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An Expired Non-Toxic Drug Acts as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Medium

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The inhibitive properties of expired non-toxic drug of ciprofloxacin (eye/ear drops) on the corrosion of mild steel strip in 1 M hydrochloric acid medium was investigated using weight loss and electrochemical (impedance) methods. The study revealed that the inhibition efficiency increases with increases in concentration of the inhibitor, immersion period (time) and temperature. Effect of temperature was investigated at temperature range (303-343 K). This inhibitor obeys Langmuir adsorption isotherm. The inhibition activity is due to the adsorption of pharmaceutically active components which are found in the inhibitor ciprofloxacin (eye/ear drops).

Keywords: Mild steel, Corrosion inhibitor, Acidic medium, Expired drug, Non-toxic, Weight loss, Impedance method.

INTRODUCTION

Mild steel has many industrial applications because of its easy availability, low cost. It is extensively used in various industries like sugar, leather, food, petrochemical, paper and textile industries. Acids are used to remove the undesirable scales and rust in several industrial processes, including pickling and rescaling operations [1-3]. Most of the studies on corrosion inhibitors reported that a large number of inhibitors are organic compounds with O, N and S atoms or N-hetero cyclic compounds with polar groups. They have higher basic properties with electron density, making them the reaction centers [4-10].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 studies have been devoted to the subject of corrosion inhibitor for mild steel in acidic media [11-14]. Most of the 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 [15-20]. 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 antimalarial drugs have been reported as good corrosion inhibitors [21-23]. In this study, the expired non-toxic drug of ciprofloxacin (eye/ear drops) drug have been selected to study anticorrosion on mild steel in 1 M hydrochloric acid medium using weight loss, electrochemical impedance spectroscopy techniques. The inhibitor is available in the brand name of Ceflox. Expired ciprofloxacin (eye/ear drops) acts as anticorrosion agent on mild steel in hydrochloric acid medium.

EXPERIMENTAL

Mild steel strips were mechanically cut into strips of size 5 cm × 1 cm × 0.2 cm, provided with a hole (2 mm) of uniform diameter at one end of the coupons for easy hooking and containing the composition of 0.034 % C, 0.259 % Mn, 0.023 % Si, 0.004 % P and the remainder Fe. For electro chemical studies, mild steel strips of the same composition were fabricated by fixing the mild steel of size 1 cm^2 to a mild steel rod of 1 mm diameter using araldite. Each specimen was polished with different grades of emery paper, degreased with acetone, washed with distilled water and properly dried prior to exposure. Accurate weight of the samples was taken using electronic balance. AnalaR grade HCl and double distilled water were used to prepare all solutions. Expired ciprofloxacin (eye/ear drops) drug obtained from Cipla Ltd.

RESULTS AND DISCUSSION

The pretreated specimen's initial weights were noted and were immersed in the experimental solution with the help of glass hooks for the period of 0.5, 2, 4, 6, 8 and 24 h. The influence of temperature on the corrosion of mild steel has also been studied at five different temperatures ranging from 303 to 343 K 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 and 1.0) for the above mentioned period. From the weight loss, the inhibition efficiency (IE %), surface coverage (θ) and corrosion rate (mpy) were calculated using the following formula:

$$\text{IE (\%)} = \frac{W_U - W_I}{W_U} \times 100$$

where, W_U and W_I are weight losses in acids without and with inhibitors respectively.

$$\text{Corrosion rate (mmpy)} = \frac{87.6 \times \text{Weight loss (mg)}}{\text{Density (g/cc)} \times \text{Area (cm}^2) \times \text{Time (h)}}$$

The maximum inhibition efficiency of 94.56 % was noted at a concentration 0.7 % of the inhibitor in 1 M HCl medium. Since more adsorption takes place on the metal surface, the inhibitor efficiency increases with an increase in immersion time. It was found that the optimum inhibition efficiency is reached in 6 h and further increase in time performance of the inhibition efficiency was found to decrease (Table-1). This may be due to prolonged immersion resulting in desorption of inhibitor molecules from the mild steel surface.

The influence of temperature on inhibitor in 1 M HCl was investigated in the temperature range, 303 to 343 K, for 0.5 h of immersion. It is found that as the temperature increases from 303 to 343 K, the inhibition efficiency also increased. The increase in inhibition efficiency was from 67.23 % at 303 K to 95.63 % at 333 K for 0.7 % concentration of inhibitor in 1 M HCl. Further rise in temperature results in slight depletion of inhibitor efficiency (Table-2). From the data, it can be inferred that the protective layer formed on mild steel surface, due to adsorption of inhibitor, which was stable up to 333 K and after that there may be desorption of inhibitor on mild steel surface.

