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Tetracycline as a Powerful Green Corrosion Inhibitor for Carbon Steel in the High-temperature with Acidic Environment

S. Shojaei Baghini, M. Shahidi Zandi*, N. Rastakhiz
Department of Chemistry, Kerman Branch, Islamic Azad University, P.O. Box: 7635131167, Kerman, Iran.

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ABSTRACT

For the first time, corrosion inhibition of carbon steel (ck45) in 0.5 M phosphoric acid was studied in the absence and presence of the Tetracycline drug as a friendly corrosion inhibitor. The corrosion resistance was calculated using electrochemical impedance spectroscopy (EIS) and the determination of the polarization curves. The corrosion tests were carried out with different inhibitor concentrations (200, 300, 600, 800, and 1000 ppm) at room temperature, and the most significant inhibitor efficiency was found to be 81 % at 1000 ppm concentration. According to the potentiodynamic polarization measurement results, Tetracycline is a mixed-type inhibitor. The activation energy, the thermodynamic parameters, and the adsorption isotherm were determined from the electrochemical data. The effect of temperature on the corrosion behavior of ck45 steel in 0.5 M H_3PO_4 with drug addition was also investigated. It was discovered that the inhibitory efficiency improves with rising temperature, reaching 95 % at 55 °C. Optical microscopy and scanning electronic microscopy (SEM) were employed to investigate the effect of the Tetracycline drug on the surface morphology of metal. Prog. Color Colorants Coat. 16 (2023), 153-164© Institute for Color Science and Technology.

1. Introduction

Corrosion is a spontaneous and natural process that changes pure metals and their alloys into a variety of stable forms, such as their hydroxides, oxides, and sulfide, among others, through chemical and electrochemical reactions with the environment [1]. The corrosion control of metallic materials in environments such as oil industries is a major issue; thus, it is critical to safeguard metal in equipment and structures in industries, hospitals, transportation, buildings, and homes from corrosion. Acidic solutions are extensively utilized in different industries for various aims. Using acids for pickling and chemical cleaning to remove oxide scales from the metal surfaces is a key and major problem in the oil industry [2].

Due to the general aggression of acid media, using effective inhibitors is one of the most reliable and cost-effective ways to reduce corrosion rates and protect metal surfaces against corrosive media [3]. Corrosion inhibitors, surface coatings, anodic and cathodic protection, and corrosion-resistant materials are all used in today's anti-corrosion procedures. When it comes to controlling, preventing, or delaying the corrosion of metals and alloys, the employment of inhibitors is a well-known method [4].

Various inorganic and organic substances have been investigated as corrosion inhibitors for metals. The existence of polar functions with O, N, or S atoms in the molecule, heterocyclic compounds, and π-electrons all contribute to the effectiveness of these organic corrosion inhibitors [5].

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*Corresponding author: *shahidi@iauk.ac.ir
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Inhibitors are chemicals that reduce electrochemical corrosion reactions on metal surfaces when applied in a small amount to corrosive conditions. The inhibitor's mechanisms are as follows: the inhibitor adsorbs on the metal surface to form a protective barrier, reducing the cathodic and/or anodic processes that cause corrosion [6]. The need for green corrosion inhibitors with the least adverse effect on the environment is high due to the poisonous behavior of traditional corrosion inhibitors and their destructive impact on the lives of living organisms and plants [7, 8]. Green corrosion inhibitors such as medications and tablets have gotten much attention in recent decades. Consider the following scenarios:

Phenylephrine's effects on mild steel and aluminum were studied by Bashir et al. [9]. The corrosion mechanism was also demonstrated with an inhibitor delaying both anodic and cathodic reactions. Tasic et al. used Azithromycin to investigate copper corrosion resistance in sodium chloride salt solution [10]. Kumar et al. and Bashir et al. investigated the inhibitory efficiency of Ethambutol and Bronopol, claiming 91.30 % at 1000 ppm for Ethambutol and 93.89 % for Bronopol [11, 12]. In the Langmuir adsorption isotherm, adsorption demonstrated the best fit. Fouda evaluated the anti-corrosion properties of expired Carvedilol, which was chemically and physically adsorbed on the sample's surface [13]. The reactivity of clozapine in sulfuric and nitric acids was studied [14]. For both chemical and physical adsorption, the Langmuir isotherm was used. The drug has an inhibitory combination effect. Haddad et al. and Khan et al. studied the behavior of Cephapirin and Ciprofloxacin as corrosion inhibitors for carbon steel in hydrochloric acid solution, respectively [15, 16]. According to the findings, the efficiency of inhibition rose with increasing concentration and decreased with increasing temperature. Cephapirin was found to be an excellent and mixed inhibitor. Adsorption obeyed Temkin adsorption isotherm.

