Application of expired Tramadol medicinal drug for corrosion inhibition of steel in acidic environment: Analytical, kinetic, and thermodynamic studies

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Abstract

Tramadol is a well-known pain reliever that is classified as a synthetic opioid; leaving it in the environment after it has expired is extremely dangerous because it is harmful to children. As a result, the current research suggests using it as a green corrosion inhibitor for steel in a 1.0 N H_2SO_4 corrosive environment. The effectiveness of expired Tramadol as a corrosion inhibitor was evaluated using three analytical techniques: gravimetric, gasometric, and acidimetric techniques. The effects of expired drug doses (100–500 ppm), reaction temperature (303–333 K), and pH were investigated. The corrosion inhibition efficiency was found to increase with increasing the concentration and pH but decreased with increasing the temperature. The maximum inhibition of 93% was achieved by using 500 ppm of the expired medicinal drug inhibitor. It's possible that the increased activation energy (E_a) for carbon steel in the presence of the expired pharmacological inhibitor than in the absence is due to physical adsorption. The increase in E_a can be explained to a significant drop in inhibitor adsorption on the carbon steel surface as temperature rises, resulting in a proportional increase in corrosion rates due to a larger area of the metal exposed to the acid environment. The decrease in carbon steel corrosion rate is primarily regulated by kinetic parameters of activation, as seen by the increase in ΔH_a with increasing inhibitor system concentrations for carbon steel corrosion. The inhibition was due to adsorption and adhesion of the drug constituents on the steel surface, and the adsorption was found to obey the Langmuir adsorption isotherm model. The techniques used are in good agreement (±2%), implying that expired Tramadol medicine could be used as a green corrosion inhibitor for steel in a 1.0 N H_2SO_4 acidic corrosive environment.

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1. Introduction

Corrosion is the process of oxidation of metals by their environment, leading to corrosion products and the destruction of the metal lattice this phenomenon represents: a terrible waste of both natural resources and money. Corrosion is an afflicting problem associated with every use of metals [1–6]. The damage by corrosion results in a high cost for maintenance and protection of materials used. Metals generally tend to move to their original state by corrosion process because corrosion is a thermodynamically feasible process as it is associated with a decrease in Gibb's free energy [7–10]. Metals prefer to return to their initial state through corrosion. Scientists working in this field face a difficult task in developing corrosion control strategies [11–15]. Among the different corrosion protection strategies explored, the employment of an inhibitor is the most appealing and practical method for protecting metals in contact with corrosion media. Inhibitors prevent metallic materials from corroding by limiting metal breakdown and consumption [15–25]. Steel corrosion control is viewed as a green process because when metal corrodes, it changes from hard and valuable metal to a corrosive substance that poses a risk to the environment [15–25]. Corrosion controlling metals has effects on technology, the economy, society, and the environment [25–30]. Because of the toxicity of commonly used corrosion inhibitors, as well as the ever-tightening environmental rules surrounding their usage and disposal, there is a lot of interest in finding effective non-hazardous alternatives. Extensive research and development over the last two decades has resulted in the discovery of new classes of corrosion inhibitors [25–34], and the importance of using a variety of medications as corrosion inhibitors has expanded [25–30]. Antibiotics and other medications have recently been studied, and their inhibitory efficacy has been connected to their heterocyclic composition [25–34]. The majority of heterocyclic medications are environmentally friendly and complement natural items well. Pharmaceutical compounds have been used to suppress corrosion in recent years because to the inclusion of hetero atoms such as nitrogen, sulphur, oxygen, and the π-bond in their structure, and are of special interest due to their safe use, high water solubility, and large molecular size. Some antimalarial and azosulpha medicines have been found to be effective corrosion inhibitors [36–42]. There have been significant efforts to employ pharmaceuticals as steel corrosion inhibitors [35–42], however the use of expired drug as steel corrosion inhibitors is limited, having only begun in 2009 by R.S. Abdel Hameed [35]. According to our understanding, R.S. Abdel Hameed started the investigation of expired medications as corrosion inhibitors in 2009 [35], when he employed expired Ranitidine as a corrosion inhibitor for aluminum in hydrochloric acid solutions [35–40]. Many scientific efforts were made after Abdel Hameed's first trial to deceive and apply expired medicines and medicinal materials as corrosion inhibitors from metals in diverse corrosive environments [35–56]. The studies have demonstrated the advantages of using expired medications as corrosion inhibitors. Some of the substances with various clinical applications that have been studied include antibiotic, antipyretic, anticonvulsant, antihypertension, gastroesophageal problems, chronic bronchospasm, mucolytic, antihistamine, anti-anxiety, anti-inflammatory, antiviral, hypogonadism, antidepressant, and anti-diabetic properties. There are several medications with multiple clinical use uses [57–59]. The purpose of the present study was to evaluate the expired Tramadol medicinal drug materials as a green corrosion inhibitor for C-steel in a corrosive sulfuric acid environment, sulfuric acid is suitable for pickling and descaling of steel. The Tramadol inhibitor's inhibitory performance was assessed using three distinct analytical techniques. Kinetics and thermodynamic parameters were calculated and discussed, as well as the effects of concentration and temperature. Tramadol is an opioid analgesic used to treat mild to moderate pain, according to a review of the literature. A synthetic opioid is a pain reliever that is similar to an opioid. It relieves pain by acting on the central nervous system (CNS). The IUPAC name for Tramadol is: 2-[(dimethylamino)methyl]-1-(3-methoxyphenyl)cyclohexanol with *R*-configuration in both stereo centers; (*R*,*R*)-enantiomer of the racemic opioid painkiller Tramadol. Its analgesic effectiveness is ten times that of the (*S*,*S*)-enantiomer. It functions as a delta-opioid receptor agonist, kappa-opioid receptor agonist, mu-opioid receptor agonist, adrenergic uptake inhibitor, antitussive, capsaicin receptor antagonist, muscarinic antagonist, nicotinic antagonist, NMDA receptor antagonist, opioid analgesic, serotonergic antagonist, serotonin uptake inhibitor, metabolite, and serotonergic antagonist. We may deduce from the literature that, the expired Tramadol medicine is highly promising because it has crucial nucleophilic function groups such as dimethyl amino group, hydroxyl group, methoxy group, and aromatic substituted benzene ring. Because of its promising chemical composition, Tramadol has the potential to be an effective corrosion inhibitor for steel in an acidic environment.

