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An Expired Non-Toxic Drug acts as Corrosion inhibitor for Mild Steel in Hydrochloric Acid Medium

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A B S T R A C T

The inhibitive properties of expired non toxic drug of Asthaline Expectorant (AE) on the corrosion of mild steel strip in 1M hydrochloric acid medium was investigated using weight loss and electrochemical methods. The study revealed that the corrosion rate increases with increases in concentration of the inhibitor, immersion period (time) and temperature. Effect of temperature was investigated at temperature range (303-343 K). Polarization curves shows that this expired non toxic drug is a mixed – type inhibitor in acidic medium. This inhibitor obeys Langmuir, Freundlich and Temkin adsorption isotherm. Surface analysis was performed to emphasis the inhibition efficiency of the studied drug inhibitor. The inhibition activity is due to the adsorption of pharmaceutically active components which are found in the inhibitor AE.

Keywords: Mild steel, Corrosion inhibitor, Acidic medium, expired drug, non-toxic, weight loss.

A R T I C L E   I N F O

CONTENTS

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1. Introduction
Mild steel has many industrial applications because of its easy availability, low cost, uncomplicated fabrication of it into water pipeline [1-3] cooling water system boilers etc. However, they are susceptible to different forms of corrosion inducted by chloride and so on. Hydrochloric acid is the most difficult of the common acids to handle from the stand points of corrosion and materials of constructions. This acid is very corrosive to most of the common metals and alloys. Due to their industrial application, 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 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 scientific studies have been devoted to the subject of corrosion inhibitor for mild steel in acidic media [11-14].Most of commercial inhibitors are toxic in nature; therefore replacement by environmentally benign

2. Materials and Methods
Mild steel strips were mechanically cut into strips of size 5 cm x1 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 cm^2 to a mild steel rod of 1mm 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 Asthaline Expectorant drug obtained

3. Evaluation
3.1 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 ( ) and corrosion rate (mpy) were calculated using the following formula.

$$Inhibition\ Efficiency(\%) = \frac{Wu-Wi}{Wu} X100 \qquad (1)$$

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 AE 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 AE is a non-toxic pharmaceutical compound used as a mucolytic agent prescribed in respiratory infection like bronchitis and brochichial asthma. The inhibitor is available in the brand name of Asthaline Expectorant. Hence, attempts are made to utilize the acid expired AE acts as anticorrosion agent on mild steel in hydrochloric acid medium. Figure 1 shows the structure of AE inhibitor.

from Cipla pharmaceutical company was used to for the study.Fig.1 shows the molecular structure of AE inhibitor.
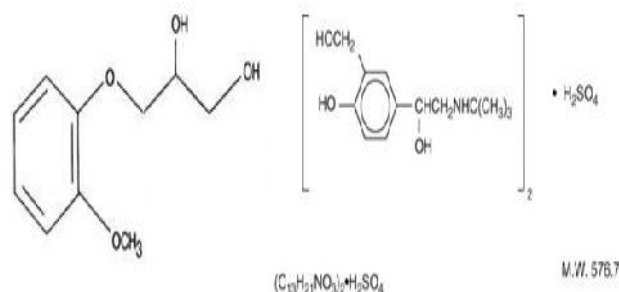

Figure 1: Structure of AE

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

$$Corrosion\ rate(mpy) = \frac{87.6 x weight\ loss(mg)}{density(gmpercc) x area(cm2) x time(hours)} \qquad (2)$$

3.2. 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 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.

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

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

3.3. Electrochemical Impedance methods

For the measurements of impendence, the cell used was same as that used for potentio dynamic 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

impendence were plotted in Nyquist plots. The charge transfer resistance (Rct) values were obtained from the plots of Z' vs. Z". The value of (Rt + Rs) corresponds to the point where the plot cuts z' and at higher frequency the difference between Rt and Rs gives the charge transfer resistance Rct values. The double layer capacitance Cdl values were obtained from the equation (4),

$$C_{d1} = \frac{1}{2\pi f_{max} R_{ct}} \tag{4}$$

Where, Cdl - double layer capacitance
Rct - charge transfer resistance
Fmax -frequency at Z" value maximum.
Besides, the above method, the inhibition efficiencies were obtained from Rp and Rct values as follows

$$\text{Inhibition efficiency} = \frac{R_{P\,(i)} - R_{P}}{R_{P\,(i)}} \times 100 \tag{5}$$

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

4. Results and Discussion

Table1: Corrosion parameter of the inhibitor on mild steel in 1M HCl for different concentrations using weight loss method.