The major goal of this study was to see if the *Tetracycline* drug could prevent carbon steel (ck45) from corroding in the 0.5 M phosphoric acid solution. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were used to study the electrochemical performance of mild steel electrodes. The influence of temperature and the amount of inhibitor added on the efficacy of the inhibition process was also investigated, and the Gibbs free energy and the adsorption isotherm were calculated to explain the inhibition mechanism. The morphology of the mild steel surface and the production of protective film on the metal surface were studied in the absence and presence of Tetracycline drug in acidic media using a scanning electron microscope and an optical microscope.

2. Experimental

2.1. Materials

The following materials and reagents were used in this work. Phosphoric acid (H_3PO_4, MW 98 g/mol), ethyl alcohol (C_2H_5OH, MW 46.07 g/mol), and acetone (C_3H_6O) were purchased from Merck Chem. Co. (Germany). All the chemical materials were used without further purification.

This investigation used a certified mild steel alloy that has been subjected to ck45 treatment. The samples were collected from a plate with a thickness of 10 mm. Table 1 shows the chemical composition of the alloy.

The exposed side of the steel sheets was polished to a mirror finish with several grades of emery papers (100, 400, and 2500). Water was used to clean the substrates, which were then degreased using acetone and ethyl alcohol, and dried at room temperature.

2.2. Solutions preparation

Dilution of phosphoric acid with double distilled water yielded a 0.5 M H_3PO_4 solution. Before each experiment, the test solutions were freshly made by adding the drug to the corrosive solution. Experiments were conducted twice to verify repeatability. For 0.5 M H_3PO_4, the inhibitor concentrations were 200, 300, 600, 800, and 1000 ppm.

Table 1: Chemical composition of mild steel (wt. %).

Mn	C	Ni	Si	Cr	Mo	S	P	Fe
0.6	0 .45	>0.4	>0.4	>0.4	>0.1	>0.035	>0.035	balance

2.3. Inhibitor

Tetracycline is an antibiotic with a broad spectrum of action. It stops cells from growing by preventing them from translating. Tetracycline is widely used in treating human diseases, animal nutrition, veterinary medicine, and as an additive in cattle feed. It treats various illnesses, including lung infections, urethritis, and severe acne. It can also be used to treat multidrug-resistant malaria [17]. The molecular formula of Tetracycline is $C_{22}H_{24}N_2O_8$, with the structure shown in Figure 1.

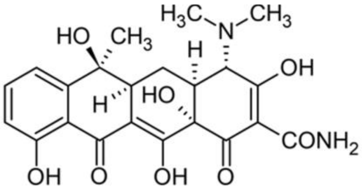

Figure 1: Molecular structure of Tetracycline.

2.4. Measurement and characterization

2.4.1. Electrochemical measurement

An Autolab (model 302N-Netherlands) potentiostat/ galvanostat was used for electrochemical investigations. The program Nova 1.10 (Utrecht, the Netherlands) was utilized to set up all experimental parameters and fit the EIS data. Three electrodes were used in a conventional electrochemical cell. The reference electrode was a saturated calomel electrode (SCE), the counter electrode was a platinum plate, and the working electrode was mild steel with an electrolyte contact surface of 1 cm^2. A 30-minute stabilization period was permitted before the electrochemical experiment, which was shown to be sufficient to achieve a stable corrosion potential value (E_{corr}).

2.4.2. Electrochemical impedance spectroscopy (EIS)

EIS uses AC excitation signals to test a material's resistance and capacitance properties. Variable frequency ranges are used to create the spectrum. The EIS measurements were performed in a frequency range of 100 kHz to 10 mHz, with an amplitude of 5 mV peak by peak, using an AC signal as corrosion potential (E_{Corr}). Nyquist plots were used to depict the impedance results. The inhibition efficiency (*IE %*) is calculated using the following equation (Eq. 1) [8]:

$$\text{IE } \% = \left(\frac{\mathrm{Rct} - \mathrm{R\prime ct}}{\mathrm{R_{ct}}}\right) \times 100 \tag{1}$$

where R_{ct} and R'_{ct} are the polarization resistance of the phosphoric acid solution with and without extract, respectively.