2. Experimental

2.1. Materials and Test Solution

The corrosive solution used in this experiment is aggressive 1.0 N sulfuric acid with a pH of 0.0, which was made from analytical grade 98 percent H_2SO_4 (Sigma Aldrich) diluted with double-distilled water, titrated against 1.0 N Na_2CO_3, and then diluted to the needed pH Sulfuric acid is suitable for pickling and descaling of steel. Each experiment was carried out in aerated stagnant solutions and was reproduced at least three times under the identical conditions to ensure reproducibility, with the average of the three replicated values being utilized for data processing. Table 1 shows the gravimetric composition of the steel materials used in this study. Its composition is comparable to that of carbon steel used in the production of petroleum pipelines [54–57].

Table 1. Shows the gravimetric composition of the steels employed.

Element	Mn	Si	S	P	C	Fe
Composition, weight %	0.517	0.201	0.009	0.007	0.157	About 99%

Tramadol, a product of the Glaxo Smith Kline (GSK) corporation in the United Kingdom, its chemical structure and content are shown in Figure 1.

Tramadol was utilized as an inhibitor in the form of pills after the expiration date had passed by six months. In this work, it is employed as a green corrosion inhibitor for steel it was used without further purifications with a concentration range (100, 200, 300, 400, and 500 ppm) in 1.0 M sulfuric acid corrosive environment.

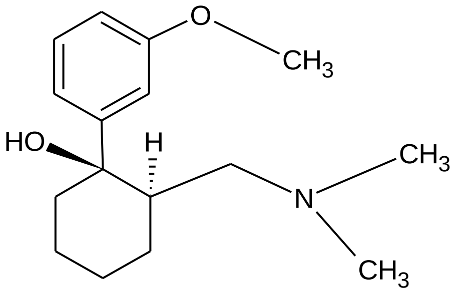
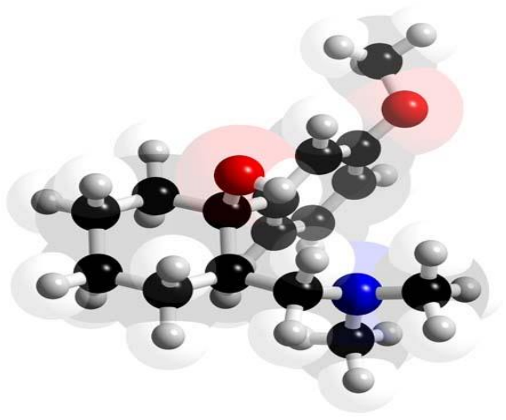
Drug name	**Tramadol**
Drug IUPAC name	(1*R*,2*R*)-2-[(dimethylamino)methyl]-1-(3-methoxyphenyl)cyclohexan-1-ol
Chemical Structural Formula	
3D Structural Formula	

Figure 1. Tramadol Drug Structure and Composition (used as inhibitor).

2.2. Gravimetric studies

The gravimetric approach is commonly utilized since it is straightforward and does not necessitate the use of complicated equipment or methods. All of the trials were repeated three times, and the recorded data was averaged with a (0.1) error. Two types of gravimetric tests were performed in this study: weight loss measurement and atomic absorption spectroscopy dosage of the metal passing in solution.

2.2.1. Weight Loss Calculation

The method is based on calculating the weight loss (WL) of a sample (coupon) of the surface (S) immersed in the aggressive solution for a period of time (t). The tests are carried out in non-aerated media in 100 mL glass vials at room temperature. The iron samples are cleaned with distilled water, degreased with acetone, and dried before and after the immersion for an

8-hour period. The determination of the corrosion rate W was made from the following relation (1):

$$W = \frac{m_\mathrm{i} - m_\mathrm{f}}{St} \tag{1}$$

where W ($\mathrm{mg \cdot cm^{-2} \cdot h^{-1}}$) is the corrosion rate, m_i (mg) and m_f (mg) are the mass before and after exposure to test solution, respectively, S ($\mathrm{cm^2}$): is the surface of area of specimen, t (h): is the immersion time. Regarding the inhibitory efficiency $\%I.E.$ and the surface coverage (θ), which represents the part of the metal surface covered by the inhibitors molecules, were calculated according to the following equations:

$$\%I.E. = \frac{W^0 - W}{W^0} \cdot 100 \tag{2}$$

$$\theta = \frac{W^0 - W}{W^0} \tag{3}$$

where W^0 and W represent the corrosion rates in the absence and presence of the inhibitors, respectively.

2.2.2. Measurements using Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy was used to quantify the number of iron ions in corrosive solutions in the absence and presence of the medications employed as corrosion inhibitors (AAS). Using Varian Spectra AA 220 atomic absorption spectroscopy, the concentration of ferric ions passing into the solution was determined. We used aqua regia to dissolve the corrosive medium in order to evaluate the quantities of iron ions in the solution while the inhibitor was absent and present [51–55].

