



Research article

Thermodynamic, Adsorption, thermal stability and optimization studies of expired valsartan drug for corrosion protection of N80 steel in a simulated acidified oil well system

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ARTICLE INFO

Keywords:

Expired valsartan

N80 steel, Corrosion inhibition

Oil well acidizing, Optimization

ABSTRACT

The use of expired pharmaceutical compounds as corrosion inhibitors represents a sustainable approach to both corrosion mitigation and pharmaceutical waste valorization. In this study, the corrosion inhibition performance of expired valsartan (VST) for N80 steel in a simulated acidized oil-well environment (1.0 M HCl) was investigated using gravimetric measurements, adsorption and thermodynamic analyses, thermal stability evaluation, and Response Surface Methodology (RSM) optimization. The novelty of this work lies in the utilization of expired valsartan as a low-cost, environmentally sustainable corrosion inhibitor while simultaneously providing an effective strategy for pharmaceutical waste reutilization. The results showed that the inhibition efficiency increased with increasing inhibitor concentration but decreased with increasing temperature and immersion time. Adsorption studies revealed that VST molecules adsorbed spontaneously onto the steel surface, predominantly through a physisorption mechanism, forming a protective barrier that reduced metal dissolution. Thermodynamic analysis further confirmed the spontaneous and protective nature of the adsorption process, while thermal analysis demonstrated that expired valsartan remained structurally stable up to approximately 260 °C, indicating adequate thermal stability for application under acidized oil-well conditions. A Box–Behnken design based on Response Surface Methodology was successfully developed to optimize the corrosion inhibition performance. The optimum conditions were identified as an inhibitor concentration of 125 ppm, a temperature of 328 K, and an immersion time of 12 h, under which an experimental inhibition efficiency of 76.8% was achieved. The findings demonstrate that expired valsartan is an effective, environmentally benign, and economically viable corrosion inhibitor for N80 steel in acidic media. This study provides a sustainable approach to corrosion control while offering a practical solution for the reutilization of expired pharmaceutical waste in petroleum industry applications.

1. Introduction

Corrosion of metallic materials remains one of the most significant technical and economic challenges in the oil and gas industry, particularly during oil-well operations where steels are exposed to aggressive environments containing mineral acids, dissolved gases, and saline brines [1,2]. N80 steel, a high-strength and cost-effective material widely used in tubing and casing applications, is especially vulnerable to corrosion during acidizing and enhanced oil recovery processes because

of prolonged exposure to hydrochloric acid (HCl) and carbon dioxide (CO₂)-containing fluids [3,4]. Dissolved CO₂ reacts with water to form carbonic acid, thereby accelerating electrochemical degradation, material loss, and equipment failure [5–7]. Beyond reducing the service life of steel components, corrosion imposes enormous economic costs estimated at trillions of dollars annually worldwide and poses serious operational, environmental, and safety risks [8–10].

Among the various corrosion control techniques, the use of corrosion inhibitors remains one of the most practical and cost-effective

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<https://doi.org/10.1016/j.nxcen.2026.100080>

Received 4 June 2026; Received in revised form 27 June 2026; Accepted 3 July 2026

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approaches for protecting steel in acidic environments [11–13]. Corrosion inhibitors function by adsorbing onto the metal surface to form a protective film that suppresses both anodic metal dissolution and cathodic hydrogen evolution reactions. Organic compounds containing heteroatoms such as nitrogen, oxygen, and sulfur, together with π -electron systems, generally exhibit excellent inhibition performance because of their strong adsorption affinity toward metallic surfaces [14–16]. However, many conventional inhibitors are associated with drawbacks including toxicity, poor biodegradability, and high production costs, thereby stimulating the search for environmentally sustainable alternatives [17,18].

Consequently, increasing attention has been directed toward green corrosion inhibitors derived from natural products and pharmaceutical compounds. Molecules containing hydroxyl (–OH), carbonyl (C=O), amide, imine (C=N), and aromatic functional groups readily adsorb onto steel surfaces through donor–acceptor interactions, electrostatic attraction, and coordinate bonding, resulting in the formation of protective surface films that mitigate corrosion [19–22]. The adsorption behavior of these inhibitors is commonly described using adsorption isotherms such as Langmuir, Freundlich, and Temkin models, which provide valuable information regarding the adsorption mechanism and inhibitor–metal interactions [23–26]. Among emerging green inhibitors, pharmaceutical compounds have attracted considerable interest because of their complex molecular structures, multiple adsorption-active functional groups, and commercial availability [27, 28]. In particular, expired pharmaceuticals provide an environmentally sustainable option by simultaneously reducing pharmaceutical waste and offering a low-cost alternative to newly synthesized corrosion inhibitors [29,30]. Several studies have demonstrated that many expired drugs retain their chemical integrity and exhibit excellent corrosion inhibition performance, making them attractive candidates for sustainable corrosion protection while supporting circular economy and green chemistry initiatives [31–34].

Valsartan (VST), an antihypertensive drug belonging to the angiotensin II receptor blocker (ARB) class, possesses a molecular structure rich in adsorption-active sites, including tetrazole, amide, carboxyl, and aromatic groups [35]. The presence of multiple heteroatoms and conjugated π -electron systems enhances its ability to adsorb onto metallic surfaces and form protective films under acidic conditions. Despite these favorable structural characteristics, the corrosion inhibition behavior of expired valsartan for N80 steel in simulated acidized oil-well environments has received little attention. Furthermore, corrosion inhibition is fundamentally governed by adsorption and thermodynamic processes that determine the spontaneity, stability, and mechanism of inhibitor adsorption on metal surfaces. Thermodynamic parameters, including activation energy, enthalpy, entropy, Gibbs free energy of adsorption, and adsorption equilibrium constants, provide important insight into whether the adsorption process is physical or chemical in nature and the strength of inhibitor–metal interactions [36–38]. In addition, statistical optimization techniques such as Response Surface Methodology (RSM) have proven effective for evaluating the combined influence of process variables, including inhibitor concentration, temperature, and immersion time, and for identifying optimum operating conditions that maximize inhibition performance [39–44].

Although pharmaceutical compounds have been extensively investigated as environmentally friendly corrosion inhibitors, comprehensive information on the inhibition performance of expired valsartan for N80 steel in acidized oil-well environments remains unavailable. To the best of our knowledge, no previous study has simultaneously evaluated the adsorption characteristics, thermodynamic behavior, thermal stability, and process optimization of expired valsartan in 1.0 M HCl using Response Surface Methodology. Therefore, the novelty of this work lies in the valorization of expired valsartan as a low-cost, environmentally benign, and sustainable corrosion inhibitor while establishing the relationship between its molecular structure, adsorption behavior, thermal stability, and corrosion inhibition performance. In addition, this study

demonstrates a practical approach for converting expired pharmaceutical waste into a value-added corrosion mitigation material, thereby contributing to sustainable corrosion protection and circular economy objectives. The optimized operating conditions obtained through RSM further enhance the potential industrial applicability of expired valsartan for corrosion protection in acidized oil-well systems.

2. Materials and methods

2.1. Materials

N80 steel, a grade extensively used in oil and gas production and transportation systems because of its excellent mechanical properties and suitability for downhole service conditions, was employed as the substrate material in this study. The chemical composition of the steel (wt.%) was as follows: C, 0.31%; Si, 0.19%; Mn, 0.92%; Cr, 0.20%; P, 0.010%; S, 0.008%; with the balance being Fe. Steel coupons with an exposed surface area of 1 cm² were prepared for the gravimetric corrosion experiments. Expired valsartan (VST) tablets were selected as the corrosion inhibitor. Prior to use, the tablets were visually inspected to ensure the absence of significant physical deterioration. They were subsequently pulverized using a clean mortar and pestle to obtain a fine, homogeneous powder. Appropriate quantities of the powdered valsartan were dissolved in 1.0 M HCl to prepare inhibitor solutions of the desired concentrations for the corrosion studies, thereby simulating acidized oil-well conditions. Hydrochloric acid solutions were prepared using analytical-grade reagents and distilled water. All chemicals used throughout the study were of analytical grade and were employed without further purification. To verify that the expired pharmaceutical retained its corrosion-inhibiting functionality, the powdered valsartan was characterized by Fourier Transform Infrared Spectroscopy (FTIR) to identify the adsorption-active functional groups responsible for interaction with the steel surface. Its thermal stability was further evaluated using Thermogravimetric Analysis/Differential Thermal Analysis (TGA/DTA) to assess its structural integrity and suitability for corrosion inhibition under the elevated-temperature conditions encountered during oil-well acidizing operations [41].

