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ENHANCING CORROSION RESISTANCE OF CARBON STEEL USING EXPIRED PHARMACEUTICAL DRUG SULPUREN: A RESPONSE SURFACE METHODOLOGY APPROACH IN ACIDIC MEDIA

Benhadria NACEUR,[a, b] Tarik ATTAR,[a,c,*] Abbes BENCHADLI[c]
and Esma CHOUKCHOU-BRAHAM[c]

[a] Higher School of Applied Sciences of Tlemcen, ESSA-Tlemcen, BP 165 RP Bel Horizon, Tlemcen 13000, Algeria
[b] Laboratory of chemistry of materials (LCM), University of Oran 1 Ahmed Ben Bella, Oran, Algeria.
[c] ToxicoMed Laboratory, University of Abou Bekr Belkaid, B.P.119, Tlemcen, 13000, Algeria

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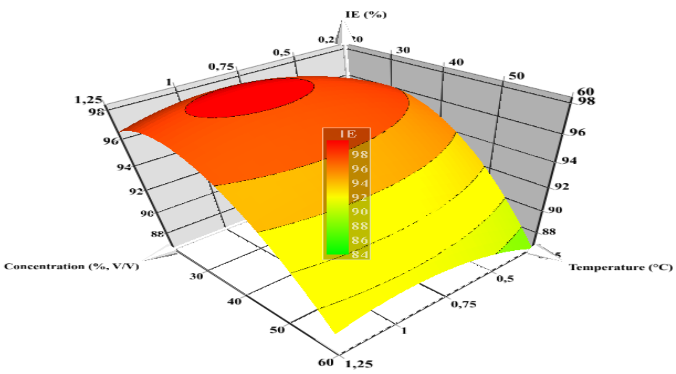
The anticorrosion potency of Sulpuren drug for carbon steel in a 0.5 M H_2SO_4 solution was studied using the weight loss method and response surface methodology (RSM). From the weight loss results, the inhibition efficiency (IE) increased when increasing Sulpuren's concentration and decreased at elevated temperatures. The data reveal that at a constant concentration of Sulpuren drug, as the temperature increases from 293 K to 333 K, the corrosion rate of carbon steel generally increases. At the highest concentration, 1.25% v/v, the protection reaches 96.03% after 6 hours of soaking at 303 K, and the maximum inhibition efficiency of 100% was achieved after 72 hours with a Sulpuren concentration of 1% v/v. The anticorrosion activity of Sulpuren drug was interpreted based on its adsorption on the carbon steel surface. The adsorption occurred according to the Langmuir isotherm model. The inhibition process was conducted by a complex mechanism involving mixed-mode interactions, including both physical and chemical adsorption, taking place simultaneously between the inhibitor molecules and the metal surface. The process of corrosion is entropically favorable, and the corrosion process follows a unimolecular reaction pathway. The second-order polynomial statistical model for corrosion IE formed using RSM is found to be favorable. It is shown that this model could successfully explain the experimental data with R^2 and R^2_{adj} values close to unity and at a 95% confidence level.



INTRODUCTION

Corrosion inhibitors are chemical compounds designed to protect metallic surfaces from the damaging effects of corrosion. When applied to metal surfaces, these inhibitors form a protective layer that prevents or reduces the corrosion process.[1] The primary function of corrosion inhibitors is to inhibit the chemical reactions that lead to the breakdown of metal structures, thereby extending the lifespan of the materials and minimizing maintenance costs.[2] These compounds

* Corresponding author: att.tarik@gmail.com / tarik.attar@essa-tlemcen.dz

can be employed in various industries, including oil and gas, manufacturing, construction, and transportation, to safeguard equipment and infrastructure from corrosion-related deterioration. Numerous inhibitors have been reported in the literature as effective solutions for safeguarding metals against corrosion.[3–6] Specifically, organic compounds containing nitrogen (N), sulfur (S), oxygen (O), and phosphorus (P) atoms, functional groups, and multiple bonds have been identified as potential corrosion inhibitors for steel in various corrosive environments.[7] These compounds exhibit a strong affinity for adsorption onto metal surfaces due to electronic interactions between the metal surface and the polar groups present in the inhibitors.[8–11]

The effectiveness of corrosion inhibitors depends on various factors, including the corrosive environment, pH, temperature, immersion time, metal composition, and the concentration and chemical properties of the inhibitor.[12,13] Exploring adsorption isotherms provides invaluable insights into the interaction between adsorbed molecules and the metal surface, revealing two fundamental types of interaction: physical and chemical adsorption. The effectiveness of the organic thin layer established post-adsorption hinges on factors such as electron density surrounding heteroatoms, the count of adsorption-active centers within the molecule and their charge density, as well as the molecule's size and structure.[14,15] Expired drugs share structural similarities with typical organic inhibitors. Numerous studies have reported their effectiveness as anticorrosion compounds.[16–22] In the field of corrosion research, numerous scientific studies have employed the design of experiments (DoE) software and techniques to optimize corrosion inhibition process parameters and predict their corresponding responses.[23–26]

The Design of Experiments is a statistical method used to plan, conduct, and analyze experiments efficiently. It involves systematically varying input factors or parameters of a process to study their effects on the output or response variable. It is widely applied in various fields, including engineering science and industry, as it helps to improve efficiency, reduce costs, and enhance product quality. RSM is a multivariate technique employed in analytical optimization that allows experimental data to be effectively fitted with a polynomial equation.[27,28] This approach aids in modeling and understanding complex relationships between variables, enabling researchers to identify optimal conditions and achieve desired outcomes efficiently.[29,30] To achieve accurate statistical predictions, the response function must accurately describe the behavior of a given data set, thereby optimizing the performance of the system.

