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THE STUDY OF EXPIRED PHARMACEUTICAL DRUG AS CORROSION INHIBITOR FOR CARBON STEEL IN ACIDIC MEDIA USING THE DESIGN OF EXPERIMENT

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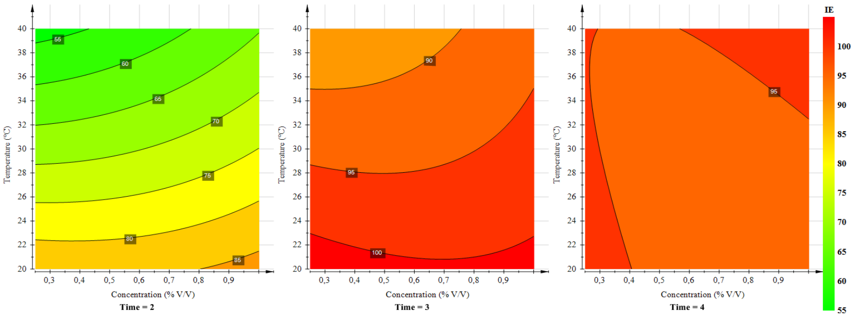

The performance of Bromhexine syrup has been investigated as a corrosion inhibitor for carbon steel (C-steel) in acid medium using the weight loss method and response surface methodology (RSM) of the design experiment. The effect of the concentration of the inhibitor, temperature and exposure time on inhibition efficiency and corrosion rate was studied. The experimental results revealed that expired drug is an effective inhibitor and its inhibition efficiency increases with the increasing concentration to attain a maximum of 97.23 % at 1.0 (v/v %) at 293 K. The thermodynamic parameters show that adsorption reaction on the C-steel surface is spontaneous and exothermic. Moreover, the energy barrier for the corrosion reaction increases in presence of the inhibitor. The individual and interactive effects of these three parameters were optimized for maximum response of inhibition efficiency using response surface methodology (RSM) within the experimental design. Second-order polynomial model was suggested to predict the inhibition efficiency as a function of three variables. The results from RSM gave a best second order polynomial model for the inhibition efficiencies (IE) with high R^2= 0.998 and R^2_{Adj}= 0.997. Moreover, the value of Q^2 greater than 0.9 indicating that the model used is excellent. This confirms a good agreement between experimental observed data and the predicted ones. The optimal inhibition efficiency (IE) obtained by RSM is 101.65 % for a concentration of 0.282 %, temperature of 20.87 ˚C and immersion time of 4 h.

INTRODUCTION

Corrosion is a real challenge that strongly affects many industries. Several options are used to change the chemical environment in order to protect metallic equipments. Among these options, is the introduction of corrosion inhibitors in the industrial circuit. Several inhibitors have been reported in literature, since they have been found as simple solution for protection of metals against corrosion.[1-3]

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In particular, organic compounds containing N, S, O and P atoms, functional groups and multiple liaisons can be used as corrosion inhibitors of steel in different corrosive media. These compounds have a great ability to be adsorbed onto a metal surface owing to their electronic interactions between the metal surface and the inhibitor's polar groups.[4-10] Expired drugs are similar in structure to general organic inhibitors. Many of them have been reported as effective anticorrosion compounds.[11–16] The inhibition efficiency analysis toward the expired drugs can be conducted by several methods such as weight loss and electrochemical routes.[17-19] The weight-loss technique involves recording the difference in weigh of a specimen before and after immersion in a corrosive media over specific time intervals. The obtained data from weight-loss measurements can be inputted in a known engineering formula and thus generate the corrosion rates and inhibition efficiency. In the context of corrosion, several scientific works have used design of experiments software and techniques in order to optimize the parameters of the corrosion inhibition process and predict their responses.[20-23] The Design of Experiments (DoE) is a tool in statistical optimization of analytical approaches can be used in reducing the number of experiments which means less time and reagent consumption. In addition, benefits can also include faster implementation and high efficiency with respect to economical cost than single experiment.[24,25] Within the design of experiments and for optimization purposes, the Response Surface Methodology (RSM) software is widely used. The RSM approach is based on a multivariate technique used in analytical optimization, by which the experimental data can be well fitted by a polynomial equation.[26, 27] For a good statistical prevision, the response function must describe the behavior of a data set in order to attain the best performance of the system. The present work investigates the inhibition efficiency of the expired drug, known as Bromhexine, on the corrosion behavior of carbon steel in acid media using the weight loss method. The collaboration effects of concentration of inhibitor, working temperature and immersion time on the activity of inhibitor have also been examined by response surface methodology (RSM).