2.3. Hydrogen Evolution Measurements (Gasometrical Measurements)

The volumetric measurement of the evolved hydrogen was used to track the development of the corrosion reaction. In a Büchner flask containing the test solution, the metal sample was placed. The flask is sealed with a rubber bung, and rubber tubing is linked to the bottom of an inverted measuring cylinder that sits above a basin via a hose barb protruding from the flask's neck. Distilled water is used to fill the cylinder and basin. The created hydrogen eventually displaces the distilled water and collects at the cylinder's top, where its volume is precisely proportional to time [51–55]. The experiment is carried out in the absence and presence of various concentrations of the inhibitor being investigated.

2.4. Acidimetric Measurements

A common BT-500 model pH meter was used to check the pH of the prepared solution before each experiment (Germany). Pre and post dipping in the tested solution for five hours, the pH was examined for the five concentrations of 50, 100, 150, 200, 250, and 300 ppm. The percent *IE* is calculated using the following equation.

$$\%IE = 1\frac{\Delta H^{+}_{\text{inh}}}{\Delta H^{+}_{\text{uninhi}}}\cdot 100 \tag{4}$$

Where $\Delta H^{+}_{\text{inh}}$ and $\Delta H^{+}_{\text{uninhi}}$ are changes in H^+ concentration with and without of the inhibitor, respectively [51–55].

3. Discussion and Results

In an acidic environment of 1.0 N H_2SO_4 solution, simple analytical procedures were utilized to estimate the corrosion rate and ferrous ion concentration in the presence and absence of Tramadol medications as green corrosion inhibitors. In this investigation, the effects of inhibitor concentration, pH, and temperatures were investigated. Different analytical techniques were employed in this study, including gravimetric, gasometrical, acidimetric, and atomic absorption spectroscopy (AAS). Tramadol, which is utilized as a green inhibitor, is represented here as Tram. The concentrations studied were 100, 200, 300, 400, and 500 ppm.

3.1. Gravimetric Measurements

3.1.1. Effect of Concentration

After 7 hours of immersion of steel coupon in the sulfuric acid corrosive environment of varying pH, gravimetric techniques were used to determine the corrosion rate and corrosion inhibition efficiency percent *I.E.* of expired Tramadol medications for various quantities of Tram inhibitor (pH 1, 2, and 3). Table 2 shows the data for corrosion rate (*W*) and corrosion inhibition effectiveness percent *I.E.* Figures 2 and 3 are also included. According to gravimetric studies, adding the expired Tramadol medications (Tram) green inhibitor reduces weight loss and, as a result, boosts inhibition efficiency, and this behavior was enhanced by increasing Tram inhibitor concentrations. It is obvious that as the inhibitor concentration rises, the inhibition efficiency rises to 93% at 500 ppm. According to equations 2 and 3 in the experimental part, the inhibitory efficiency percent *I.E.* and the surface coverage (θ), which reflects the portion of the metal surface covered by the inhibitor's molecules, were computed. Table 2 shows that the values of inhibition efficiency rise with increasing drug concentration and decrease with decreasing medium pH. Figure 2 shows that raising the concentrations of expiring Tram medicines reduces the weight loss of carbon steel samples, demonstrating that the presence of these compounds reduced iron dissolving in 1.0 N H_2SO_4 solution, implying that these medications function as inhibitors. In both uncontrolled and inhibited 1.0 N H_2SO_4, the relationship between weight loss and time is linear. This shows that during corrosion, there are no insoluble surface coatings. In this situation, the inhibitors are adsorbed into the metal surface and then prevent corrosion by either blocking reaction sites (anodic and cathodic) or changing the mechanism of the anodic and cathodic partial processes [25–31]. When compared to the efficiency obtained in the stated references (prior works) [25–31], the maximal inhibition efficiency obtained utilizing 500 ppm of expired Tramadol medications is 93%, which is higher. This result could be owing to the presence of nucleophilic functional groups (methylamino, methoxy, and hydroxyl groups) in addition to the aromatic substituted benzene ring, which are electron donating groups.

Table 2. Shows the effect of increasing TRAM medication concentrations on steel corrosion characteristics in H_2SO_4 solutions of various pH determined from weight loss measurements at 303 K.

Expired drug concentration, ppm	**pH=1**			**pH=2**			**pH=3**		
	W **mg/(cm^2·h)**	***I.E.*** **%**	**θ**	***W*** **mg/(cm^2·h)**	***I.E.*** **%**	**θ**	***W*** **mg/(cm^2·h)**	***I.E.*** **%**	**θ**
Blank	9.00	–	–	7.9	–	–	7.1	–	–
100	1.35	85.0	0.85	1.12	85.8	0.858	0.84	88.2	0.882
200	1.23	86.3	0.86	0.96	87.8	0.878	0.76	89.3	0.893
300	1.11	87.7	0.877	0.73	90.7	0.907	0.63	91.1	0.91
400	0.95	89.4	0.894	0.67	91.5	0.915	0.54	92.4	0.924
500	0.88	90	0.90	0.58	92.6	0.926	0.48	93.2	0.932

