Colorimetric evaluation of the corrosion rate of steel in acidic media in the presence of pentoxifylline drug and KI

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Abstract

This work employed a simple colorimetric method (UV-Vis spectroscopy) to measure the concentration of ferrous ions resulting from steel corrosion by using the *ortho*-phenanthroline method. *ortho*-Phenanthroline is a chelating agent that forms a stable ferrous complex with ferrous ions. Thus, this colorimetric method was used to measure the characteristics of corrosion and inhibition processes. Consequently, the properties of the expired pentoxifylline medication were assessed as an anti-corrosion agent for steel in a 0.2 M HCl solution. The concentration of dissolved iron was used to calculate the inhibition efficiency and corrosion rate. Additionally, studies on the synergistic impacts of pentoxifylline and potassium iodide (KI) have been conducted. After adding potassium iodide, the maximal pentoxifylline inhibitory efficiency of 88% rose to 94%. The free energy of adsorption was computed by fitting several adsorption isotherms. The limitations of this method include the use of the Beer–Lambert equation, which limits the measurement of ferrous ions in corrosive environments to a maximum of 21 parts per million.

1. Introduction

Corrosion is a phenomenon that is the main cause of damage to many machines and metal structures and is limited not only to metals but also to polymers and ceramics. The term "corrosion" refers to the degradation of a substance induced by an electrochemical or chemical reaction with its environment [1]. Corrosion causes annual losses estimated at millions or even billions of dollars, as it turns metal structures into broken structures. In addition, corrosion can contaminate canned foods and medicines, which directly affects human health. Although corrosion can be controlled by selecting highly resistant materials, it is better to use affordable metallic materials in conjunction with efficient corrosion prevention measures due to cost considerations. Steel alloys are among the most commonly used building materials in a wide range of sectors, for example, for oil and gas production; for the design of various reaction vessels and tanks; and for the handling of various corrosive liquids and aggressive solutions, including acidic, basic, and salt solutions. Steel is

commonly used due to its remarkable features, such as low cost, easy availability, high strength, and durability. Steel alloys are frequently exposed to acid, such as acid cleaning, acid descaling, acid pickling, and various petrochemical processes [2–4]. An acidic environment easily corrodes steel, in which H^+ ions and dissolved oxygen are known as natural motors of corrosion. As a result, the structures need to be protected against corrosion attacks. Several methods, such as coating, cathodic and anode protection, and the use of inhibitors, have been used to resist corrosion. Inhibitors are extensively used, especially in acidic environments. Inhibitors are compounds that cause a decrease in the corrosion rate of metal when supplied in suitable amounts without significantly changing the concentration of other agents [5]. The inhibitors typically interact chemically with the metal and the nearby environment or are adsorbed from the solution to form a layer on the metal surface. By enhancing the anodic or cathodic polarization or both, slowing the migration of ions towards the metal surface, or increasing the electrical resistance at the metal–electrolyte interfaces, the protective layer reduces corrosion. Many corrosion inhibitors have been explored for mild steel under acidic conditions. Most of the well-known corrosion inhibitors are organic compounds that contain N, O, S, P and multiple bonds or aromatic rings in their structure [6–16]. The loosely bonded π electrons and lone pairs in these functional groups are key features that determine the corrosion inhibition efficiency. Although a large spectrum of chemical compounds is accessible, the majority of studied inhibitors are costly, nonbiodegradable and harmful to humans and the environment. The drawbacks of synthetic corrosion inhibitors include the need to replace them with environmentally safe inhibitors, such as naturally occurring plant products, which are inexpensive, nontoxic, eco-friendly, green, and corrosion inhibitors. Moreover, nontoxic, expired medications have been employed to shield metals and their alloys. Therefore, it is possible to look into outdated medications that are useless for corrosion inhibition. Therefore, medications are a promising class of inhibitors [17–20].

There are numerous non-destructive detection technologies, including electromagnetic, radiographic, ultrasonic and acoustic methods. However, destructive techniques, such as linear polarized resistance, electrical resistance, and electrochemical impedance spectroscopy, include coupons and probes [21]. However, these techniques often result in expensive and time-consuming cleaning and inspection of tanks, which can influence normal production [22]. These techniques were developed over time to help with the challenge of corrosion and to minimize its risks and damage, so they vary depending on the purpose of the study.

Corrosion inhibitor research employing expired medications is still ongoing. In this context, the purpose of this investigation was to study the inhibitory effect of pentoxifylline (Figure 1) on steel corrosion in a 0.2 M hydrochloric acid solution by a colorimetric technique as part of an investigative study in our laboratory.
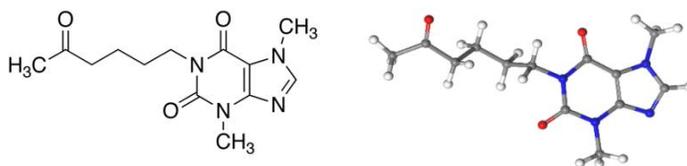
Figure 1. Chemical structure of pentoxifylline.