This research delves into the inhibitive potential of SULPUREN, an expired pharmaceutical drug, in mitigating the corrosion of carbon steel within acidic environments. The weight loss technique was utilized to evaluate the inhibition process. Furthermore, the interactive impacts of inhibitor concentration, operational temperature, and immersion duration on inhibitory performance were probed using response surface methodology (RSM).

MATERIAL AND METHOD

Specimen preparation

Analytical-grade chemical reagents, including HCl (37%), HNO_3 (65%), H_2SO_4 (96%), H_3PO_4 (60%), and $HClO_4$ (70–72%), were purchased from Sigma-Aldrich for this study. The expired pharmaceutical drug SULPUREN®, obtained from a local medical practitioner (SAIDAL®), was also utilized. Commercially available carbon steel sample is employed as working specimen with the following element composition (wt%): C (0.37), Mn (0.68), Cu (0.16), Cr (0.077), Ni (0.059), Si (0.023), S (0.016), Ti (0.011), Co (0.009), with the remaining portion being Fe.

Before any experimentation, all specimens underwent meticulous preparation. This process included polishing with various grades of emery paper, degreasing with acetone, washing with deionized water, and final drying using a hot air blower. To prepare the solutions, the commercial acids were diluted with distilled water. Different percentage solutions of the expired drug, ranging from 0.25% to 1.25% (v/v), were then prepared in a one normal acid solution.

Weight Loss Method

The main approaches to studying corrosion are gravimetric (weight-loss method) and electrochemical methods, which are not discussed in this work. The former technique is one of the most common methods to quantify corrosion rates (CRs), as it is a simple technique that does not involve measurements of currents or voltages.[31] The weight loss method provides a more accurate depiction of uniform corrosion compared to electrochemical techniques, as they closely mirror real-world experimental conditions. This alignment ensures the reliability and practicality of the results obtained.[9,27] Several research studies utilizing the gravimetric method have been published. These studies delve into the effectiveness, mechanisms, and outcomes of weight loss achieved through this method, providing valuable insights into its applications and implications for managing body weight.[32–35] One of the key advantages of the weight-loss method is its simplicity and ease of implementation. It does not require sophisticated equipment or specialized expertise, making it accessible to researchers across various disciplines. Additionally, it provides a direct and tangible measure of corrosion damage, making it particularly suitable for comparative studies and practical applications.[36]

This method is used to evaluate the corrosion rate of a metal sample by measuring the loss of its mass over a period of exposure to a corrosive environment. In a typical procedure, a clean and pre-weighed metal specimen is immersed or exposed to the corrosive medium, and after a predetermined time, the sample is removed, cleaned, and re-weighed. The difference in weight before and after exposure is used to calculate the corrosion rate and inhibition efficiency. The change in weight of samples before and after immersion in the acid solution, with or without the inhibitor, was measured using a digital balance. The immersion time varied from 1 to 6 hours, with temperatures ranging from 293 to 333 K. All measurements were performed in triplicate, and the average weight loss value was recorded. The inhibition efficiency (IE), corrosion rate (CR), and surface coverage (θ) were calculated according to the following formulas:[37–39]

$$\mathrm{IE} = 100 \times (\mathrm{CR}' - \mathrm{CR}) / \mathrm{CR}' \qquad (1)$$

$$\mathrm{CR} = \Delta W / (S \times t) \qquad (2)$$

$$\theta = \mathrm{IE} / 100 \qquad (3)$$

In the above equations, ΔW represents the weight loss in grams (g), S denotes the total area of the specimen in square centimeters (cm²), t stands for the exposure time in hours (h), CR' and CR are the corrosion rates of carbon steel samples in the absence and presence of the inhibitor, respectively, measured in grams per square centimeter per hour (g/cm·h).

Design of experiments study

Response Surface Methodology (RSM) is a mathematical and statistical approach used for modeling and analyzing processes that involve multiple variables. This method inhibition efficiency (IE) and corrosion rate (CR), by employing techniques like Partial Least Squares (PLS)[40] or Multiple Linear Regression (MLR)[41] enables the assessment of the effects of various factors and their interactions on one or more response variables. Consequently, RSM can be employed to optimize corrosion process parameters, such as to estimate model coefficients.

The experimental design and statistical analysis in this study were performed using MODDE Software Version 9.1. The standard Response Surface Methodology (RSM) based on the Multiple Linear Regression method was employed to decipher the individual and interactive effects of the corrosion process on the independent factors. In our study, we investigated the process variables in phosphoric acid, namely the concentration of inhibitor (X1), temperature (X2), and immersion time (X3). Each of these three variables was examined at three different levels, as shown in Table 1. The inhibition efficiency (Y) was chosen as the response function, which was represented by the second-order polynomial equation (eq. 4). The equation demonstrates a combination of the individual effects of each variable and the interaction effects between them, making it a more suitable model than others for our analysis

$$Y = a_0 + \sum_i a_i X_i + \sum_i a_{ii} X_i^2 + \sum_{ij} a_{ij} X_i X_j + \varepsilon \qquad (4)$$

where: 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.

Table 1

Levels of variables and factors considered for experimental design

Factors	Levels		
	–1	0	+1
Concentration (% V/V)	0.25	0.75	1.25
Temperature (°C)	20	40	60
Time of immersion (h)	2	4	6

RESULTS AND DISCUSSION

Effect of Acid Medium

According to the data presented in Table 2, it is evident that Sulpuren is most effective in inhibiting carbon steel corrosion when used in combination with sulfuric acid. This is because the combination of Sulpuren and sulfuric acid achieves the highest inhibition efficiency compared to other acid media. The observed trend in inhibition efficiencies across various acid media suggests that the inhibitive performance of Sulpuren is influenced by the nature of the acid used. It is worth noting that sulfuric acid provides the most conducive environment for enhancing the bonding capability of the various components present in Sulpuren on the carbon steel surface.