Conc. (% v/v)	CR(mpy)					
	1/2 Hours	2 Hours	4 Hours	6 Hours	8 Hours	24Hours
B	111.90	529.39	156.87	194.48	538.17	114.05
0.1	95.85	406.79	79.97	113.31	346.89	74.16
0.2	84.70	345.50	67.71	102.16	302.31	67.33
0.3	78.02	323.21	60.46	85.45	248.12	58.42
0.4	70.88	273.05	52.94	74.30	230.01	55.63
0.5	62.41	222.90	45.69	66.87	220.11	51.31
0.6	57.95	195.04	40.40	57.58	198.10	45.51
0.7	52.60	167.18	29.26	48.30	181.52	43.74
0.8	46.14	144.89	16.44	35.29	143.49	41.56
0.9	42.13	111.45	8.08	27.86	128.31	36.31
1.0	49.04	128.17	17.27	33.44	152.97	42.49
1.1	53.50	156.03	25.08	42.72	176.79	50.90

4.2. Thermodynamic Consideration

Table 3 shows the calculated values of activation energy (Ea), free energy of adsorption (Gads), the enthalpy of adsorption (H) and the entropy of adsorption (S) for mild steel in 1M HCl with and without AE inhibitor. Figure 3 shows Arrhenius plot of the corrosion rate of mild steel in 1M HCl in the presence and absence of the inhibitor at different temperature. From the table 2 it is evident that the addition of AE inhibitor led to abrupt decrease in the apparent activation energy (Ea) to a value less than that of the uninhibited solution followed by the monotonous decrease with increase in inhibitor concentration indicates that the inhibitory action of AE on mild steel in 1 M HCl occurs via chemical adsorption (Sankarapapavinasam 1989).The negative value of free energy of adsorption (Gads) indicates the spontaneous adsorption and the positive values of enthalpy indicate an endothermic reaction

suggesting that a high temperature favors the complexation process and it is in good agreement with the increase in stability with the temperature. These also support the assumption of chemical adsorption.

4.3. Adsorption Consideration

To explain the nature of the adsorption of the inhibitor, Langmuir's, Freundlich's and Temkin adsorption isotherm were studied. It is generally accepted that the studied expired drugs, compounds inhibit the corrosion process by adsorbing at the metal/solution interface [24]. In this case, the plots of C/ versus C yield a straight line with intercept of (1/ Kads) and with slope approximately equal unity were obtained. The small deviation from unity is generally attributed to the interaction of the adsorbed inhibitor molecules on heterogeneous carbon steel surface. This indicates that, the adsorption of inhibitor on the mild steel

surface in 1M HCl solution follows Langmuir's adsorption isotherm which is showed in the Figure 4. Figure 5 show that the inhibitor also follows the Temkin adsorption isotherm for the chemisorptions of species to form a monolayer on the metal surface. Similar trend was observed in many corrosion inhibitors such as Sehaibani 2000. 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 ( ) was plotted against log C for the inhibitor. The plot of log   Vs log C is shown in Figure 6.

The linearity shows that the adsorption of the inhibitor on mild steel surface follows Freundlich adsorption isotherm.