2.4.3. Potentiodynamic polarization

Potentiodynamic polarization curves were swept at a rate of 1 mV/s at 298 K from a cathodic potential of -200 mV to an anodic potential of -900 mV vs. free corrosion potential (E_{corr}). The corrosion current densities (i_{corr}) were calculated by extrapolating the anodic and cathodic curve slopes to corrosion potential. The *IE %* was computed using the following equation (Eq. 2) [18]:

$$\text{IE } \% = \frac{\mathrm{i_{corr}} - \mathrm{i'_{corr}}}{\mathrm{i_{corr}}} \times 100 \tag{2}$$

where i and i′ are the solution's current densities in the inhibitor's absence and presence, respectively.

2.5. Temperature

The influence of temperature on the corrosion rate of mild steel in acid solution with and without the best inhibitor concentration was evaluated using the potentiodynamic polarization technique in the temperature range of 25-55±1 °C.

2.6. Surface characterization

The mild steel specimens were immersed in 0.5 M phosphoric acid solution for 24 hours at room temperature in the presence and absence of the optimum inhibitor concentration. The steels were then cleaned and dried after being removed from the solution. The scanning electron microscope (SEM, Regulus8220; Japan) and optical microscope (Leica zoom 2000 model) were used to examine the surface morphology of the alloys.

3. Results and Discussion

3.1. Electrochemical impedance spectroscopy

The EIS method was used to study the current flow and the resistance value occurring on the mild steel surface in the inhibitor-free solution and the inhibitor-containing solution at room temperature. Figure 2a depicts the inhibition behavior of the Tetracycline drug on the corrosion of ck45 alloy in an acidic environment. It could be observed when the concentration of the extract was raised, the diameter of Nyquist plots grew larger, which could be related to the strengthened inhibitive film on the mild steel surface [19]. When compared to the blank solution, Tetracycline extract operated as a concentration-independent inhibitor with a low optimal concentration value of 1000 ppm and showed 81 % inhibitory performance at 1000 ppm.

In Table 2, the parameters of impedance are gathered. In this table, C_{dl}, R_{ct}, ω_{max} and *IE %* are double-layer capacitance, charge transfer resistance, high frequency, and inhibition efficiency, respectively.

The values of the C_{dl} was calculated using Eq. 3 [8]:

$$C_{dl}=\frac{1}{2\pi\omega_{max}R_{ct}} \tag{3}$$

The *IE* % of the inhibitor was determined using Eq. 1.

According to Table 2, as the amount of inhibitor was increased, the charge transfer resistance and inhibition efficiency rose. The fact that a charge transfer process controls steel corrosion was proven by this increase in R_{ct} [20]. Also, as expected, the C_{dl} value decreases as the inhibitor concentration rises, owing to a drop in the local dielectric constant or an increase in the thickness of the electrical double-layer capacitor [21]. It is revealed that the inhibitor molecules, rather than water molecules, are found on the steel surface and act through adsorption at the electrode/solution contact. The decrease in C_{dl} values is due to the inhibitor adsorption on the metal surface, which causes a film or complex to form from the acidic solution [22].

All of the processes involved in the system's electrical response were fitted against an equivalent Randle CPE circuit model in Figure 2b. The ohmic resistance is described by solution resistance (R_s). Still, the charge transfer resistance (R_{ct}) is inversely related to the corrosion rate and shows the inhibitor's resistance to oxidation of the metal surface. A constant phase element (*CPE*) is used instead of a pure double-layer capacitor (C_{dl}) to justify the semicircle form of the Nyquist plot [23].

Table 2: Corrosion parameters derived from Nyquist curves for ck45 alloy in 0.5 M H_3PO_4 solution in the absence and presence of different concentrations (0-1000 ppm) of Tetracycline.

C/ppm	ω_{max}	C_{dl}/μF.cm^{-2}	R_{ct}/Ω.cm^{2}	IE %
Blank	25.90	84	73	---
200	20.00	69	116	37
300	11.10	81	178	59
600	12.70	54	232	69
800	8.80	64	281	74
1000	7.30	56	389	81