2. Theory

A spectrophotometer now offers a method of quantitative analysis with a better level of accuracy than is feasible with other techniques [23]. To investigate the concentration of dissolved iron in the aqueous phase, a colorimetric method was used with oligophenanthroline [24–26]. Saywell [27] noted that ferrous *ortho*-phenanthroline complex ions exhibit a highly stable, vivid red colour, the intensity of which is directly proportional to the amount of iron. *Ortho*-phenanthroline reacted instantaneously with divalent Fe, forming a colored complex of $[Fe(C_{12}H_8N_2)_3]^{+2}$. Pyenson [23] reported that for the most accurate determination of minute quantities of iron, the use of *ortho*-phenanthroline is recommended [25]. Thus, the benefits of using *ortho*-phenanthroline to determine iron content can be described as follows: (1) it gives a relatively more intense color for a given iron concentration; (2) the orange-red complex produced is stable, and no fading has been observed for as long as six months; (3) color formations occur in acid solution, eliminating the difficulties usually caused by precipitation of metal hydroxides and hydrated oxides in alkaline solution [23, 26]; and (4) the method is most sensitive for concentrations of approximately 0.5 ppm [28]. In this method, it is necessary to reduce any ferric ions to ferrous ions before the addition of *ortho*-phenanthroline. Therefore, it was decided to utilize a concentrated solution of hydroxylamine hydrochloride. According to Rao and Somidevamma [29], hydroxylamine converts ferric ions in acidic solutions to ferrous ions. Saywell discovered that a hydroxylamine hydrochloride solution at a concentration of 10% worked well as a reducing agent for the measurement of iron [23]. This was followed by the addition of 10% hydroxylamine hydrochloride solution, shaking, and the addition of 0.5 ml of *ortho*-phenanthroline solution. This technique has the benefit of being applicable to the evaluation of iron in food, biological materials, and analytical reagents because it can detect iron at concentrations as low as 0.5 ppm [23].

Johnsson [24] used a colorimetric technique to measure the quantity of dissolved iron in an aqueous phase to explore the rates of steel corrosion [25]. *Ortho*-phenanthroline was utilized as a reagent, and it immediately interacted with divalent Fe to generate the coloured $[Fe(C_{12}H_8N_2)_3]^{+2}$ complex [25].

The corrosion rate and inhibition efficiency were calculated by using the following equations:

$$CR = \frac{C}{A_s \cdot t} \qquad (1)$$

$$\mathrm{Inh\%} = \left(1 - \frac{R_{\mathrm{inh}}}{R_0}\right) \times 100 \qquad (2)$$

where C is the dissolved iron concentration in millimolar (mM), A_s is the surface area of the steel coupon, t is the time (1.5 hours), and R_0 and R_{inh} are the corrosion rates in the absence and presence of the inhibitor, respectively.

3. Materials and Methods

3.1. Materials

All the analytical reagent-grade chemicals were utilized. The expired 400 mg of pentoxifylline was manufactured by Santa Farma/Turkey. The molecular formula of the drug is ($C_{13}H_{18}N_4O_3$), and its chemical structure is shown in Figure 1. The experiments were performed on steel cylinders with the following chemical compositions: C (0.33), Si (0.17), Mn (0.72), P (0.013), S (0.002), and Fe (98.77). The specimens were obtained from the Musrata steel factory in Libya. The specimens used were mechanically cut into 4.0 cm long and 1 cm in diameter pieces and then abraded with 400–1200 grit SiC abrasive papers. The length and diameter of steel samples were measured to determine the surface area, which were calculated by: $A = 2\pi r L + 2(\pi r^2)$ [30]. Before being subjected to corrosion tests, the samples were cleaned in 100% ethanol and acetone, dried at room temperature and maintained in desiccators free of moisture.

3.2. Instrumentation

An Evolution™ UV-Visible/300 spectrophotometer (Thermo-Electron) was used to measure the absorbance of the tested solution. A thermostatically controlled water bath was used (Clifton Bata-England).

