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Study of Inhibition and Adsorption Properties of Expired Pharmaceutical Norfloxcin Drug for Mild Steel Corrosion in Hydrochloric Acid Media

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ABSTRACT

This experiment avoids pollution and recycles of the drugs and also promotes economically benefited inhibitor. In this test expired norfloxcin drug was examined for testing its inhibitive impact on mild steel in 1 M HCl corrosive medium with the weight reduction and electrochemical strategies. The Various parameters were figured, for example, corrosion rate, inhibition efficiency and surface scope. The weight reduction technique demonstrates that the inhibition efficiency increments when inhibitor concentration, immersion period and temperature increments. Acquired outcomes in electrochemical Impedance and weight reduction studies are especially phenomenal concurrence with each other. Thermodynamic parameter like free vitality esteem was negative, which shows unconstrained adsorption of inhibitor on the surface of the mild steel. The adsorption way of the inhibitor on the surface of mild steel was under similarity with Langmuir adsorption isotherm. The mild steel surface morphology, with and without inhibitor was contemplated by utilizing scanning electron microscopy.

Keywords: Mild steel, Acidic medium, Expired drug, Electrochemical impedance, Mild steel, Surface morphology

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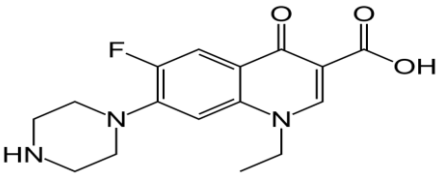
INTRODUCTION

Simple accessibility, minimal cost of mild steel has numerous mechanical applications. It is widely utilized as a part of different enterprises like sugar, petrochemical, paper and material businesses. In most mechanical procedures, the acidic solutions are normally utilized for the pickling, acid cleaning and acid de-scaling and so on. The decreasing consumption rate of metals spares the current assets (minerals) and thus creates practical advantages amid the modern applications. The lifetime of types of materials can be expanded and effective corrosion inhibition will diminish the disintegration of harmful metals from the parts into the environment [1-3]. Hydrochloric acid is the most destructive with the greater part of the common metals and alloys, troublesome of this acid to deal with from corrosion and materials of developments, because of its mechanical applications the corrosion inhibitors turned into a response for corrosion attack which prompt to metal damage and furthermore substitution of the metal. Many reviews on corrosion inhibitors tells that a large portion of the inhibitors are organic compounds N, O and S atoms or with polar groups of N- hetero cyclic compounds. They have essential properties with high electron density, making them the reaction centers, these block the dynamic corrosion destinations by adsorption on the metallic surface and the majority of them are exceedingly poisonous to the individuals and in addition the environment [4-10]. Henceforth substitution by eco-accommodating inhibitors is fundamental. The utilization of pharmaceutical compounds which contains hetero atoms in their structure, high solubility and high molecular weight offers fascinating potential outcomes for corrosion inhibition [11-20]. Few drugs like azosulpha and antimalarial have been accounted for that they are great corrosion inhibitors on mild steel [21-22]. In this review Norfloxcin drug (Eye/Ear Drops) that has been lapsed is chosen for the corrosion inhibition on mild steel in 1 M HCl medium by utilizing weight reduction, electrochemical spectroscopy strategies. Norfloxcin is a non-dangerous pharmaceutical prescription used to counteract or treat a wide assortment of bacterial infections. It has a place with a class of medications known as amino glycoside antibiotics, it contain N-molecule having high electron density to block the active destinations of corrosion [23-29]. The inhibitor is accessible in the brand name of Norflox produced in India by CIPLA LTD it goes about as anticorrosion specialist on mild steel in hydrochloric acid medium.



Norfloxcin

EXPERIMENTAL

Materials

Mild steel strips mechanically cut into size of 5 × 1 × 0.2 cm, with an opening (2 mm) with equal diameter at one end for simple snaring and its composition Mn (0.256%), C (0.034%), Si (0.023%), P (0.004%) and remaining Fe. For electrochemical study, mild steel strips of a similar composition were manufactured by fixing the mild steel 1 cm^2 to a mild steel rod with measurement 1mm utilizing araldite. Every sample was cleaned with various evaluations of emery paper, diminished with acetone, washed with refined water dried and put away in desiccators. Exact weights of the strips were taken utilizing electronic balance. Analar grade HCl and double time distilled water was utilized to set up all solutions. Expired Norfloxcin drug got from restorative shop and utilized for this review with no further cleansing.

