linearity shows that the adsorption of the inhibitor on mild steel surface follows Freundlich isotherm.

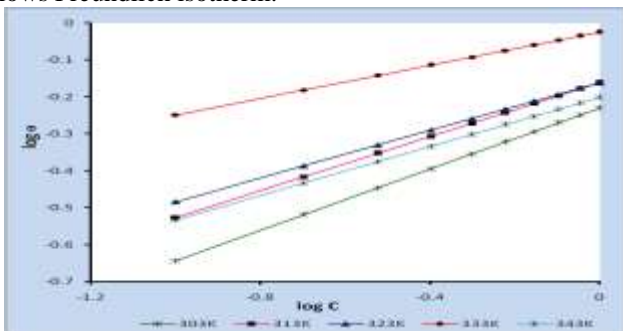


Fig 4. Freundlich isotherm plot for the adsorption of the inhibitor in 1 M HCl solution

Tafel Polarization Studies

The electrochemical parameter obtained from the Tafel polarization studies observed that the i_{corr} values decreased from 0.412 A/cm² to 0.157 A/cm² with increased concentration of LF inhibitor. Fig. 5 shows Potentiodynamic polarization curves for mild steel in 1M HCl in the absence and presence of different concentrations of the inhibitor. The inhibition value is also found to increase from 32.62% to 88.46%. The calculated polarization resistance (R_p) had increased from 67.03 Ωcm² to

160.5 Ωcm² with increase of inhibition efficiency from 30.11% to 58.24% for the concentration of 0.2% to 0.9%. Table 3 shows the Tafel polarization behaviors of mild steel in 1M HCl in the presence of the inhibitor. From the graph it is observed that LF inhibitor behaved like a mixed type of inhibitor (Kann et al 2006).

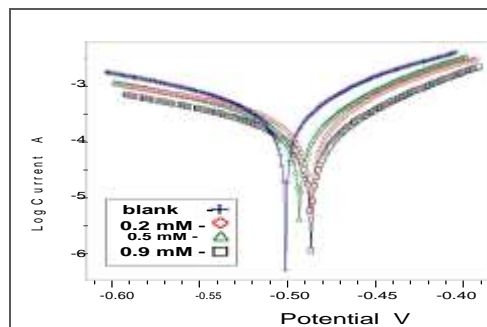


Fig. 5 Potentiodynamic polarization curves for mild steel in 1M HCl in the absence and presence of different concentrations of the inhibitor.

Electrochemical Impedance Measurement

The impedance parameters for mild steel in 1M H Cl with and without LF inhibitor are given in Table 4. It was observed that the charge transfer resistance (R_{ct}) values had increased from 26.67 to 88.08 Ωcm² and in double layer capacitance (C_{dl}) the values had decreased from 641.4 to 492.2 μF/Cm² with increase in LF inhibitor concentrations. The decrease in C_{dl} values indicates the adsorption of inhibitor constituents in the acid solution of the inhibitor on the mild steel surface and also the metal-solution interface. The maximum inhibition efficiency obtained for this inhibitor is 70.86 % at 0.9% concentration.

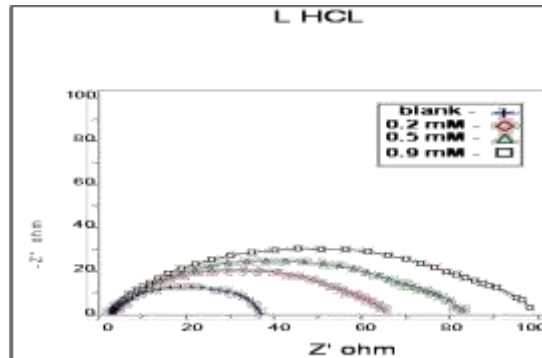


Fig 6. Impedance diagram for mild steel in 1M HCl in the presence and absence of different concentrations of the inhibitor

Conclusion

The LF inhibitor acts as good and efficient inhibitor for the corrosion of mild steel in 1 M hydrochloric acid medium. The maximum inhibition efficiency was found to increase with concentration, immersion period and temperatures studied. The effect of immersion time of the inhibitor at the optimum concentration showed maximum efficiency in 4h immersion time at 323K and found sufficient for pickling. A Potentiodynamic polarization study reveals that the extract acts through mixed mode of inhibition. The impedance method revealed that charge transfer process mainly controls the corrosion mild steel. The thermodynamic parameters such as activation energy (Ea) and free energy of adsorption (Gads) obtained from this study indicated spontaneous adsorption of inhibitor on the surface of the metal.