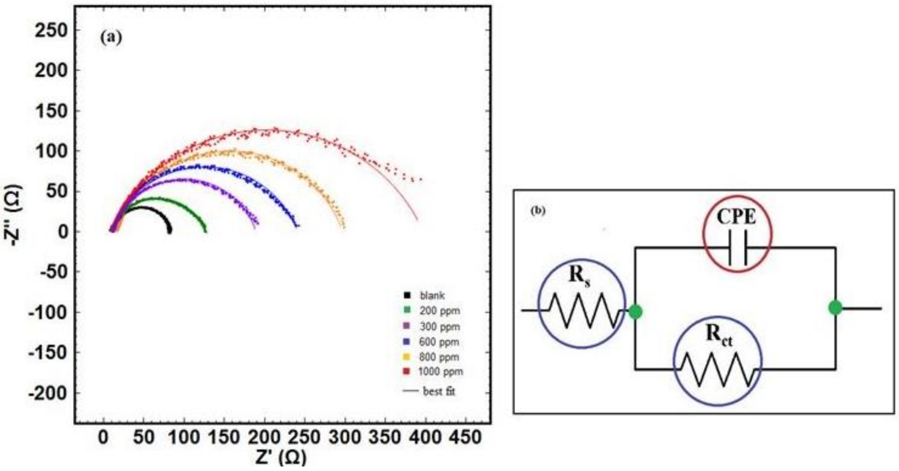

Figure 2: a) Nyquist plots and b) Equivalent circuit for ck45 alloy in 0.5 M H_3PO_4 in the different concentrations (0-1000 ppm) of Tetracycline.

Table 3: Corrosion parameters derived from polarization curves for ck45 alloy in 0.5 M H_3PO_4 solution in the absence and presence of different concentrations (0-1000 ppm) of Tetracycline.

C/ppm	i_{corr}/µA.cm^{-2}	E_{corr}/mV	β_c/mV.dacade^{-1}	β_a/mV.dacade^{-1}	θ	IE%
Blank	132	-533	80	161	---	---
200	45	-519	49	150	0.66	66
300	43	-529	60	134	0.67	67
600	40	-530	58	168	0.70	70
800	32	-510	45	170	0.76	76
1000	29	-504	38	208	0.78	78

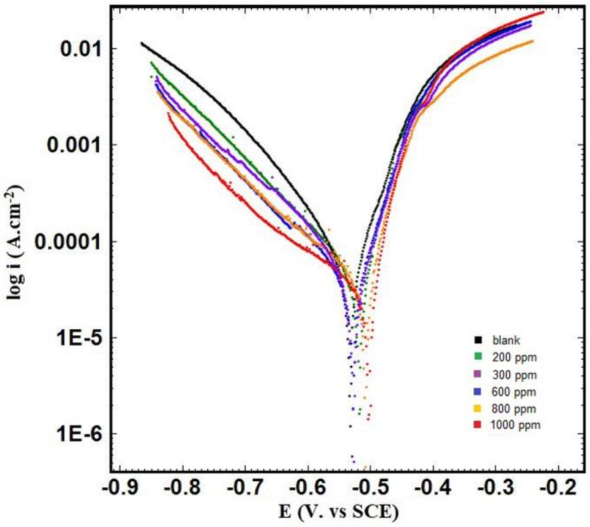

Figure 3: Polarization curves for ck45 alloy in 0.5 M H_3PO_4 in the different concentrations (0-1000 ppm) of Tetracycline.

3.1.1. Potentiodynamic polarization analysis

This experiment aimed to determine the type of corrosion inhibition activity of the investigated inhibitor on the mild steel surface. Figure 3 depicts the results of an electrochemical investigation that used Tetracycline as a green metal inhibitor in an acidic solution at room temperature. In Table 3, some dependent parameters are listed, including anodic and cathodic Tafel slopes (β_a and β_c), corrosion current density (i_{corr}), corrosion potential (E_{corr}), the inhibition efficiency (*IE* %), and the degree of surface coverage (θ). The intercept of extrapolated cathodic and anodic Tafel lines at the corrosion potential (E_{corr}) was used to calculate corrosion current density (i_{corr}). And The *IE* % was determined from Eq. 2. Table 3 shows that the i_{corr} decreases as the inhibitor increases, with the inhibitor showing 78 % of *IE %* at 1000 ppm, which was the highest when compared to the blank solution. This behavior is due to the drug molecules blocking the metal surface's reaction sites and forming a protective layer on it [24].

After utilizing the drug as an inhibitor, the shape of the anodic and cathodic curves and the Tafel parameter (β_c and β_a) did not change considerably, indicating that the drug is a both an anodic and cathodic inhibitor (mixed one). On the other hand, if the change in corrosion potential values in the inhibited solution compared to the uninhibited solution is 85 mV, the inhibitor can be classified as either cathodic or anodic [25]. In this study, the change in the corrosion potential, E_{corr}, stayed between 3–29 mV compared to the blank, indicating that the compound is a mixed-type inhibitor.