Table 2

Variation of inhibition efficiency with different acid medium for carbon steel (SULPUREN® drug 1% (V/V) for 4 h and at 303 K)

Acidic Medium	HNO_3	HCl	$HClO_4$	H_3PO_4	H_2SO_4
IE (%)	10	19	24	27	93

This enhanced bonding allows Sulpuren to form a strong protective layer on the metal, effectively preventing corrosion. These results indicate that the performance of this drug as a corrosion inhibitor is less effective in hydrochloric acid, nitric acid, perchloric acid, and phosphoric acid compared to sulfuric. These results highlight the importance of the specific acid medium in which the corrosion inhibition is being assessed and the potential of Sulpuren to provide excellent protection under certain conditions.

Effect of immersion time at different concentrations of Sulpuren

The immersion time is crucial in determining how well a substance can protect metal surfaces from corroding. In Fig. 1, we can see the effectiveness of Sulpuren in preventing corrosion at different amounts and soaking times in sulfuric acid. Inhibition efficiency describes how well the expired drug can shield carbon steel from rusting. Upon examining the data, we notice a consistent trend: the longer the metal stays immersed in Sulpuren and the higher the Sulpuren concentration, the better it guards against corrosion. For instance, at the lowest Sulpuren concentration of 0.25% v/v, the protection starts at 43.09% after one hour of immersion and rises to 95.39% after six hours. When the concentration of inhibitor increases to 0.5% v/v, it results in a noticeable improvement in protection. An inhibition efficiency of 43.27% was achieved after 1 hour of reaction, and after 6 hours of reaction, an inhibition efficiency of 95.53% was obtained. Similarly, at a concentration of 0.75% v/v, protection continues to improve, ranging from 43.49% to 95.61%. At the highest concentration tested, 1.25% v/v, the protection reaches 96.03% after six hours of soaking. However, it becomes apparent that protection levels start to level with increasing concentration and soaking time, suggesting that there may be an optimal point beyond which further increases do not significantly enhance protection. Furthermore, the findings reveal that a maximum inhibition efficiency of 100% was achieved after 72 hours of contact time with a Sulpuren concentration of 1% v/v. This suggests that after 72 hours of exposure to sulfuric acid with this specific Sulpuren concentration, the surface of the carbon steel is completely shielded from corrosion.

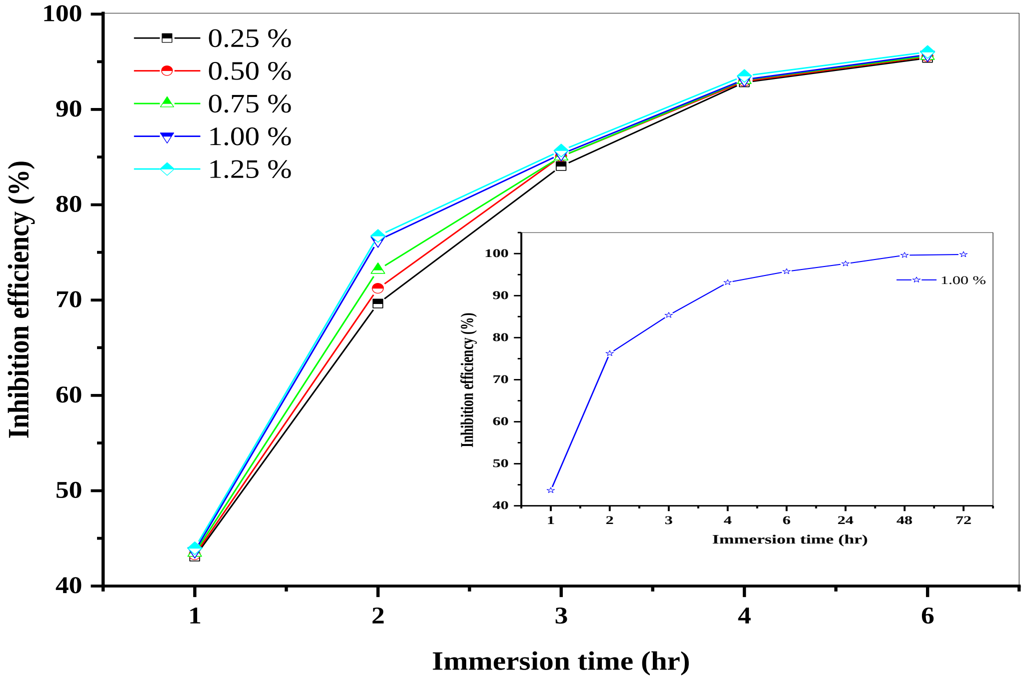


Fig. 1 – Variation of inhibition efficiency with time for carbon steel immersed in 0.5 M H_2SO_4 solution with expired SULPUREN® drug as inhibitor at 303 K.