MATERIAL AND METHOD

Specimen preparation

The corrosion study was conducted on C-steel metal surface, and its composition is as presented in Table 1. Before any use, all the specimens were polished with different grades of emery paper, degreased with acetone, washed with deionised water and finally dried using a hot air blower. The chemicals reagents used in this study are of analytical grade including HCl (37%), HNO_3 (65%), H_2SO_4 (96%), H_3PO_4 (60%) and $HClO_4$ were purchased from Sigma-Aldrich. The expired drug (Bromhexine) was procured from a local medical practitioner (SAIDAL®). The solutions were prepared by dilution of the commercial acids using distilled water. The expired drug solutions of different percentages from 0.25 to 1.0 % (v/v) were prepared in one normal of acid solution.

Table 1

The chemical composition of C-steel metal.

Element	C	Mn	Cu	Cr	Ni	Si	S	Ti	Co	Fe
Wt%	0.37	0.68	0.16	0.077	0.059	0.023	0.016	0.011	0.009	balance

Weight Loss Method

Loss in weight of samples before and after insertion in acid solution with or without inhibitor was recorded by using a digital balance (± 0.0001 g). The time of the immersion was variable from 1 to 6 h with temperature range from 293 to 323 K. All measurements were done in triplicate, and the average value of the weight loss was noted. The inhibition efficiency (IE), corrosion rate (CR) and surface coverage (θ) were calculated as follows:[21, 22]

$$\mathrm{IE} = \frac{\mathrm{CR}' - \mathrm{CR}}{\mathrm{CR}'} \cdot 100 \tag{1}$$

$$\mathrm{CR} = \frac{\Delta W}{S \cdot t} \tag{2}$$

$$\theta = \frac{\mathrm{IE}}{100} \tag{3}$$

where ΔW is the weight loss, g; S is the total area of the specimen, cm^2; t is the exposure time, h; CR′ and CR are the corrosion rates of C-steel samples in the absence and presence of inhibitor, respectively, g/h·cm^2.

Design of experiments study

The response surface methodology (RSM) is a mathematical and statistical tool for modeling and analyzing processes with different variables. The method allows to evaluate the effects of multiple factors and their interactions on one or more response variables. Hence, the RSM can be used in optimization of corrosion process parameters such as inhibition efficiency (IE) and corrosion rate (CR) by using partial Least Squares (PLS)[28] or Multiple Linear Regression (MLR)[29] for estimating the coefficients of a model. The response of a system can be accurately analyzed by the following quadratic equation (eq. 4):

$$\mathbf{Y} = a_0 + \sum{}_i a_i X_i + \sum{}_i a_{ii} X_i^2 + \sum{}_{ij} a_{ij} X_i X_j + \varepsilon \qquad (4)$$

where: $\mathbf{Y}$ is the matrix of responses; X_i and X_j are the independent coded variables; a_0 is the intercept; a_i, a_{ii} and a_{ij} represent the linear pure quadratic and interaction regression coefficients; and ε is the statistical random error term. In this paper, the experimental design and statistical analysis were conducted by MODDE Software Version 9.1. The individual and interactive effects of the corrosion process on the independent factors were resolved by the standard RSM based on Multiple Linear Regression method. In our case, the process variables investigated in phosphoric acid were concentration of inhibitor (X_1), temperature (X_2) and immersion time (X_3). These three variables were considered at three levels. The settings and the levels of each parameters are given in Table 2. On other hand, the inhibition efficiency ($\mathbf{Y}$) was selected as response function given by the second order polynomial equation (eq. 4).

Table 2

Levels of experimental parameters selected for RSM

Variables	Levels		
	− 1	0	+ 1
X_1 Inhibitor concentration (v/v %)	0.25	0.625	1.0
X_2 Temperature (K)	293	308	323
X_3 Immersion time (h)	2	4	6

It is clear from eq. 4, that the model is a mixture of individual effect of each variable and the interaction effect between them, which makes it more suitable than other models.

RESULTS AND DISCUSSION

Effect of medium acid

Acidic solutions have been widely applied in industry, *e.g.*, in the removal of mill scale from metal surfaces, acid pickling, acid descaling, acidizing oil wells and industrial acid cleaning. In this study, the inhibition efficiencies of bromhexine are mainly applied in different acid media. It can be seen from Fig. 1 that the maximum of Inhibition efficiency was obtained with phosphoric acid. Such results suggest that the high inhibitive performance of bromhexine may be due to the higher bonding ability of various components of the syrup on the carbon steel surface in the presence of phosphoric acid. The Inhibition efficiencies of bromhexine in different acid medium are in the following order: $H_3PO_4 > H_2SO_4 > HClO_4 > HCl > HNO_3$

The lower efficiency of inhibitor observed for HNO_3 at room temperature can be explained by the high aggressive acid environment to this metal compared to that of others.

