OPTIMIZATION AND THERMODYNAMIC CHARACTERISTICS OF COPPER CORROSION INHIBITION BY EXPIRED TOPLEX SYRUP IN SULFURIC ACID

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ABSTRACT

This study investigates the effectiveness of expired Toplex syrup as a sustainable and eco-friendly corrosion inhibitor for copper in 0.5 M sulfuric acid (H_2SO_4), using weight loss measurements to assess its performance. The influence of critical parameters inhibitor concentration (0.1 - 0.4 % v/v), temperature (293 - 323 K), and immersion time (0.5 - 1.5 h)-on corrosion rate and inhibition efficiency were comprehensively examined. Experimental results revealed a direct correlation between inhibition efficiency and both Toplex concentration and temperature, with peak efficiency (95.55 %) was achieved at 0.385 % v/v, 322.5 K, and 1 h of immersion. Optimization using Response Surface Methodology (RSM) with a central composite design yielded a statistically robust and predictive model (R^2 = 0.994, Q^2 = 0.946). Adsorption behaviour followed both the Langmuir and Temkin isotherms, while thermodynamic analysis confirmed a spontaneous physisorption mechanism, as evidenced by negative Gibbs free energy values (ΔG_{ads} = - 11.69 to - 17.46 kJ mol^{-1}). Activation energy calculations indicated an endothermic corrosion process, with significantly higher energy barriers observed in the presence of the inhibitor supporting a predominantly physical adsorption mechanism. Furthermore, Scanning Electron Microscopy (SEM) revealed the formation of a uniform and protective film on the copper surface, confirming the role of Toplex syrup in mitigating acid-induced degradation. These findings highlight the potential of expired Toplex syrup as an effective, low-cost, and environmentally benign corrosion inhibitor for copper in acidic environments, with promising implications for industrial applications.

Keywords: *toplex syrup, copper, sulfuric acid, corrosion inhibition, optimization.*

INTRODUCTION

Corrosion represents a major challenge for industries such as electronics, marine, energy, and manufacturing, where material degradation compromises the durability, safety, and efficiency of metallic components [1]. Copper, prized for its superior electrical and thermal conductivity, mechanical workability, and moderate corrosion resistance, is widely utilized in applications including wiring, heat exchangers, pipelines, and industrial machinery [2 - 4]. However, in aggressive acidic environments, such as sulfuric acid, copper is prone to severe corrosion due to the absence of a stable protective oxide layer, leading to substantial economic

losses and operational inefficiencies [5]. To address this, corrosion inhibitors are employed to form protective films on metal surfaces, reducing direct exposure to corrosive agents and extending equipment lifespan [6]. Organic compounds with heteroatoms (e.g., N, S, O) and π-conjugated systems exhibit high efficacy due to their strong adsorption onto metal surfaces through electron-donor interactions [7, 8]. In recent years, the repurposing of expired pharmaceuticals as corrosion inhibitors has emerged as a promising eco-friendly strategy [9]. These compounds, often structurally like conventional organic inhibitors, possess polar functional groups and aromatic systems that facilitate robust adsorption. Expired drugs, retaining chemical stability beyond their expiration dates, offer a sustainable, low-cost alternative to traditional toxic inhibitors due to their biodegradability, widespread availability, and minimal environmental impact. This approach aligns with the growing demand for green chemistry solutions in corrosion management, reducing reliance on hazardous chemicals while valorising pharmaceutical waste. The effectiveness of corrosion inhibitors depends on factors such as inhibitor concentration, temperature, immersion time, and the corrosive medium's properties [10]. To optimize these parameters efficiently, statistical tools like Design of Experiments (DoE) and Response Surface Methodology (RSM) are increasingly utilized. RSM, employing polynomial modelling, enables the systematic analysis of variable effects and interactions, minimizing experimental runs while maximizing precision, cost-effectiveness, and predictive accuracy [11, 12].

Expired pharmaceuticals present a sustainable strategy for corrosion control, combining waste reduction with eco-friendly metal protection. This work investigates the inhibitory performance of expired Toplex syrup on copper in 0.5 M H_2SO_4. The influence of concentration, temperature, and immersion time was optimized using Response Surface Methodology. Thermodynamic analysis and SEM observations further confirm its adsorption-driven protective action and film formation.

EXPERIMENTAL

Spaceman preparation and weight loss measurements

Weight loss experiments were conducted to evaluate the corrosion inhibition performance of expired Toplex syrup on copper in 0.5 M H_2SO_4. Rectangular copper specimens, with a composition of 99.9 % Cu, were polished using emery papers (grades 600 to 1200), cleaned with double-distilled water, degreased with acetone (99 %, Sigma-Aldrich, Germany), dried, and weighed using an analytical balance (precision 0.1 mg). A 0.5 M H_2SO_4solution was prepared by diluting 98 % sulfuric acid (Merck, Germany) with double-distilled water. Each specimen was immersed in 100 mL of the test solution, either without or with varying concentrations of Toplex syrup (0.1 % to 0.4 % v/v), at temperatures ranging from 293 to 323 K for immersion periods of 0.5 to 1.5 h. Post-immersion, specimens were retrieved, rinsed with double-distilled water, dried, and reweighed to determine weight loss. All measurements were performed in triplicate to ensure reproducibility, with mean values reported. The corrosion rate (CR, mg cm^{-2} h^{-1}), inhibition efficiency (IE, %), and surface coverage (θ) were calculated using the following Eq. (1) and Eq. (2) [13]:

$$IE\ (\%) = 100 \times (CR_0 - CR_{inh}) / CR_0 \quad (1)$$

$$CR = (m_i - m_f) / t \times S \quad (2)$$

where m_i and m_f are the initial and final masses (mg) of the specimen, S is the surface area (cm^2), t is the immersion time (h), and CR_0 and CR_{inh} are the corrosion rates in the absence and presence of the inhibitor, respectively. These measurements provided reliable data for assessing the inhibitory efficacy of Toplex syrup and its adsorption characteristics on the copper surface.