3.1.2. Effect of temperature on inhibitor efficacy of thyme extract

Temperature is a key factor in metal dissolving research. Many factors that affect corrosion in acid solutions are affected by temperature. The comparison of corrosion activation energies in the absence and presence of an inhibitor, and the temperature dependency of inhibition efficiency, may provide some insights into the likely mechanism of inhibition adsorption. The effect of temperature on potentiodynamic polarization curves for mild steel in 0.5 M H_3PO_4 solution is illustrated in Figure 4a and b. Table 4 shows the several corrosion parameters (E_{corr}, i_{corr}, and *IE*) that were investigated in 0.5 M H_3PO_4 solution at a temperature ranging from 25 to 55±1 °C in the presence and absence of the best inhibitor concentration.

The current density is always significantly lower in the presence of the inhibitor than it is in the absence of the inhibitor, which reveals that in the studied temperature range, Tetracycline is an effective inhibitor.

From data in Table 4b, Potentiodynamic polarization studies revealed a slight increase in the corrosion current density (i_{corr}) with increasing temperature and corrosion inhibition efficiency. Inhibition of corrosion may be caused by the adsorption of inhibitor's organic components on steel surfaces, and higher temperatures do not lead to the desorption of these components, and this is not owing to a decrease in the adsorption process's strength at higher temperatures.

The Arrhenius behavior for the reaction between the mild steel and the phosphoric acid is given in Figure 4. The activation energy value of the corrosion process was also calculated using the Arrhenius equation (Eq. 4) [26]:

$$i_{corr}=A\exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

The pre-exponential factor, the gas constant, the absolute temperature, the corrosion current density, and the activation energy are represented by *A*, *R*, *T*, i_{corr}, and E_a, respectively. In this situation, the correlation between *ln* (i_{corr}) and (*1/T*) is clearly fit by straight lines.

The results are listed in Table 4, and the E_a values were obtained by linear regression of *ln* (i_{corr}) vs. *1/T* data (Figure 5). E_a values in the blank and inhibitory solution are 80.60 and 31.55 *kJ/mol*, respectively, as shown in Table 4. An inhibitor increases the activation energy by about 2.5 times in the absence of an inhibitor. The chemisorption mechanism of Tetracycline on the mild steel surface is supported by an increase in inhibition efficiency with increasing temperature and a comparable decrease in corrosion activation energy in the presence of an inhibitor compared to its absence.

3.2. Adsorption isotherm

Adsorption isotherms are vital because they provide detailed information about the interaction between drug molecules and the metal surface. The measurements of surface coverage (θ) at various inhibitor concentrations in acid were used to describe the optimal isotherm for determining the adsorption process. The findings were fitted using different adsorption isotherms to derive the adsorption process and adsorption equilibrium constant (K_{ads}). The Langmuir adsorption model was used to discuss the inhibitory effect of Tetracycline on acid corrosion of mild steel.

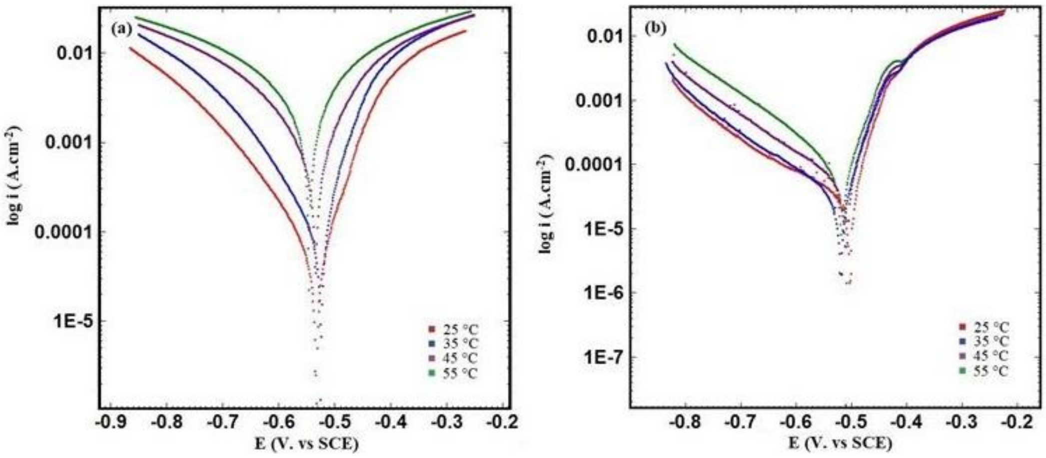

Figure 4: Polarization curves for ck45 alloy in 0.5 M H_3PO_4 at different temperatures a) without Tetracycline b) with 1000 ppm of Tetracycline.