2.2. Methods

2.2.1. Weight loss (gravimetric) measurements

The weight loss test was conducted to determine the corrosion of N80 steel at 318, 328 and 338K. Steel coupons were polished, washed with water, degreased in acetone, dried and weighed. These were then immersed in 1.0 M HCl solutions with and without inhibitor for a certain duration. The coupons were then taken out, cleaned, dried and reweighed for the weight loss (ΔW). The corrosion rate (CR), the inhibition efficiency (IE%) and surface coverage (Θ) were determined by the following equations [38,45]:

$$CR = \frac{\Delta W}{At} \quad (1)$$

$$I.E(\%) = \frac{W_{blank} - W_{inh}}{W_{blank}} \times 100 \quad (2)$$

$$\Theta = \frac{W_{blank} - W_{inh}}{W_{blank}} \quad (3)$$

where: ΔW is a weight loss (g), A is a surface area of the coupon (cm²), t is a immersion time (h), W_{blank} and W_{inh} are weight losses in absence and presence of inhibitor, respectively.

2.2.2. Electrochemical measurements

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) studies were carried out with a three-electrode system of N80 steel (working electrode), Ag/AgCl (reference electrode) and

platinum (counter electrode). From the polarization curves, the corrosion current density (i_{corr}), corrosion potential (E_{corr}) and Tafel slopes (β_a and β_c) were determined [37].

The polarization data based inhibition efficiency was calculated using:

$$I.E(\%) = \frac{i_{corr_{blank}} - i_{corr_{inh}}}{i_{corr_{blank}}} \times 100 \quad (4)$$

Where $i_{corr_{blank}}$ is the corrosion current density without inhibitor and $i_{corr_{inh}}$ corrosion current density with inhibitor.

The electrochemical impedance spectroscopy (EIS) measurements were carried out on OCP using a 5 mV AC signal in the frequency range of 100 kHz to 0.01 Hz. The charge transfer resistance (R_{ct}) was determined by fitting the Nyquist plot and the inhibition efficiency (IE) was computed using the equation:

$$I.E(\%) = \frac{R_{ct_{blank}} - R_{ct_{inh}}}{R_{ct_{blank}}} \times 100 \quad (5)$$

The double layer capacitance (Cdl) was calculated using:

$$Cdl = \frac{1}{2\pi f_{max} R_{ct}} \quad (6)$$

2.3. Adsorption studies

The adsorption behavior of expired valsartan (VST) molecules on the surface of N80 steel was evaluated using four adsorption isotherm models, namely Langmuir, Freundlich, Temkin, and El-Awady. The surface coverage values (θ), calculated from the gravimetric weight-loss measurements, were fitted to these adsorption models to elucidate the adsorption mechanism, determine the nature of the inhibitor-metal interactions, and assess the adsorption characteristics of VST on the steel surface [46,47].

2.3.1. Langmuir adsorption isotherm

The Langmuir adsorption isotherm assumes monolayer adsorption of inhibitor molecules on a homogeneous metal surface containing a finite number of energetically identical adsorption sites. The model further assumes that each adsorption site accommodates only one inhibitor molecule and that there are no lateral interactions between adjacent adsorbed species. The Langmuir isotherm is widely employed to describe the adsorption behavior of corrosion inhibitors and is expressed as:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (7)$$

In which: C is the concentration of inhibitor (g/L), θ is the surface coverage, K_{ads} is the equilibrium constant of adsorption.

Plotting C/θ versus C gives a linear relationship, where the intercept is $1/K_{ads}$. The standard Gibbs free energy of adsorption (ΔG°_{ads}) was calculated using:

$$\Delta G_{ads} = -RT \ln[55.5 K_{ads}] \quad (8)$$

This value can be used to determine the spontaneity and type of adsorption process.

2.3.2. Freundlich adsorption isotherm

The Freundlich isotherm is an adsorption isotherm used to model multilayer adsorption. It is expressed as:

$$\text{Log } \theta = \ln K_{ads} + \frac{1}{n} \text{Log } C \quad (9)$$

Where, n = adsorption intensity parameter. The graph between $\log \theta$ and $\log C$ is linear. Values $0 < 1/n < 1$ suggests good adsorption and a heterogeneous metal surface.

2.3.3. Temkin adsorption isotherm

The Temkin isotherm considers adsorbate-adsorbate interactions and uses a linear adsorption heat decrease function. It is expressed as:

$$\theta = \frac{1}{f} \ln(K_{ads} C) \quad (10)$$

Where, f is Temkin constant related to adsorbate-adsorbate interactions. The adsorption parameters are obtained from a plot of θ versus $\ln C$. This isotherm helps in getting information about the nature of the interaction of the inhibitor molecules with the metal surface.

2.3.4. El-Awady adsorption isotherm

The El-Awady isotherm (kinetic-thermodynamic model) gives information about the number of active sites occupied by inhibitor molecules. It is expressed as:

$$\log \left(\frac{\theta}{1-\theta} \right) = \log K_{ads} + y \log C \quad (11)$$

Where y is the number of inhibitor molecules occupying one active site.

A plot of $\text{Log} \left(\frac{\theta}{1-\theta} \right)$ versus $\log C$ yields a straight line. The value of $\frac{1}{y}$ reveal the mode of adsorption.

2.4. Thermodynamic studies

Thermodynamic studies have been performed to evaluate the influence of temperature on the corrosion process and to get insight into the mechanism by which the corrosive process of N80 steel is inhibited by the expired VST in the acid oil well environment. Thermodynamic parameters such as activation energy (E_a), enthalpy of activation (ΔH) and entropy of activation (ΔS) were obtained from the corrosion rate data obtained from the weight loss measurements as a function of temperature at 318, 328 and 338K. The activation energy (E_a) of the corrosion process was determined from the Arrhenius equation [47]:

$$\log CR = \log A - \frac{E_a}{2.303RT} \quad (12)$$

CR is the corrosion rate, A is the pre-exponential factor, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (K). A straight-line plot is obtained when $\log CR$ is plotted against $1/T$ and the slope gives the value of activation energy.

The transition state equation was used to calculate the enthalpy (ΔH) and entropy (ΔS) of activation:

$$\log \left(\frac{CR}{T} \right) = \log \left(\frac{R}{Nh} \right) + \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (13)$$

where N is Avogadro's number and h is Planck's constant. A plot of $\log (CR/T)$ versus $1/T$ produces a straight line, with slope equal to $-\frac{\Delta H}{2.303RT}$ and intercept equal to $\log \left(\frac{R}{Nh} \right) + \frac{\Delta S}{2.303R}$

2.5. Optimization using Response Surface Methodology (RSM)

Response Surface Methodology (RSM) was employed to evaluate the combined effects of the experimental variables and to determine the optimum conditions for maximizing the corrosion inhibition performance of expired valsartan (VST) on N80 steel. RSM is a statistical and mathematical optimization technique widely used to model, analyze, and optimize processes involving multiple independent variables while minimizing the number of experimental trials required compared with conventional one-factor-at-a-time approaches.