Adsorption isotherm and thermodynamic parameter determination

To investigate the adsorption behaviour of expired Toplex syrup on copper surfaces in 0.5M H_2SO_4, surface coverage data, obtained from weight loss measurements, were analysed using multiple isotherm models: Langmuir, Freundlich, Frumkin, Temkin, Flory-Huggins, and El-Awady. These models were selected to capture diverse adsorption characteristics, such as uniform monolayer formation, heterogeneous surface interactions, intermolecular forces, changes in adsorption energy with coverage, replacement of water molecules by inhibitor molecules, and the number of active sites occupied per inhibitor molecule. Linearized versions of

each model were used to relate inhibitor concentrations (0.1 - 0.4 % v/v) to surface coverage (θ), calculated as ($\theta = IE / 100$), where IE is the inhibition efficiency from weight loss experiments [13]. The Langmuir model assumes identical, non-interacting adsorption sites; the Freundlich model accounts for variable surface energies; the Frumkin model incorporates lateral interactions among adsorbed molecules; the Temkin model assumes a linear decrease in adsorption energy; the Flory-Huggins model considers water molecule displacement; and the El-Awady model evaluates active site occupancy. The fit of each model was assessed by calculating the linear regression coefficient using standard statistical software.

Thermodynamic parameters were determined to characterize the adsorption process of Toplex syrup on copper. The Gibbs free energy of adsorption (ΔG_{ads}) was calculated using the adsorption equilibrium constant (K_{ads}) derived from the isotherm models, employing the Eq. (3) [13]:

$$\Delta G_{ads} = - RT \times \ln (K_{ads} \times 55.5) \quad (3)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature in Kelvin, and 55.5 is the molar concentration of water in the solution (mol L^{-1}). The enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) of adsorption were determined using the Gibbs free energy relation Eq. (4) [14]:

$$\Delta G_{ads} = \Delta H_{ads} - T \times \Delta S_{ads} \quad (4)$$

A linear regression of ΔG_{ads} versus temperature was performed to obtain ΔH_{ads} (intercept) and $- \Delta S_{ads}$ (slope). Experiments were conducted at temperatures of 293, 303, 313, and 323 K, with surface coverage and K_{ads} values derived from weight loss data at varying Toplex concentrations (0.1 - 0.4 % v/v). All calculations were performed using standard statistical software to ensure precision and consistency.

Thermodynamic activation parameters analysis

The temperature dependence of corrosion rates provides critical insights into the reaction kinetics and inhibitor mechanism [15]. We employed fundamental thermodynamic relationships to characterize the activation barrier and molecular interactions during the corrosion process. The activation energy (E_{act}) was evaluated using the Arrhenius equation Eq. (5) to determine the energy barrier associated with the corrosion reaction [16]:

$$CR = A \cdot \exp (- E_{act} / RT) \quad (5)$$

where CR is the corrosion rate (mg cm^{-2} h^{-1}), A is the Arrhenius pre-exponential factor, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K). Experimental corrosion rates, measured at various temperatures (293 - 323 K), were converted into natural logarithms and plotted as lnCR versus 1/T. The slope of the resulting straight line ($- E_{act}/R$) was used to calculate the activation energy. To further examine the transition-state parameters, the activation enthalpy (ΔH_{act}) and activation entropy (ΔS_{act}) were obtained from the transition state theory (Eyring) equation Eq. (6) [16]:

$$\ln(CR / T) = [\ln(R / Nh) + (\Delta S_{act} / R)] - \Delta H_{act} / RT \quad (6)$$

where N is Avogadro's number (6.022×10^{23} mol^{-1}), and h is Planck's constant (6.626×10^{-34} J s). A linear plot of $\ln(C_R/T)$ versus 1/T was constructed, where the slope ($- \Delta H_{act}/R$) yielded ΔH_{act} and from the intercept of the dependence on the ordinate axis can be determined ΔS_{act}.

The activation Gibbs free energy (ΔG_{act}) at 308 K was calculated using Eq. (4), while the values of ΔH_{act} and ΔS_{act} were previously determined from Eq. (6). This parameter reflects the spontaneity and feasibility of the corrosion process in the presence and absence of the inhibitor.

Experimental precision was enhanced by carefully calibrating the test environment and correcting for any slight variations in sample surface area or solution temperature. This comprehensive evaluation of activation parameters provides deeper insight into the corrosion mechanism and the inhibitive action of the expired drug [17].