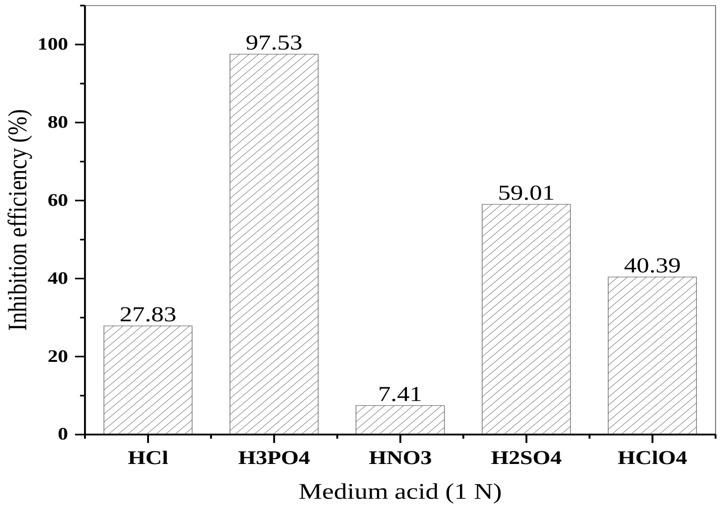

Fig. 1 – Inhibition efficiency as a function of acid media.

Study of the effects of different parameters in phosphoric acid

The effects of bromhexine concentration, temperature and immersion time on corrosion rate (CR) and inhibition efficiency IE (%) of carbon steel are summarized in Table 3. The weight loss method was used to determine all the parameters in 1N acid with or without inhibitor with different immersion periods. As seen in Table 3, since more adsorption takes place on the metal surface, the inhibitor efficiency increases with increasing immersion time. It was found that the maximum inhibition efficiency of 97.23% is reached with 1.0% (v/v) inhibitor during 6 h and at 293 K. It is observed from the Table 3, little change in the values of IE and corrosion rate on increasing the concentration of the inhibitor when the immersion period is constant.

Table 3

Corrosion rate and inhibition efficiency for carbon steel in 1 M H_3PO_4 in the absence and presence of Bromhexine syrup at different temperature and immersion time

Temperature (K)	Time (hrs)	Acid	0.25 %		0.50 %		0.75 %		1.0 %	
		CR’ (g/h·cm^2)	CR (g/h·cm^2)	IE (%)	CR (g/h·cm^2)	IE (%)	CR (g/h·cm^2)	IE (%)	CR (g/h·cm^2)	IE (%)
293	1 h	0.00219	0.00071	67.37	0.00069	68.41	0.00069	68.49	0.00068	68.99
	2 h	0.01067	0.00163	84.74	0.00154	85.59	0.00141	86.74	0.00141	86.79
	4 h	0.05868	0.00265	95.48	0.00259	95.59	0.00219	96.26	0.00202	96.55
	6 h	0.07950	0.00257	96.77	0.0025	96.85	0.00239	96.99	0.0022	97.23
303	1 h	0.01010	0.00538	46.69	0.00538	46.73	0.00538	46.77	0.00537	46.83
	2 h	0.01858	0.00603	67.56	0.00602	67.61	0.00601	67.66	0.00600	67.69
	4 h	0.06659	0.00398	94.03	0.0039	94.15	0.00386	94.21	0.00376	94.35
	6 h	0.08741	0.00398	95.45	0.00396	95.47	0.00392	95.51	0.00388	95.56
313	1 h	0.02264	0.01422	37.17	0.01421	37.23	0.01417	37.39	0.01417	37.41
	2 h	0.03198	0.01819	43.12	0.01354	57.65	0.01167	63.51	0.01117	65.06
	4 h	0.07999	0.00577	92.79	0.0054	93.25	0.00538	93.27	0.00534	93.33
	6 h	0.10081	0.00478	95.26	0.00466	95.38	0.00461	95.43	0.00455	95.49
323	1 h	0.03128	0.02576	17.66	0.02573	17.73	0.02571	17.81	0.02567	17.95
	2 h	0.04062	0.02885	28.97	0.02863	29.51	0.02841	30.07	0.02836	30.19
	4 h	0.08863	0.00895	89.90	0.00883	90.04	0.00799	90.99	0.00784	91.15
	6 h	0.10945	0.00656	94.01	0.00616	94.37	0.00595	94.56	0.0059	94.61