RESULTS AND DISCUSSION

Weight loss method

The pretreated sample's initial weights are noted triplicate was inundated in the 100 ml experimental solution (1 M HCl) in existence and absence 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 time of 0.5, 2, 4, 6, 8 and 24 h with help of hooks made of glass after the analysis time the final weights are additionally noted. Likewise examined impact of temperature on the corrosion of mild steel at five distinct temperatures ranges starting from 303K up to 343K. From this strategy the corrosion rate (mils per year), inhibition efficiency (IE%) and surface coverage (θ) were ascertained by utilizing the accompanying formula.

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

Where, WU and WI are weight losses in acids with and without the inhibitors individually.

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

Corrosion parameters obtained from this method are given in Tables 1 and 2. It uncovers that, the efficiency of inhibition expanded with the increase of concentration, immersion period and temperature of the inhibitor it is shown in Figures 1 and 2. The most extreme inhibition efficiency 92.25% was seen in 6 h immersion period at room temperature (303K) with the concentration of 0.9%. This outcome demonstrated that the inhibitor could go about as viable corrosion inhibitor for mild steel in 1 M HCl medium.

Table 1: Influence of concentration of expired norfloxcin (Eye/Ear drops) on the corrosion of 1 M HCl at room temperature (303K) and different time periods

Time	½ h		2 h		4 h		6 h		8 h		24 h	
Inhibitor Conc. (%V/V)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
Blank	590.34		647.62		714.18		733.26		764.23		783.11	
0.1	469.03	40.13	397.60	44.36	313.64	49.26	342.01	53.23	371.02	49.23	394.23	45.26
0.2	433.99	48.15	349.23	52.26	263.12	56.93	289.32	60.31	310.23	58.22	319.21	49.62
0.3	398.95	56.26	306.63	60.35	220.13	64.29	246.32	67.11	272.65	64.71	294.35	56.34
0.4	363.90	61.21	270.95	66.29	175.65	69.01	194.11	72.63	220.32	69.21	239.24	62.52
0.5	336.95	65.23	228.64	68.65	142.31	72.22	164.30	75.84	189.65	73.05	206.98	66.92
0.6	309.99	68.54	199.41	72.26	121.36	74.98	143.21	78.10	168.32	76.21	188.36	69.23
0.7	280.34	72.38	164.82	75.13	104.28	78.56	121.02	83.11	144.11	78.99	163.58	73.03
0.8	258.43	75.12	139.36	77.65	89.67	83.99	102.32	88.61	123.08	83.09	139.55	75.69
0.9	233.12	78.65	117.99	80.36	76.29	86.24	90.08	92.25	111.35	86.19	126.65	80.31
1.0	247.62	74.36	134.87	78.21	84.23	83.06	106.32	87.42	119.32	82.11	135.21	77.26

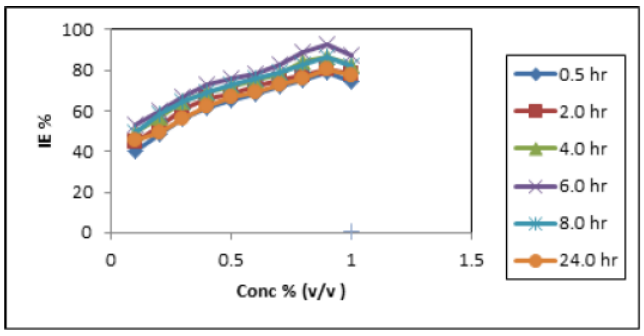


Figure 1: Inhibition efficiency of the norfloxcin inhibitor with different concentrations and different time periods at room temperature (303 K)