Design of experiments study

The experimental design for this study was established using Response Surface Methodology (RSM), a statistical technique that combines experimental design, regression modelling, and optimization to evaluate the influence of multiple factors and their interactions on a target response while minimizing the number of experiments. Design and analysis were performed

using MODDE® 9.1 software (Sartorius, Germany), which facilitated the construction of a central composite face-centered (CCF) design [18]. This design was used to examine both individual and interactive effects of three independent variables: inhibitor concentration (X_1), temperature (X_2), and immersion time (X_3). Each factor was tested at three coded levels (- 1, 0, +1) as shown in Table 1. The design included 17 experiments, comprising factorial, axial, and center points to ensure accurate estimation of curvature and model validation.

The correlation between the variables (X_1, X_2, X_3) and inhibition efficiency (IE) was described by a second-order polynomial model Eq. (7) :

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + \varepsilon \quad (7)$$

where Y is the response (IE), b_0 is the intercept, b_1, b_2, b_3 are linear coefficients, b_{11}, b_{22}, b_{33} are quadratic coefficients, b_{12}, b_{13}, $b_{23}$are interaction coefficients, and ε is the statistical random error term. Multiple Linear Regression (MLR) within the RSM framework was used to estimate the coefficients, evaluate factor significance, and generate 3D surface and contour plots. Model reliability was confirmed through statistical indicators including R^2, Q^2, and ANOVA, ensuring that the model was both accurate and predictive [18]. Optimization of inhibition efficiency (IE) was achieved by analysing the response surfaces, which enabled the identification of optimal experimental conditions. The RSM approach reduced experimental effort, minimized resource use, and provided valuable insights into the interactive effects among the studied variables.

RESULTS AND DISCUSSION

Adsorption isotherm and thermodynamic parameters

The suitability of various adsorption isotherm models was assessed by analysing the R^2 values presented in Table 2. Although the data exhibited reasonable correlation with multiple models - including Freundlich, Langmuir, Temkin, Flory-Huggins, El-Awady, and Frumkin-the Langmuir and Temkin isotherms yielded the highest R^2 values across all studied temperatures. This indicates that these two models provide the most accurate description of the adsorption behaviour of Toplex syrup on copper in 0.5M H_2SO_4. Consequently, both isotherms were used to calculate the adsorption parameters.

Table 2 shows that the R^2 values for Langmuir and Temkin exceed 0.99 at 293 K, confirming a strong linear relationship between the surface coverage and inhibitor concentration. The Langmuir model suggests monolayer adsorption on a homogeneous surface, while the Temkin model accounts for adsorbate-adsorbate interactions, implying that both mechanisms could contribute to the inhibitor's adsorption. From the Langmuir and Temkin plots, the equilibrium adsorption constant (K_{ads}) was determined, enabling the calculation of the standard free energy of adsorption (ΔG_{ads}). As shown in Table 3, K_{ads} values are positive and increase with temperature, suggesting enhanced adsorption at higher temperatures

Table 1. Experimental range and coded levels for Toplex syrup corrosion inhibition.

Factors	Names	Units	Low (-1)	Middle (0)	High (+1)
X1	Concentration	%, V/V	0.1	0.25	0.4
X2	Temperature	°C	20	35	50
X3	Time	h	0.5	1	1.5

Table 2. R^2 values for the various adsorption isotherms considered.

T (K)	Langmuir	Temkin	Freundlich	Flory-Huggins	El-Awady	Frumkin
293	0.992	0.995	0.989	0.534	0.965	0.874
303	0.995	0.958	0.976	0.972	0.937	0.753
313	0.976	0.943	0.935	0.935	0.891	0.709
323	0.981	0.948	0.940	0.932	0.889	0.713

Table 3. Adsorption parameters for copper corrosion in H_2SO_4 medium with Toplex syrup.

	Langmuir			Temkin		
T (K)	K_{ads}, L mol^{-1}	$-\Delta S_{ads}$, J $K^{-1}mol^{-1}$	$-\Delta G_{ads}$, kJ mol^{-1}	K_{ads}, L mol^{-1}	$-\Delta S_{ads}$, J $K^{-1}mol^{-1}$	$-\Delta G_{ads}$, kJ mol^{-1}
293	2.38	54.98	11.89	0.78	56.72	11.68
303	5.69	45.57	14.49	0.94	52.17	12.49
313	10.43	37.54	16.55	1.00	48.69	13.06
323	11.98	33.59	17.45	1.04	45.54	13.59

[19]. The enthalpy value (ΔH_{ads} = - 28.30 kJ mol^{-1}) indicates that the adsorption of Toplex syrup on copper is an exothermic process, implying that energy is released as inhibitor molecules adhere to the metal surface. The negative entropy values (ΔS_{ads}) obtained from both Langmuir (- 54.98 to - 33.59 J mol^{-1} K^{-1}) and Temkin (- 56.72 to - 45.54 J mol^{-1} K^{-1}) models reflect a decrease in disorder at the metal-solution interface. This reduction is likely due to the formation of a compact and ordered layer of inhibitor molecules, limiting their freedom of movement compared to their state in solution.