Table 1: Corrosion parameters of the LF inhibitor on mild steel in 1M HCl at different immersion periods from weight loss method at room temperature

Conc. (v/v %)	Corrosion Rate (mpy)					
	2 Hrs	2 Hrs	4 Hrs	6 Hrs	8 Hrs	24 Hrs
BL	193.25	206.18	283.25	312.69	114.24	320.11
0.1	148.67	139.31	165.34	190.69	76.62	244.88
0.2	133.74	122.60	116.08	135.60	57.12	216.09
0.3	126.16	106.44	109.58	128.26	48.76	145.94
0.4	120.14	89.16	90.08	107.74	41.79	131.13
0.5	108.55	66.87	75.23	88.55	39.01	118.65
0.6	102.53	50.15	56.67	72.44	30.65	107.36
0.7	92.50	42.35	39.95	60.07	26.47	99.22
0.8	85.15	32.88	31.60	58.83	23.68	84.82
0.9	67.98	27.31	21.87	43.21	20.20	66.56
1	80.24	33.44	34.35	56.91	27.86	91.07
1.1	88.05	38.45	56.64	66.20	34.83	100.36

Table 2. Thermodynamic data for mild steel in 1M HCl in the presence and absence of acid LF inhibitor at 303 K to 343 K

CON (%V/V)	Ea KJ/mol	$\Delta G_{KJ/mol}$					$\Delta S_{KJ/mol}$	$\Delta H_{KJ/mol}$
		303K	313K	323K	333K	343K		
blank	54.77							
0.1	52.26	-12.86	-14.83	-16.14	-17.79	-15.21	-0.078	10.17
0.2	53.02	-12.24	-13.67	-16.37	-17.39	-13.76	-0.075	10.21
0.3	52.46	-12.75	-14.42	-16.18	-17.57	-13.40	-0.086	14.13
0.4	52.13	-12.81	-14.84	-15.76	-17.46	-13.69	-0.092	16.24
0.5	52.96	-13.61	-14.96	-15.74	-17.40	-14.67	-0.083	13.37
0.6	51.41	-14.10	-15.26	-16.31	-17.53	-15.36	-0.092	16.37
0.7	50.79	-14.28	-15.46	-16.69	-17.66	-15.58	-0.091	15.91
0.8	49.93	-14.56	-15.62	-16.88	-17.83	-16.06	-0.094	16.51
0.9	52.96	-14.85	-16.17	-18.32	-20.18	-16.30	-0.093	15.48
1.0	54.25	-13.86	-15.24	-16.24	-17.37	-14.68	-0.069	9.04
1.1	53.81	-13.19	-14.36	-15.12	-16.47	-12.88	-0.068	9.46

Table 3. Electrochemical polarization (Tafel) Parameters for the corrosion of mild steel in 1M HCl containing with and without LF inhibitor at room temperature

conc. (v/v%)	E.corr (mV)	I cor. A/cm ²	I corr % IE	ba mV/dec	bc mV/dec	Rp Ωcm ²	Rp % IE
0.2	491.2	0.278	32.52	70	137	95.91	30.11
0.5	485.5	0.269	34.71	74	149	98.5	31.95
0.9	483.1	0.157	61.89	68	135	160.5	58.24

Table 4: Electrochemical impedance parameters for mild steel in 1M HCl containing different concentrations of the inhibitor at room temperature

Conc. (%)	R _{ct} (Ωcm ²)	C _{dl} μF/cm ²	IE (%)
blank	25.67	641.4	-
0.2	46.09	531.5	44.30
0.5	57.22	497.9	55.14
0.9	88.08	492.2	70.86

Results obtained in weight loss method were very much in good agreement with the electrochemical methods

Scope for future research

Surface examination of mild steel specimen may be carried out using Atomic Force Microscopy (AFM) and X-ray Diffraction (XRD) studies.

The expired non-toxic drug studied under investigation may be applied in industries for acid pickling, acid descaling and oil well acidizing purposes.

Studies may be performed with the expired non-toxic drug to know the difference in cost of corrosion, the economic importance and also would be helpful in predicting the exact mechanism of inhibition of corrosion.

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