Table 2: Effect of temperature on the corrosion of MS in the presence of various concentration of expired norfloxcin (Eye/Ear Drops) in 1 M HCl

Temperature	303K		313K		323K		333K		343K	
Inhibitor Conc. (%V/V)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
Blank	590.34		1386.23		3149.23		6991.23		14681.23	
0.1	469.03	40.13	943.27	44.28	2130.71	50.36	4942.23	55.65	10284.26	48.65
0.2	433.99	48.15	806.01	52.64	2085.61	59.82	4313.21	65.63	9716.54	56.32
0.3	398.95	56.26	755.48	60.98	1798.23	65.32	3298.23	69.36	8847.45	63.21
0.4	363.90	61.21	666.92	67.36	1411.65	72.16	2885.65	74.32	7981.45	68.65
0.5	336.95	65.23	576.23	71.58	1225.19	76.21	2372.61	78.61	6313.60	73.63
0.6	309.99	68.54	422.58	74.36	1081.32	79.45	2054.25	82.65	5647.58	77.65
0.7	280.34	72.38	365.23	77.26	836.65	82.01	1737.54	85.65	4917.23	80.65
0.8	258.43	75.12	336.41	80.13	682.25	85.75	1390.85	87.65	4125.36	82.31
0.9	233.12	78.65	387.65	82.25	785.32	87.06	1586.32	89.31	3421.68	84.65
1.0	247.62	74.36	401.75	78.26	956.32	83.22	1850.23	86.32	4021.10	80.65

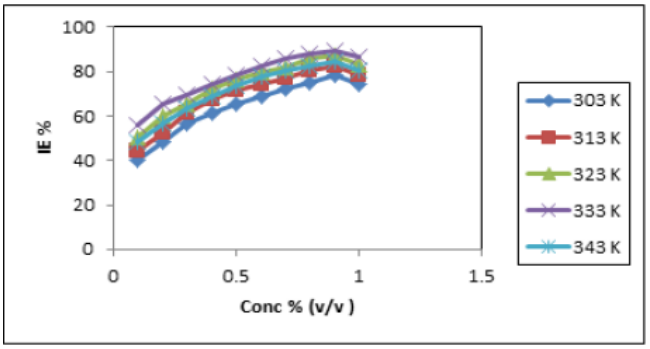


Figure 2: Inhibition efficiency of the Norfloxcin inhibitor with concentrations and different temperatures

Electrochemical impedance strategies

In the estimations of electrochemical impedance, cell same as utilized for potentiodynamic polarization. An AC potential 50 mV was super forced on the unfaltering open circuit potential. The genuine part (Z') and the fanciful part (Z") were measured at different frequencies in the scope of 10 kHz to 10 MHz. The genuine and imagined parts of the impendence were plotted in Nyquist plots. From the plots of Z' versus Z," the charge transfer resistance (Rct) values were obtained. The estimation of (Rt+Rs) relates to the point where the plot cuts z' and at a higher frequency, the distinction amongst Rt and Rs gives the charge transfer resistance Rct values. The double layer capacitance Cdl values were gotten from the equation:

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

Where, Cdl-double layer capacitances, Rct-charge exchange resistance, f_{max}-frequency at Z value maximum.

The inhibition efficiencies were acquired from Rp and Rct values as it takes after

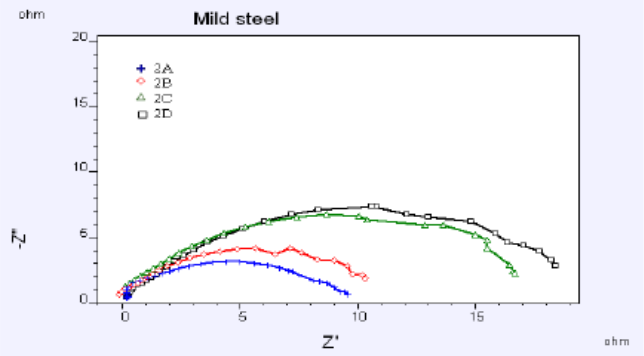
$$\text{Inhibition efficiency} = \frac{R_{ct\ (i)} - R_{ct}}{R_{ct\ (i)}} \text{ x } 100$$

Where, Rct (i) and Rct are charge transfer resistance in the existence and absence of the inhibitor. Nyquist plots shows Figure 3 for the estimations of the genuine part (Z') and imaginary part (Z"). We can conclude the corrosion is mainly controlled by charge transfer process from the semi-circle curves of impedance.

