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Short Communication

# **Expired Desloratidine Drug as Inhibitor for Corrosion of Carbon Steel Pipeline in Hydrochloric acid Solution**

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The expired desloratidine drug was examined as an inhibitor for carbon steel (X52) corrosion in 1M HCl solution. The inhibition conduct of desloratidine was studied utilizing potentiodynamic polarization and weight loss techniques. The drug efficacy as inhibitor was found to rise by increasing the desloratidine concentration and reduces by increasing temperature. Morphology of the surface and the adsorption isotherm were also studied. The heat of adsorption ( $Q_{ads}$ ) and activation energy ( $E_a$ ) were computed and elucidated. Based on adsorption of desloratidine molecules on carbon steel surface leading to conserve the carbon steel surface from the offensive ions, the inhibition conduct was explicated.

**Keywords:** Reusing – Drug - Desloratidine – Carbon Steel – Corrosion – Inhibitor.

#### 1. INTRODUCTION

Iron is the fourth most widespread element in the Earth's crust. It is utilized to form numerous alloys. One of the utmost common utilized materials in numerous industries is carbon steel (CS). But, it suffers from corrosion in numerous applications which cause loss of millions of dollars [1-3].

Acidic solutions notably of hydrochloric acid solution are immensely utilized in numerous industrial operations like acid pickling, acid cleaning and acid descaling of metals and their alloys [1, 4-5]. Utilizing inhibitors is one of the utmost effective processes for metal preservation against corrosion [6-8]. Numerous researches were executed to reduce carbon steel corrosion in acidic solution [9–12]. But the elevated price and the undesirable effects on the environment are considered disadvantages of inhibitors.

Drugs industry is one of the most important industries in the world. Every year billions of dollars are spent in this industry. Some drugs are returned to these companies because it will be expired, which

causes money losses to this companies. The returned medicines (or expired) containing a treasure trove of chemicals, which can be recycled in another application, like prevention of corrosion [13-22].

The objective of this paper is to investigate the inhibiting conduct of returned medicine (or expired) desloration on the corrosion of carbon steel X52, which utilized in Mustorod petroleum pipe Co. in Egypt, in 1M HCl solution. Potentiodynamic polarization, weight loss, AFM and SEM techniques were utilized in the study.

# 2. EXPERIMENTAL

#### 2.1. Test solutions.

Distilled water and analytical grade chemicals were utilized to prepare all solutions. The desloratidine was obtained from deslorate drug manufactured by Eva Pharma Company in Egypt. Each 5ml from the drug contains 2.5 mg of desloratidine. The volume for the desired concentration was calculated and then the required concentrations were prepared by dilution. Desloratidine has the molecular formula  $C_{19}H_{19}ClN_2$  and molar mass of 310.82 g/mol. The structure of desloratidine, 8-Chloro-11-piperidin-4-ylidene-6,11-dihydro-5H-benzo[5,6]cyclohepta[1,2-b]pyridine, is presented in Fig. (1).

# 2.2. Weight loss experiments.

Carbon steel (CS-X52) specimens (from Mustorod petroleum pipe Co.) which have the following composition: 0.28 % C, 1.4 % Mn, 0.03 % P, 0.03 %S,  $\leq$  0.06 % Np,  $\leq$  0.06 % Ti,  $\leq$  0.06 % V and the residue Fe, were utilized in weight loss experiments. Rectangular coupons from CS-X52 with dimensions of ( $40 \times 14 \times 12$  mm) have been utilized for weight loss experiments. The coupons have been polished mechanically with different grade emery papers, rinsed with dist. H<sub>2</sub>O, acetone and distilled water another time. The coupons have been weighted rightly, subsequently sunken in 1 M HCl acid solution with and without different quantities of desloration at temperatures of 303 K. Afterward 1 day exposure, the coupons were removed, rinsed thoroughly with dist. H<sub>2</sub>O, desiccated subsequently weighted carefully. All experiments in this research have been done under natural aerated statuses [1, 23-24].

#### 2.3 Potentiodynamic polarization experiments.

The working electrode have been made of carbon steel X52 inserted in epoxy holders with area,  $2.24 \text{ cm}^2$ . Prior to utilizing the electrode, it polished with different grades of emery papers until  $2.5 \times 10^3$  grade, degreased with acetone and posteriorly swilled with dist. H<sub>2</sub>O. Pt counter electrode and Hg/Hg<sub>2</sub>Cl<sub>2</sub>/Cl<sup>-</sup> reference electrode, have been utilized in this research. Potentiodynamic polarization experiments were achieved utilizing a PS remote potentiostat with PS6 software at scan rate  $1 \times 10^{-3}$ V/sec, in Benha University in Egypt [1, 25-26].