In this study, three independent variables were selected based on their significant influence on the corrosion process: inhibitor concentration (X_1), temperature (X_2), and immersion time (X_3). The response

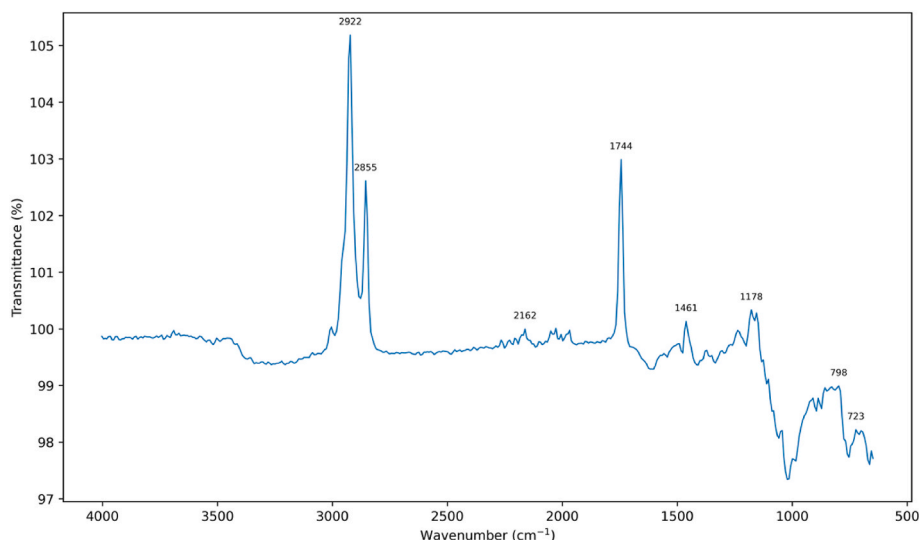


Fig. 1. FTIR plot of expired VST.

variable (Y) was the inhibition efficiency (IE%) obtained from the gravimetric measurements. Each factor was investigated at three coded levels (−1, 0, and +1), corresponding to the low, center, and high experimental levels. The temperature range investigated was 318–338 K, while the ranges of inhibitor concentration and immersion time were established from preliminary corrosion experiments. A Box–Behnken Design (BBD) was adopted to generate the experimental matrix because of its efficiency in fitting second-order response surfaces while requiring fewer experimental runs than a full factorial design. The design comprised 60 experimental runs, including 12 center-point replicates, to estimate the experimental error, evaluate model adequacy, and improve the reliability of the statistical analysis. The experimental data were fitted to a second-order (quadratic) polynomial model to describe the relationship between the independent variables and the response, as expressed by the following equation [41,44]:

$$Y = \beta_0 + \sum B_i X_i + B_{ii} X_i^2 + \sum B_{ij} X_i X_j + \epsilon \quad (14)$$

where Y is the predicted response, β_0 is the intercept term, β_i represents

the linear coefficients, β_{ii} the quadratic coefficients, β_{ij} the interaction coefficients, and ϵ is the random error. X_i and X_j are the coded independent variables.

3. Result and discussion

3.1. FTIR study

The FTIR spectrum of expired valsartan (VST) confirmed the presence of the characteristic functional groups responsible for its corrosion inhibition performance. The major absorption bands corresponded to O–H/N–H stretching, aliphatic C–H stretching, carbonyl (C=O) stretching, aromatic C=C vibrations, C–N stretching, and C–O stretching vibrations. The abundance of oxygen- and nitrogen-containing functional groups, together with the conjugated aromatic π -electron systems within the valsartan molecule, provides multiple adsorption-active centers capable of interacting with the N80 steel surface. The preservation of these characteristic absorption bands indicates that the expired valsartan retained its molecular structure and adsorption-active

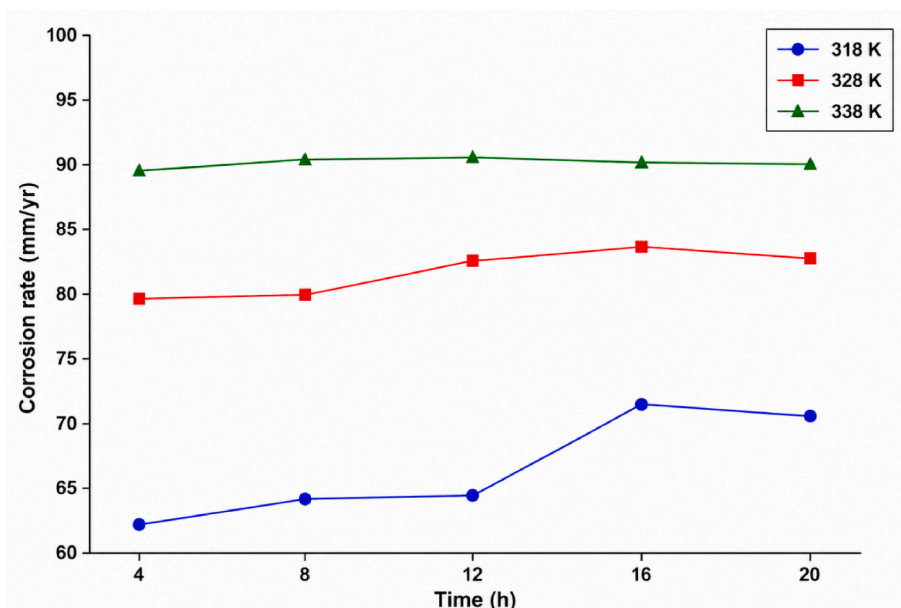


Fig. 2. Corrosion -Time plots for N80 steel in VST inhibitor at vary temperatures.

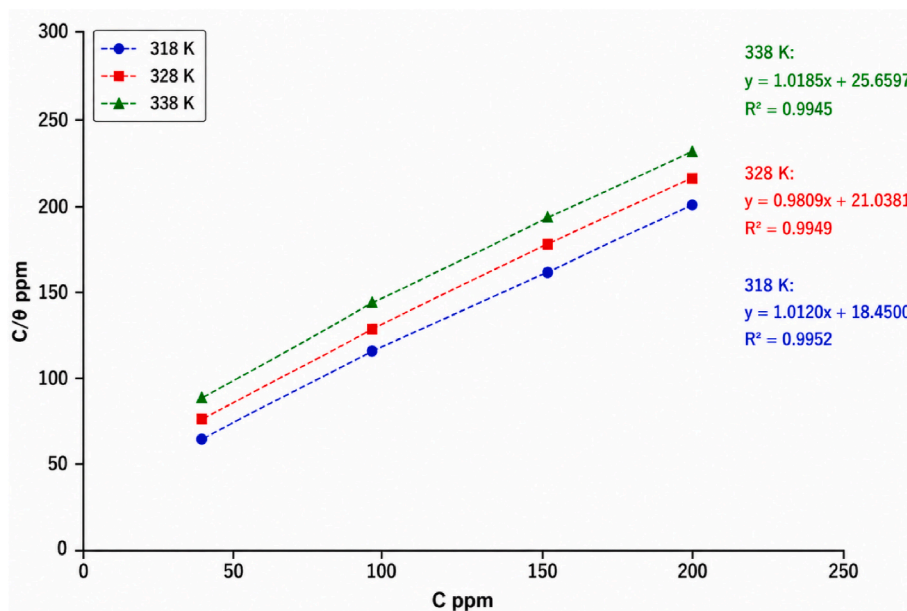


Fig. 3. Langmuir adsorption isotherm for plots for N80 steel in VST inhibitor at vary temperatures.

functional groups despite exceeding its pharmaceutical shelf life. These adsorption centers facilitate the interaction of VST molecules with the steel surface through electron donation and electrostatic interactions, resulting in the formation of a stable protective adsorbed film that suppresses metal dissolution in the acidic medium. The retention of these functional groups explains the observed corrosion inhibition performance of expired valsartan. The FTIR results confirm that the chemical integrity of expired valsartan remained largely unaffected after expiration, supporting its suitability as an environmentally sustainable corrosion inhibitor for N80 steel in simulated acidized oil-well environments [41] (see Fig. 1).

3.2. Weight loss analysis

The corrosion rate–immersion time plots presented in Fig. 2 illustrate the combined influence of temperature and exposure time on the corrosion behavior of N80 steel in 1.0 M HCl containing expired valsartan (VST). As shown in Fig. 2, the corrosion rate increased with both increasing temperature and prolonged immersion time, indicating that the corrosion process is strongly dependent on these two variables. The increase in corrosion rate with temperature is attributed to the acceleration of electrochemical reactions resulting from the higher kinetic energy of the reacting species, enhanced ionic mobility within the electrolyte, and an increased rate of anodic metal dissolution. Elevated temperatures also reduce the stability of the adsorbed inhibitor film by promoting thermal agitation and partial desorption of VST molecules from the steel surface, thereby exposing additional active sites to the corrosive medium [46]. Consequently, the highest corrosion rates were recorded at 338 K, demonstrating that the protective adsorption layer became progressively less effective under elevated-temperature conditions.