In Table 3, impedance parameters for mild steel in 1 M HCl with and without inhibitor are given. The (Rct) values had increased from 3.43 Ω cm^2 to 15.91 Ω cm^2 and simultaneously the (Cdl) values had decreased from 438-88 μF/cm^2 with increase inhibitor concentrations.

Table 3: Electrochemical impedance parameters for the corrosion on mild steel in 1M HCL containing with and without inhibitor at room temperature

Conc. (%)	R_{ct} (Ωcm^2)	C_{dl} ($\mu F/cm^2$)	IE (%)
blank	3.43	438	-
0.4	8.747	220	60.80
0.7	14.07	121	75.62
0.9	15.39	161	77.64



1A=BLANK, 1B=0.4%, 1C=0.7%, 1D=0.9%

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

Thermodynamic consideration

The activation energy at various concentrations at different temperatures was calculated from the Arrhenius equation:

$$\mathrm{Log}\,\frac{\rho_2}{\rho_1} = \frac{E_a}{2.303 \times R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Where, ρ1 corrosion rate at T1 and ρ2 at T2 temperature. 'R' is a real gas constant. The change in free energy at various temperatures comparison with room temperature for various concentration of inhibitor was ascertained utilizing the accompanying equation:

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

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

Where, Surface coverage (θ), Concentration (C), Temperature (T) and Equilibrium constant (K).

The change in adsorption enthalpy (ΔH) and change in adsorption entropy (ΔS) can be computed by utilizing the accompanying equations:

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

$$\Delta H = E_a - RT$$

For mild steel in 1 M HCl acid with and without the inhibitor, the calculated values of the activation energy (Ea), free energy (ΔGads), the entropy (ΔS) and the enthalpy (ΔH) are shown in activation energy (Ea), free energy (ΔGads), the entropy (ΔS) and the enthalpy (ΔH) are given in the Table 4. Value of Ea for blank is 68.91 kJ/mol and 57.85 kJ/ mol for 0.9% inhibitor concentration, it is clear that addition of the inhibitor leads to the decrease of obvious Ea with a value which is lesser than the value of uninhibited solution which is trailed by the dull decrease with increase in inhibitor concentration which points out the action on the mild steel in the 1M HCl acid takes place through via the chemical adsorption. Negative estimation of the ΔGads points out spontaneous adsorption. Positive values of the enthalpy suggest that high temperature favors complexation process and same in excellent agreement with the increasing stability with temperature. The negative values of ΔSact pointed to a greater order produced during the process of activation. This can be achieved by the formation of activated complex and it represents the association or fixation with the consequent loss in degrees of freedom of system in this process. This also supports supposition of the chemical adsorption.

Figure 4 represents the Arrhenius plot for dissolution of mild steel in the 1 M HCl acid with and without the inhibitor at various temperatures.

Table 4: Thermodynamic data for mild steel in 1 M HCl in the presence and absence of expired norfloxcin (Eye/Ear drops) in 1M HCl for ½ h period