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 1 M HCl with and without inhibitor showed in Table-3.

The negative value of free energy of adsorption (ΔG_{ads}) indicates the spontaneous adsorption. Energy of activation (E_a) was calculated by Arrhenius equation:

TABLE-1
INFLUENCE OF CONCENTRATION OF EXPIRED CIPROFLOXACIN (EYE/EAR DROPS) ON THE CORROSION OF MILD STEEL IN 1 M HCl AT ROOM TEMPERATURE (298 K) AT DIFFERENT TIME PERIODS

Inhibitor conc. (% v/v)	Time (h)											
	0.5		2		4		6		8		24	
	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
Blank	514.52	–	590.34	–	633.18	–	647.62	–	699.58	–	714.34	–
0.1	472.69	40.23	500.21	54.36	506.64	63.23	514.68	72.36	546.24	68.36	564.38	60.36
0.2	408.64	44.63	395.64	58.32	391.12	67.23	386.98	75.36	402.82	70.23	445.67	63.12
0.3	321.76	46.23	314.06	63.25	306.16	72.36	293.19	81.26	308.19	74.26	348.68	68.23
0.4	249.08	52.65	238.18	67.99	229.06	75.32	221.98	85.32	240.68	79.65	279.98	71.65
0.5	187.23	58.63	180.64	72.65	174.33	81.25	166.82	87.36	184.96	83.2	223.14	76.33
0.6	146.72	63.26	138.21	75.26	130.28	86.32	123.04	90.23	142.08	89.63	180.86	78.04
0.7	118.66	64.23	107.82	78.63	98.67	89.02	91.98	94.56	106.82	90.23	139.68	84.65
0.8	124.28	59.02	111.36	75.65	102.29	83.26	95.89	92.36	111.21	86.32	145.68	79.99
0.9	129.66	53.65	118.99	69.36	110.28	77.26	102.29	89.36	117.08	79.23	156.69	73.26
1.0	136.78	48.36	123.87	62.36	116.72	70.36	110.88	82.36	126.66	73.69	176.95	65.86

TABLE-2
EFFECT OF TEMPERATURE ON THE CORROSION OF MILD STEEL IN 1 M HCl IN THE PRESENCE OF VARIOUS CONCENTRATION OF EXPIRED CIPROFLOXACIN (EYE/EAR DROPS) IN 1 M HCl

Inhibitor conc. (% v/v)	Temperature (K)									
	303		313		323		333		343	
	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
Blank	655.95	–	1539.18	–	3519.25	–	8109.48	–	16527.78	–
0.1	465.32	40.99	1006.36	47.34	2432.69	56.62	5257.26	72.63	11063.23	61.73
0.2	315.66	45.02	821.63	52.36	1802.69	59.82	3806.23	75.63	7706.21	65.78
0.3	230.65	47.32	563.21	55.34	1698.31	63.36	2722.61	79.36	5423.65	69.02
0.4	183.61	53.26	390.23	60.23	1230.65	67.08	1960.23	83.61	3994.25	73.42
0.5	145.11	59.31	269.32	65.39	893.22	73.65	1426.33	86.12	2904.66	77.39
0.6	90.36	63.99	188.78	72.11	647.23	76.36	999.69	89.45	1725.36	81.02
0.7	78.11	67.23	161.08	75.63	459.29	78.84	685.25	95.63	1329.99	84.23
0.8	89.32	62.36	182.55	67.23	526.21	73.26	826.32	88.61	1689.45	81.23
0.9	86.23	56.32	188.36	62.35	538.62	69.86	965.32	83.21	1698.32	74.11
1.0	94.26	49.63	196.32	54.66	578.95	64.79	1069.66	75.41	1856.01	70.23

TABLE-3
THERMODYNAMIC DATA FOR MILD STEEL IN 1 M HCl IN THE PRESENCE AND ABSENCE OF EXPIRED CIPROFLOXACIN (EYE/EAR DROPS) FOR 0.5 h PERIOD