#### 2.4 SEM and AFM measurements.

The carbon steel X52 coupons have been abraded utilizing several emery papers up to 2500 grit size then keeping for 24 hrs in 1 M HCl in the lack and existent of  $19.3 \times 10^{-5}$  M of desloration. After this inundation time, the coupons have been rinsed with dist. H<sub>2</sub>O, subsequently carefully desiccated and put into the spectrometer. The SEM observation is done utilizing JSM-6510LV, in Mansoura University in Egypt. While the AFM was executed in Nano Technology center, Mansoura University.

**Figure 1.** The structure of desloratidine).

#### 3. RESULTS AND DISCUSSION

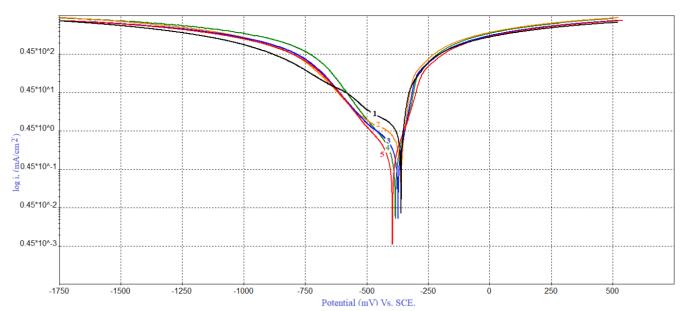
## 3.1. Potentiodynamic polarization.

The influence of different concentrations of desloratedine on Potentiodynamic polarization curves of CS-X52 in 1M HCl solutions; has been studied at a scan rate of  $1\times10^{-3}$ V/sec and presented in Fig (2). The competent electrochemical parameters e.g. corrosion current ( $i_{corr}$ ), cathodic and anodic Tafel slopes ( $\beta_c$  and  $\beta_a$ ), corrosion potential ( $E_{corr}$ ) and the percentage of inhibition efficacy (%IE) are presented in table (1). The inhibition efficacy were calculated by utilizing the next equation [25, 27]:

$$\%$$
 IE =  $(1 - i_{Inh}/i_{Free}) \times 100$ 

where  $i_{\text{Free}}$  and  $i_{\text{Inh}}$  are the corrosion current of CS-X52 electrode in the absence and presence of the examined drug, respectively.

Inspection of table (1) shows that the corrosion current ( $i_{corr}$ ) reduces while the inhibition efficacy % IE rises with increasing the quantity of the desloratedine, pointing out the inhibiting influence of the examined drug toward the corrosion of CS-X52 in the hydrochloric acid solution. The values of corrosion potential not affected upon the addition of increasing concentrations of desloratedine, while the values of cathodic Tafel constants were affected. These findings suggest that desloratedine act as slightly cathodic inhibitor [25, 28-31].



**Figure 2.** Potentiodynamic polarization curves for CS-X52 electrode in 1 M HCl solution containing: 1) 0 2) 3.2 3) 6.4 4) 12.8 5)19.3  $\times 10^{-5}$  M of desloratedine at a scan rate of  $1\times 10^{-3}$  V/sec.

**Table 1.** Corrosion parameters obtained from Potentiodynamic polarization curves of CS-X52 electrode in 1 M HCl solution including different concentrations of desloratadine at 30 °C.

Concentration,	βa	<b>-β</b> c	Ecorr	icorr	%IE	θ
$\mathbf{M}$ mV.		mV.	mV	μA		
	decade <sup>-1</sup>	decade <sup>-1</sup>	(SCE)			
0	41	267	-367	1210	-	-
3.2 ×10 <sup>-5</sup>	25	299	-351	473	60.9	0.609
6.4×10 <sup>-5</sup>	30	178	-364	218	82.0	0.820
12.8×10 <sup>-5</sup>	42	130	-372	188	84.5	0.845
19.3×10 <sup>-5</sup>	56	136	-388	179	85.2	0.852

## 3.2 Weight loss studies.

The influence of increasing the desloratedine concentration on weight loss, inhibition efficacy (%IE) and the extent of surface coverage ( $\theta$ ) for the corrosion of CS-X52 in 1 M HCl solution after 24 hours was presented in Table (2). The equations utilized to calculate %IE and  $\theta$  are presented below [1, 32]:

% IE = 
$$(1 - W_{Inh}/W_{Free}) \times 100$$
  
 $\theta = 1 - W_{Inh}/W_{Free}$ 

where  $W_{Free}$  and  $w_{Inh}$  are the weight loss of CS-X52 in 1 M HCl after 24 hours in the lack and existent of the desloratedine, respectively. Inspection of table (2) shows that the weight loss reduces, whilst inhibition efficacy and surface coverage rise with increasing the concentration of the desloratedine.