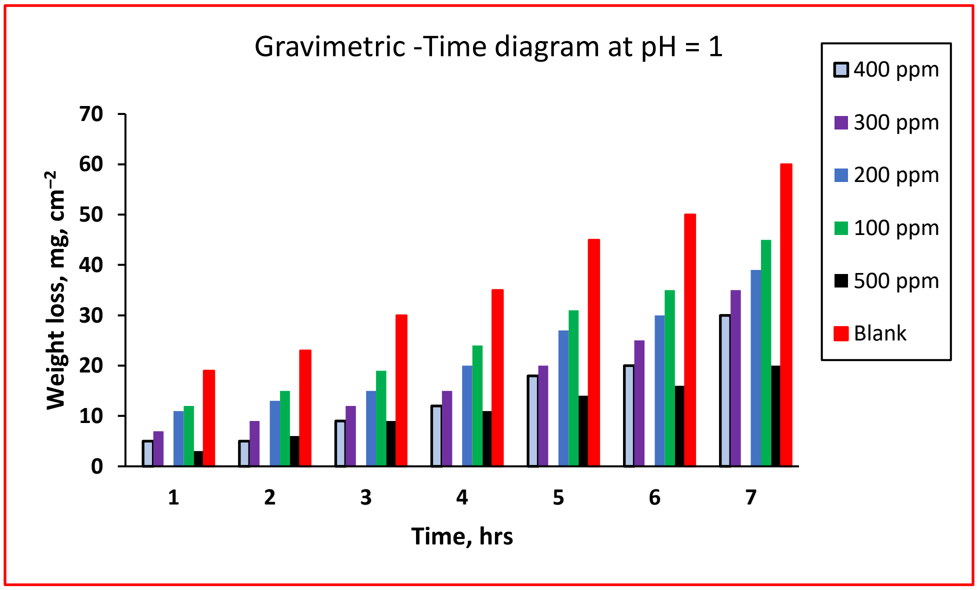


Figure 2. Steel weight loss as a function of time in 1.0 N H_2SO_4 in the absence and presence of expired TRAM medicines as a green steel corrosion inhibitor.

3.1.2. Effect of temperature

Gravimetric (weight loss) tests were done at various temperatures, such as 303, 313, 323, 333 K, to understand the mechanism of inhibition and identify the kinetic parameters of the corrosion process. Figure 3 depicts the influence of temperature on the percentage inhibition efficiency of steel in the presence of the inhibitor. It is clear that as the temperature rose, the percent *I.E.* values declined. The protective coating of these compounds generated on the steel surface becomes less stable at higher temperatures, which could be owing to the desorption of certain adsorbed molecules from the steel surface at higher temperatures, exposing a larger area of the metal to the acidic environment [25–31]. All of the trials were repeated three times, and the recorded data was averaged with a (0.1) error.

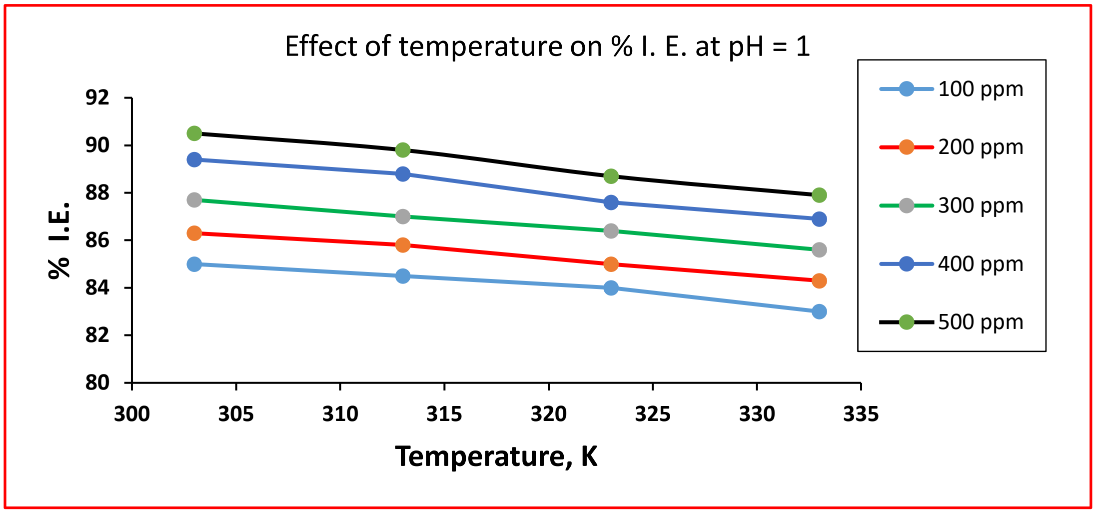


Figure 3. Effect of temperature on steel percent I.E. in 1.0 N H_2SO_4 in the presence of various doses of expired TRAM medicines as a green inhibitor, data from weight loss at pH=1.

The percent *I.E.* values clearly reduced as the temperature increased, implying that the protective coating created on the steel surface by these chemicals is less stable at higher temperatures. This could be because certain adsorbed molecules desorb from the steel's surface at higher temperatures, exposing a larger area of the metal to the acidic environment [25–30].

3.1.2. Kinetics and Thermodynamic Parameters

The Arrhenius equation and the transition state equation [25–30] can be used to express the relationship between corrosion rate and temperature:

$$\ln R_{\mathrm{corr}} = \exp\left(\frac{-E_{\mathrm{a}}}{RT}\right) + A \tag{5}$$

where E_a is the apparent activation energy, R is the universal gas constant, A is Arrhenius pre-exponential factor, T is the absolute temperature.

Figure 4 shows an Arrhenius curve for carbon steel submerged in 1.0 M sulfuric acid in the absence and presence of different drug inhibitor concentrations in the absence and presence of different drug inhibitor concentrations. The plots obtained are straight lines, with the slope of each straight line corresponding to the apparent activation energy, as given in Table 3. The higher value of E_a for carbon steel in the presence of the expired drug inhibitor compared to that in the absence of the expired drug inhibitor could be attributed to its physical adsorption in the current investigation. The increase in E_a can be explained by a significant drop in inhibitor adsorption on the carbon steel surface as temperature rises, resulting in a commensurate increase in corrosion rates due to a larger area of the metal exposed to acid environment [25–31].