The high IE at the first two hours of reaction can be attributed to the high adsorption rate of the expired medicinal compound. These results show that the expired drug could act as efficient corrosion inhibitor. Without inhibitor, there is rapid enhancement of corrosion rate from 1h to 6 h when working temperature is 293 K, while for higher temperature, the results show a slight increase of CR, this could be referred to the effect of temperature which enhances the adsorption rate of corrosive agent at the first contact time. In the presence of inhibitor, the CR decreases slightly at constant period of immersion in phosphoric acid solution. While on enhancing the exposure time in the presence of the expired drug, the CR increases slowly for 2 h and then decreases up to 6 h, while IE increased substantially after 4h and then slightly increased. This behavior was observed in particular at temperatures of 303, 313, and 323 K. This can be explained by the synergetic effect of both temperature and inhibitor concentration. The thermal activation of the reaction increases the molecular agitation and hence the speed of reactants. Consequently, the mass transfer of organics within the solution is favored as well as the percentage of inhibition efficiency will increase.

It is clear after adsorption equilibrium; the excess inhibitor molecules didn't take part in the inhibition process and became inactive. On the other hand, the less concentration of active compounds present in the inhibitor composition may lead to a limited number of functional groups that bind to the metal steel surface to stop or reduce its corrosion. The corrosion rate was subject to increase when enhancing temperature. As seen from Table 3, as temperature increases, corrosion rate substantially increases and conversely inhibition efficiency decreases for the blank and inhibited samples after 6h of reaction. Typically, CR increases from ~ 0.079 to ~ 0.11 g/h·cm^2 as temperature increases from 293 to 323 K for the acid sample, while with 0.25% inhibitor, CR increases from ~ 0.0026 to ~ 0.0065 g/h·cm^2. The inhibition efficiency after 6h of reaction slightly decreased from 96.77 to 94.01 %. The increase in CR is due to the evolution of hydrogen gas with higher dissolution of metal. So, bromhexine syrup has been found to work properly at lower temperatures than that at higher temperatures.[30]

Adsorption considerations

The nature of metal–inhibitor interaction can be established by the adsorption isotherm. In the current study, the adsorption isotherm was better fitted with Langmuir adsorption isotherm[31]

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{5}$$

where C is the concentration of inhibitor, K_{ads} is equilibrium constant of adsorption, and θ is surface coverage. As seen from Fig. 2, the plot of C/θ against C yields a straight line with correlation coefficient close to unity.

This shows that the dynamical data were well fitted with the Langmuir adsorption isotherm at studied temperature. This result indicates that the drug inhibitor was strongly adsorbed on the metal surface with the formation of a thin layer which promoted anticorrosion. The equilibrium constant of adsorption process (K_{ads}) was calculated from the intercept of C/θ axis. The standard free energy change of adsorption (ΔG_{ads}) and the adsorption constant (K_{ads}) is related by the following expression[32]

$$\Delta G_{ads} = -RT \ln(1000 K_{ads}) \tag{6}$$

where 55.5 is the molar concentration of water in the solution and T is the absolute temperature.

Further, the relation of $\Delta G^{o}_{\text{ads}}$ with enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) was written as follows[33]

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \tag{7}$$

where ΔH_{ads} and ΔS_{ads} are the enthalpy and entropy of adsorption, respectively.

The thermodynamic parameters are collected in Table 4. The negative values of ΔH_{ads} indicate that the adsorption process is exothermic with very high value achieved after 6h of reaction. Moreover, the observed negative value of ΔG_{ads} with the range from − 26.39 to − 36.31 kJ/mol further confirms the spontaneous nature of the adsorption process. This can be explained by the fact that the drug's inhibitor was adsorbed on the surface of metal steel by both physisorption and chemisorption processes.[34] In addition, the entropy change is positive which means an increase in randomness as a result of adsorption of the inhibitor on the metal surface. The values of K_{ads} are positive, which means that the adsorption process is well favored on the metal surface.