3.3. Reagents and solutions

A stock solution of 5.0 N HCl acid was prepared and standardized by titration with standard sodium carbonate (Na_2CO_3). A stock solution of 1000 ppm expired pentoxifylline was prepared and used in this study at concentrations ranging from 50 to 500 ppm. Sodium acetate (44 g) was dissolved in 500 ml of a volumetric flask to prepare the acetate buffer. Hydroxylamine hydrochloride (10%) was also prepared. A saturated solution of *ortho*-phenanthroline monohydrate was dissolved in 0.5 g of deionized water in 500 ml of water. The following reagents were added to each 50 ml volumetric flask for each experiment: 4.0 ml of acetate, 5.0 ml of *ortho*-phenanthroline, and 0.5 ml of hydroxylamine hydrochloride. After each addition, the flask was shaken, and water was then added to fill the volume.

3.4. Standard curve

After dissolving 0.0702 g of ferrous ammonium sulfate in 2.5 ml of 1 M sulfuric acid, enough water was added to obtain 500.0 ml of a 50 ppm iron standard solution. Aliquots of 0, 1, 2, 4, 7 and 21 ppm of the standard iron solutions were accurately measured in a 50 ml standard flask, and the reagents were added as described above. For iron determination, the spectrophotometer was set at 200–800 nm, and the peak of the absorption band was located at 510 nm. The sample's concentration can be ascertained using the Beer's law formula, which can be expressed mathematically as the following equation:

$$A = \varepsilon bc \qquad (3)$$

where A represents absorbance, ε denotes molar absorptivity, b denotes the sample's path length, and c denotes the sample's concentration. The data obtained for the standard curve were plotted (absorbance against the concentration). The five points determined for this curve follow a straight line and thus conform closely to Beer's law.

3.5. Procedure

The steel samples were dipped in 0.2 N HCl solution with or without different concentrations of pentoxifylline (50, 100, 150, 200, 300, 400 and 500 ppm) at the desired temperature (293.15±0.01 and 303.15±0.01 K). After 90 min, 0.5 ml was withdrawn from the test solution and placed in standard 50 ml flasks. Then, hydroxylamine hydrochloride, sodium acetate and *ortho*-phenanthroline were added, and the mixture was shaken after each addition. A permanent orange–red complex $[Fe(C_{12}H_8N_2)_3]^{+2}$ developed. The intensity is proportional to the iron content (Figure 2). The iron concentration was determined directly from the standard reference curve.

| 0.2 M HCl | 0.2 M HCl+Pentoxifylline | 0.2 M HCl+Pentoxifylline+KI |

Figure 2. Forming a coloured complex with ferrous ions in a corrosion environment.

4. Results

4.1. Linearity and limits of detection

A standard calibration curve was generated to measure the iron concentration using the colorimetry method. The absorbance values at λ_{max} were plotted against the ferrous ion concentration in ppm according to the Beer–Lambert equation (Figure 3A). The maximum

wavelength (λ_{max}) was 510 nm for an *ortho*-phenanthroline iron (II) complex, as shown in Figure 3B. Three analyses were performed at each concentration level in a three-level calibration series. Nine points in the calibration curve were obtained at ferrous iron concentrations up to 0.08 mM (21 ppm). For the calibration curve, the method demonstrated satisfactory linearity at up to 21 ppm. The least-square regression technique was used to obtain the regression equations (Table 1). The accuracy of the calibration curve was evaluated using the correlation coefficient. The linearity of the method was determined by the calibration equation ($A=23.84C+0.01$), where A is the absorbance and C is the concentration.
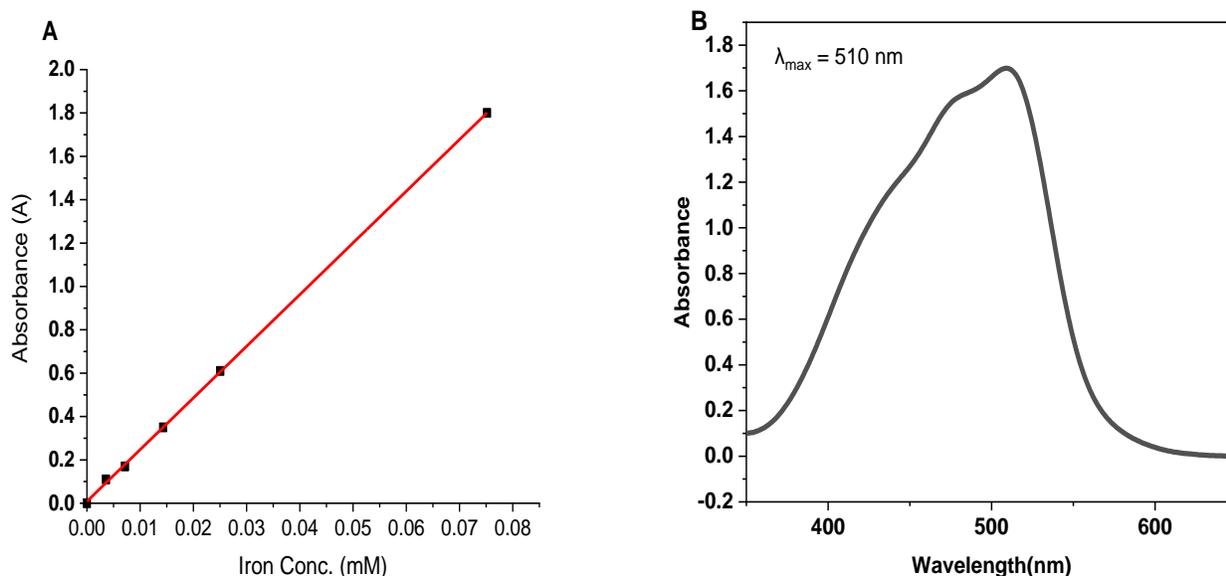
Figure 3. A) Standard calibration curve for iron concentration determination; B) maximum wavelength determination.