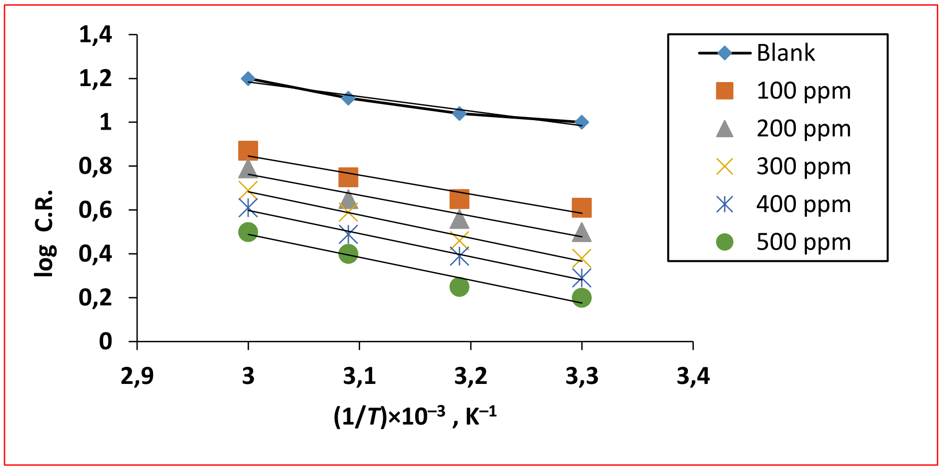


Figure 4. Arrhenius plot for carbon steel in 1.0 N H_2SO_4 solution with and without varied amounts of the expired Tramadol pharmacological inhibitor.

Table 3. Values of activation parameters for carbon steel in 1.0 N H_2SO_4 in the absence and presence of different concentrations of the expired drug inhibitor.

Inhibitor	Inhibitor concentration (ppm)	E_a (kJ·mol^{-1})	ΔH_a (kJ·mol^{-1})	$-\Delta S_a$ (kJ·mol^{-1})
Blank	Free acid (1.0 N H_2SO_4)	53.2	48	144
Expired Tramadol Drug	100	61.7	53	139
	200	64.5	55	136
	300	66.4	58	128
	400	68.2	61	125
	500	69.8	63	122

An alternative form of Arrhenius equation is the transition state equation [55–58]:

$$CR = \left(\frac{RT}{Nh}\right)\exp\left(\frac{\Delta S_a}{R}\right)\exp\left(\frac{-\Delta H_a}{RT}\right) \tag{6}$$

where, h is the Plank constant, N is the Avogadro number, ΔS_a is the entropy of activation, and ΔH_a is the enthalpy of activation. A plot of $\log(CR/T)$ *vs.* $1/T$ as shown in Figure 5 gave a straight line with a slope of $(-\Delta H/2.303R)$ and an intercept of $[\log(R/Nh)+(\Delta S/R)]$, from which the values of ΔH_a and ΔS_a were calculated and listed in Table 3.

The endothermic nature of the metal dissolving process is reflected by the positive values of ΔH_a for corrosion of carbon steel in the presence and absence of the inhibitor. The decrease in carbon steel corrosion rate is primarily regulated by kinetic parameters of activation, as seen by the increase in ΔH_a with increasing inhibitor system concentrations [25–31]. The entropy of activation values for inhibited solutions is less negative than for uninhibited solutions. This shows that as the reactants progressed to the active complex, the unpredictability increased [55–59].

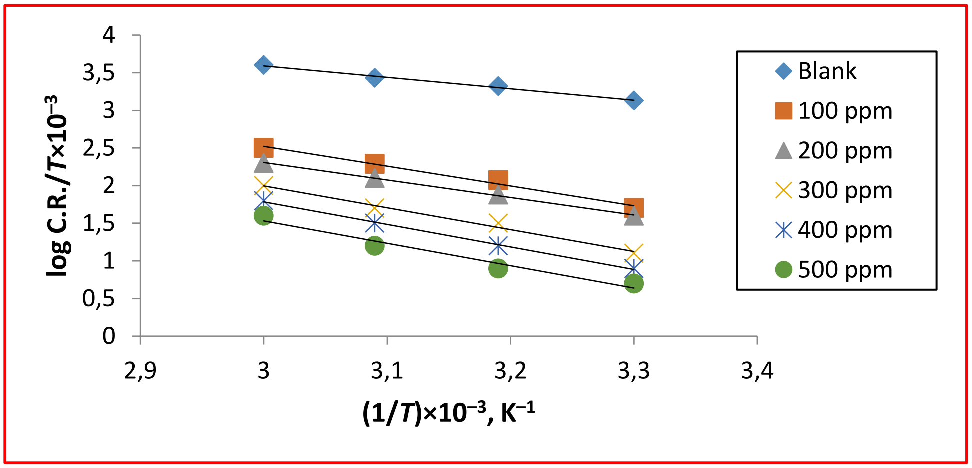


Figure 5. Transition state map for carbon steel in 1.0 N H_2SO_4 in the presence of various Tramadol inhibitor doses.