Inhibitor conc. (% v/v)	E_a (KJ/mol)	-ΔG (KJ/mol)										-ΔS (KJ/mol)	-ΔH (KJ/mol)
		θ	303 K	θ	313 K	θ	323 K	θ	333 K	θ	343 K	303 K	303 K
Blank	70.151	–	–	–	–	–	–	–	–	–	–	–	–
0.1	69.027	0.4099	15.00	0.4734	16.16	0.5662	17.68	0.7263	20.19	0.6173	19.38	0.271	67.380
0.2	68.569	0.4502	13.66	0.5236	14.88	0.5982	16.17	0.7563	18.71	0.6578	17.91	0.263	66.049
0.3	68.415	0.4732	12.88	0.5534	14.14	0.6336	15.49	0.7936	18.18	0.6902	17.17	0.260	65.895
0.4	67.334	0.5326	12.75	0.6023	13.91	0.6708	15.16	0.8361	18.17	0.7342	16.96	0.256	64.814
0.5	66.291	0.5931	12.81	0.6539	13.91	0.7365	15.41	0.8612	18.09	0.7739	16.94	0.253	63.771
0.6	65.196	0.6399	12.85	0.7211	14.73	0.7636	15.69	0.8945	19.98	0.8102	17.69	0.249	62.676
0.7	61.669	0.6723	12.82	0.7563	14.32	0.7884	15.27	0.9365	19.56	0.8423	17.25	0.238	59.149
0.8	65.349	0.6236	11.95	0.6723	12.90	0.7326	14.09	0.8861	17.42	0.8123	16.27	0.247	62.829
0.9	65.824	0.5632	11.02	0.6235	12.04	0.6986	13.32	0.8321	15.84	0.7411	14.75	0.245	63.304
1.0	66.329	0.4963	10.08	0.5466	10.94	0.6479	12.42	0.7541	14.22	0.7023	13.90	0.244	63.809

$$\log\frac{\rho_2}{\rho_1}=\frac{E_a}{2.303\times R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

where, ρ_1 = corrosion rates at T_1 temperature, ρ_2 = 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:

$$\Delta G_{ads}=-2.303\times 8.314\times T\times\log(K\times 55.5)$$

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

where, θ = surface coverage of the metal surface; C = concentration of the inhibitor in percentage; T = temperature in Kelvin; K = equilibrium constant.

The change in enthalpy of adsorption (ΔH) and change in entropy of adsorption (ΔS) can be calculated using the following equations:

$$\Delta H=E_a-RT$$

$$\Delta S=\frac{\Delta H-\Delta G}{T}$$

Activation energy (E_a) value for blank is 70.15 kJ/mol and 61.66 kJ/mol for 0.7 % concentration of the inhibitor. Fig. 1 illustrated the Arrhenius plot for the dissolution of mild steel in 1 M HCl with and without inhibitor at various temperatures. The magnitude of E_a show that the chemical adsorption is involved [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 (θ/(1–θ) against log C (Fig. 2) shows a straight line indicating that adsorption from the acid follows the Langmuir adsorption isotherm. 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.

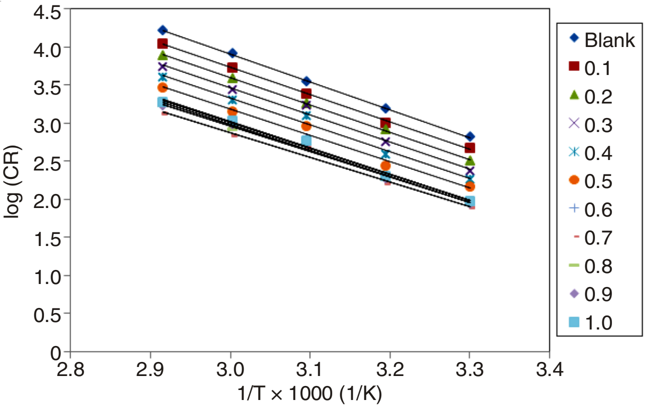

Fig. 1. Arrhenius plots for dissolution of mild steel in 1 M HCl with and without inhibitor at 303 to 343 K

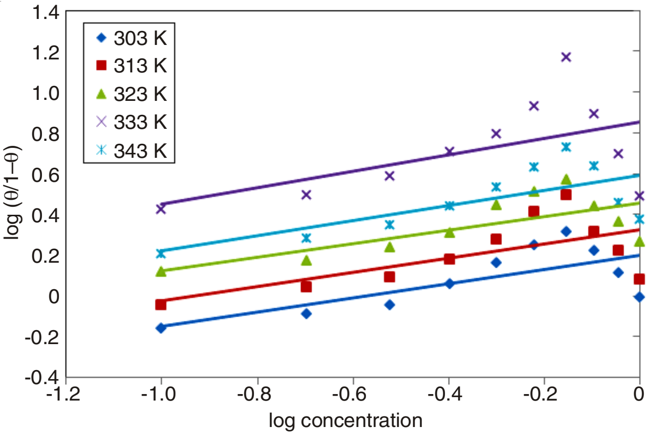

Fig. 2. Langmuir isotherm plots for the adsorption of inhibitor in 1 M HCl solution on the surface of mild steel