Table 1. Summary of quantitative parameters and statistical data from the calibration curve.

Parameter	Value
Linear range µg/mL	0–0.08
LOD	0.001
LOQ	0.002
Slope	23.84
Intercept	0.01±0.01
Correlation coefficient	1

The limits of detection (LODs) and limits of quantitation (LOQs) were determined using the following formulas:

$$LOD = 3.3(\sigma/S) \tag{4}$$

$$LOQ = 10(\sigma/S) \tag{5}$$

where σ is the standard deviation of the intercept and S is the slope. The LOD and LOQ were 0.001 and 0.002, respectively. Thus, the proposed method demonstrated good linearity, and the LOD and LOQ were found to be within acceptable limits, indicating the method's sensitivity.

4.2. Determination of the dissolved iron concentration

The slope of the straight line ($A = 23.84C + 0.01$) was used to measure the dissolved iron concentration (in millimolar) after dissolution (due to steel corrosion) in 0.2 M HCl. The corrosion experiments of the steel coupons in HCl solution were performed at different concentrations of the pentoxifylline drug and at temperatures of 293.15 and 303.15 K. The absorbance was recorded after each experiment to estimate the dissolved iron concentration using a standard curve equation. The obtained absorbance and corresponding iron concentration data are shown in Table 2 and presented in Figure 4.

Table 2. Absorbance and dissolved iron concentration.

Pentoxifylline conc. (ppm)	293.15 K		303.15 K	
	Abs.	Fe conc. (ppm)$\times 10^{-2}$	Abs.	Fe conc. (ppm)$\times 10^{-2}$
0	1.83	7.64	1.94	7.93
100	1.32	5.51	1.57	6.54
200	0.73	3.03	1.47	6.13
300	0.50	2.06	1.40	5.84
400	0.22	0.88	1.33	5.55
500	0.33	1.34	1.39	5.77

Figure 4 and Table 2 show that the concentrations of dissolved iron in the presence of free acid were greater than those in the presence of a pentoxifylline inhibitor. Additionally, the dissolved iron concentration decreases as the inhibitor concentration increases, which indicates that the presence of pentoxifylline prevents the steel corrosion.
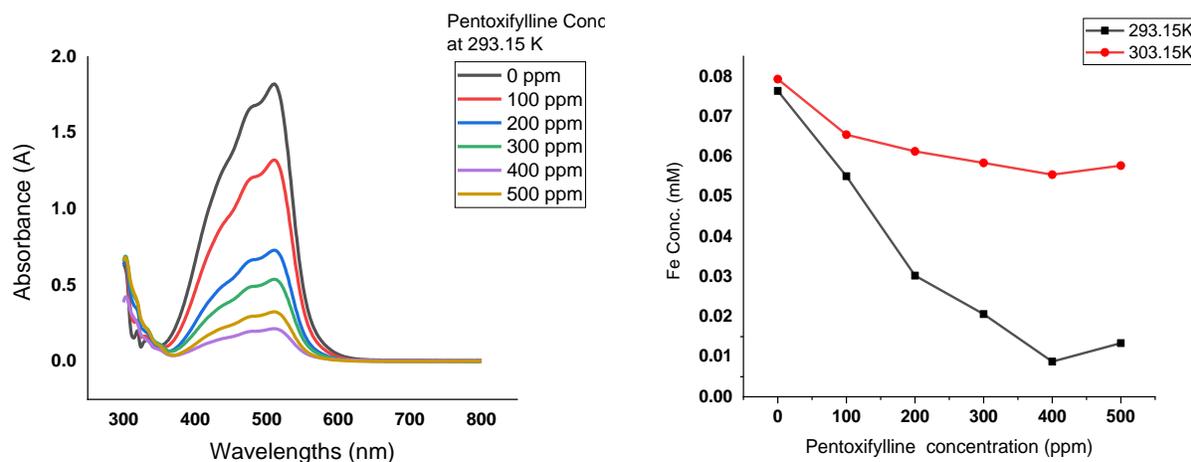
Figure 4. Dissolved iron concentration at different temperatures and pentoxifylline concentrations.