Inhibitor Conc. (%V/V)	Ea (KJ/mol)	- ΔG (KJ/mol)										-ΔS (KJ/mol)	ΔH (KJ/mol)
Temperature		**θ**	**303K**	**θ**	**313K**	**θ**	**323K**	**θ**	**333K**	**θ**	**343K**	**303K**	**303K**
blank	68.91												66.39
0.1	66.95	0.401	14.91	0.442	15.40	0.503	15.89	0.556	16.38	0.486	16.88	0.268	64.43
0.2	66.80	0.481	13.98	0.526	14.44	0.598	14.91	0.656	15.37	0.563	15.83	0.258	64.28
0.3	65.53	0.562	13.78	0.609	14.24	0.653	14.69	0.693	15.15	0.632	15.60	0.257	63.01
0.4	65.14	0.612	13.57	0.673	14.02	0.721	14.47	0.743	14.92	0.686	15.37	0.252	62.62
0.5	63.07	0.652	13.45	0.715	13.89	0.762	14.33	0.786	14.78	0.736	15.22	0.251	60.55
0.6	62.84	0.685	13.36	0.743	13.80	0.794	14.25	0.826	14.69	0.776	15.13	0.243	60.32
0.7	61.89	0.723	13.44	0.772	13.88	0.820	14.33	0.856	14.77	0.806	15.22	0.243	59.37
0.8	58.99	0.751	13.46	0.801	13.91	0.857	14.35	0.876	14.79	0.823	15.24	0.240	56.47
0.9	57.85	0.786	13.67	0.822	14.12	0.870	14.57	0.893	15.02	0.846	15.47	0.227	55.33
1.0	60.63	0.743	12.80	0.782	13.22	0.832	13.64	0.863	14.06	0.806	14.49	0.234	58.11

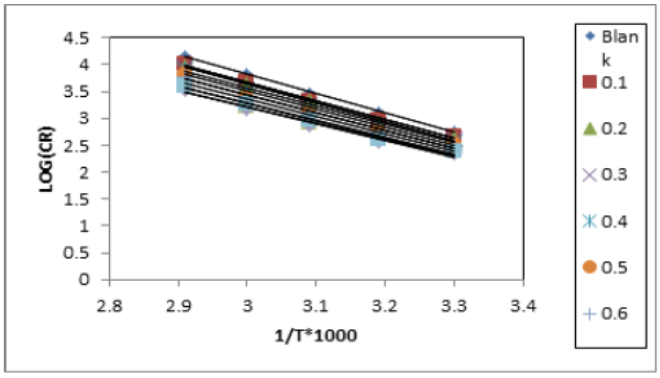


Figure 4: Arrhenius plot for dissolution of mild steel in 1 M HCl with and without inhibitor from 303K to 343 K temperature

Adsorption consideration

Corrosion Inhibition is identified with the adsorption of inhibitor mol on metal surface. Surface coverage (θ) = IE/100. In order to find out the adsorption isotherm for present review, a plot C/θ and C ought to be straight. This is demonstrative the adsorption takes after Langmuir adsorption isotherm. These isotherms give the best fit with the correlation co efficient almost near to (0.9998) unity. In Figure 5 shows a straight line showing that Langmuir adsorption isotherm. Organic molecules contain polar atoms which are adsorbed on metal surface and interact with mutual attraction or repulsion. Because this plot is straight, the angles are never solidarity, Langmuir adsorption isotherm shown as:

$$C/\theta=1/K+C$$

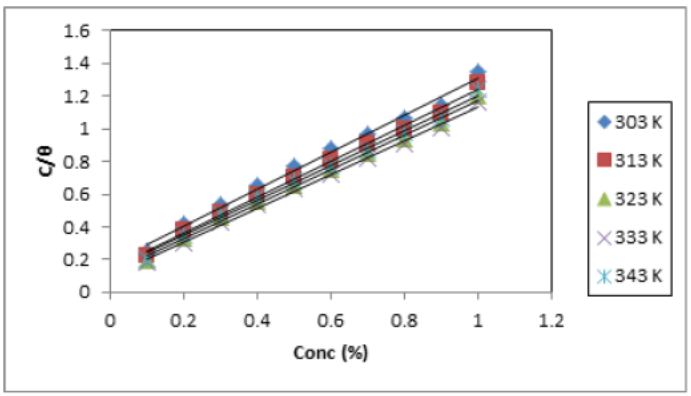


Figure 5: Langmuir isotherm plot for the adsorption of inhibitor in 1 M HCl solution on the surface of mild steel

Morphology examination

The photos of mild steel in acid medium containing without and with the inhibitor are shown in Figures 6 and 7. It is watched that the assault of mild steel within the existence of inhibitor in 1 M HCl is less compared to the nonappearance of inhibitor, because of the presence of adsorbed layer of the inhibitor which blocks corrosion rate of metal evidently. This is ascribed to the contribution of the compound of the interaction of the inhibitor with active sites on surface of metal, thus results in enhanced surface coverage of the metal so that there is decrease in contact amongst aggressive medium and the metal.