3.2. Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) allows for significant simplification of techniques for analyzing aqueous, acidic, or basic solutions, resulting in cost savings. The use of atomic absorption for routine analysis in industry is separated into four areas: 1. raw material inbound inspection; 2. production testing; 3. final product inspection; 4. environmental analysis. Atomic absorption is primarily of indirect benefit for rapid analysis during the manufacturing process because, due to the sequential nature of the technique, it cannot be employed for entire steel or slag analysis in two to three minutes [51–55]. Based on the fundamental chemistry of the solubility of corrosion products, AAS was used to estimate corrosion rates in various media, including acidic, basic, and neutral. Fe ions in mineral waters and natural waters were determined using the AAS technique [51–55]. The concentration of iron ions released into solution owing to corrosion was evaluated using a calibration curve and atomic absorption spectroscopy. High salinity, falling pH, the presence of chloride ions, and temperatures increased the corrosion of iron samples in solution [51–55]. When iron is exposed to oxygen and humidity, corrosion occurs, which is aggravated by the presence of anions (chloride ions, sulfate, nitrate, *etc.*). The cost of corroding iron structures or other components can be calculated by looking at the qualities of the corroding material [51–55]. The quantities of ferrous ions Fe^{+2} that occur from steel corrosion by acidic H_2SO_4 of various pH were determined using atomic absorption spectroscopy in this work (AAS). AAS was used to determine the amounts of ferrous ions inside corrosive solution while the green inhibitor was missing and present. Table 4 and Figure 6 show that raising inhibitor concentration and lowering pH of the solution decreased ferrous ion Fe^{+2} concentrations in the corrosive medium. The concentration of ferrous ions in the solution is plotted as a function of corrosion rate; as the concentration of ferrous ions in the solution rises, so does the corrosion rate, and vice versa. The addition of inhibitor has an impact on all processes. The results obtained by the gravimetric (weight loss) method agree well with those obtained by the expired (TRAM) drug, indicating that the addition of expired (TRAM) drug inhibits steel corrosion in acidic environments and reduces the iron dissolution process (ferrous ion concentration Fe^{+2}) in this environment at lower pH values.

Table 4. Effect of pH and inhibitor concentrations on ferrous ion concentrations as result of AAS technique.

Sample	**Inhibitor concentration ppm**	**Ferrous ion concentration [Fe^{+2}], ppm**		
		pH=1	**pH=2**	**pH=3**
Blank	1.0 N H_2SO_4	133	115	102
Expired Tramadol	100	41	27	21
	200	35	22	14
	300	20	18	10
	400	17	14	8
	500	15	10	7

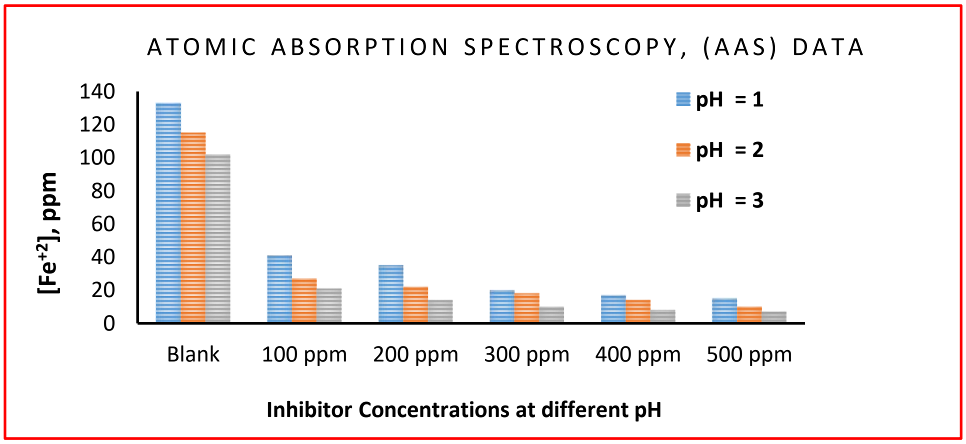


Figure 6. Effect of expired medicines (TRAM) inhibitor concentrations on ferrous ion concentration [Fe^{+2}] in the presence of 1.0 N H_2SO_4 as measured by atomic absorption spectroscopy (AAS) at various pH levels.

3.3. Hydrogen Evolution Method (Gasometrical technique)

In the absence and presence of inhibitors in an acidic environment, gasometrical approaches are based on detecting the evolved hydrogen gas over time. For the evaluation of expired Tramadol, TRAM as green corrosion inhibitors for carbon steel alloy in acidified hydrochloric acid solution of varied lower pH, a gasometrical methodology (hydrogen evolution method) was applied (pH 1, 2, and 3). Because iron is an active metal with a greater oxidation potential, it may quickly replace the hydrogen in acid, resulting in metal salt and the release of hydrogen in the form of gas. In the absence and presence of different concentrations of expired TRAM medicines as green inhibitor, 100, 200, 300, 400, and 500 ppm, the volume of hydrogen evolved during the corrosion reaction of iron acidic H_2SO_4 medium. At room temperature, time was measured (30°C). The following equation [51–55] was used to compute the inhibitory efficiency.

$$\%I.E.=\left[1-\left(\frac{V_{\text{inh}}}{V_{\text{free}}}\right)\right]\cdot 100 \qquad (7)$$

where, V_{inh} is the volume of hydrogen gas evolved for inhibited solution and V_{free} for the uninhibited solution.

Table 5 shows the values of evolved hydrogen volumes and inhibition efficiencies at various doses of the green inhibitor TRAM. As the inhibitor concentration is increased, the efficiency of inhibition improves. This suggests that the pharmacological inhibitor chemicals act as a good carbon steel inhibitor in an acidic H_2SO_4 environment.

Table 5. Hydrogen volumes and percentage inhibition efficiency for steel corrosion in an acidic H_2SO_4 solution of various pH with and without varying concentrations of expired TRAM medication after 8 hours at room temperature.