4.3. Inhibition properties of the expired pentoxifylline drug.

The corrosion rate was calculated from the dissolved iron concentration divided by the area and time at different temperatures (293.15 and 303.15 K), and the results are shown in Table 3.

Table 3. Corrosion and inhibition efficiency of the test solutions.

Pentoxifylline conc. (ppm)	293.15 K		303.15 K	
	$CR \cdot 10^{-3}$, (mM·cm^{-2}·h^{-1})	**Inh%**	$CR \cdot 10^{-3}$, (mM·cm^{-2}·h^{-1})	**Inh%**
0	3.45	–	3.58	–
100	2.46	28.56	2.92	18.19
200	1.30	62.05	2.74	23.17
300	0.95	72.10	2.59	27.48
400	0.38	88.45	2.39	32.93
500	0.6	82.32	2.6	27.15

Figure 5 shows the plot of the corrosion rate against the concentration in the presence and absence of the inhibitor. The inhibitor lowers the rate of corrosion more than it does when it is absent, based on the data. The corrosion rate decreases with increasing concentrations of the inhibitor due to the formation of a pentoxifylline layer on the steel surface by adsorption. According to the obtained results, the rate of corrosion increases with increasing temperature, which can be attributed to the increase in the reaction rate, which leads to an increase in dissolved iron. Table 3 displays the inhibition efficiency values for

steel dissolution in hydrochloric acid at various pentoxifylline concentrations at 293.15 K. Accordingly, the inhibition efficiency increases with increasing inhibitor concentration due to an increase in the inhibitor coverage on the surface of the steel.
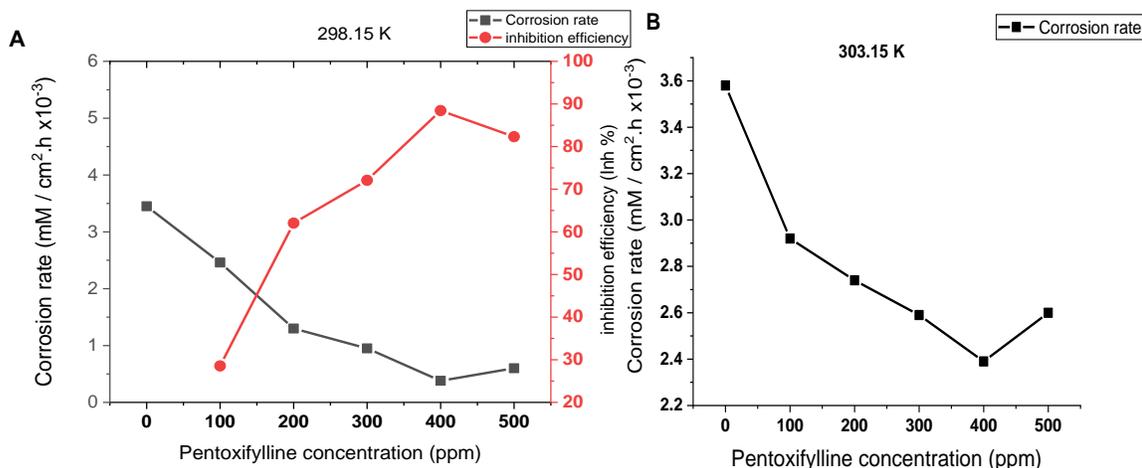
Figure 5. The corrosion rate and inhibition efficiency at A) 293.15 K and B) 303.15 K.

4.4. The synergistic effect at 303.15 K

Using the ultraviolet–visible approach, the impact of potassium iodide (synergistic) on the corrosion inhibition of steel dissolved in hydrochloric acid was examined. Different concentrations of potassium iodide were used in the presence of 200 ppm pentoxifylline at room temperature. The presence of iodide ions decreases the corrosion rate and increases the inhibition efficiency of pentoxifylline due to the synergistic effect. The absorbance, dissolved iron concentration, corrosion rate and inhibition efficiency are listed in Table 4 and displayed in Figure 6.

Table 4. The absorbance, dissolved iron concentration, corrosion rate and inhibition efficiency at 200 ppm of pentoxifylline and different concentrations of KI.