Table 4: Corrosion parameters were calculated from polarization measurements in 0.5 M H_3PO_4 solution at different temperatures a) without Tetracycline and b) with 1000 ppm of Tetracycline.

temperature/°C	$i_{corr}/\mu A.cm^{-2}$	$-E_{corr}/mV$	IE%
a) blank			
25	132	-533	---
35	160	-526	---
45	1020	-535	---
55	1966	-547	---
b) Tetracycline			
25	29	-504	78
35	33	-519	79
45	46	-510	95
55	96	-518	95

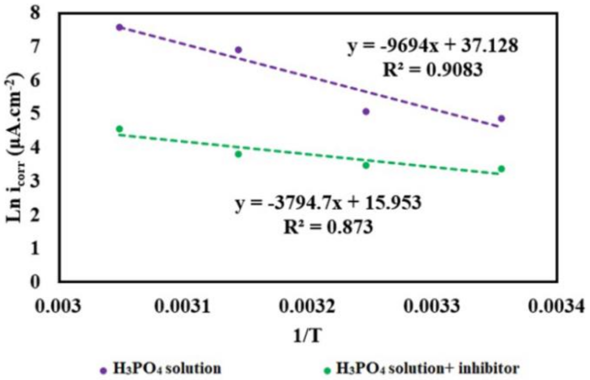

Figure 5: Arrhenius slopes determined from corrosion current density for ck45 alloy in acidic media, without Tetracycline and with Tetracycline.

Figure 6 illustrates the relationship between the portion of the surface protected by adsorbed molecules and the inhibitor concentration (C_{inh}), as defined by Eq. 5:

$$C_{inh}/\theta=1/K_{ads}+C_{inh} \tag{5}$$

Simple linear regression analysis was used to assess the goodness of fit. The Langmuir isotherm's regression coefficient is almost close to unity (0.9958). The intercept of the Langmuir isotherm diagram was used to study the K_{ads} value (K_{ads}=0.012).

3.3. Thermodynamic parameters

Thermodynamic/kinetic parameters for inhibitor adsorption, such as the standard free energy of adsorption (ΔG°_{ads}), entropy (ΔS°_{ads}), enthalpy (ΔH°_{ads}), and activation energy (E_a), might give helpful information regarding the corrosion inhibition process. The standard free energy of adsorption calculation shows how strong the molecule's adsorption is on the surface.

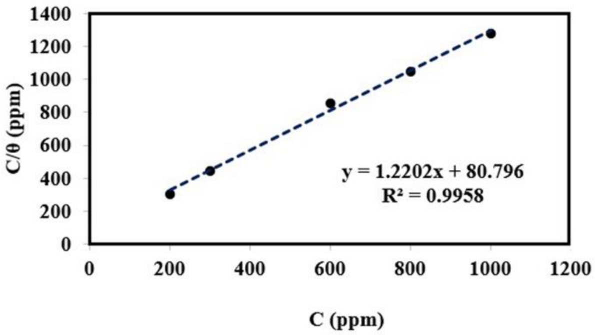

Figure 6: The Langmuir adsorption isotherm plots for ck45 alloy in 0.5 M H_3PO_4 in the different concentrations (200-1000 ppm) of Tetracycline by polarization technique.

The value of free adsorption energy was determined using the following equation after measuring K_{ads} in the previous section (Eq. 6):

$$\Delta G^{o}_{ads} = -RT\ln(1 \times 10^{6} K_{ads}) \qquad (6)$$

where 1×10^{6} indicates the concentration of water in milligrams per liter when employed in dilute solutions. The standard adsorption heat (ΔH°_{ads}) and the standard adsorption entropy (ΔS°_{ads}) can also be calculated using the following equations (Eqs. 7 and 8):

$$\frac{\theta}{1-\theta} = AC\exp\left(-\frac{\Delta H^{o}_{ads}}{RT}\right) \qquad (7)$$

and,

$$\Delta G^{o}_{ads} = \Delta H^{o}_{ads} - T\Delta S^{o}_{ads} \qquad (8)$$

where *T*, *A*, *C*, *R*, and *θ* are the reaction temperature in kelvin, a constant, the inhibitory concentration, the universal gas constant, and the inhibitory molecules' surface coating, respectively. The plot of $\mathrm{Ln}(\frac{\theta}{1-\theta})$ vs. 1/T is shown in Figure 7. For measuring ΔH°_{ads}, $-\Delta H^{\circ}_{ads}/R$ is determined from the slope of the linear parts of the graph.