At 318 K, the corrosion rate remained relatively low during the initial 12 h of immersion, indicating effective adsorption of VST molecules and the formation of a stable protective film on the steel surface. However, a gradual increase in corrosion rate was observed after prolonged immersion (16–20 h), suggesting progressive deterioration of the adsorbed inhibitor layer with increasing exposure time. Despite this increase, the corrosion rates at 318 K remained substantially lower than those measured at higher temperatures, confirming the superior inhibition performance of VST under lower-temperature conditions.

At 328 K, the corrosion rate increased moderately with immersion

time, indicating that although VST continued to provide appreciable corrosion protection, the stability of the adsorbed film was reduced by thermal agitation. The inhibitor layer remained largely intact but became less compact than that formed at 318 K, resulting in a gradual decline in inhibition efficiency.

The highest corrosion rates were consistently observed at 338 K, where the corrosion rate approached an approximately constant value of 90 mm y^{-1} throughout the immersion period. The relatively small variation with time suggests that the inhibitor film formed at this temperature was comparatively unstable and provided limited resistance to the corrosion process. This reduction in inhibition efficiency with increasing temperature is characteristic of a predominantly physisorption-controlled mechanism, in which physically adsorbed inhibitor molecules are more readily desorbed from the metal surface as temperature increases. Overall, the results demonstrate that expired valsartan provides effective corrosion protection for N80 steel, particularly at lower temperatures. Its inhibition performance is primarily attributed to the adsorption of inhibitor molecules onto the steel surface, forming a protective barrier that suppresses electrochemical corrosion reactions. However, increasing temperature and prolonged immersion reduce the stability of the adsorbed film, resulting in progressive desorption of inhibitor molecules and a corresponding increase in corrosion rate [47].

3.3. Adsorption model and thermodynamic analysis

The adsorption and thermodynamic analyses provide important insights into the corrosion inhibition mechanism of expired valsartan (VST) on N80 steel in 1.0 M HCl. The adsorption isotherm models and thermodynamic parameters collectively indicate that VST molecules adsorb spontaneously onto the steel surface, forming a protective layer that isolates the metal from the aggressive acidic environment. The adsorption behavior was evaluated using the adsorption equilibrium constant (K_{ads}), Gibbs free energy of adsorption (ΔG_{ads}), activation energy (E_a), enthalpy of adsorption (ΔH_{ads}), entropy of adsorption (ΔS_{ads}), and the temperature dependence of the inhibition efficiency. The Langmuir adsorption isotherm (Fig. 3) exhibited excellent linearity ($R^2 = 0.9945\text{--}0.9952$), indicating that the adsorption of VST molecules follows the Langmuir model and occurs predominantly through monolayer coverage on a relatively homogeneous steel surface. The slopes of the fitted plots were close to unity, further confirming the applicability

Table 1
Adsorption isotherms parameters for VST.

Isotherm Model	Temp. (K)	Slope	Intercept	R ²	K _{ads} /K	n	1/y	a	ΔG _{ads}
Langmuir	318	1.012	18.45	0.9952	0.0542	—	—	—	−2.91
	328	0.9809	21.0381	0.9949	0.0475	—	—	—	−2.65
	338	1.0185	25.6597	0.9945	0.039	—	—	—	−2.17
Freundlich	318	0.4757	−2.0448	0.9992	0.1294	2.1	—	—	−5.21
	328	0.4373	−2.0386	0.9994	0.1302	2.29	—	—	−5.39
	338	0.4349	−2.1232	0.9996	0.1197	2.3	—	—	−5.32
Temkin	318	0.1772	0.1456	0.9989	—	—	—	2.27	−12.76
	328	0.1678	0.0422	0.9985	—	—	—	1.29	−11.65
	338	0.1542	0.0536	0.9978	—	—	—	1.42	−12.39
El-Awady	318	0.8691	−5.3421	0.9992	0.00479	—	1.15	—	3.5
	328	0.8392	−5.5108	0.9991	0.00404	—	1.19	—	4.1
	338	0.7934	−5.6557	0.9986	0.0035	—	1.26	—	4.63

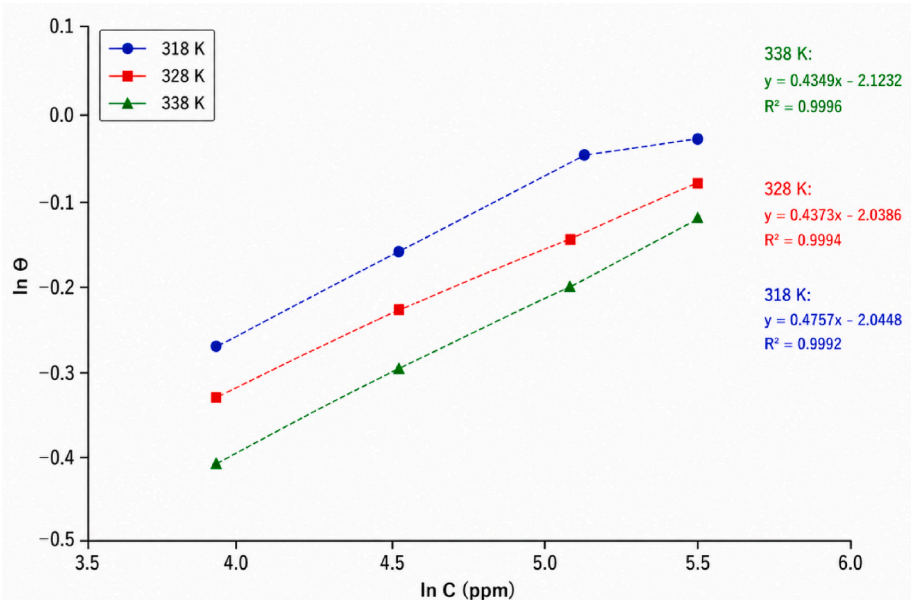


Fig. 4. Freundlich adsorption isotherm for plots for N80 steel in VST inhibitor at vary temperatures.

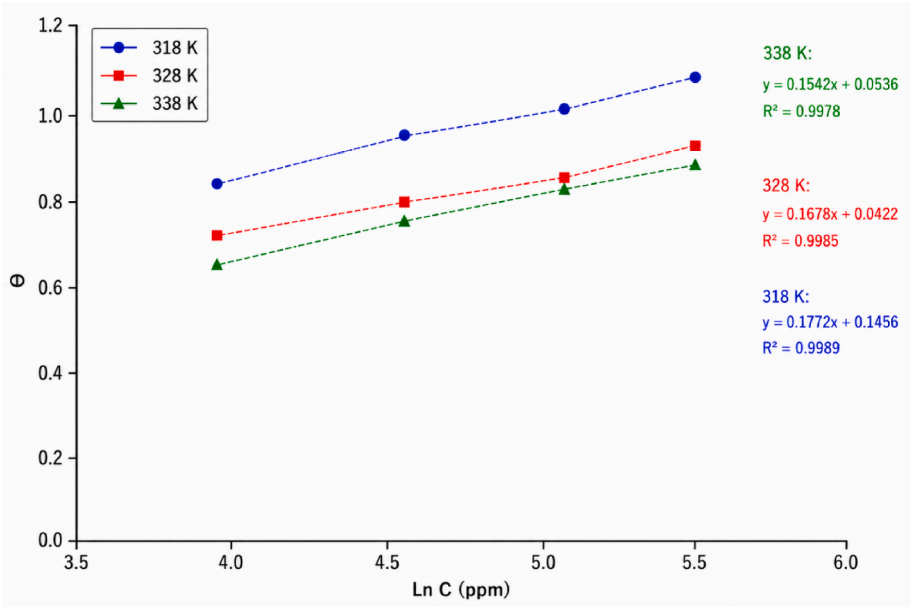


Fig. 5. Temkin adsorption isotherm plots for N80 steel in VST inhibitor at vary temperatures.