Inhibitor conc. (ppm)	Abs.	Fe conc. (mM·10^{-2})	CR (mM·cm^{-2}·h^{-1})	Inh%
0	1.47	6.13	2.74	–
50	0.15	0.57	0.23	91.76
100	0.14	0.54	0.22	91.89
150	0.13	0.53	0.20	92.72
200	0.1	0.37	0.18	93.57
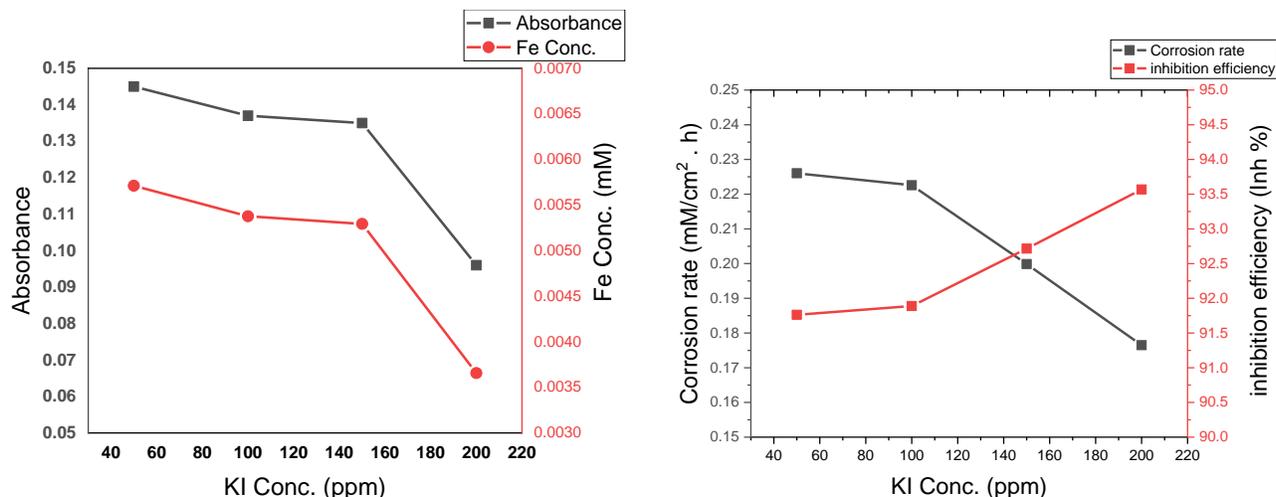
Figure 6. Corrosion rate and inhibition efficiency versus different concentrations of KI in the presence of 200 ppm PTX.

The effect of different concentrations of pentoxifylline on the steel corrosion rate in the presence of 100 ppm potassium iodide was studied, and the calculated corrosion rates and their corresponding inhibition efficiency values are listed in Table 5 and displayed in Figure 7.

Table 5. Absorbance and dissolved iron concentration at 100 ppm of KI in the presence of different concentrations of pentoxifylline.

Pentoxifylline conc. (ppm)	Abs.	Fe conc. (mM·10^{-2})	CR (mM·cm^{-2}·h^{-1})	Inh%
0	1.41	5.87	3.16	–
100	0.16	0.94	0.47	85.02
200	0.14	0.71	0.37	88.43
300	0.12	0.63	0.31	90.25
400	0.10	0.37	0.17	94.52

Figure 7 shows that the corrosion rate decreases with increasing concentration. Since the surface area increased and the dissolved iron concentration decreased, the rate of corrosion in the presence of potassium iodide and pentoxifylline was lower than the rate of corrosion in the presence of pentoxifylline alone. When potassium iodide solution was added to the pentoxifylline solution, the efficiency of the inhibition increased.
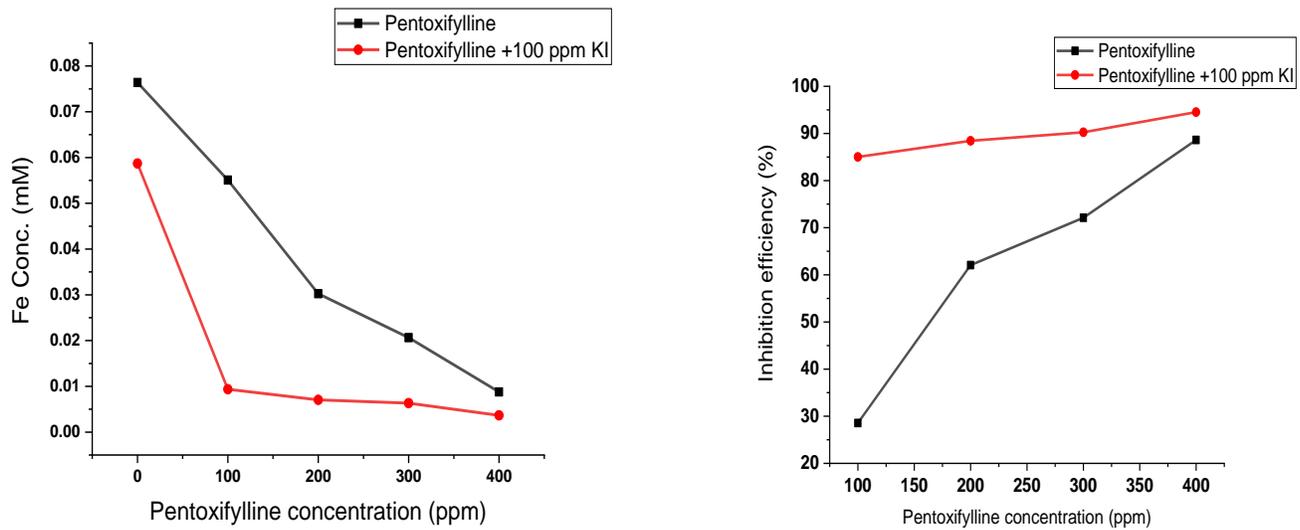
Figure 7. Corrosion rate and inhibition efficiency *versus* different concentrations of pentoxifylline in the presence of 100 ppm of KI.