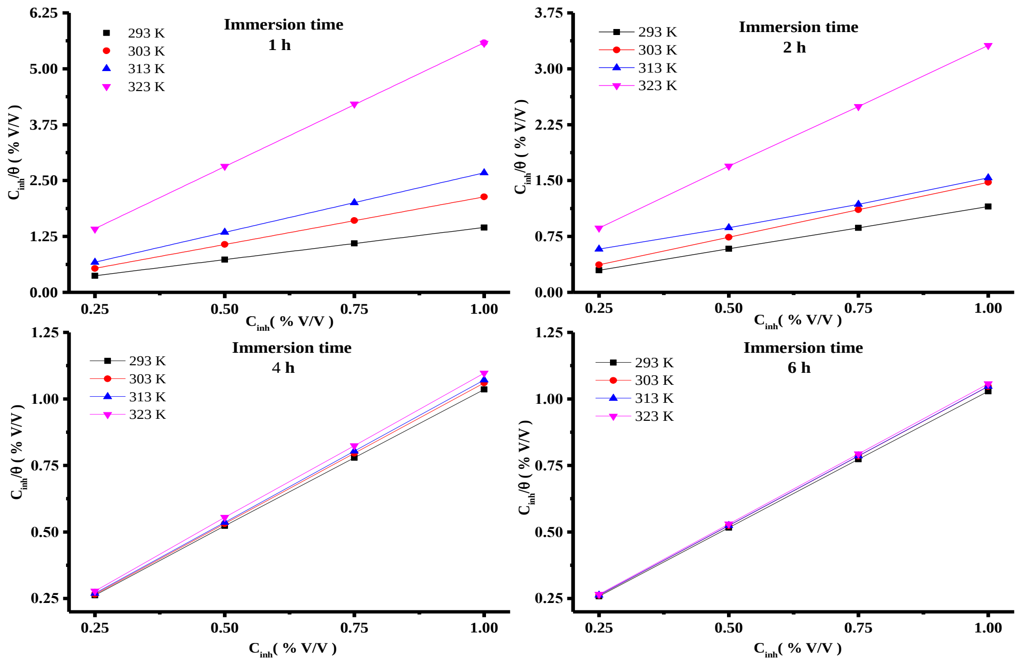

Fig. 2 – Langmuir isotherm for the adsorption of bromhexine on C steel surface in 0.33 M H_3PO_4.

Table 4

Thermodynamic parameters at different times of immersion

Immersion time (h)	Temperature (K)	R^2	K_{ads}	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol K)	ΔG_{ads} (kJ/mol)
1	293	0.999	84.846	-35.25	94.23	-27.64
	303	1	364.545		106.35	-32.26
	313	0.999	132.522		97.94	-30.69
	323	0.999	24.904		84.05	-27.18
2	293	0.999	90.851	-79.20	94.65	-27.81
	303	1	871.319		113.45	-34.45
	313	0.996	4.083		68.87	-21.63
	323	0.999	18.534		81.45	-26.39
4	293	0.999	181.746	-6.51	100.66	-29.50
	303	1	682.775		111.66	-33.84
	313	1	559.071		110.00	-34.43
	323	0.999	138.989		98.43	-31.80
6	293	0.999	448.212	-4.30	108.17	-31.69
	303	1	1824.412		119.84	-36.31
	313	1	1070.597		115.41	-36.12
	323	1	423.999		107.71	-34.79

Thermodynamic activation parameters

The activation energy (E_a) of corrosion process can be determined from the following Arrhenius equation. [35]

$$\mathrm{CR} = A \times exp\left(-\frac{E_a}{RT}\right) \tag{8}$$

where CR is the corrosion rate, R the gas constant, T the absolute temperature, and A the pre-exponential factor. The values of E_a were extracted from the plot of ln(CR) against $1/T$ (Table 7) and the values of activation enthalpy ΔH and activation entropy ΔS can be calculated using the following transition state equation (9).[35]

$$ln\left(\frac{CR}{T}\right)=\left[ln\left(\frac{R}{Nh}\right)+\frac{\Delta S}{R}\right]-\frac{\Delta H}{RT} \qquad (9)$$

where N is Avogadro number and h is Plank's constant. A plot of ln(CR/T) against 1/T gave a straight line. The slope and incept of the straight line give rise to the adsorption values of ΔH and ΔS, respectively (Table 5). The calculated parameters at different concentrations of bromhexine in 0.33 M H_3PO_4 with variable immersion periods are presented in Table 5. It is clearly seen, after each time of immersion and compared to the blank experiment, the activation energy and activation enthalpy substantially increases at the first addition of inhibitor (0.25%) and slightly increases up to 1.0% of bromhexine. This indicated that the energy barrier for the corrosion reaction increases in presence of inhibitor.[36]