Additionally, the negative free energy values (ΔG_{ads}) ranging between - 11.68 and - 17.45 kJ mol^{-1} confirm the spontaneous nature of the adsorption. The relatively small magnitude of ΔG_{ads} (< - 20 kJ mol^{-1}) supports the conclusion that the process is primarily governed by physisorption, involving weak electrostatic interactions rather than chemical bonding.

Determination of thermodynamic activation parameters

The thermodynamic parameters: activation energy (E_{act}), activation enthalpy (ΔH_{act}), activation entropy (ΔS_{act}), and activation Gibbs free energy (ΔG_{act}) were analysed for copper corrosion in 0.5 M H_2SO_4, with and without Toplex syrup (Table 4). These values provide insights into energy barriers, spontaneity, and the mechanism of inhibition. E_{act} represents the minimum energy required for corrosion to occur. In inhibitor free solution, Eact is higher, indicating a significant barrier for copper dissolution. With Toplex syrup, E_{act} decreases, implying that the inhibitor modifies the reaction pathway by adsorbing on the surface and forming a protective layer. This reduction in E_{act} supports a physisorption mechanism where weak, reversible interactions dominate [20]. The positive ΔH_{act} values confirm that copper dissolution is an endothermic process. The gradual decrease of ΔH_{act} with increasing inhibitor concentration suggests that Toplex reduces the energy required for the transition state formation, correlating with its inhibition efficiency. ΔS_{act} values are negative, signifying a transition from a disordered state in solution to a more ordered activated complex at the metal interface [7]. As inhibitor concentration increases, ΔS_{act} becomes more negative, reflecting the compact, organized arrangement of Toplex molecules on the surface, which restricts the mobility of reacting species. The positive ΔG_{act} values indicate that the formation of the activated complex is non-spontaneous and requires energy input. The increase of ΔG_{act} in the presence of Toplex suggests that the inhibitor makes corrosion thermodynamically less favourable by increasing the energy barrier. The close agreement between E_a and ΔH_a (where $E_{act} - \Delta H_{act} \approx RT$) validates the consistency of the thermodynamic data and indicates the involvement of hydrogen evolution as a parallel reaction. Overall, these findings confirm that Toplex syrup inhibits copper corrosion primarily through physical adsorption, forming a stable film that increases order at the interface and slows down the corrosion process.

Optimization of inhibition efficiency using response surface methodology

Optimization of inhibition efficiency using RSM

Response Surface Methodology (RSM) was employed to develop a predictive model and optimize the corrosion inhibition efficiency (IE) of copper in 0.5 M H_2SO_4 using expired Toplex syrup. A second-order polynomial model was used to evaluate the influence of three independent variables: inhibitor concentration

Table 4. Effect of Toplex syrup concentration on activation parameters for copper in acidic medium.

C, %V/V	$R^2_{(Eq.5)}$	E_{act}, kJ mol^{-1}	$R^2_{(Eq.6)}$	ΔH_{act}, kJ mol^{-1}	$-\Delta S_{act}$, J mol.K^{-1}	ΔG_{act}, kJ mol^{-1}
-	0.991	43.43	0.989	40.88	183.09	97.27
0.1	0.999	23.54	0.999	20.98	252.67	98.80
0.2	0.996	23.90	0.995	21.34	253.32	99.36
0.3	0.991	14.40	0.988	11.84	287.84	100.49
0.4	0.997	9.67	0.995	7.12	304.76	100.98

(X_1), temperature (X_2), and immersion time (X_3) on IE (%). A total of 17 experimental trials were conducted to determine the combined and individual effects of these parameters (Table 5). The highest IE (88.12 %) was observed at 0.40 % (v/v) inhibitor concentration, 323K and 1.5 h immersion time, as predicted by the model.

The quadratic regression model Eq. (8) describes the relationship between IE% and the input factors:

$$IE, \% = 54.474 + 16.130x_1 + 18.747x_2 + 3.068x_3 + 6.225x_1^2 + 4.980x_2^2 - 12.635x_3^2 - 1.3125x_1x_2 - 0.020x_1x_3 - - 0.040x_2x_3 \quad (8)$$

The diagnostic plot (Fig. 1) demonstrated a strong linear correlation between the observed and predicted IE values, confirming the reliability and robustness of the model.

The positive linear coefficients of X_1 (16.13) and X_2 (18.75) indicate that increasing concentration or temperature significantly improves IE, with temperature having the strongest effect.

The smaller positive coefficient of X_3 (3.07) suggests a moderate enhancement with immersion time. The quadratic terms X_1^2 (6.22) and X_2^2 (4.98) also contribute positively, implying that higher values of these factors favor inhibition efficiency up to an optimum point. In contrast, the negative quadratic term X_3^2 (- 12.63) suggests that excessively long immersion times reduce efficiency, likely due to partial desorption of inhibitor molecules from the copper surface. Interaction terms such as X_1X_2 (- 1.31), X_1X_3 (- 0.02), and X_2X_3 (- 0.04) are negative, indicating that simultaneous increases in these pairs of variables slightly counteract each other's positive effects. This reflects the complex interplay between concentration, temperature, and time in controlling inhibitor adsorption and stability on the surface. Fig. 2 presents the coefficient plot derived from the polynomial model, highlighting the influence of each parameter on the inhibition efficiency (IE) of Toplex syrup. Positive coefficients indicate that the variable enhances IE (synergistic effect), while negative coefficients suggest a reduction in efficiency due to antagonistic or diminishing interactions.