4.5. Adsorption isotherms

In this work, surface coverage (θ) was used to construct various adsorption isotherms that better represent the pentoxifylline behavior on steel surfaces. Therefore, the Freundlich, El-Awady, and Langmuir adsorption isotherms have proven accurate. The equations that define these isotherms and the parameters of the obtained straight lines are expressed in Table 6. Figure 8 shows that all the tested isotherms produced straight lines. Furthermore, the various properties of the isotherms under study are summarized in Table 7.

Table 6. Equations for the studied isotherms and their straight line parameters.

	Isotherms equations	**Solutions**	R^2
Langmuir	$\dfrac{C}{\theta} = \dfrac{1}{K_{\text{ads}}} + C$	Pentoxifylline	0.83
		Pentoxifylline+KI	1
El-Awady	$\log \dfrac{\theta}{1-\theta} = \log k' + y \log C$	Pentoxifylline	0.96
		Pentoxifylline+KI	1
Freundlich	$\log \theta = \dfrac{1}{n} \log C + \log K_{\text{ads}}$	Pentoxifylline	0.97
		Pentoxifylline+KI	1

where C is concentration, θ is surface coverage, K_{ads} is equilibrium constant and $K_{\text{ads}} = K'^{1/y}$, and $1/y$ is active sites occupied by an inhibitor molecule.

The obtained results reveal that all the linear regression coefficients (R^2) and the slopes are close to unity and become closer after adding 100 ppm of KI. The Langmuir adsorption isotherm was studied using the form C_{inh} *vs*. C_{inh}/θ graph, in which the values of the different