Table 5

The activation parameters for bromhexine protection onto carbon steel

Time (h)	Concentration (v/v %)	R^2	E_a (kJ/ mol)	R^2	ΔH (kJ/ mol)	$E_a - \Delta H$ (kJ/ mol)	ΔS (J/mol K)	ΔG (kJ/mol)
1	-	0.893	69.69	0.885	67.13	2.556	-64.27	85.96
	0.25	0.913	92.94	0.908	90.38	2.556	6.30	88.53
	0.50	0.910	93.68	0.905	91.13	2.559	8.66	88.59
	0.75	0.910	93.70	0.905	91.15	2.563	8.71	88.59
	1.0	0.909	94.07	0.904	91.51	2.551	9.85	88.62
2	-	0.970	35.96	0.965	33.40	2.556	-168.09	85.18
	0.25	0.957	76.89	0.954	74.34	2.556	-43.14	87.63
	0.50	0.977	75.63	0.975	73.07	2.556	-48.00	87.86
	0.75	0.969	76.35	0.967	73.79	2.556	-46.18	88.02
	1.0	0.967	75.95	0.965	73.40	2.556	-47.56	88.05
4	-	0.985	11.18	0.976	8.62	2.556	-238.94	82.13
	0.25	0.995	31.61	0.995	29.05	2.556	-195.03	89.13
	0.50	0.985	31.45	0.983	28.89	2.556	-195.83	89.21
	0.75	0.987	33.23	0.984	30.67	2.556	-190.62	89.38
	1.0	0.980	34.87	0.977	32.31	2.556	-185.56	89.47
6	-	0.985	8.66	0.971	6.11	2.556	-244.99	81.57
	0.25	0.970	23.60	0.962	21.05	2.556	-222.16	89.48
	0.50	0.952	22.64	0.939	20.09	2.556	-225.54	89.56
	0.75	0.935	22.91	0.917	20.35	2.556	-224.88	89.62
	1.0	0.912	24.68	0.891	22.12	2.556	-219.37	89.69

Furthermore, the process of metal dissolution is endothermic and non-spontaneous. The $\Delta \underline{S}$ values are higher in presence of inhibitor than that of the blank solutions. This behavior can be referred to the increase in randomness when going from reactants to the activated complex. The mean value of the difference E_a–ΔH was 2.556 kJ/mol for all concentrations. This value is equal to about RT. This can be explained by the fact that the corrosion process proceeded by unimolecular reaction with the evolution of hydrogen gas.[26]

Optimization of inhibition efficiency by RSM

The RSM was used to fit the empirical models to the experimental data obtained in relation to experimental design. For this reason, square polynomial function is employed to give information on the system studied and, consequently, to explore experimental conditions until its optimization. In our case, working temperature, immersion period and inhibitor concentration were defined as independent variables, while the response function was referred to the inhibition efficiency. For this, 17 experimental trials were carried out to obtain the responses of the dependent variables presented in the experimental plan. Table 6, shows the experiments performed for optimization of IE using nonlinear regression analysis. As seen from Table 6, the largest inhibition efficiency was obtained with the expired drug concentration of 0.625 v/v (%), exposure time of four hours, and working temperature of 20°C. The right optimum conditions with highest IE were found by using RSM.

For three factor inputs, the second order polynomial equation is given below (eq.10):

$$IE(\%) = 93.9151 + 1.442x_1 - 6.03801x_2 + 11.631x_3 + 1.43114x_1^2 + 0.691125x_2^2 - 12.1939x_3^2 + 2.1325x_1x_2 - 2.0875x_1x_3 + 7.1875x_2x_3 \quad (10)$$

Table 6

Experimental design of the independent factors and their anticipated estimations of inhibition efficiency

Exp No	Exp Name	Run Order	Concentration (% V/V)	Temperature (°C)	Time (h)	IE (%)
1	N1	12	0.25	20	2	84.74
2	N2	2	1.0	20	2	86.79
3	N3	13	0.25	40	2	52.71
4	N4	3	1.0	40	2	65.06
5	N5	1	0.25	20	6	96.77
6	N6	11	1.0	20	6	92.24
7	N7	15	0.25	40	6	95.26
8	N8	10	1.0	40	6	97.49
9	N9	16	0.25	30	4	94.03
10	N10	17	1.0	30	4	96.35
11	N11	8	0.625	20	4	99.63
12	N12	5	0.625	40	4	89.27
13	N13	6	0.625	30	2	69.64
14	N14	4	0.625	30	6	93.49
15	N15	7	0.625	30	4	94.08
16	N16	14	0.625	30	4	93.98
17	N17	9	0.625	30	4	94.31

It is clear from eq.10, that the inhibition efficiency function is a combination of interactions between second order, first-order and three interlinked effects with a constant. The model was obtained with a confidence level of 95%. Table 7 presents the analysis of variance for corrosion inhibition parameters. The values of R^2 and R^2_{adj} were near unity, which means that the data was better fitted with the model. The Q^2 value is greater than 0.9 indicating that the obtained model is excellent. Moreover, for a good model, the difference between R^2 and Q^2 should be smaller than 0.3. The residual standard deviation (RSD) for the model was about 0.772. The low value of RSD, confirmed that the predicted inhibition efficiency was in a good agreement with experimental one. The values of P were used to check whether or not each the interactions among the variables are significant. From the results obtained by the variance analysis, any probability value smaller than < 0.05 confirmed the validity of the suggested model.