4.4. Tafel Polarization Studies

The electrochemical parameter obtained from the Tafel polarization studies observed that the i_{corr} values decreased from 0.412 A/cm^2 to 0.182mA/cm^2 with increased concentration of AE ionhibitor showed in the Table 3. The inhibition value is also found to increase from 21.84% to 55.83%. The calculated polarization resistance (R_p) had increased from 67.03 cm^2 to 136.00 cm^2 with increase of inhibition efficiency from 21.11% to 50.71% for the concentration of 0.2% to 0.9%. Figure 7 shows the Tafel polarization behaviours of mild steel in 1M HCL in the presence of AE inhibitor. From the graph it is observed that AE inhibitor behaved like a mixed type of inhibitor (Kann et al 2006).
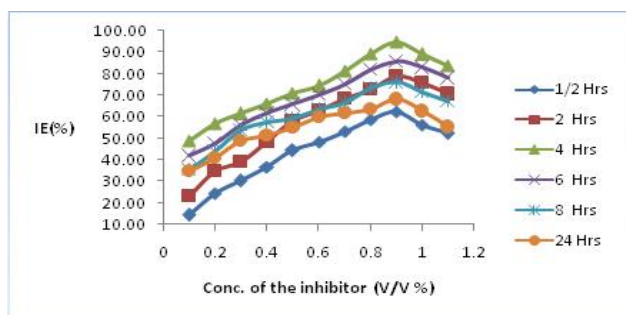

Figure 2: Inhibition efficiency of the AE inhibitor at various temperature in absence and presence of the inhibitor
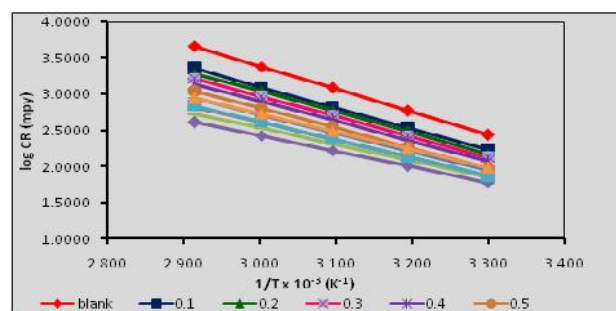

Figure 3: Arrhenius plot for dissolution of mild steel in 1M HCl with and without inhibitor at 303 K to 343 K
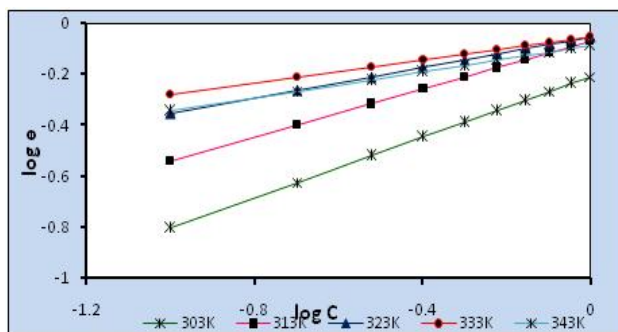

Figure 4: Langmuir's adsorption isotherm plot for dissolution of mild steel in 1M HCl with and without inhibitor at 303 K to 343 K.
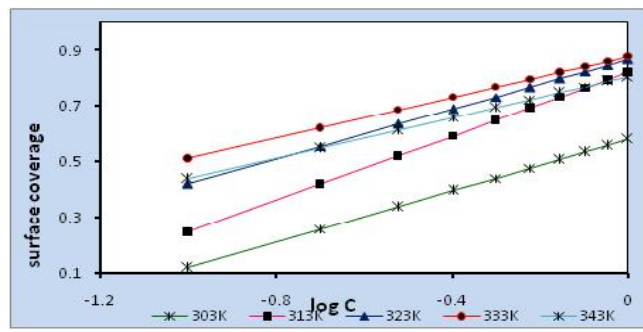

Figure 5: Temkin adsorption isotherm plot for mild steel in 1M HCl with and without inhibitor at 303 K to 343.
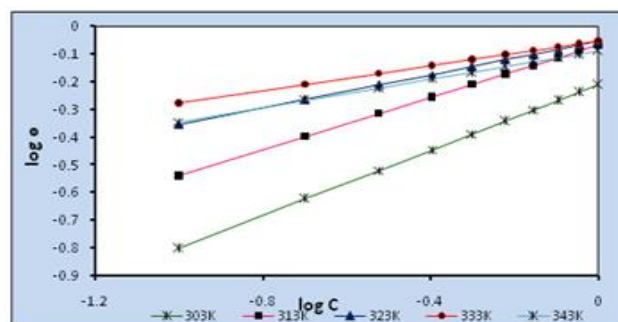