Effect of concentration and temperature on the corrosion rate

The experimental results reveal important insights into the behavior of the Sulpuren drug as a corrosion inhibitor for carbon steel. The data from Fig. 2 indicates that as the concentration of Sulpuren drug increases from 0.25% to 1.25% v/v, the corrosion rate of carbon steel tends to decrease. This suggests that higher concentrations of the expired drug are more effective in reducing the corrosion rate, making it a promising corrosion inhibitor. Furthermore, the inhibition efficiency of the drug shows an increasing trend with its concentration. As the concentration of Sulpuren drug increases, its ability to protect carbon steel from corrosion becomes more pronounced. This is due to a higher driving force propelled by a concentration gradient that overcomes mass transfer resistance between the adsorbent surface and the inhibitor acid solution. Additionally, the effect of temperature on the corrosion rate of carbon steel was also examined. The data reveals that at a constant concentration of Sulpuren drug, as the temperature increases from 293K to 333K, the corrosion rate of carbon steel generally increases[42]. This observation suggests that higher temperatures promote a more aggressive corrosion process. The corrosive agent can readily access the metal surface and continue reacting with the metal, leading to faster corrosion rates. Moreover, the enhancement of the rate of corrosion is due to the increase in temperature, and this behavior can also be attributed to the desorption of the inhibitor from the metal surface. At higher temperatures, the thermal energy disrupts the interactions between the inhibitor molecules and the metal surface, causing the inhibitor to detach from the metal. As a result, a greater area of the metal surface is left exposed to the corrosive acid, leading to an accelerated corrosion rate.[43,44] Upon comparing the corrosion rates at various concentrations and at specific temperatures, the changes in Sulpuren drug concentration lead to a not important variation in the corrosion rate of carbon steel. It is important to note that there might be an optimal concentration for the inhibitor where the corrosion rate reduction is most effective. Beyond this concentration, adding more inhibitors may not lead to a significant improvement in the inhibitive effect. This variation in corrosion rate is attributed to a slight increase in the adsorption of the inhibitor on the metal surface as the concentration increased; subsequently, a decrease in the corrosion rate will result.

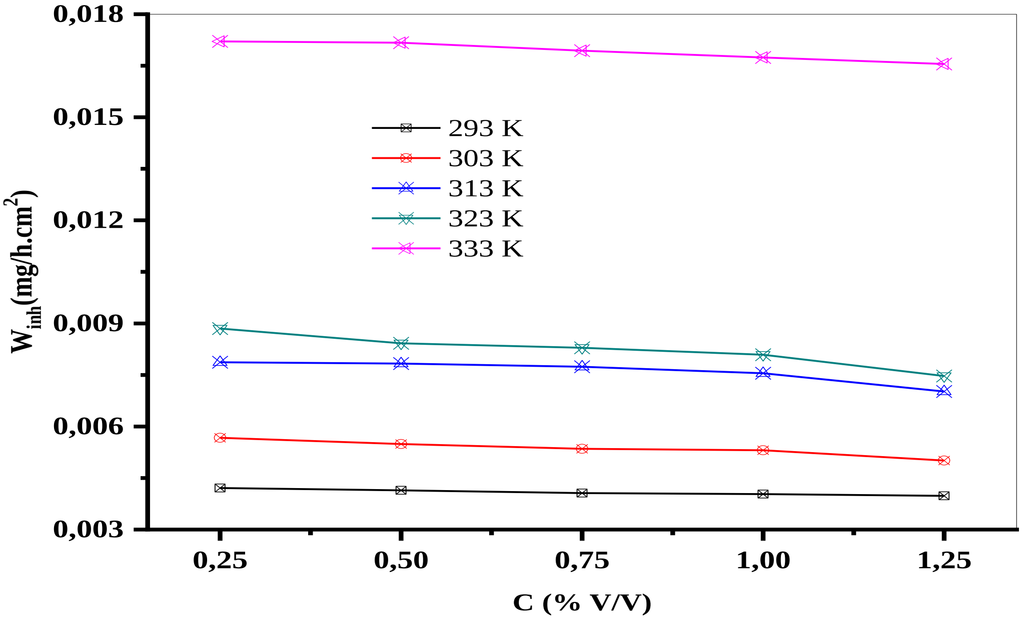


Fig. 2 – The relation between corrosion rate and concentration of SULPUREN® drug at different temperatures for 4 h.

Adsorption Isotherm

In the context of corrosion inhibition, adsorption isotherm plays a crucial role in understanding the interaction between the inhibitor molecules and the metal surface. Adsorption isotherm provides information on the extent of inhibitor adsorption on the metal surface as a function of inhibitor concentration. The data obtained from the experiment was analyzed graphically using various isotherms, including Langmuir, Temkin, and Frumkin. Among these isotherms, the Langmuir adsorption isotherm was determined to be the most suitable for describing the adsorption behavior. The Langmuir adsorption isotherm is one of the most commonly used models to describe the adsorption behavior in the corrosion inhibition process. It is based on the assumption that the adsorption sites on the metal surface are uniform and that only monolayer coverage of the inhibitor molecules occurs.

The evaluation of the free energy of inhibitor adsorption on the carbon steel surface involves employing the following equation:[45]

$$\Delta G_{ads} = -RT\ln(55.5K_{ads}) \quad (5)$$

where R represents the gas constant (J·mol/K), and T denotes the absolute temperature (K). The constant value of 55.5 corresponds to the concentration of water in the solution (mol/L) and K_{ads} represents the equilibrium constant of adsorption and indicates the strength of the interaction between the inhibitor and the metal surface. The determination of the adsorption process's equilibrium constant (K_{ads}) was achieved by analyzing the Langmuir isotherm graphically.

Table 3

Thermodynamic parameters for the adsorption of SULPUREN® drug in 0.5 M H_2SO_4 solution on carbon steel at different temperatures

T (K)	R^2	K_{ads}	ΔG_{ads} (kJ/mol)
293	1	558.621	–25.19
303	0.999	206.954	–23.55
313	0.999	152.769	–23.53
323	0.999	127.640	–23.80
333	0.999	238.195	–26.27

The adsorption equilibrium constants demonstrate positive values, indicating the feasibility of the inhibitors' adsorption to the carbon steel surface. This result corroborates the trend observed in the inhibitor's higher inhibition efficiency. The negative value of the free energy adsorption signifies the spontaneity of the adsorption process and it is energetically favorable. The negative value shows that the system releases energy when the inhibitor molecules are adsorbed, leading to a decrease in the overall energy of the system. Typically, if the ΔG_{ads} values exceed −20 kJ/mol, physisorption is favored, whereas values of −40 kJ/mol or lower suggest chemisorption. In Table 3, the obtained ΔG_{ads} values range from −23.53 to −26.27 kJ/mol, positioning it between −20 and −40 kJ/mol. The findings suggest a complex mechanism involving mixed-mode interactions including both physical and chemical adsorption are taking place simultaneously between the inhibitor molecules and the metal surface.