concentrations of pentoxifylline in the presence and absence of KI were used. The correlation coefficients (R^2) and their related straight lines were between 0.827 to 0.998. The values of K_{ads} are shown in Table 7. The linear relationship of the Freundlich adsorption isotherm indicates that the $1/n$ values are less than unity, which is in the range of $0 < 1/n < 1$, indicating the ease of adsorption [31, 32].
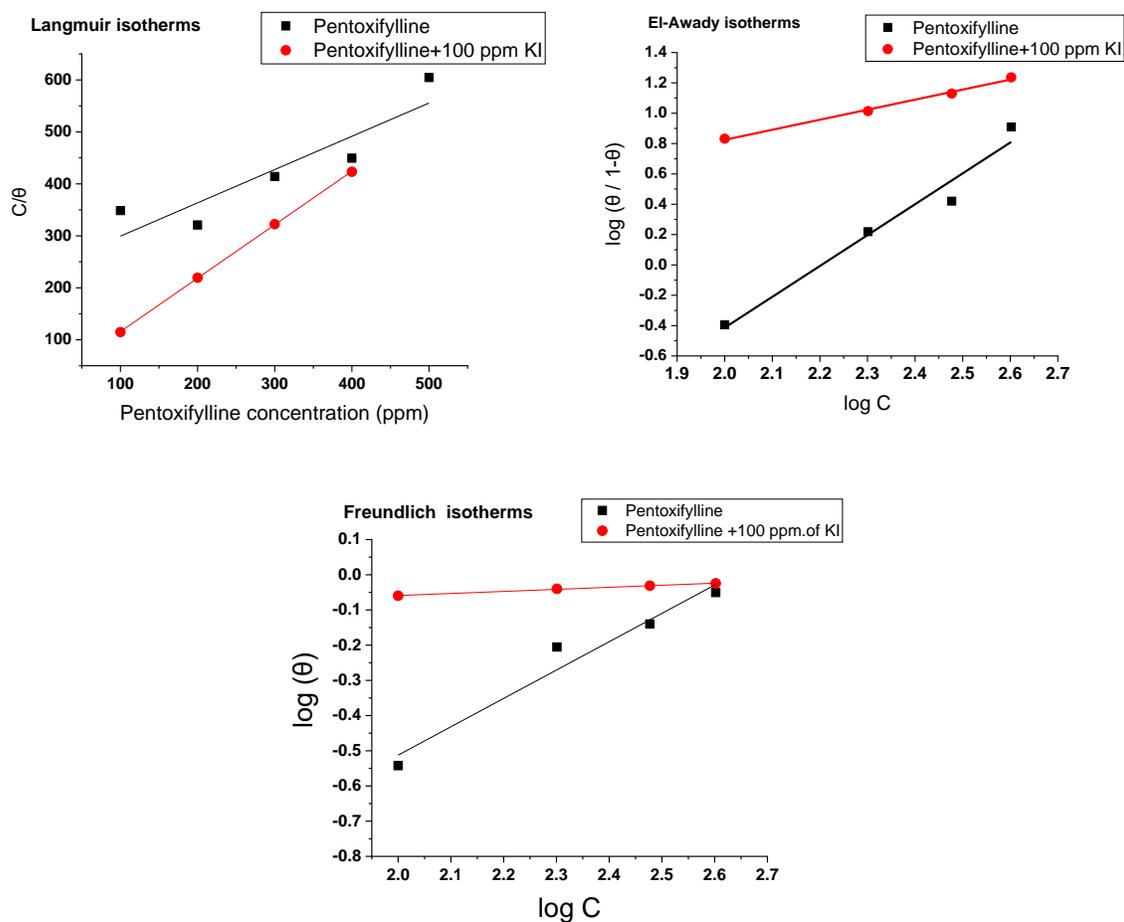
Figure 8. Fitting of the experimental data to the Langmuir, El-Awady and Freundlich adsorption isotherms.

The suitability of the El-Awady models for the adsorption of pentoxifylline on steel surfaces was confirmed by the comparatively high linear regression coefficients (R^2). Table 6 clearly shows that the correlation coefficients of the El-Awady models are closer to unity than are those of the other isotherms. Thus, this isotherm better reflects the pentoxifylline behaviour concerning steel corrosion in 0.2 M HCl. With respect to the El-Awady model, the values in the pentoxifylline system and the pentoxifylline +KI system yielded inverse slopes ($1/y$) of 0.49 and 1.5, respectively. In the presence of pentoxifylline, the number of surface active sites occupied by one molecule of pentoxifylline was less than unity, which indicates that two pentoxifylline molecules occupy one active site, which leads to less coverage and less inhibition efficiency. On the other hand, one pentoxifylline

molecule was shown to occupy more than one active site in the presence of KI, indicating that one pentoxifylline molecule occupies some active sites [33–35].

Table 7. Adsorption parameters obtained from the Langmuir, Freundlich and El-Awady isotherms.

Isotherms	Parameters	Pentoxifylline	Pentoxifylline+KI
Langmuir	K_{ads}	0.01	0.08
El-Awady	K_{ads}	0.01	0.18
	$1/y$	0.49	1.5
	y	2.03	0.66
Freundlich	K_{ads}	0.01	0.67
	$1/n$	0.81	0.06

The values of the adsorption equilibrium constant are deduced from the parameters of the modified Langmuir isotherm (the intercept of the straight lines). The K_{ads} values were used to calculate the free energy of adsorption. Larger K_{ads} values indicate better adsorption efficiency [36–39].

5. Conclusion

The colorimetry method was used to evaluate the corrosion inhibition of steel by the pentoxifylline mixture in 0.2 M HCl. The main findings of this study are as follows:

- Pentoxifylline acts as a good inhibitor of steel corrosion in 0.2 M HCl, and its inhibition efficiency increases with increasing concentration.
- Synergistic effects between Pentoxifylline and KI have been observed. The addition of KI to PTFs markedly enhanced the corrosion inhibition efficiency.
- The adsorption of pentoxifylline on steel surfaces obeys the Langmuir, El-Awady, and Freundlich adsorption isotherms.
- The adsorption of pentoxifylline and (pentoxifylline+KI) onto a mild steel surface is a spontaneous process.

Ethics

Authors should address any ethical issues that may arise after the publication of this manuscript.

Conflict of interest

The authors declare that they have no conflicts of interest associated with this manuscript.

Author contributions

Dr. AL-Abbasi supervised the project, developed the theoretical formalism, performed the analytic calculations and wrote the manuscript. H. Sida carried out the experiments and contributed to the review of the final version of the manuscript.

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