Figure 6: Freundlich's adsorption isotherm plot for mild steel in 1M HCl with and without inhibitor at 303 K to 343K
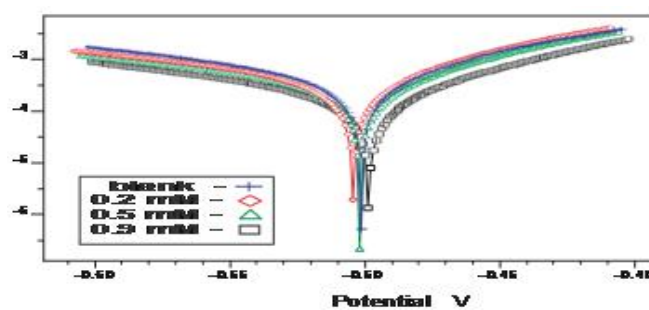

Figure 7: Potentiodynamic polarization curves for mild steel in 1M HCl in the absence and presence of the inhibitor at different concentration of the AE

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

Conc. (%V/V)	Ea KJ/mol	- GKJ/mol					- S KJ/mol	H KJ/mol
		303K	313K	323K	333K	343K		
blank	68.86							
0.1	57.18	11.39	14.02	16.33	18.03	16.85	0.1491	32.84
0.2	56.74	11.29	13.18	15.31	16.50	15.89	0.1253	26.04
0.3	56.21	11.03	13.30	15.01	16.07	15.40	0.1152	23.03
0.4	55.58	11.02	13.58	15.28	15.97	15.26	0.1085	20.84
0.5	54.99	11.26	14.04	15.53	16.41	15.21	0.1028	18.71
0.6	52.18	11.20	14.10	15.66	16.52	15.55	0.1111	21.29
0.7	50.86	11.29	14.60	15.93	16.88	15.76	0.1121	21.33
0.8	48.58	11.55	14.93	16.24	17.25	16.24	0.1170	22.56
0.9	46.27	11.63	15.38	16.79	17.96	16.46	0.1225	23.91
1.0	53.78	10.72	14.09	15.44	16.20	14.45	0.0957	16.72
1.1	56.13	10.08	12.87	14.29	15.24	13.23	0.0868	14.90

Table 3: Tafel parameters for the corrosion of mild steel in 1M HCl containing with and without inhibitor at room temperature

Conc. (%)	E. corr (mV)	I cor. A/cm2	I corr % IE	Ba mV/dec	Bc mV/dec	Rp Ohm	Rp % IE
blank	503.9	0.412		83	125	67.03	
0.2	502	0.322	21.84	75	141	84.97	21.11
0.5	500	0.281	31.80	75	141	95.33	29.69
0.9	496.2	0.182	55.83	73	127	136	50.71

4.5. Electrochemical Impedance Measurement

The impedance parameters for mild steel in 1M HCL with and without AE inhibitor are given in Table 4. It was observed that the charge transfer resistance (Rct) values had increased from 25.67 to 57.10 cm2 and in double layer capacitance (Cdl) the values had decreased from 67 to 527 $\mu F/Cm^2$ with increase in inhibitor concentrations. The semi circle curves of impedance indicate that the corrosion of mild steel is mainly controlled by charge transfer process. Figure 8 shows the Nyquist representation of impedance behaviours of mild steel in 1M HCL with and without AE inhibitor. There is a relatively good agreement between the polarization resistances, obtained from both electrochemical methods.
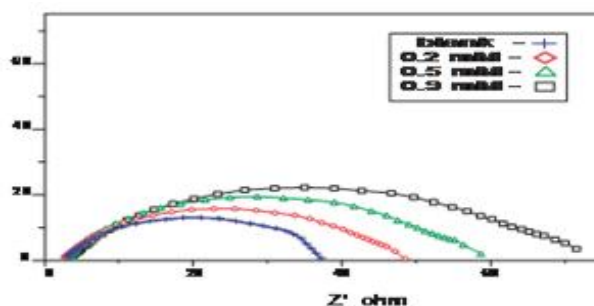