Thermodynamic and kinetic parameters

The data obtained from the weight loss measurements were analyzed and plotted using the Arrhenius equation. The Arrhenius equation is a widely used empirical formula in corrosion studies that relates the corrosion rate to temperature. It is expressed as follows:[46,47]

$$\mathrm{CR} = A \times \exp(-\Delta E_{act} / RT) \quad (6)$$

where E_{act} is activation energy [kJ/mol], R is gas constant [J·mol/K], T is absolute temperature [K], and A is a pre-exponential factor.

By plotting the lnCR against the reciprocal of temperature ($1/T$), a straight line is obtained, and the slope of this line represents the activation energy (E_{act}) of the corrosion process. The activation energy provides valuable information about the energy barrier that the corrosion reaction must overcome to proceed. Moreover, the activation enthalpy (ΔH_{act}) and activation entropy (ΔS_{act}) are important thermodynamic parameters that provide insights into the corrosion inhibition process. These parameters can be calculated using the transition state equation, which relates the corrosion rate to ΔH_{act} and ΔS_{act}. The transition state equation is given as:[48]

$$\ln(\mathrm{CR}/T) = [\ln(R/Nh) + (\Delta S_{act}/R)] - \Delta H_{act}/RT \quad (7)$$

where N is Avogadro's number, h is Planck's constant, T is absolute temperature and R is gas constant.

The change in free Gibbs energy can be deduced at 313 K by eq. 8

$$\Delta G_{act} = \Delta H_{act} - \mathrm{T}\Delta S_{act} \quad (8)$$

The plot of ln(CR/T) as a function of $1/T$ gives a straight line. The values of ΔH_{act} and ΔS_{act} can be extracted from the slope and intercept of the linear form of the equation (7). The calculated thermodynamic parameters at different concentrations of Sulpuren drug in 0.5 mol/L H_2SO_4 are collected in Table 4. As shown in Table 4, the activation energy (E_{act}) of inhibited solutions is higher than that of the blank solution. The observed result can be attributed to the physical adsorption of the inhibitor on the metal surface.[49]

The rise in activation energy can be ascribed to a notable reduction in inhibitor adsorption on the steel surface as temperature increases. This leads to an associated escalation in corrosion rates, primarily because a larger metal surface area is exposed to the corrosive solution.[50]

Table 4

The thermodynamic activation functions of carbon steel dissolution in 0.5 mol/L H_2SO_4 without and with different concentrations of SULPUREN® drug by applying Arrhenius and transition state plots

C_{inh} (% V/V)	R^2	E_{act} (kJ/mol)	R^2	ΔH_{act} (kJ/mol)	$-\Delta S_{act}$ (J/Kmol)	$\Delta G_{act\,(313K)}$ (kJ/mol)
−	0.98001	12.40	0.96968	9.81	235.02	83.37
0.25	0.91381	26.30	0.89634	23.70	209.77	89.35
0.50	0.89278	26.38	0.87141	23.78	209.70	89.41
0.75	0.89339	26.56	0.87229	23.96	209.26	89.45
1.00	0.88513	26.34	0.86235	23.74	210.09	89.49
1.25	0.84361	26.12	0.81350	23.52	211.18	89.61

From Table 4, the calculated values of enthalpy for the corrosion of carbon steel in uninhibited H_2SO_4 are 9.81 kJ/mol, which increased to 23.7 and 23.52 kJ/mol in the presence of 0.25 and 1.25 % v/v inhibitor concentrations, respectively. The values of enthalpy are all positive, indicating the endothermic nature of the reaction and suggesting that higher temperatures favor the metal dissolution process.[51,52] An important observation is that the activation energy values (E_{act}) are notably higher than the corresponding values of ΔH_{act}, signifying the involvement of a gaseous reaction, specifically the hydrogen evolution reaction.[53] Additionally, the average discrepancy between E_{act} and ΔH_{act}, quantified at 2.59 kJ/mol, is nearly equivalent to the average RT value. This alignment suggests that the corrosion process follows a unimolecular reaction pathway, as expressed by the following equation:[54]