Table 7

Variance analysis of corrosion parameters for inhibition efficiency

IE	Coeff. SC	Std. Err.	*P*	Conf. int(±)
Constant	93.9151	0.330174	1.75272E-015	0.780748
Con	1.442	0.244006	0.000593657	0.57699
Temp	-6.03801	0.244006	4.48709E-008	0.57699
Tim	11.631	0.244006	4.67846E-010	0.57699
Con*Con	1.43114	0.471405	0.0189563	1.11471
Temp*Temp	0.691125	0.471405	**0.186051**	1.11471
Tim*Tim	-12.1939	0.471405	3.29972E-008	1.11471
Con*Temp	2.1325	0.272807	0.00010564	0.645094
Con*Tim	-2.0875	0.272807	0.000120956	0.645094
Temp*Tim	7.1875	0.272807	2.90508E-008	0.645094
N = 17 DF = 7	Q^2 =0.979 R^2 =0.998 R^2_{Adj}. =0.997	Cond. no. =4.438 RSD =0.7716 Conf. lev. =0.95		

The results of Table 7 show that most of the interaction and individual influences of factors are significant and must be considered. It is observed from the analysis of variance, that only the second order effect of temperature is insignificant because the *P*-value is higher than (0.05); indicating there is no inter-correlation with the second order interaction of temperature. Based on analysis of the polynomial coefficients, the results show that the pure effect of (Tim*Tim), (Temp*Tim), Tim and Con is the most influential and greater than that of the effect of (Con*Temp), (Con*Tim), (Con*Con), and Con.

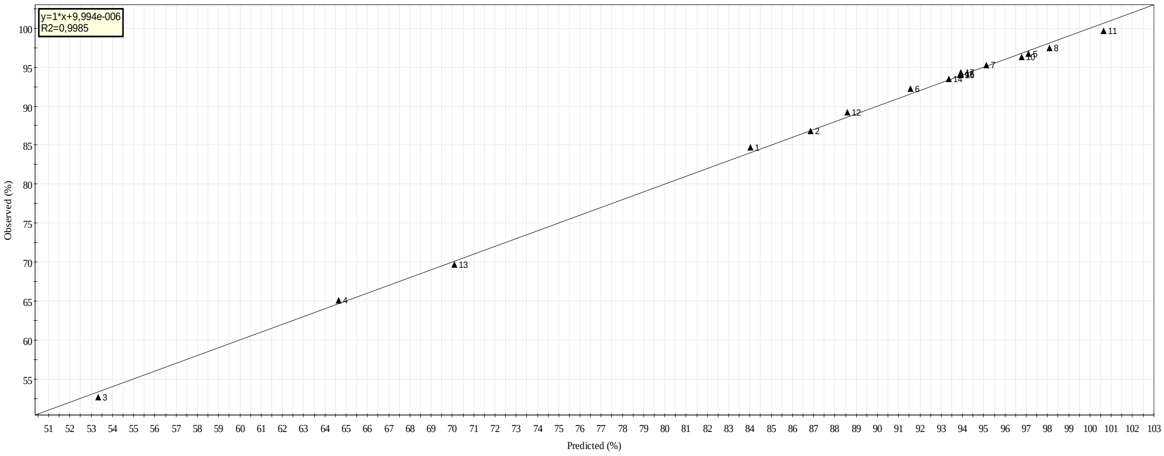

Fig. 3 – Performance of the second order mathematical model.

The relationship between predicted and experimental inhibition efficiency is shown in Fig. 3. As seen in Fig. 3, the plot gives a straight line which means that the design model is suitable to predict the inhibition efficiency of the expired drug for corrosion process. In order to localize the optimum zone of the IE, the surface plot of IE with contour plots have been plotted (Figs. 4, 5). Since the inhibition efficiency was affected by the process variables, so it is necessary to investigate them by construction a contour plot as a function of two independent variables (working temperature and concentration of inhibitor) at different periods of immersion.