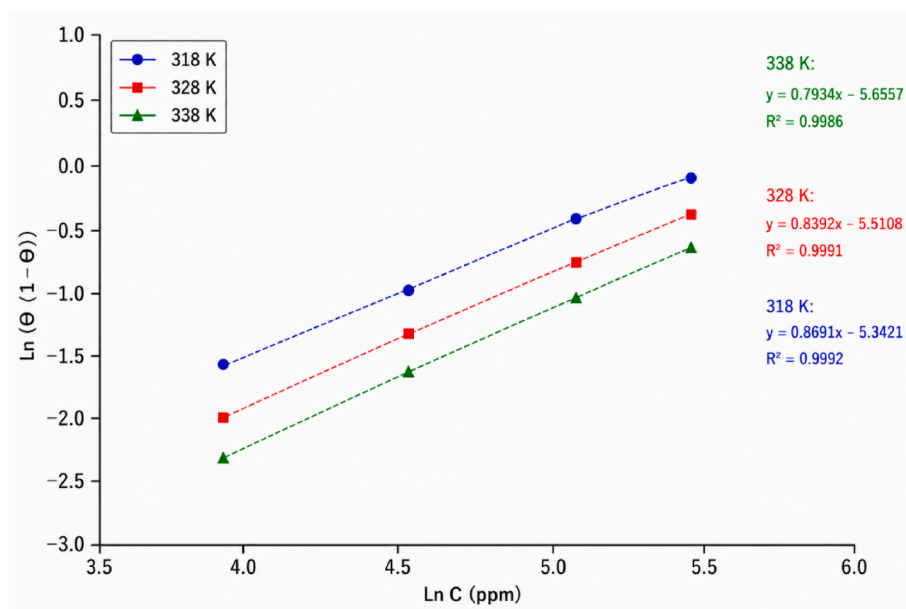


Fig. 6. El-Awady adsorption isotherm plots for N80 steel in VST inhibitor at vary temperatures.

of the model. As summarized in Table 1, the adsorption equilibrium constant K_{ads} decreased from 0.0542 at 318 K to 0.0390 at 338 K, demonstrating that the adsorption strength weakened with increasing temperature. This decrease in K_{ads} , together with the increase in corrosion rate and the reduction in inhibition efficiency at elevated temperatures, indicates progressive desorption of inhibitor molecules from the steel surface, which is characteristic of a predominantly physisorption-controlled process.

The Gibbs free energy of adsorption (ΔG_{ads}) values obtained from the Langmuir model were negative, ranging from -2.91 to -2.17 kJ mol^{-1} , confirming that the adsorption process occurred spontaneously. The relatively low magnitude of ΔG_{ads} suggests that adsorption was primarily governed by weak electrostatic interactions rather than chemical bond formation. This interpretation is further supported by the observed decrease in adsorption strength with increasing temperature and the corresponding reduction in inhibition efficiency. In addition, the

positive values of ΔH_{ads} indicate that the adsorption process is endothermic, whereas the negative ΔS_{ads} values suggest increased ordering of inhibitor molecules at the metal–solution interface during the formation of the protective adsorbed film. The Freundlich adsorption isotherm (Fig. 4) also showed excellent agreement with the experimental data ($R^2 > 0.999$), indicating favorable adsorption on a heterogeneous steel surface. Furthermore, the adsorption intensity parameter ($n > 1$) confirms the strong affinity of VST molecules for the steel surface. Likewise, the Temkin adsorption isotherm (Fig. 5) exhibited excellent linearity ($R^2 = 0.9978$ – 0.9989), suggesting that interactions between adjacent adsorbed inhibitor molecules contribute to the overall adsorption process. Although the Temkin model produced slightly more negative ΔG_{ads} values than the Langmuir model, this observation does not necessarily indicate chemisorption. Instead, it reflects the contribution of lateral interactions among neighboring adsorbed molecules, which enhance the stability of the protective inhibitor film.

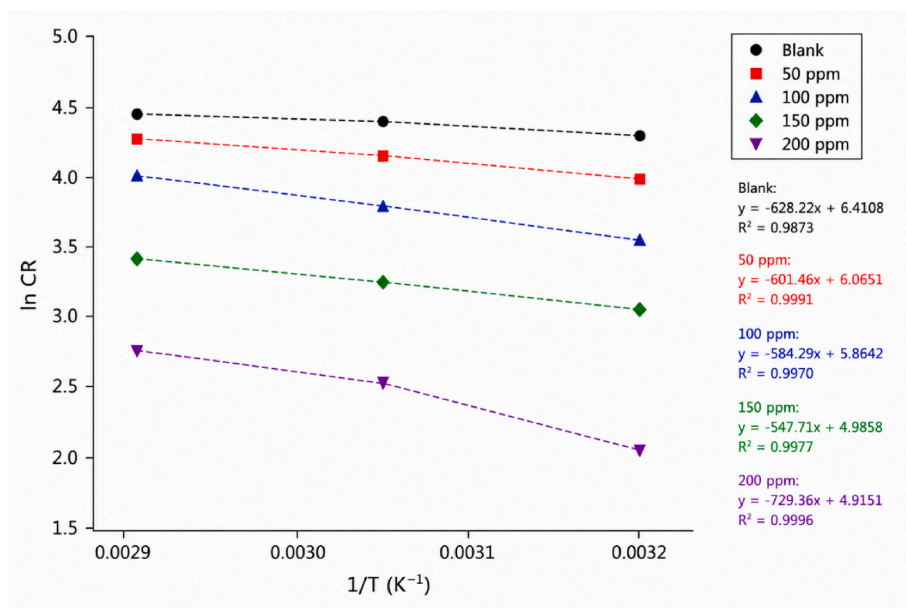


Fig. 7. Arrhenius plots for N80 steel in VST inhibitor at vary concentrations.

Table 2

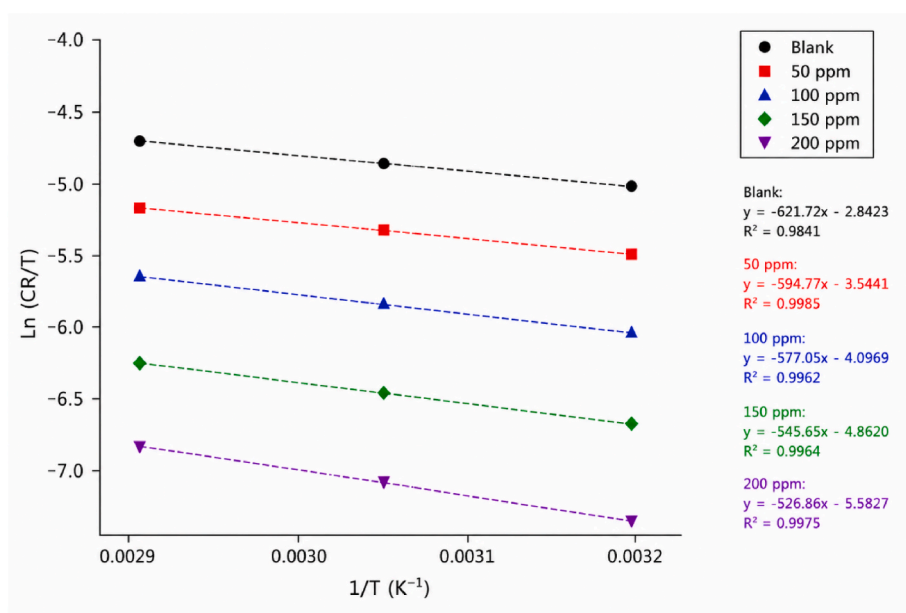
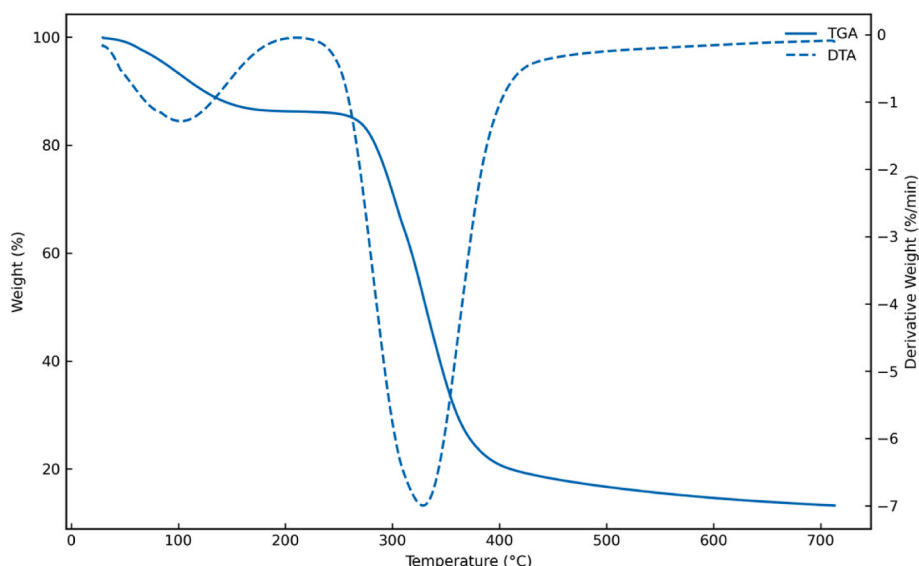
Thermodynamic parameters for VST.