$$E_{act} - \Delta H_{act} = RT \qquad (9)$$

Moreover, the study's findings reveal negative entropy values, which indicate that the process of corrosion is entropically favorable. This insight signifies the creation of a structured and stable film comprising inhibitor molecules on the metal surface. This film serves as an effective barrier, impeding the interaction between the metal and corrosive agents, thus resulting in enhanced corrosion protection. The significantly negative value of ΔS_{act} in acid medium without inhibitor suggests that the reaction of the formation of activated complex is the rate-determining step during the corrosion process. This finding emphasizes the role of the inhibitor in the corrosion inhibition mechanism, meaning that a decrease in disordering takes place on going from reactants to the activated complex.[55] The data presented in Table 4 clearly indicate that ΔS_{act} increased (with lower negative values) in the presence of the investigated inhibitor compared to the free acid solution. In the case of the free acid solution, this phenomenon can be explained as follows: The transition state of the rate-determining recombination step exhibits a more organized arrangement compared to the initial state, resulting in a higher value for the activation entropy. However, in the presence of an inhibitor, the rate determining step is the discharge of hydrogen ions to form adsorbed hydrogen atoms. As the surface becomes coated with inhibitor molecules, this process hinders the release of hydrogen ions at the metal surface, leading to an increase in the entropy of activation. The large negative values in ΔS_{act} ranging from − 209.77 to − 211.18 J/Kmol as the inhibitor concentration increases indicate a greater degree of disorder during the transition from reactants to the activated complex. This phenomenon can be attributed to the process of replacing water molecules during the adsorption of Sulpuren drug onto the carbon-steel surface.[56] The positive values of ΔG_{act} indicate that the corrosion process is characterized by non-spontaneity and is thermodynamically unfavorable. This suggests that the corrosion reaction requires an input of energy to proceed. Furthermore, the observed increase in ΔG_{act} values in the presence of the inhibitor compared to its absence suggests that the inhibitor's introduction enhances the thermodynamic barrier against the corrosion reaction. This phenomenon can be attributed to physisorption mechanisms,[57-58] where the inhibitor molecules adsorb onto the metal surface through weaker intermolecular forces. These forces contribute to a higher energy barrier for the corrosion reaction to occur, leading to the observed increase in ΔG_{act} values. This additional resistance against the corrosion process emphasizes the inhibitive effectiveness of the introduced inhibitor and its ability to create a protective layer on the metal surface.

Optimization of inhibition efficiency by RSM

The primary goal of utilizing Design of Experiments (DOE) is to streamline the experimental process and anticipate the maximum outcome (Y) based on chosen variables and their levels while conducting the fewest possible experiments. Numerous computer-assisted optimization techniques are available for DOE, with Response Surface Methodology (RSM) being notably effective.[59] RSM combines statistical and mathematical approaches that are pivotal in the development, enhancement, and optimization of processes. In RSM, the initial objective is to identify the optimal response (Y), followed by comprehending how Y changes in specific directions through graphical representations. In this context, the inhibitor's efficiency serves as the response variable, expressed as a function of three independent variables. From Table 5, it has been seen that the most elevated effectiveness is achieved in the trial with a drug concentrate of 0.75 v/v (%), 0.5 mol/L H_2SO_4, an operating temperature of 40 °C, and a working time of 6 h.

The multivariate regression empirical formula between IE and process factors was then established, as shown in the following equation (eq. 10):

$$IE = 90.9352 + 1.987\,x_1 - 5.323\,x_2 + 12.414\,x_3 - 1.54162\,x_1^2 - 3.9316\,x_2^2 - 6.22662\,x_3^2 + 0.240003\,x_1x_2 - 1.165\,x_1x_3 + 4.085\,x_2x_3 \quad (10)$$

Table 5

Results of the experiments conducted for the corrosion inhibitor (Sulpuren)

Exp No	**Exp Name**	**Run Order**	**Concentration (% V/V)**	**Temperature (°C)**	**Time (h)**	**IE (%)**
1	N1	1	0.25	20	2	69.63
2	N2	7	1.25	20	2	76.43
3	N3	16	0.25	60	2	57.31
4	N4	6	1.25	60	2	63.57
5	N5	9	0.25	20	6	95.39
6	N6	4	1.25	20	6	96.03
7	N7	15	0.25	60	6	85.91
8	N8	3	1.25	60	6	89.01
9	N9	17	0.25	40	4	88.16
10	N10	2	1.25	40	4	91.23
11	N11	13	0.75	20	4	93.08
12	N12	14	0.75	60	4	81.53
13	N13	8	0.75	40	2	72.64
14	N14	11	0.75	40	6	97.38
15	N15	5	0.75	40	4	90.32
16	N16	12	0.75	40	4	90.57
17	N17	10	0.75	40	4	90.71

The model was established with a 95% confidence level (Table 6). The analysis yielded R^2 and adjusted R^2 values that are nearly equal to one, signifying a strong alignment of the data with the model. The Q^2 value surpassing 0.9 indicates the excellence of the model. Furthermore, the difference between R^2 and Q^2, being less than 0.3, reaffirms the quality of the model. The residual standard deviation (RSD) for the model was 0.687, underscoring the agreement between the predicted inhibition efficiency and the actual experimental outcomes.

Table 6

The results of Q^2 and R^2

	R^2	R^2 **Adj.**	Q^2	**SDY**	**RSD**	**Model Validity**	**Reproducibility**
IE	0.998558	0.996703	0.982843	11.9662	0.68707	0.287242	0.999727
			Cond. no. = 4.438		**Conf. lev.** = 0.95		

Figure 3 illustrates the main effect coefficient plot for carbon steel in the H_2SO_4 acid solution, revealing that the majority of interactions of the process parameters exert a noteworthy influence on the response variable, except for the interlinked impact of concentration and temperature, which is found to be positive and negligible. This suggests the absence of a substantial inter-correlation between the interlinked effects of temperature and concentration. Upon careful examination of the main effect coefficient plot, it becomes clear that a negative sign signifies the antagonistic effect of the factors, while a positive sign indicates their synergistic effect.