The values of measured kinetic and thermodynamic factors are shown in Table 5. The little positive value of ΔG°_{ads} implies that the inhibitor molecules are slightly non-spontaneously adsorbed on the mild steel alloy's surface. When the ΔG°_{ads} is more positive than -20 *kJ/mol*, the adsorption of inhibitor molecules on the steel surface is mostly performed by electrostatic action, which is physical adsorption. When ΔG°_{ads} is more negative than -40 *kJ/mol*, chemical adsorption takes over. The computed ΔG°_{ads} in our case is 1.01 *kJ/mol* at 298 *K*, showing that Tetracycline drug molecules are adsorbing on the steel surface via a physical process.

The positive values of ΔH_{ads} reflect the endothermic behavior of mild steel dissolution in a sulfuric acid environment. This study's entropy of adsorption in the solutions is also low and favorable. This positive value is due to substituting Tetracycline molecules with water molecules, which might increase solvent entropy and a higher positive water desorption entropy.

3.4. Surface observations

The morphology of mild steel surfaces immersed in 0.5 M phosphoric acid was studied with and without Tetracycline medication for roughly 24 hours by a scanning electron microscope and an optical microscope (Figure 8). In the absence of the examined compound, the blank pictures (Figure 8a and c) indicate a very rough and heavily corroded surface. Pits and cracks are apparent in these images.

Figure 8 b and d shows that when the inhibitor is present, the damage to the steel surface is reduced, and the rough, corroded steel surface displaces to a much smoother surface with just a slight shallower pitting corrosion. According to the previous findings, inhibitor molecules can adsorb on the metal surface and form a protective inhibitor layer.

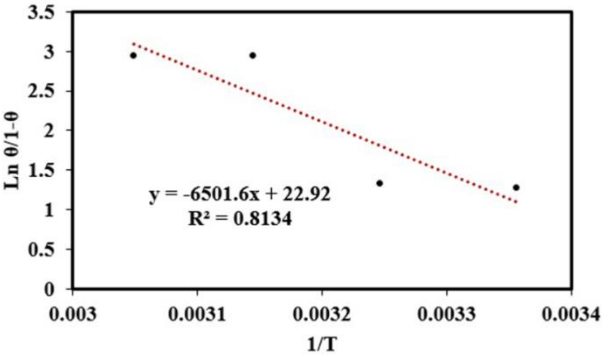

Figure 7: Plots of Ln (θ/1-θ) versus 1/T for ck45 alloy in 0.5 M H_3PO_4 containing 1000 ppm of Tetracycline *e*, at different temperatures.

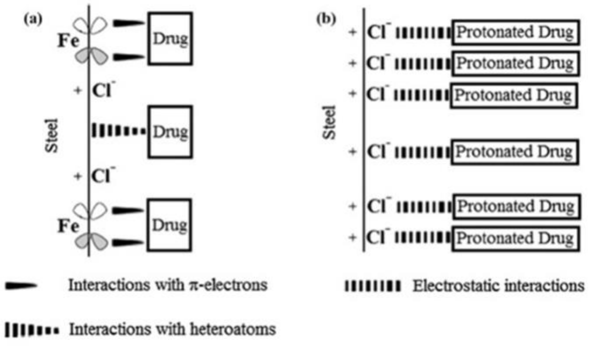

Figure 8: The images of ck45 alloy surface after 24 h immersion in 0.5 M H_3PO_4 solution in the (a) absence and (b) presence of 1000 ppm of Tetracycline drug using SEM and (c) without and (d) with 1000 ppm of Tetracycline drug using optical microscopy.

Table 5: Kinetic and Thermodynamic parameters for adsorption of Tetracycline in 0.5 M H_3PO_4 on the ck45 alloy surface.