S. No	VST (System) Conc.(g/L)	Ea (KJ/mol)	$-\Delta G_{\text{ads}}$ (KJ/mol)			ΔH_{ads} (KJ/mol)	ΔS_{ads} (KJ/mol)
			318K	328K	338K		
1	0	5.22	12.83	13.24	13.64	5.17	-0.024
2	50	5	13.79	14.22	14.65	4.94	-0.028
3	100	4.86	14.72	15.18	15.64	4.8	-0.031
4	150	4.55	15.63	16.12	16.61	4.54	-0.034
5	200	6.06	16.56	17.08	17.6	4.38	-0.037

Similarly, the El-Awady adsorption isotherm (Fig. 6) produced excellent correlation coefficients ($R^2 > 0.998$), indicating that VST adsorption may involve the occupation of multiple active sites on the N80 steel surface. The good agreement obtained with all four adsorption models demonstrates the complexity of the adsorption process while confirming the strong interaction between the inhibitor molecules and

the steel surface. The combined adsorption and thermodynamic results demonstrate that the corrosion inhibition of expired valsartan is spontaneous and predominantly governed by physical adsorption. The nitrogen- and oxygen-containing functional groups, together with the aromatic π -electron systems present in the valsartan molecule, facilitate adsorption through electrostatic interactions and donor-acceptor interactions with the steel surface. The resulting protective adsorbed film effectively suppresses anodic metal dissolution and retards the corrosion process. However, increasing temperature weakens the adsorption strength, promotes partial desorption of inhibitor molecules, and consequently reduces the inhibition efficiency, further confirming the predominance of a physisorption-controlled corrosion inhibition mechanism [48–51].

The activation and thermodynamic parameters provide further insight into the corrosion inhibition mechanism of expired valsartan (VST) on N80 steel in 1.0 M HCl. The Arrhenius plots in Fig. 7 and Table 2 showed that the apparent activation energy (Ea) generally

**Fig. 8.** Transition state plots for N80 steel in VST inhibitor at vary concentrations.**Fig. 9.** TGA and DTA plots of VST inhibitor.

decreased with increasing inhibitor concentration, indicating that the adsorption of VST molecules promoted the formation of a protective barrier on the steel surface. The lower activation energies observed for the inhibited systems suggest that corrosion protection was primarily achieved through surface coverage by adsorbed inhibitor molecules, thereby reducing the number of active corrosion sites. However, at 200 ppm, a slight increase in activation energy was observed, which may be attributed to the formation of a more compact inhibitor film or to structural rearrangement of the adsorbed layer at higher surface coverage [51].

The transition-state thermodynamic plot in Fig. 8 and Table 2 further support the proposed adsorption mechanism. The positive enthalpy values (ΔH_{ads}) indicate that the adsorption process is endothermic, while the negative entropy values (ΔS_{ads}) suggest a decrease in randomness at the metal–solution interface during adsorption. This reduction in entropy is attributed to the orderly arrangement of VST molecules on the N80 steel surface as the protective film is formed. The Gibbs free energy of adsorption (ΔG_{ads}) became more negative with increasing inhibitor concentration, indicating that the adsorption process became increasingly spontaneous as more inhibitor molecules became available to occupy the active sites on the steel surface. Nevertheless, despite the endothermic nature of the adsorption process, the observed decrease in adsorption equilibrium constant (K_{ads}) and inhibition efficiency with increasing temperature indicates that elevated temperatures promote partial desorption of the adsorbed inhibitor layer. This behavior is consistent with a predominantly physisorption-controlled mechanism, in which adsorption is governed mainly by weak electrostatic interactions. The activation and thermodynamic analyses demonstrate that expired valsartan inhibits the corrosion of N80 steel through spontaneous adsorption and the formation of a protective surface film. Although the adsorption process is predominantly physical in nature, the nitrogen- and oxygen-containing functional groups together with the aromatic π -electron systems present in the valsartan molecule may contribute to stronger donor–acceptor interactions with the steel surface. These interactions enhance the stability of the adsorbed film without providing conclusive evidence for significant chemisorption [25,47,52–57].

3.4. Thermal stability analysis

The combined TGA–DTA thermogram depicted in Fig. 9 demonstrated that expired valsartan (VST) possesses excellent thermal stability over a broad temperature range, highlighting its suitability as a corrosion inhibitor for acidized oil-well environments. Thermal analysis was performed to evaluate the structural integrity of the inhibitor and to determine whether the adsorption-active functional groups remained stable under the elevated temperatures encountered during corrosion protection applications. The initial weight loss observed below approximately 170 °C was attributed to the removal of physically adsorbed moisture and other volatile components. The relatively small mass loss within this region indicates that the inhibitor undergoes negligible thermal degradation at low and moderate temperatures. Between 170 and 260 °C, the TGA curve exhibited only a slight decrease in mass, suggesting that the molecular structure of valsartan remained largely intact. This thermal stability is advantageous because the adsorption-active functional groups responsible for interaction with the N80 steel surface are preserved under temperatures commonly encountered during oilfield acidizing operations.

The principal thermal decomposition stage occurred between approximately 260 and 400 °C, where a significant reduction in sample mass was accompanied by a pronounced DTA peak at 330–340 °C, corresponding to the maximum decomposition rate. This stage is associated with the breakdown of the valsartan molecular structure and the progressive loss of adsorption-active functional groups. Since the onset of significant thermal decomposition occurs well above the temperatures typically encountered during acidized oil-well operations, expired

Table 3

Design Matrix and result for inhibiting N80 steel corrosion in 1M HCl with VST.

Std	Run	Factor 1	Factor 2	Factor 3	Response 1
		A:Time	B:Temperature	C:Concentration	Inhibition efficiency
		h	K	ppm	%
50	1	4	318	50	66.80
11	2	4	318	100	78.50
22	3	4	318	150	85.60
18	4	4	318	200	98.20
48	5	4	328	50	67.95
44	6	4	328	100	78.45
5	7	4	328	150	82.70
53	8	4	328	200	92.30
25	9	4	338	50	55.30
12	10	4	338	100	63.67
39	11	4	338	150	69.59
16	12	4	338	200	88.50
15	13	8	318	50	67.40
27	14	8	318	100	76.40
55	15	8	318	150	87.40
57	16	8	318	200	93.25
34	17	8	328	50	66.69
8	18	8	328	100	74.60
46	19	8	328	150	86.24
38	20	8	328	200	96.74
20	21	8	338	50	82.10
6	22	8	338	100	76.30
54	23	8	338	150	72.56
24	24	8	338	200	88.56
4	25	12	318	50	65.73
13	26	12	318	100	75.83
47	27	12	318	150	88.34
32	28	12	318	200	98.56
31	29	12	328	50	55.62
52	30	12	328	100	70.63
59	31	12	328	150	74.57
28	32	12	328	200	87.64
9	33	12	338	50	53.10
17	34	12	338	100	66.45
19	35	12	338	150	78.12
23	36	12	338	200	92.25
36	37	16	318	50	66.40
56	38	16	318	100	76.50
37	39	16	318	150	87.30
42	40	16	318	200	93.44
49	41	16	328	50	56.45
26	42	16	328	100	65.38
14	43	16	328	150	74.22
41	44	16	328	200	88.45
29	45	16	338	50	54.45
60	46	16	338	100	68.23
3	47	16	338	150	66.45
45	48	16	338	200	91.43
43	49	20	318	50	62.14
51	50	20	318	100	72.00
40	51	20	318	150	83.3
58	52	20	318	200	96.45
33	53	20	328	50	55.63
30	54	20	328	100	65.75
7	55	20	328	150	80.42
21	56	20	328	200	85.29
1	57	20	338	50	56.40
2	58	20	338	100	66.48
35	59	20	338	150	76.29
1	60	20	338	200	84.28

valsartan is expected to retain its corrosion inhibition capability under normal field operating conditions. Beyond 400 °C, the rate of decomposition decreased markedly, and the TGA curve gradually approached a residual mass of approximately 13% at 720 °C. The residual mass is attributed to the formation of thermally stable carbonaceous residues generated during thermal degradation. The presence of this residue demonstrates the material's resistance to complete thermal decomposition and further confirms its thermal robustness. The TGA–DTA results

Table 4
ANOVA of VST inhibition efficiency for mitigating N80 steel corrosion in 1M HCl.