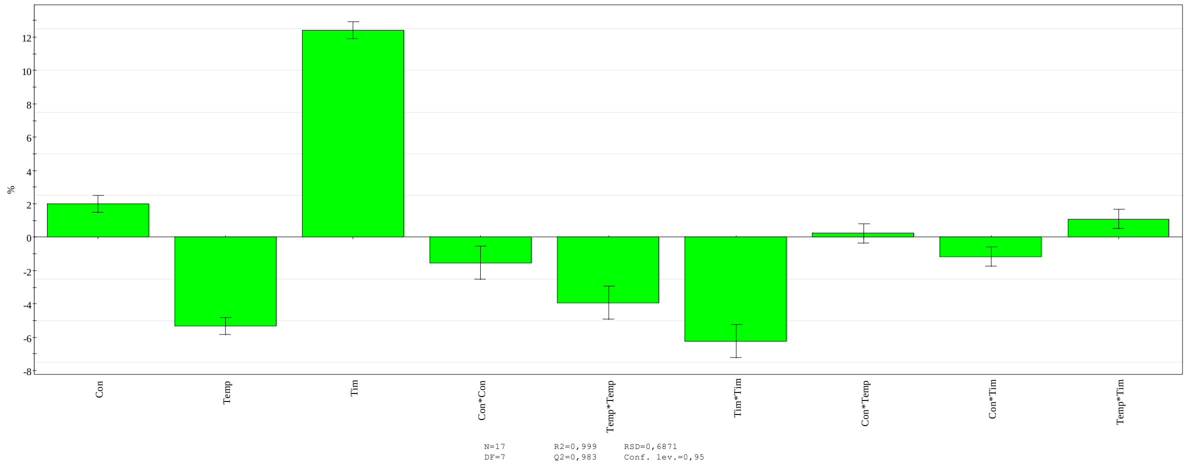


Fig. 3 – Main effect coefficients plot.

To delineate the optimal range for achieving optimal inhibition efficiency (IE), we generated surface plots and contour plots (Figs. 4 and 5). The IE was observed to be distinctly affected by the variables that govern the process, specifically the working temperature and the concentration of the inhibitor. Through a meticulous analysis of these variables using contour plots, we were able to delve into their impacts on the IE within a specific immersion time of 6 hours. The surface plot depicted in Fig. 4 and the corresponding contour plot illustrated in Fig. 5, portraying the inhibition efficiency, vividly showcase that a decrease in working temperature while maintaining a constant inhibitor concentration leads to an augmentation in inhibition efficiency. This intriguing trend can be elucidated by attributing it to the physical adsorption phenomenon of the inhibitor onto the surface of the carbon steel. Consequently, this adsorption process results in a reduction in the corrosion rate. Lower temperatures promote favorable adsorption of the inhibitor, thereby increasing its inhibitory effectiveness.

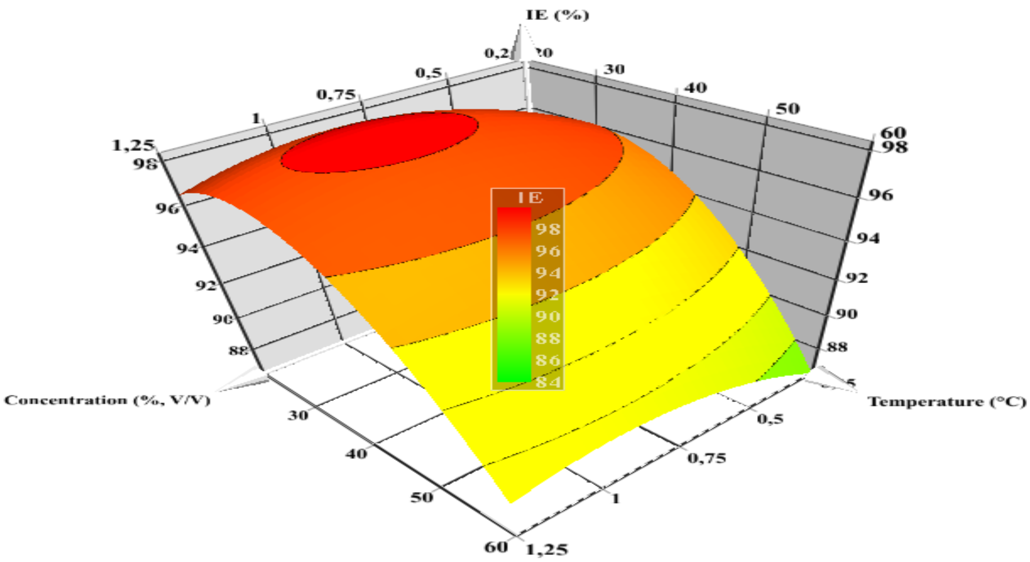


Fig. 4 – 3-D surface plot showing the relationship between inhibition efficiency (%), inhibitor concentration and temperature.

As seen from Fig. 4, there was an accompanying progressive increase in Inhibition Efficiency (%IE) and surface coverage with an increase in inhibitor concentration up to a point, which led to a significant decline in the rate and extent of aggressiveness of the acid on the carbon steel; a wider surface coverage was attained which got improved as the drug's concentration was increased. This observation is attributable to the effectiveness of the inhibitor in protecting the metal surface against acid attack. Moreover, there was a synergetic effect between acid and temperature toward the enhancement of metal surface attack when increasing temperature. From Fig. 5, it can be seen that the inhibition efficiency of the Sulpuren drug is a function of concentration and temperature, attaining a maximum value of 98.34% at an optimum inhibitor concentration of 0.867% v/v and a working temperature of 29.46 °C during a 6-hour reaction. The Prediction Plot Wizard enabled independent variation of each variable. Enhanced surface coverage facilitates the increased availability and adsorption of the active inhibitor components onto the corroding metal surface. As depicted in Fig. 6, the highest inhibition efficiency was achieved at about 1% v/v concentration of Sulpuren drug, a temperature of 20°C, and an immersion time of six hours, out of the various levels of factors considered.