Statistical test and analysis of models

The model was developed with a 95 % confidence level (Table 6), showing excellent agreement between the experimental data and the predicted values. The analysis yielded an R^2 value of 0.994 and an adjusted R^2 of 0.987, indicating that more than 99 % of the variation in inhibition efficiency (IE) is accurately explained by the quadratic model [21]. The Q^2 value of 0.946 further confirms the strong predictive power of the model. The small difference between R^2 and Q^2 (0.048 < 0.3) demonstrates that there is no risk of overfitting, and the model remains statistically reliable [22]. The residual standard deviation (RSD = 2.336) is low, reflecting minimal deviation between the observed and predicted values. Additionally, the reproducibility value of 0.999 highlights the model's ability to produce highly consistent results across repeated experimental runs. The F-value (135.92) from the ANOVA analysis (Table 6) is considerably high, while the p-value (p = 0.000) is well below 0.05, confirming that the regression model and its terms are statistically significant at the 95 % confidence level [23].

The total sum of squares (SS = 55614.5) reflects the overall variability in inhibition efficiency (IE), with the regression SS (6674.9) showing the portion explained by the model factors and the residual SS (38.19) representing minimal unexplained variation. The low residual SD (2.33) confirms that predicted values closely match experimental data, indicating strong model accuracy. The higher regression SD (27.23) further emphasizes the dominant influence of temperature,

Table 5. Responses of experimental design for inhibition process of copper in the presence of Toplex syrup in 0.5 M H_2SO_4.

Exp No	Factors			Response, %	
	X1, %. V/V	X2, °C	X3, h	IE_{Obs}	IE_{Pred}
1	0.10	20	0.5	15.78	13.72
2	0.40	20	0.5	48.16	48.65
3	0.10	50	0.5	54.18	53.92
4	0.40	50	0.5	85.09	83.60
5	0.10	20	1.5	19.05	19.98
6	0.40	20	1.5	55.13	54.82
7	0.10	50	1.5	61.07	60.02
8	0.40	50	1.5	88.12	89.61
9	0.10	35	1.0	42.15	44.56
10	0.40	35	1.0	77.03	76.82
11	0.25	20	1.0	39.78	40.70
12	0.25	50	1.0	76.91	78.20
13	0.25	35	0.5	35.47	38.77
14	0.25	35	1.5	45.99	44.90
15	0.25	35	1.0	55.73	54.47
16	0.25	35	1.0	55.95	54.47
17	0.25	35	1.0	56.18	54.47

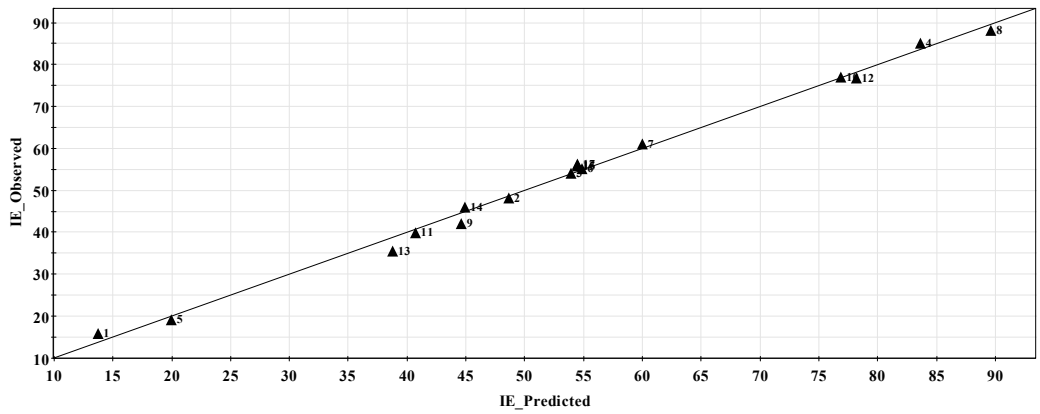


Fig. 1. Diagnostic representation of predicted versus observed inhibition efficiency.

concentration, and immersion time on IE.

Main effects

The main effect plots (Fig. 3) highlight the individual contributions of inhibitor concentration, temperature, and immersion time to the corrosion inhibition efficiency (IE%) of copper in 0.5M H_2SO_4. An appreciable rise in IE % was recorded with increasing concentration and temperature, indicating that a higher availability of active inhibitor molecules and enhanced molecular mobility promote stronger adsorption onto the copper surface. The maximum efficiency was observed at 0.4 % (v/v) Toplex syrup and 323 K, consistent with the formation of a compact and strongly adherent protective layer. Of all factors, temperature demonstrated the most pronounced positive impact, supporting the notion that the adsorption