<b>Table 2.</b> The influence of the addition of different concentrations of desloratadine on weight loss, % IE
and $(\theta)$ of carbon steel in 1 M HCl solution at 303 K.

Inh. Conc. 10 <sup>-5</sup> × M	Weight loss (10 <sup>-4</sup> × g.cm <sup>-2</sup> )	IE%	θ	
0	197.6	-	-	
3.2	25.9	86.9	0.869	
6.4	23.6	88.1	0.881	
12.8	20.6	89.6	0.896	
19.3	14.4	92.7	0.927	

# 3.3 Adsorption isotherm

Desloratadine's adsorption performance on the surface of carbon steel may be interpreted by seeking a convenient isotherm. The equation that matches our results, gained from measurements of weight loss, is attributable to Langmuir isotherm [12, 33], given by the following equation:

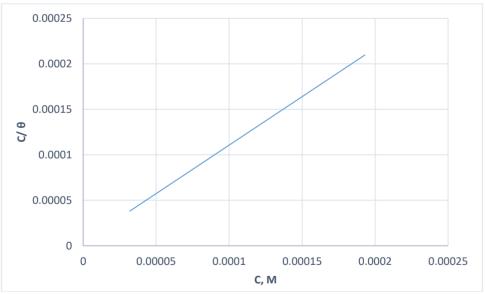
$$C/\theta = 1/K + C$$

where C is desloratedine concentration and K is the equilibrium constant. A plot C/ $\theta$  against C is shown in fig (3). The free energy of adsorption,  $\Delta G^o{}_{ads}$ , can be computed utilizing the next equation [32, 36]:

$$K=1/55.5 \exp \left(-\Delta G^{o}_{ads}/RT\right)$$

where R is the ideal gas constant (8.314 J. mol<sup>-1</sup>.K<sup>-1</sup>) and T is the absolute temperature.

K and  $\Delta G^o_{ads}$  are equal 25×10<sup>4</sup> and -41.43 kJ. Mol<sup>-1</sup>, respectively. The negative value of  $\Delta G^o_{ads}$  implies that the desloratedine's adsorption process on the surface of carbon steel is a spontaneous [32, 34].



**Figure 3.** The relation between C/ $\theta$  and C, M for carbon steel electrode.

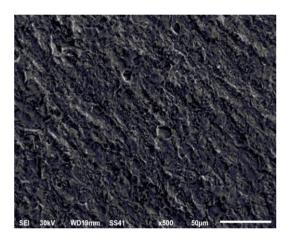
# 3.4 Morphology studies

The surface morphologies served as a perfect indicator of the sharpness of corrosion attack. The SEM and AFM observation of CS-X52 coupons after immersion in 1 M HCl in the lack and existent of  $19.3 \times 10^{-5}$  M from desloratedine are presented in Fig. (4).

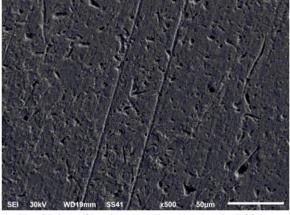
In the lack of the drug, from SEM results, the morphology of CS-X52 coupon in 1 M HCl showed that the surface is badly damaged. But, in the existent of desloratedine the surface of CS-X52 becomes smooth and less.

AFM provides images with atomic or near-atomic-resolution surface topography, able to calculate surface roughness of coupons. The values of roughness average are 978.76 and 124.81 nm, while the root mean square values are 1234.9 and 160.72 nm for CS-X52 coupons after inundation in 1 M HCl in the lack and existent of 19.3×10<sup>-5</sup> M from desloratedine, respectively. The average roughness and the root mean square for the metal surface in 1M HCl have greater values than the protected steel.

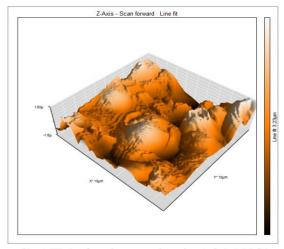
These results prove that the drug formed a protective film by adsorption on CS-X52 surface, leads to protect the carbon steel from the aggressive ions [35-37].