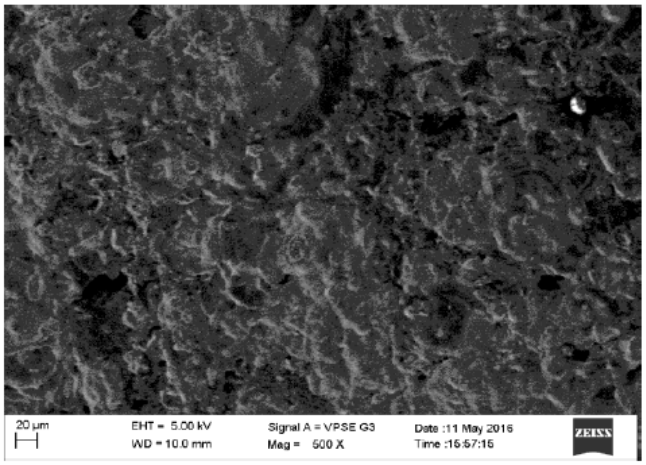


Figure 6: SEM photograph of mild steel immersed in 1 M HCl without inhibitor

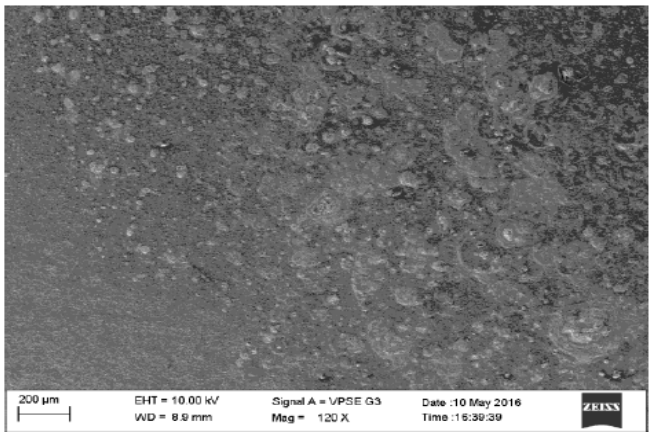


Figure 7: SEM photograph of mild steel immersed in 1 M HCl containing 0.9% of inhibitor

CONCLUSION

The expired norfloxcin (Eye/Ear drops) pharmaceutical drug acts as excellent, efficient and economically benefitted inhibitor on corrosion of mild steel in the 1 M HCl acid medium. The inhibitor efficiency is found to increase with period of immersion, temperatures and concentration. The Inhibitor with concentration (0.9%) showed maximum efficiency (92.25%) in 6 h immersion period at room temperature (303K) and found sufficient for pickling. The chemical adsorption mechanism of the inhibition process was conformation with the data obtained; Langmuir adsorptions were best fitted into the obtained results. Thermodynamic parameters like activation energy (Ea) values also conformed to a chemical adsorption mechanism. Free energy (Gads) of absorption values are –ve which called attention to inhibitor adsorption on surface of metal. The positive values of Enthalpy are proposing high temperature favors inhibition efficiency. The semi-circle bends of impedance points out that corrosion is controlled mostly by charge transfer phenomena. High performance of effect on inhibitive effect upon mild steel surface has confirmed protective film SEM morphology. Acquired outcomes in electrochemical and weight reduction studies are especially fabulous concurrence with each other (Table 5). This experiment promotes eco-friendly and economically benefitted inhibitor and also avoids pollution and recycles the drugs.

Table 5: Inhibition efficiency competition of inhibitor for mild steel in 1 M HCl from weight loss, polarization and impedance for ½ h studies

Conc. (%)	Inhibition efficiency (%)	
	Weight loss	Impedance
0.4%	63.21	60.80
0.7%	69.28	75.62
0.9%	76.65	77.64

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