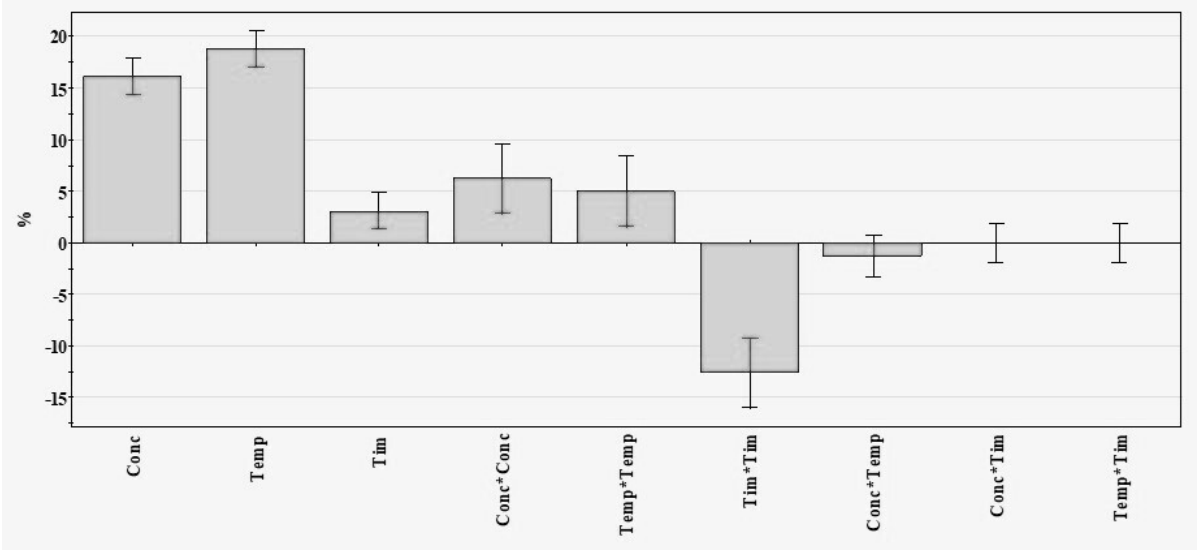


Fig. 2. Coefficients plot.

Table 6. Analysis of variance for the quadratic model of inhibition efficiency.

	DF	Sum of squares	Mean square	F	p	SD
Total	17	55614.5	3271.44			
Constant	1	48901.4	48901.4			
Total Corrected	16	6713.1	419.569			20.4834
Regression	9	6674.9	741.656	135.921	0.000	27.2334
Residual	7	38.1957	5.45653			2.33592
		R^2 = 0 .994	R^2 Adj. = 0.987	Q^2 = 0.946		
		Reproducibility = 0.999		RSD = 2.336		
		Cond. No. = 4.438		Conf. level = 0.95		

mechanism is largely dominated by physisorption, with possible minor contributions from chemisorptive interactions that improve film stability [24]. Immersion time exerted a moderate effect; IE % increased steadily up to 1 h but showed little change beyond this point. This behaviour can be attributed to the saturation of adsorption sites, while extended exposure might lead to partial desorption or weakening of the inhibitor film. The optimum protection corresponding to 0.4 % (v/v), 323 K, and 1 h immersion represents a balance between surface coverage, adsorption dynamics, and thermal stability of the protective film.

Response surface and contour plots

Response surface and contour plots (Figs. 4 and 5) elucidate the combined influence of inhibitor concentration (0.1 - 0.4 % v/v), temperature (293 - 323 K), and immersion time (0.5 - 1.5 h) on the inhibition efficiency (IE) of copper in sulfuric acid medium using expired Toplex syrup as a corrosion inhibitor. Three-dimensional (3D) and four-dimensional (4D) visualizations, the latter representing multi-variable interactions, reveal that IE rises with increasing temperature and inhibitor concentration. This trend indicates the formation of a denser, more stable adsorbed film on the copper surface, which significantly reduces the corrosion rate [3, 25]. As depicted, contour plots highlight the synergistic effects of concentration and temperature, with IE peaking at approximately 318 K and 0.4 % v/v. Extending immersion time beyond 1 h yields minimal further improvement, suggesting optimal adsorption occurs within this period. (Fig. 5) The response surface model predicts a maximum IE of 95.55 % at 0.385 % v/v, 322.5 K, and 1 h immersion, confirming the robustness and precision of the response surface methodology (RSM) optimization (Fig. 4).

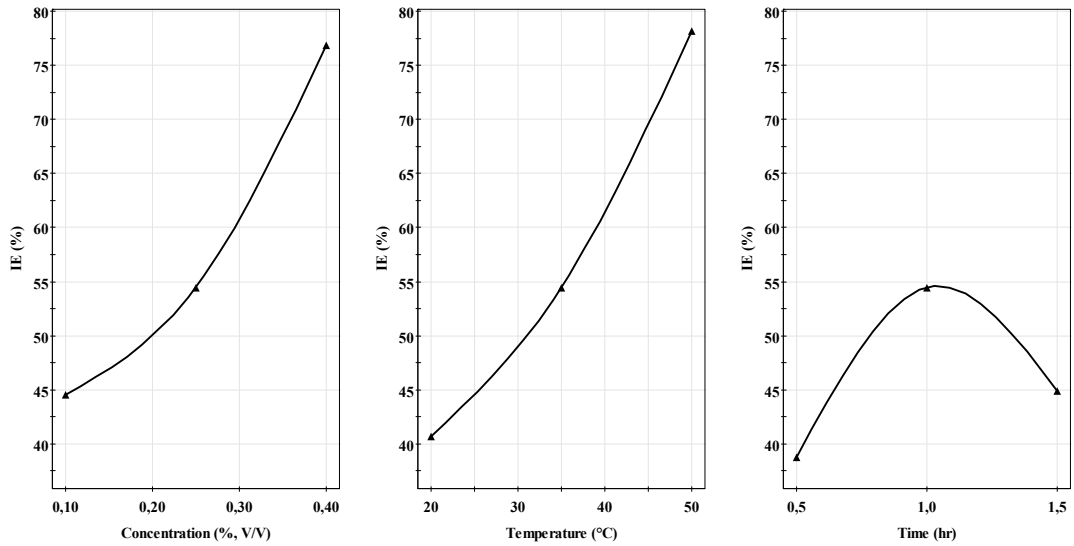


Fig. 3. Main graph plot for inhibition efficiency.