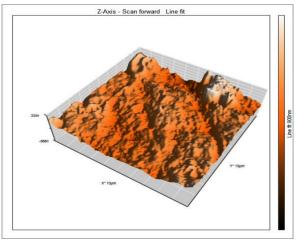
A) SEM after immersion in 1 M HCl only



B) SEM after immersion in 1 M HCl in existence of  $19.3 \times 10^{-5}$  M from desloratadine



C) AFM after immersion in 1.0 M HCl only



D) AFM after immersion in 1.0 M HCl in existence of  $19.3 \times 10^{-5}$  M from desloratadine

**Figure 4.** SEM and AFM for CS-X52 coupons after inundation in 1 M HCL in the absence and presence of the desloratedine.

## 3.5. Thermodynamic calculations

Table 3 shows the impact of rising temperature on the weight loss and corrosion rate of CS-X52 in 1 M HCl in the lack and existence of  $19.3 \times 10^{-5}$  M desloratedine after 24 hours. The data exposes that the desloratidine acts at high temperature as an beneficial inhibitor and the inhibition efficacy diminishes with increasing the temperature.

Utilizing the next Arrhenius type equation, the activation energy  $E_a$  for the corrosion of CS-X52 in 1 M HCl in the lack and existent of  $19.3 \times 10^{-5}$ M desloratedine has been calculated [32, 38-39]:

$$log (R_{T2}/R_{T1}) = (E_a/2.303R)((1/T_1) - (1/T_2))$$

where  $E_a$  is the apparent activation energy, R is the ideal gas constant, T is the absolute temperature,  $R_{T1}$  and  $R_{T2}$  are the corrosion rate which calculated after 24 hours at temperature  $T_1$  and  $T_2$ , respectively. The values of  $E_a$  has been computed and presented in Table (3). This value is more than the blank gained value and less than the threshold value of 80 kJ mol<sup>-1</sup> necessary for the chemical mechanism [32, 40-41]. This indicates that the drug adsorbed by physical mechanism [28].

The heat of adsorption of desloratadine was computed utilizing the next equation [32, 42-45]:

$$Q_{ads} = [T_1 T_2 / (T_2 - T_1)] \times [\log (\theta_2 / (1 - \theta_2)) - \log (\theta_1 / (1 - \theta_1))] \times [2.303 \text{ R}]$$

where,  $\theta_1$  and  $\theta_2$  are the quantity of surface coverage at temperature  $T_1$  and  $T_2$ , respectively.

The computed value of  $Q_{ads}$  has been presented in Table 3 .It has minus value, suggesting that the examined drug adsorbed exothermically on carbon steel surface.

The entropy for the adsorption of desloratidine on CS-X52 surface was computed utilizing the next equation [28, 32]:

$$\Delta S^{o}_{ads} = (\Delta G^{o}_{ads} - \Delta H^{o}_{ads})/T$$

Table 3. presented the computed value of entropy changes, also. From the gained results, the entropy of the adsorption has a minus value.

**Table 3.** The values of adsorption parameters of carbon steel in 1 M HCl and 19.3×10<sup>-5</sup> M desloratidine.

Sol.	wt <sub>1</sub> 293 K	wt <sub>2</sub> 323 K	R <sub>1</sub> 303 K g.cm <sup>-2</sup> .d <sup>-1</sup>	R <sub>2</sub> 323 K g.cm <sup>-2</sup> .d <sup>-1</sup>	θ <sub>1</sub> 303 K	$\frac{\theta_2}{323K}$	E <sub>a</sub> kJ. mol <sup>-1</sup>	-Q <sub>ads</sub> kJ. mol <sup>-1</sup>	$\Delta S_{ads}$ J. mol <sup>-1</sup> .K <sup>-1</sup>
Free	0.4774	1.1145	0.01976	0.04613	-	-	34.5	-	-
Inh.	0.0347	0.1201	0.001436	0.004971	0.9273	0.8922	50.52	17.6	-78.65

# 3.6 Mechanism of inhibition.

From the obtained data, desloratidine adsorption on the surface of carbon steel may be explicated the inhibition conduct. The presence of nitrogen atoms and unsaturated bonds in desloratidine molecule facilitates its adsorption on the carbon steel surface. These adsorbed desloratidine molecules lead to conserve the carbon steel surface from the offensive ions [46-49].

#### 4. CONCLUSIONS

- The addition of desloratidine restrains carbon steel corrosion.
- The inhibition efficacy was found to rise with increasing desloration and reduces with increasing temperature.
- The adsorption of desloratidine on carbon steel surfaces in HCl solution follows Langmuir isotherm.
- The inhibition conduct could be explicated based on adsorption of desloratidine molecules on carbon steel surface leading to conserve the iron surface from the offensive ions.

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