Expired drug concentration ppm	**pH=1**		**pH=2**		**pH=3**	
	Volume of hydrogen (ml/cm^2)	***I.E.*%**	**Volume of hydrogen (ml/cm^2)**	***I.E.*%**	**Volume of hydrogen (ml/cm^2)**	***I.E.*%**
Blank	49	–	45	–	38	–
100	7	85.7	6.2	86.2	4.6	87.8
200	6	87.7	5.4	88.0	3.9	89.7
300	5.2	89.3	4.4	90.2	3.5	90.8
400	4.9	90.0	3.8	91.5	2.9	90.4
500	4.3	90.2	3.2	92.8	2.4	93.6

3.5. Acidimetric measurements

Pre and post dipping in the tested solution for 8 hours, the pH was examined for the five concentrations of 100, 200, 300, 400, and 500 ppm. In each case, [H$^+$] was calculated.

The following equation was used to calculate the corrosion rate (*W*) of steel samples:

$$W(\text{mole}\cdot\text{dm}^{-3}\cdot\text{cm}^{-2}\cdot\text{h}^{-1})=\frac{\Delta\text{H}^+}{At} \tag{8}$$

where [ΔH$^+$] is the variation between the first and last concentration of *H*$^+$, *A* the surface area of coupon in cm^2 and *t*, the time in hours. The *%I.E.* values were computed utilizing the following equation:

$$\%I.E.=1-\left(\frac{\Delta\text{H}^+_{\text{inh}}}{\Delta\text{H}^+_{\text{uninh}}}\right)\cdot 100 \tag{9}$$

where ΔH$^+_{\text{inh}}$ and ΔH$^+$ are changes in H$^+$ concentration with and without the presence of green inhibitor, TRAM, respectively.

The values of surface coverage (θ), was computed utilizing the next equation [51-55]:

$$\theta=1-\left(\frac{\Delta\text{H}^+_{\text{inh}}}{\Delta\text{H}^+_{\text{uninh}}}\right) \tag{10}$$

As indicated in Table 6, increasing the concentration of green inhibitor TRAM increased corrosion inhibition efficacy and surface coverage, owing to lower hydrogen ion concentrations in the medium, as the inhibitor molecule acts as a ligand for protons in acidic media [51–55].

Table 6. The percent *I.E.* values for expired Tramadol inhibitor in 1.0 N H_2SO_4 at 303 K determined using the acidimetric method.

Expired drug Concentrations ppm	**pH=1**			**pH=2**			**pH=3**		
	ΔH$^+$·10^4 mol·L^{-1}	**θ**	**%*I.E.***	**ΔH$^+$·10^4 mol·L^{-1}**	**θ**	**%*I.E.***	**ΔH$^+$·10^4 mol·L^{-1}**	**θ**	**%*I.E.***
Blank	96	–	–	89	–	–	82	–	–
100	14	0.854	85.4	12	0.87	86.5	11	0.87	86.6
200	12	0.875	87.5	11	0.88	87.6	9	0.89	89.0
300	11	0.885	88.5	10	0.89	89	8	0.9	90
400	10	0.895	89.5	8	0.91	91	6	0.93	93
500	8	0.916	91.6	7	0.92	92	5	0.94	0.94

3.6. Corrosion Inhibition Mechanism

The adsorption of inhibitor onto the metal surface is the mechanism of corrosion inhibition in an acidic medium. The first step in the inhibition mechanism in acidic media is inhibitor adsorption at the metal/solution interface. During inhibition involving organic molecules at the metal/solution interface, four types of adsorption can occur [25–27]:

1. interaction of the metal with unshared electron pairs in the molecule;
2. electrostatic attraction between charged molecules and charged metals;
3. interaction of π-electrons with metal, and
4. a combination of the above.

The inhibition efficiency of inhibitors is affected by several factors, including the number of adsorption sites and their charge density, molecular size, the heat of hydrogenation, mode of interaction with the metal surface, and the formation of metallic complexes [30–35]. Physical adsorption necessitates the presence of both an electrically charged metal surface and charged species in the solution's bulk; the presence of metal with a vacant low-energy electron orbital and an inhibitor with molecules with relatively loosely bound electrons or a heteroatom with lone pair electrons. However, the reported compound can be protonated in an acidic medium. As a result, they become cations, coexisting with the corresponding molecular form:

$$[\mathrm{TRAM}] + x\mathrm{H}^+ \rightarrow [\mathrm{TRAM}_x]^{x+} \tag{11}$$

where [TRAM] represents the Tramadol molecule and H^+ represents the hydrogen proton from the acidic corrosive environment. Because the steel surface has a positive charge in the H_2SO_4 medium, the protonated TRAM could be attached to the carbon steel surface via electrostatic interaction between SO_4^{-2} and protonated $[\mathrm{TRAM}_x]^{x+}$ [25–27]. This could be explained further by assuming that in the presence of SO_4^{-2}, negatively charged SO_4^{-2} attaches to positively charged surfaces, resulting in protonated TRAM being adsorbed to the metal surface. Aside from electrostatic interaction, chemical interaction is also present. Non-bonding electrons of oxygen atoms, nitrogen atoms, and benzene ring – electrons [25–27], caused chemical interaction.

3.7. Adsorption Isotherm

The main factors influencing the adsorption process are the charge, the nature of the metal surface, its electronic properties, the reaction's temperature, the presence of electrorepelling or electron-donating groups in the derivatives, the electrochemical potential of the solution interfaces, the solvent's adsorption, and other ionic species.