Surface morphology characterization

In 0.5 M H_2SO_4, copper dissolution proceeds via successive oxidation from Cu^0 to Cu^{2+}, with Cu^+ as an intermediate [26]. Sulfate anions adsorb on the copper surface, inducing a negative charge that favours electrostatic attraction with protonated Toplex molecules, initiating physisorption through displacement of interfacial water Eq. (9):

$$Inh_{(sol)} + x\,H_2O_{(ads)} \leftrightarrow Inh_{(ads)} + x\,H_2O_{(sol)} \quad (9)$$

Subsequently, chemisorption strengthens protection: heteroatoms (O, N, S) in Toplex donate electron pairs to Cu 3d orbitals, while aromatic π-systems promote π-back-donation. In parallel, Cu(I) - Toplex complexes form Eq. (10) and Eq. (11):

$$Cu + Inh \rightarrow Cu - Inh_{(ads)} \quad (10)$$

$$Cu^+_{(aq)} + Inh_{(aq)} \rightarrow Cu(I)Inh_{(s)} + H_{(aq)} \quad (11)$$

This dual mechanism - adsorption plus Cu(I) complexation creates a compact protective barrier. The synergistic combination of physisorption, coordination bonding, and π-interactions explains the high inhibition efficiency of Toplex in acidic media.

This mechanistic interpretation is strongly supported by the SEM results shown in Fig. 6. Polished copper (Fig. 6a) displays a smooth, uniform surface, serving as the reference. After immersion in 0.5M H_2SO_4 without inhibitor (Fig. 6b), the surface exhibits severe degradation, with evident pitting, roughness, and localized corrosion, confirming the aggressiveness of the acidic medium. In contrast, (Fig. 6c) (copper + 0.4 % v/v expired Toplex syrup) shows a much smoother and more homogeneous surface, with a marked reduction in defects and corrosion sites. This improvement highlights the formation of a protective film by Toplex molecules, limiting direct metal-acid interaction [27]. The preservation of surface integrity observed in SEM images is consistent with the high inhibition efficiencies obtained from weight loss measurements, confirming the dual adsorption–complexation mechanism proposed above [28]. These results further support the hypothesis that inhibitor molecules adsorb onto the copper surface, forming a protective film that minimizes corrosion [29].

CONCLUSIONS

Expired Toplex syrup has demonstrated remarkable efficiency as a green corrosion inhibitor for copper in 0.5M H_2SO_4. Through weight loss experiments combined with Response Surface Methodology (RSM), optimal inhibition efficiency reached 95.55 % under the conditions of 0.385 % v/v, 322.5 K, and 1 h immersion. The statistical robustness of the RSM model ($R^2 = 0.994$, $Q^2 = 0.946$) identified temperature and inhibitor concentration as the most significant parameters affecting corrosion resistance. Adsorption

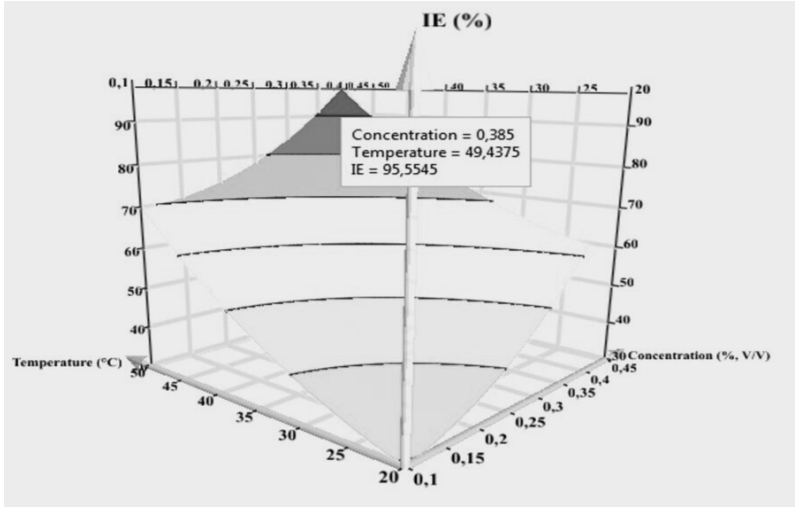


Fig. 4. Interactive effects of temperature and concentration on IE represented by response surface plot.