Electrochemical impedance method: For the measurements of impendence, the experiments were carried out in a conventional three electrode cell assembly. The working electrode was mild steel specimen with exposed area of 1 cm^2 and the rest being covered with insulation tape. A rectangular platinum foil was used as the counter electrode. To exert uniform potential field on the working electrode, it is designed in a way that the counter electrode is much larger in area compared to working electrode the reference, working and counter electrodes were assembled in position and electrical connections were given. 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 10 MHz. The real and imaginary parts of the impendence were plotted in Nyquist plots (Fig. 3).

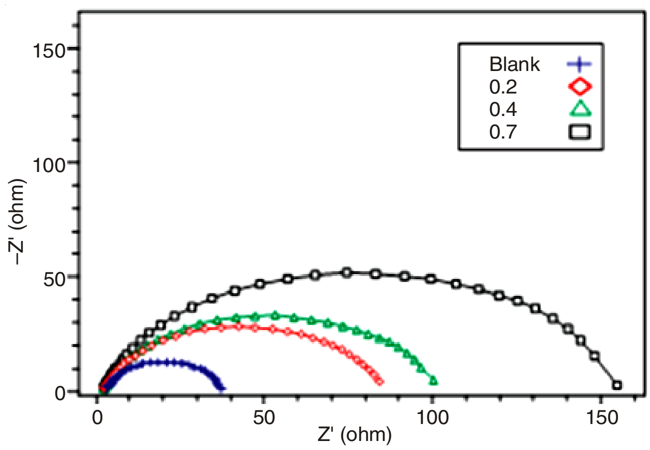

Fig. 3. Impedance diagram for mild steel in 1 M HCl in the presence and absence of different concentrations of the inhibitor

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:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}}$$

where, C_{dl} = double layer capacitance; R_{ct} = charge transfer resistance; f_{max} = frequency at Z″ value maximum.

The values of R_{ct} and C_{dl} are given for difference concentration of inhibitor in Table-4.

TABLE-4
ELECTROCHEMICAL IMPEDANCE PARAMETERS OF EXPIRED CIPROFLOXACIN (EYE/EAR DROPS) IN 1 M HCl

Inhibitor conc. (% v/v)	R_{ct} (Ω cm^2)	C_{dl} (μF/cm^2)	IE (%)
Blank	22.08	45.73	–
0.2	41.65	38.22	46.98
0.4	49.31	30.27	53.76
0.7	73.58	28.61	69.99

Besides, the above method, the inhibition efficiencies were obtained from R_p and R_{ct} values as follows:

$$\text{Inhibition efficiency (IE, \%)} = \frac{R_{ct(i)} - R_{ct}}{R_{ct(i)}} \times 100$$

where, $R_{ct(i)}$ and R_{ct} are the charge transfer resistance in the presence and absence of inhibitor. In the comparison of inhibition efficiency the results obtained in weight loss method were in good agreement with the electrochemical (impedance) method. The compared results are given in Table-5.

TABLE-5
COMPARISON INHIBITION EFFICIENCY OF EXPIRED CIPROFLOXACIN (EYE/EAR DROPS) OF MILD STEEL IN 1 M HCl FROM WEIGHT LOSS, IMPEDANCE TECHNIQUES FOR 0.5 h STUDIES

Inhibitor conc. (% v/v)	Inhibition efficiency (%) for 0.5 h	
	Weight loss	Impedance
0.2	45.02	46.98
0.4	53.26	53.76
0.7	67.23	69.99

Conclusion

The expired non-toxic drug of ciprofloxacin (eye/ear drops) acts as good and efficient inhibitor for the corrosion of mild steel in1 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 ciprofloxacin (eye/ear drops) inhibitor at the optimum concentration (0.7 %) showed maximum efficiency (95.63 %) in 6 h immersion time at 333 K and found sufficient for pickling. The impedance method revealed that charge transfer process mainly controls the corrosion mild steel. The adsorption of the ciprofloxacin (eye/ear drops) on mild steel obeys Langmuir's, adsorption isotherm. The thermodynamic parameters such as activation energy (E_a) and free energy of adsorption (G_{ads}) obtained from this study indicated spontaneous adsorption of inhibitor on the surface of the metal. The inhibitive action of the inhibitor may be due to strong chemisorptions of the active ingredients of the acid extract. Results obtained in weight loss method were in good agreement with the electrochemical (impedance) method.

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