The surface coverage (θ) values were calculated using weight loss data in the presence of various inhibitor concentrations, and numerous adsorption isotherms were used to find the one that fit the data the best. However, the obtained results are perfectly consistent with the Langmuir adsorption isotherm as stated in the following mathematical equation [25–30]:

$$\frac{C_\mathrm{i}}{\theta} = \frac{1}{K_\mathrm{ads}} + C_\mathrm{i} \tag{12}$$

where, K_ads and C_i are the constant of the adsorption process and the concentration of the drug, respectively [25–30].

Figure 7 shows a straight line shape as the graphic representation of C_i/θ against C_i. The obtained straight line's slope is approximately equal to 1 and its intercept is equal to K. The following mathematical equation provides the typical free energy for the adsorption process ΔG^0_ads:

$$K_\mathrm{ads} = \frac{1}{55.5}\exp\left(\frac{-\Delta G}{RT}\right) \tag{13}$$

where K_ads is the adsorption process' equilibrium constant, the water content in the majority of the solution (measured in moles per liter), T is the absolute temperature, and R is the gas constant. ΔG_ads has been determined at 303 K to be (–38.75 kJ/mole). The drug molecules spontaneously adsorb on the metal surface, as seen by the negative value of the free energy of adsorption (ΔG_ads) [25]. However, the obtained result (–40 kJ/mol) is lower than the reported amount. a requirement for chemical adsorption. This finding suggests that the adsorption process is of the physical adsorption variety [25–30]. Conclusion: The adsorption of the constituent molecules of the expired medicinal ingredients on the metal/electrolyte interface inhibits corrosion. Some researchers believe that the formation of a passive film from the solid organic drug molecule on the atoms of the metal at the surface is the most acceptable in this case [25–30]. Because the Tramadol drug is a highly promising chemical compound including organic additives and efficient functional groups containing combination of the aromatic nucleus with a methoxy group, *ortho*-substituted cyclohexane ring, hydroxyl group, and tertiary amine base side chain. All those mentioned chemical functional groups are responsible for the formation of a stronger adhesive film on the steel surface, preventing the steel from corrosion.

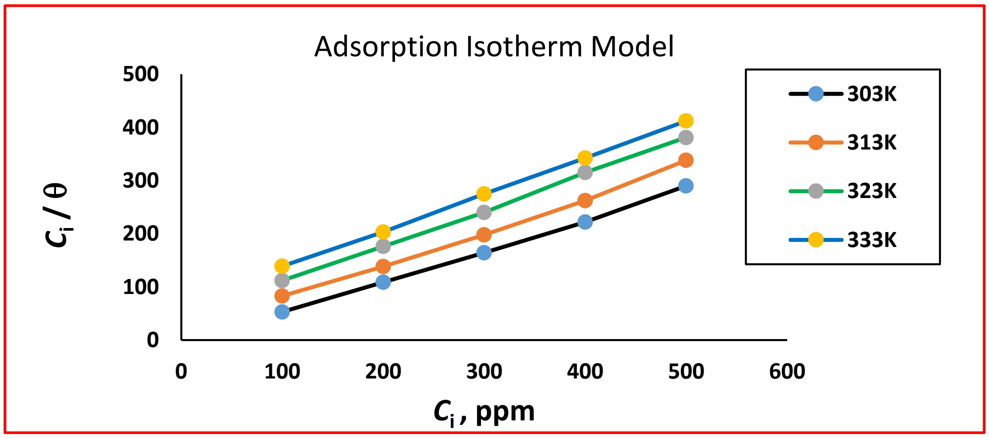


Figure 7. Langmuir adsorption isotherm model for the adsorption of steel immersed in 1.0 M sulfuric acid solution at different temperatures.

Conclusions

1. Expired Tramadol medicines are considered green corrosion inhibitors since they are innocuous to humans, especially at extremely low concentrations. Furthermore, preventing steel corrosion is important for the environment because corrosion is a dreadful waste of both natural resources and money.
2. By raising tramadol (TRAM) inhibitor concentrations to 500 ppm, the corrosion inhibition efficiency is increased to 93 percent, and consequently, the ferrous ion concentration [Fe+2] is decreased in the corrosive solution.
3. Corrosion rate was shown to rise as concentration was reduced and temperature was raised.
4. The inhibition due to adsorption and adhesion of drug constituent on the steel surface without modifying the mechanism of corrosion, and the adsorption found to obey Langmuir isotherm model.
5. Physical adsorption may account for the increased activation energy (E_a) for carbon steel in the presence of the expired pharmacological inhibitor compared to that in the absence. The increase in E_a can be explained to a significant drop in inhibitor adsorption on the carbon steel surface as temperature rises, resulting in a proportional increase in corrosion rates due to a larger area of the metal exposed to the acid environment.
6. The decrease in carbon steel corrosion rate is primarily regulated by kinetic parameters of activation, as seen by the increase in H_a with increasing inhibitor system concentrations.
7. The ferrous ion Fe^{+2} concentrations were decreased by increasing inhibitor concentration and increased by lowering the pH of the solution, according to AAS results.
8. Increasing the concentrations of expiring TRAM inhibitors decreased the amount of hydrogen evolved during the corrosion reaction of steel in acidic H_2SO_4 media, probably because inhibitor chemicals restrict the reaction of hydrogen evolution.
9. As a result of the inhibitor’s ability to bind protons in an acidic environment, the acidimetric approach’s findings indicate that the concentrations of hydrogen ions in the medium were lowered.
10. The outcomes of a number of analytical methods are in good accord with (±2%), demonstrating that the presence of expired Tramadol medications inhibits steel corrosion in acidic conditions and slows the process of iron dissolution in these situations. Therefore, expired Tramadol, signed as TRAM, may function as a green corrosion inhibitor.

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