Figure 8: Impedance diagram for mild steel in 1M HCl in the absence and presence of different concentration of the AE inhibitor

4.6. Morphology examination of mild steel with AE inhibitor

The photograph for iron in 1M HCl containing with and without AE inhibitor is given in Figures 9 and 10. It is observed that from the photographs, the attack of mild steel in the presence of AE inhibitor in 1M HCl is very less in comparison with attack in 1M HCl in the absence of the inhibitor. The SEM morphology of the adsorbed protective film on the mild steel surface has confirmed performance of inhibitive effect of inhibitor.
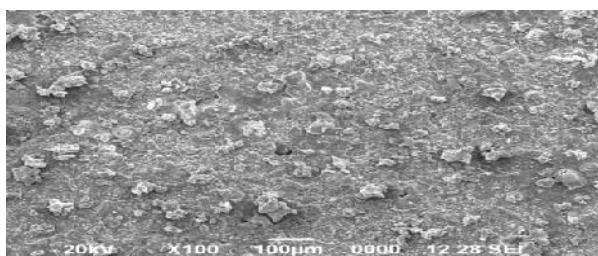

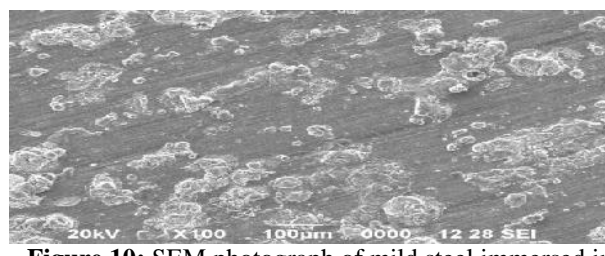**Figure 9:** SEM photograph of mild steel immersed in 1M HCl

Figure 10: SEM photograph of mild steel immersed in 1M HCl containing 0.9% of AE inhibitor

4.7. Mechanism of Inhibition

The AE inhibitor was found to contain Salbutamol sulphate and Guaiphenesin compound having the molecular formulae C13H21NO3.SO4 and C10H14O4 respectively. FTIR spectrum confirms the presence of NH, OH and electrons of aromatic ring. This indicates that the expired non-toxic pharmaceutical compound is involved in complex formation with the metal through its functional groups and electrons of aromatic ring.

4.8. Evaluation of Inhibition Efficiency of AE Inhibitor obtained from Different Techniques

The inhibition efficiency obtained by the Weight loss measurements, polarization and electrochemical impedance techniques are given in the Table 5. The inhibition efficiency of the AE inhibitor studied by various techniques is almost similar. Hence the inhibitor can be effectively used as an anti corrosion agent for static and dynamic conditions.

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

conc.(%)	Rct (cm^2)	Cdl ($\mu F/Cm^2$)	% IE
blank	25.67	670	
0.2	34.66	630	25.94
0.5	43.3	531	40.72
0.9	57.1	527	55.04

Table 5: Inhibition efficiency of AE inhibitor for mild steel in 1M HCl from weight loss, polarization and impedance techniques

Conc. (%)	Inhibition efficiency (%)			
	Weight loss	Polarization		Impedance
		I_{corr}	R_p	
0.2	24.30	21.84	21.11	25.94
0.5	44.22	31.80	29.69	40.72
0.9	62.35	55.83	50.71	55.04

4. Conclusion

The expired non-toxic drug of AE 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 AE inhibitor at the optimum concentration showed maximum efficiency in 6h 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 adsorption of the AE on mild steel obeys Langmuir's, Freundlich's and Temkin adsorption isotherm. 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. The inhibitive action of the inhibitor may be due to strong chemisorptions of the active ingredients of the acid extract. The SEM morphology of the adsorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the AE inhibitor. Results obtained in weight loss method were very much in good agreement with the electrochemical methods

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