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	8034.29	9	892.70	36.56	<0.0001 significant
A-Time	229.08	1	229.08	9.38	0.0035
B-Temperature	710.40	1	710.40	29.10	<0.0001
C-Concentration	6970.59	1	6970.59	285.51	<0.0001
AB	0.3188	1	0.3188	0.0131	0.9095
AC	39.71	1	39.71	1.63	0.2081
BC	15.40	1	15.40	0.6306	0.4309
A ²	13.46	1	13.46	0.5515	0.4612
B ²	29.08	1	29.08	1.19	0.2804
C ²	26.25	1	26.25	1.08	0.3047
Residual	1220.73	50	24.41		
Cor Total	9255.01	59			
Std. Dev.	4.94		R²	0.8681	
Mean	76.27		Adjusted R²	0.8444	
C.V. %	6.48		Predicted R²	0.8084	
			Adeq Precision	21.3431	

demonstrate that expired valsartan maintains its structural integrity up to approximately 260 °C, which is substantially higher than the temperatures encountered in most oilfield acidizing operations. This excellent thermal stability ensures the preservation of adsorption-active functional groups required for protective film formation, thereby supporting the practical application of expired valsartan as a corrosion inhibitor for N80 steel in aggressive acidic oil-well environments [41].

3.5. Experimental design matrix and ANOVA of the RSM model

The experimental design matrix together with the corresponding inhibition efficiency (IE) values for the corrosion inhibition of N80 steel in 1.0 M HCl is presented in Table 3. The investigated process variables were immersion time (4–20 h), temperature (318–338 K), and inhibitor concentration (50–200 ppm). The experimental inhibition efficiencies ranged from 53.10% to 98.56%, demonstrating that the selected operating variables exerted a significant influence on the corrosion inhibition performance of expired valsartan (VST). The highest inhibition efficiencies were achieved at higher inhibitor concentrations and lower temperatures, indicating that the corrosion protection performance of VST is strongly governed by surface coverage and the stability of the adsorbed inhibitor film. The adequacy and statistical significance of the developed quadratic Response Surface Methodology (RSM) model were evaluated using analysis of variance (ANOVA), as summarized in Table 4. The model exhibited a high F-value of 36.56 with a corresponding p-value <0.0001, confirming that the regression model is highly significant and accurately describes the relationship between the process variables and the inhibition efficiency within the investigated experimental domain. Among the linear model terms, inhibitor concentration (C) was identified as the most influential factor, with an F-value of 285.51 and $p < 0.0001$. This result demonstrates that increasing the VST concentration significantly enhances the adsorption of inhibitor molecules on the N80 steel surface, resulting in improved surface coverage and greater corrosion protection. Temperature (B) also exhibited a significant effect ($F = 29.10$, $p < 0.0001$), confirming that increasing temperature adversely affects inhibitor performance by reducing the stability of the adsorbed film and promoting the desorption of physically adsorbed inhibitor molecules from the steel surface [41]. Immersion time (A) was likewise statistically significant ($p = 0.0035$), indicating that prolonged exposure influences the stability and compactness of the protective inhibitor layer during the corrosion process.

In contrast, the interaction terms (AB, AC, and BC) and the quadratic terms (A², B², and C²) were statistically insignificant ($p > 0.05$), indicating that within the investigated experimental range, the inhibition efficiency was predominantly controlled by the individual linear effects of inhibitor concentration, temperature, and immersion time rather than

by interaction or curvature effects.

The goodness-of-fit statistics further demonstrated the predictive capability of the developed model. The coefficient of determination ($R^2 = 0.8681$) indicates that 86.81% of the variation in inhibition efficiency is explained by the regression model. Furthermore, the close agreement between the adjusted coefficient of determination (Adjusted $R^2 = 0.8444$) and the predicted coefficient of determination (Predicted $R^2 = 0.8084$) confirms the robustness and predictive reliability of the model. The relatively low coefficient of variation ($CV = 6.48\%$) reflects good experimental precision and reproducibility, while the Adequate Precision value of 21.3431, which is substantially greater than the recommended minimum value of 4, demonstrates an excellent signal-to-noise ratio and confirms the suitability of the model for navigating the design space. The statistical analysis confirms that the developed RSM model provides a reliable and accurate tool for predicting and optimizing the corrosion inhibition performance of expired valsartan for N80 steel in simulated acidized oil-well environments. The results further demonstrate that inhibitor concentration is the dominant process variable governing inhibition efficiency, whereas elevated temperature remains the principal factor limiting corrosion protection because of the reduced stability of the adsorbed inhibitor film [58].

3.6. RSM coded regression modeling

The coded regression model developed using Response Surface Methodology (RSM) is presented in Eq. (15). This model enables prediction of the response at any selected combination of independent variables within the investigated experimental domain. The corresponding regression equation expressed in terms of the actual (uncoded) process variables is provided in Eq. (16), allowing direct prediction of the response using real experimental units.

$$IE\% = 75.03 - 1.76A - 4.21B + 14.46C + 0.1263AB + 1.54AC - 0.8324BC - 1.13A^2 + 1.48B^2 + 1.49C^2 \quad (15)$$

$$\text{Inhibition efficiency} = +1748.19815 - 0.759982\text{Time} - 9.98912\text{Temperature} + 0.459804\text{Concentration} + 0.001578\text{Time} * \text{Temperature} + 0.002573\text{Time} * \text{Concentration} - 0.001110\text{Temperature} * \text{Concentration} - 0.017693\text{Time}^2 + 0.014767\text{Temperature}^2 + 0.000265\text{Concentration}^2 \quad (16)$$

The response surface plots illustrating the effects of the process variables on the inhibition efficiency (IE) of expired valsartan (VST) for N80 steel in 1.0 M HCl are presented in Fig. 10a–d. The parity plot (Fig. 10a) demonstrates excellent agreement between the experimental and model-predicted inhibition efficiencies, as evidenced by the close distribution of the data points along the diagonal line. This agreement confirms the adequacy of the developed quadratic RSM model for