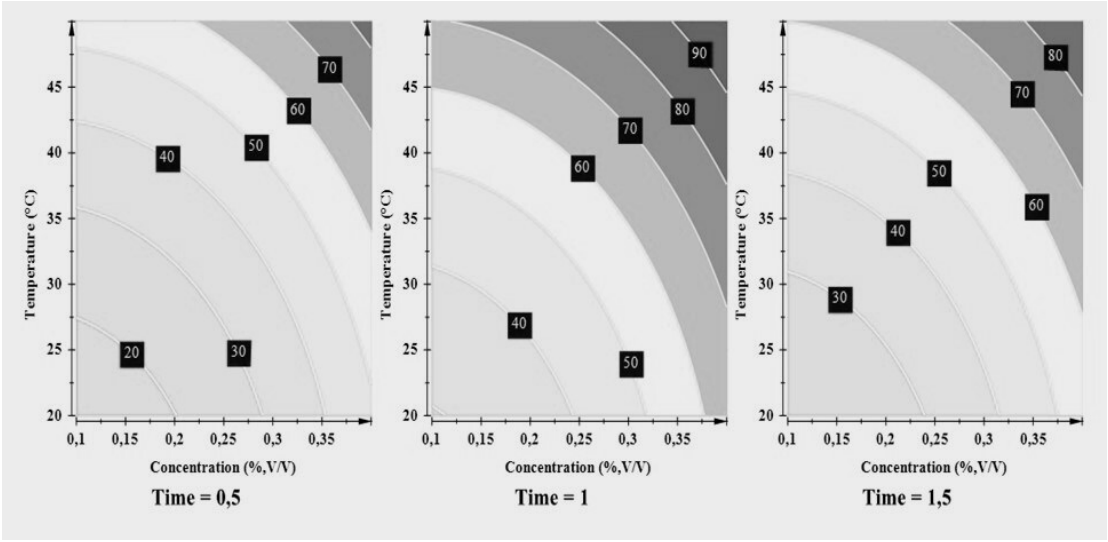
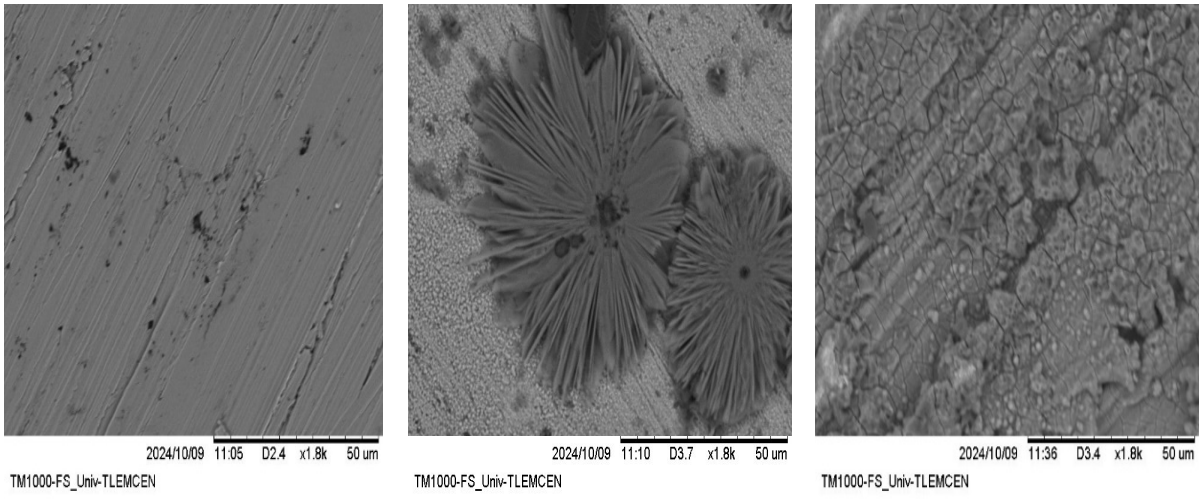


Fig. 5. 4D Contour visualization of key parameters affecting inhibition efficiency.



(a) (b) (c)

Fig. 6. SEM micrographs of copper surface: (a) polished, (b) after corrosion in 0.5M H_2SO_4, (c) after inhibition treatment with 0.4 % (v/v) expired Toplex syrup.

analyses revealed that the inhibition mechanism aligns with both Langmuir and Temkin isotherms, suggesting mixed monolayer coverage with lateral interactions. Thermodynamic data, including negative ΔG_{ads} values (- 11.68 to - 17.45 kJ mol^{-1}) and an exothermic ΔH_{ads} (- 28.3 kJ mol^{-1}), confirm a spontaneous and primarily physisorptive adsorption process. Kinetic and energetic evaluations further support the formation of a stable, adherent inhibitor layer on the copper surface.

This was visually confirmed by Scanning Electron Microscopy (SEM), which showed a significant reduction in surface degradation and corrosion features when Toplex syrup was present-indicating effective film formation and surface protection.

Altogether, this study highlights expired Toplex syrup as a low-cost, environmentally friendly, and efficient inhibitor, offering a dual benefit: prolonging the service life of copper in acidic conditions and contributing to pharmaceutical waste valorisation in line with green chemistry principles.

Authors' contributions

K.B: Design of anticorrosion tests and experiments; D. Y: Analysis, Writing - Original Draft; B. A: performed the experiments; and A. T: Methodology, analysed and interpreted the data.

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