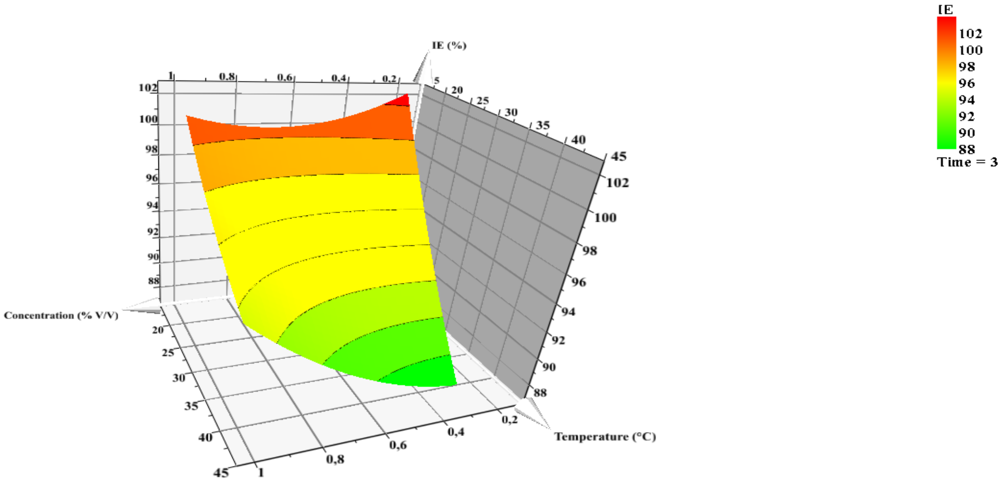

Fig. 4 – Surface plot of inhibition efficiency at optimum conditions.

The surface and contour plot for inhibition efficiency are shown in Figs. 4 and 5, respectively. As seen in Figs. 4 and 5, the inhibition efficiency increases with decreasing temperature for a given inhibitor concentration. This can be attributed to the physical adsorption of the inhibitor on the surface of the carbon steel and thereby reducing the corrosion rate. We take into account the interactive effects between the variables, the optimum conditions for maximum inhibition efficiency were obtained by solving the second order polynomial equation (10). As a result, a high percentage of inhibition efficiency (101.65%) was obtained with concentration of 0.282% v/v, 20.87°C and 4 h of immersion time.

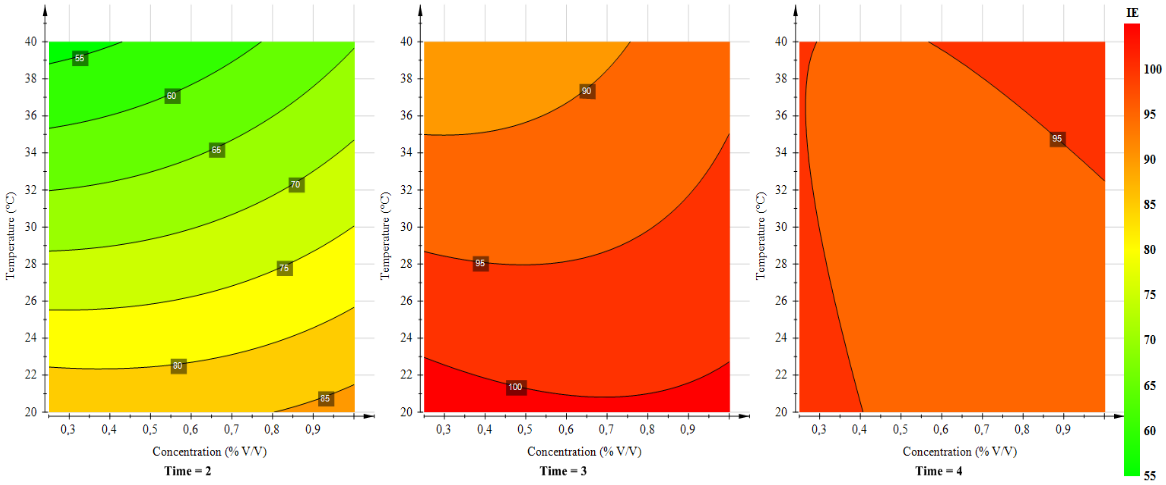

Fig. 5 – Contour plots at various times studying the effect of temperature versus concentration on the inhibition efficiency.

CONCLUSION

In this paper the expired bromhexine syrup was used as inhibitor for carbon steel corrosion in phosphoric acid solution. The study was conducted by using a weight loss method and the surface response methodology. The inhibition efficiency increases with increasing the concentration of the inhibitor. While the temperature has the inverse effect, so IE decreases when temperature increases. The performance of inhibitor comes from the formation of protective layer on the surface of the metal. The study shows also that the adsorption of the examined drug obeys Langmuir's adsorption isotherm at all temperatures, and the process of adsorption is exothermic and spontaneous in nature. According to the values of ΔG^{o}_{ads}, the pharmaceutical drug was adsorbed onto the metal surface by both physisorption and chemisorption processes. The link between the three studied parameters was also investigated by using the response surface methodology. The results revealed a best second order polynomial model was obtained for the inhibition efficiency with high correlation coefficients. The Q^2 values greater than 0.9 confirmed that the model used is excellent. All of these coefficients are an index of a good agreement between observed data and the predicted ones. The optimal inhibition efficiency obtained by RSM is 101.65%.

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