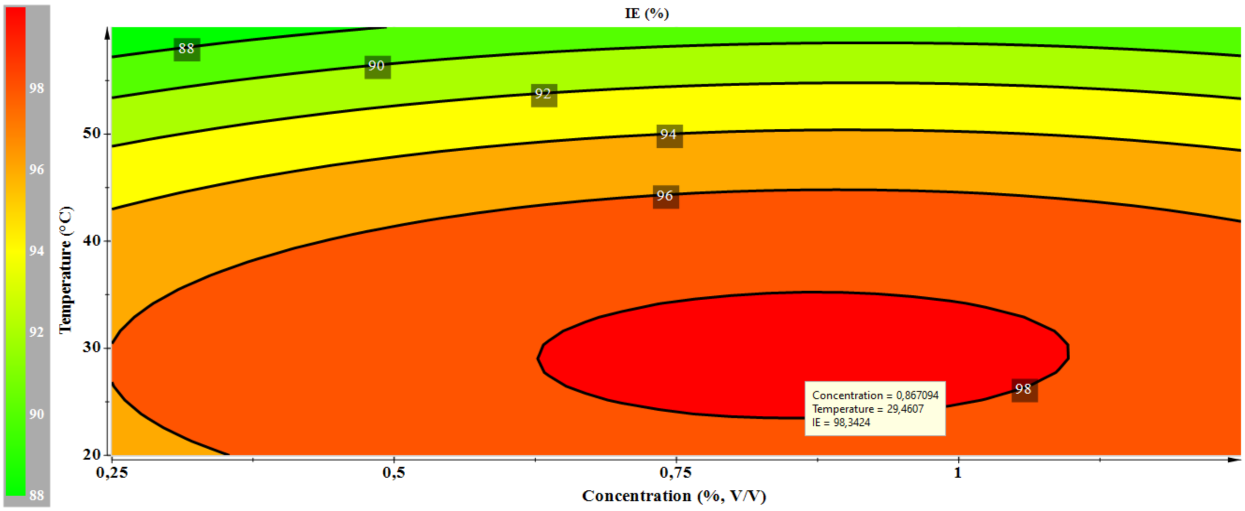


Fig. 5 – 2D contour plot of temperature and concentration effects on inhibition efficiency (IE) for 4 h.

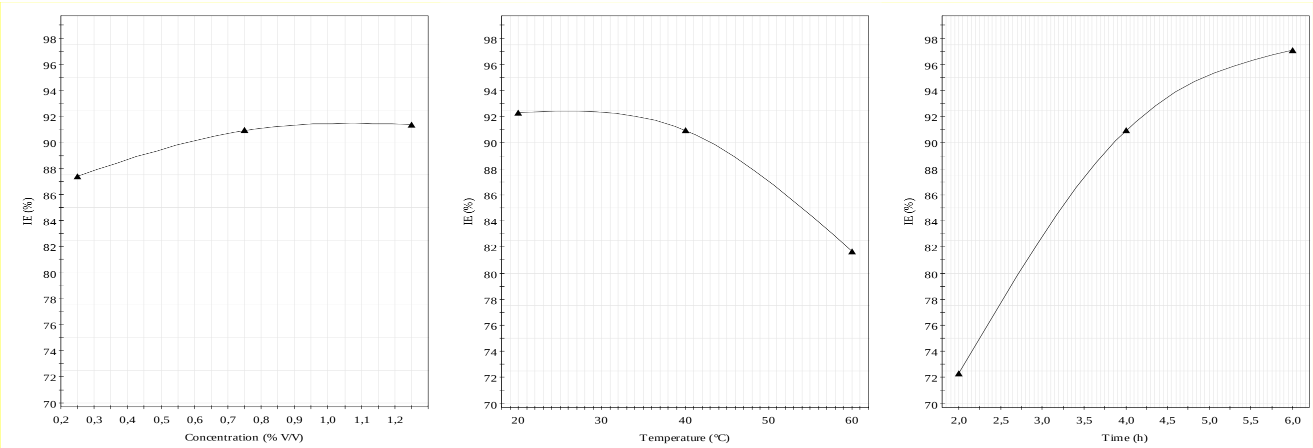


Fig. 6 – Prediction plot of inhibition efficiency (IE) in Sulpuren drug.

CONCLUSION

Response Surface Methodology (RSM) was expertly employed to comprehensively investigate and statistically assess the potential of Sulpuren, an expired pharmaceutical drug, as a corrosion inhibitor for carbon steel in a 0.5 mol/L sulfuric acid aqueous solution. The collected experimental data underwent rigorous analysis to ensure both coherence and significance. The experimental results revealed that the Sulpuren drug acts as a good inhibitor for the corrosion of carbon steel in the acid solution. Inhibition efficiency increases with increasing inhibitor concentration but decreases with an increase in temperature. The adsorption process of the expired pharmaceutical drug is spontaneous and obeys the Langmuir adsorption isotherm. Through the integration of RSM, a quadratic model equation was formulated, illuminating the intricate relationships between the aforementioned parameters and the resulting inhibition efficiency. This in-depth examination provided insights into how these variables interacted and influenced the corrosion inhibition process. The practical application of the derived models enabled the identification of optimal conditions to maximize the inhibition efficiency. Importantly, the projected inhibition efficiencies harmonized well with the actual experimental results, thereby validating the reliability and precision of the models. The optimization outcomes conclusively demonstrated that an impressive inhibition efficiency of 98.66% in the optimal conditions of 1 % v/v of Sulpuren concentration, at a temperature of 20°C, and for 6 hours. From RSM results, the values of R^2 and R^2_{adj} were close to unity, indicating a good fit of the data with the model. Overall, the study demonstrates the potential of Sulpuren as an effective corrosion inhibitor, providing valuable insights into its adsorption mechanism and performance under different experimental conditions. These findings open up new possibilities for utilizing expired pharmaceutical drugs as environmentally friendly and cost-effective corrosion inhibitors in various industrial applications.

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