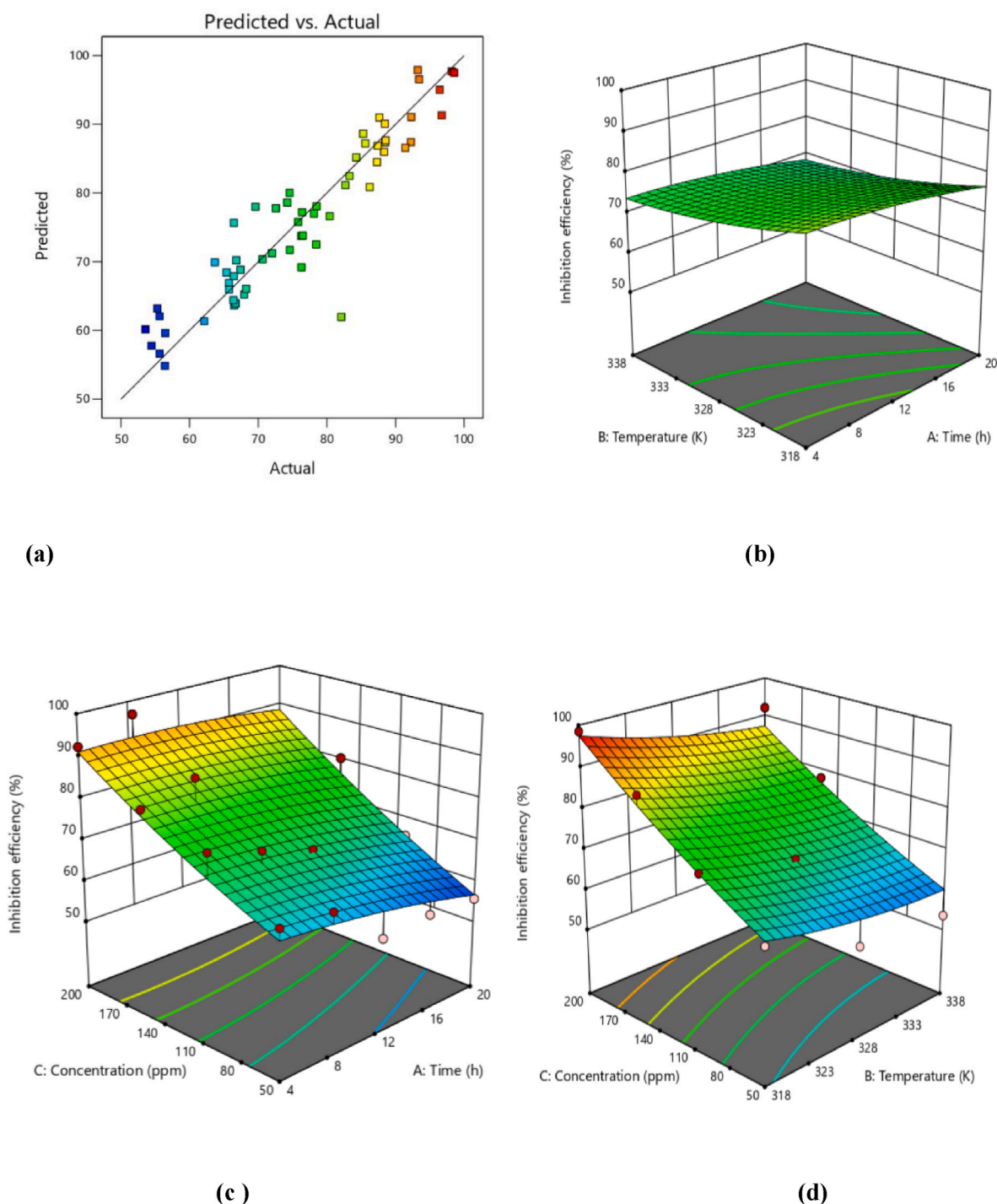


Fig. 10. (a) RSM experimental vs predicted IE (b) 3 dimensional plot of IE versus temperature and time (c) 3D Dimensional diagnostic plot of IE versus concentration and time (d) diagnostic plot of IE versus inhibitor concentration and temperature.

predicting the corrosion inhibition performance within the investigated experimental domain. The three-dimensional response surface plots (Fig. 10b–d) illustrate the combined effects of inhibitor concentration, immersion time, and temperature on the inhibition efficiency. The response surfaces reveal that inhibitor concentration exerts the greatest influence on corrosion protection, with inhibition efficiency increasing markedly as the concentration of VST increases. This behavior is attributed to the greater availability of inhibitor molecules for adsorption onto the N80 steel surface, leading to improved surface coverage and the formation of a more compact and protective adsorbed film.

In contrast, increasing temperature generally reduced the inhibition

efficiency because elevated temperatures promote thermal agitation and partial desorption of physically adsorbed VST molecules from the steel surface, thereby weakening the protective film. Immersion time also influenced the inhibition performance, although its effect was less pronounced than that of inhibitor concentration. Prolonged exposure resulted in a gradual reduction in adsorption stability due to progressive deterioration of the protective inhibitor layer. The response surface plots further indicate the existence of an optimum operating region where the combined effects of inhibitor concentration, temperature, and immersion time produced maximum corrosion protection. Under the optimized conditions predicted by the RSM model, an experimental inhibition

Table 5

Validation of optimal parameters.

System	Optimal inhibition Conc.ppm)	Optimal temperature (K)	Optimal time(h)	Optimal inhibitor efficiency
N80 steel in 1M HCl with VST	125	328	12	76.8

efficiency of 98.56% was achieved, demonstrating the excellent corrosion inhibition performance of expired valsartan for N80 steel in 1.0 M HCl. The close agreement between the predicted and experimental results further validates the reliability of the developed optimization model and confirms its suitability for predicting optimum operating conditions for corrosion protection in acidized oil-well environments [59].

3.7. RSM model validation

The optimized operating conditions for minimizing the corrosion of N80 steel in 1.0 M HCl using expired valsartan (VST), together with the corresponding inhibition efficiency (IE), are presented in Table 5. Under the optimum conditions, an experimental inhibition efficiency of 76.8% was achieved, demonstrating that expired valsartan provides effective corrosion protection for N80 steel in the investigated acidic medium. The observed inhibition performance is attributed to the presence of multiple adsorption-active functional groups, including tetrazole, amide, carboxyl, and aromatic moieties, together with nitrogen- and oxygen-containing heteroatoms and conjugated π -electron systems within the valsartan molecule. These structural features promote the adsorption of VST molecules onto the steel surface, leading to the formation of a stable protective film that suppresses anodic metal dissolution and reduces the overall corrosion rate. The validity of the developed optimization model was verified experimentally by comparing the predicted inhibition efficiency with the measured value under the optimum operating conditions. The experimental result showed excellent agreement with the model prediction, with a deviation of only 2.6%, confirming the accuracy, reliability, and predictive capability of the developed Response Surface Methodology (RSM) model. These findings demonstrate that the model is suitable for predicting and optimizing the corrosion inhibition performance of expired valsartan for N80 steel in simulated acidized oil-well environments [43].

4. Conclusion

This study demonstrated that expired valsartan (VST) is an effective, low-cost, and environmentally sustainable corrosion inhibitor for N80 steel in a simulated acidized oil-well environment (1.0 M HCl). The inhibition efficiency increased with increasing inhibitor concentration but decreased with increasing temperature and immersion time, indicating that the adsorption stability of the inhibitor is influenced by operating conditions. Adsorption and thermodynamic analyses revealed that VST adsorbs spontaneously onto the steel surface, forming a protective barrier that suppresses metal dissolution through a predominantly physisorption-controlled mechanism. The adsorption behavior was satisfactorily described by the Langmuir, Freundlich, Temkin, and El-Awady isotherm models, confirming favorable interaction between VST molecules and the N80 steel surface. Thermal analysis further demonstrated that expired valsartan retained its structural integrity up to approximately 260 °C, indicating sufficient thermal stability for corrosion protection under typical oilfield acidizing conditions. Response Surface Methodology (RSM) successfully optimized the corrosion inhibition process, identifying an optimum inhibitor concentration of 125 ppm, a temperature of 328 K, and an immersion time of 12 h, at which an experimental inhibition efficiency of 76.8% was

achieved. The close agreement between the predicted and experimental results confirmed the reliability and predictive capability of the developed optimization model. The findings demonstrate that expired valsartan offers a practical approach to corrosion mitigation while simultaneously providing a sustainable strategy for the reutilization of expired pharmaceutical waste. Consequently, this work contributes to the advancement of environmentally benign corrosion protection technologies and supports circular economy principles in the petroleum industry. A limitation of the present study is the absence of direct surface characterization of the inhibited steel specimens. Future work should therefore incorporate advanced surface analytical techniques, including Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM/EDS), Atomic Force Microscopy (AFM), and X-ray Photoelectron Spectroscopy (XPS), to directly characterize the morphology, composition, and chemical nature of the protective adsorbed film and to further elucidate the corrosion inhibition mechanism of expired valsartan.

Availability of data and materials

The datasets used and/or analyzed during the current paper are available from the corresponding author on reasonable request.

CRediT authorship contribution statement

Silas O. Okuma: Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Supervision, Writing – original draft, Writing – review & editing. **Cynthia C. Nwaeju-Okechukwu:** Formal analysis, Investigation, Writing – review & editing. **Ejovi O. Oga-gavwodia:** Formal analysis, Methodology, Resources, Writing – review & editing. **Clever Kate Ojoba:** Writing – review & editing. **Martins Obaseki:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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