Medium	E_a ($kJ.mol^{-1}$)	ΔH^o_{ads} ($kJ.mol^{-1}$)	ΔG^o_{ads} ($kJ.mol^{-1}$)	ΔS^o_{ads} ($kJ.mol^{-1}.K^{-1}$)
Phosphoric acid	80.60	----	----	----
Phosphoric acid and inhibitor	31.55	54.05	1.01	0.18

Figure 9 depicts the inhibition behavior of *Tetracycline* drug on the corrosion of ck45 alloy in 1 M HCl solution. In Table 5, the parameters of impedance are gathered. A comparison of the inhibition efficiency of tetracycline drug in 1 M HCl and 0.5 M H_3SPO_4 should reveal the principal modes of adsorption of the drug. If corrosion inhibition is due exclusively to protonated species that adsorb electrostatically, the drug should be more effective in 1 M HCl; if not, then the inhibiting effect should be comparable in both acid solutions.

According to data in Table 5, tetracycline drug showed better performance in HCl solution than in H_3PO_4 solution. Thus, it can be stated that the adsorption mode of Figure 8b was more favored than that of Figure 8a. This means that tetracycline was adsorbed mainly through electrostatic interactions between the protonated molecules and the negatively charged metal surface.

3.5. Theoretical study

To investigate the interaction of tetracycline with carbon steel, quantum chemical calculations were carried out using the methodology of the density functional theory (DFT) method. Generally, the adsorption of the inhibitor molecules on a metallic surface occurs via a donor-acceptor interaction between the π-electrons of the organic inhibitor and the orbital of the metallic atom. Thus, the energies of HOMO and LUMO of the inhibitor are very important for the investigation of the inhibitor interaction with the metal surface. The vacant orbital of the metallic atom can interact with the HOMO of the inhibitor, and the 4s orbital of the metallic atom interacts with the LUMO of the inhibitor atom. The inhibitor molecule with the less negative energy of HOMO tends to be more donating and that with the lower energy of LUMO (more negative) tends to be more accepting. Therefore, the IE value will be increased by increasing the HOMO energy and decreasing LUMO energy [3]. Furthermore, by decreasing the energy gap (ΔE) between HOMO and LUMO, the interactions between the inhibitor molecule and metal atom become stronger and the inhibition efficiency will be increased. The quantum chemical parameters of tetracycline are presented in Table 6.

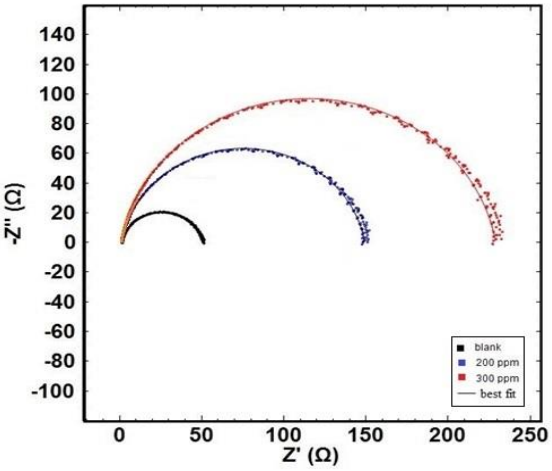

Figure 9: Nyquist plots for ck45 alloy in 1M HClsolution containing different concentrations (0, 200 and 300 ppm) of *Tetracycline*.

Table 5: Corrosion parameters derived from Nyquist curves for ck45 alloy in 0.5 M H_3PO_4 and 1M HCl solutions in the absence and presence of different concentrations of *Tetracycline*.

Medium	C/ppm	$R_{ct}/\Omega.cm^2$	IE%
H_3PO_4	Blank	73	---
	200	116	37
	300	178	59
HCl	Blank	47	---
	200	153	69
	300	233	80

Table 6: Quantum chemical parameters for effects of Tetracycline on carbon-steel.

Inhibitor	E_{HOMO} (ev)	E_{LUMO} (ev)	ΔE (ev)	μ (D)
Tetracycline	-6.44	-2.21	4.23	5.27

3.6. Surface observations

The morphology of mild steel surface immersed for roughly 24 hours in 0.5 M phosphoric acid with and without the best dose of Tetracycline medication was studied using a scanning electron microscope and an optical microscope (Figure 10). In the absence of the examined compound, the blank pictures (Figure 10a and c) indicate a very rough and heavily corroded surface. Pits and cracks are very clear in these images.

Figure 10 b and d shows that when the inhibitor is present, the damage to the steel surface is reduced, and the rough, corroded steel surface displaces to a much smoother surface with just a slight bit shallower pitting corrosion. According to the foregoing findings, inhibitor molecules can adsorb on the metal surface and form a protective inhibitor layer.

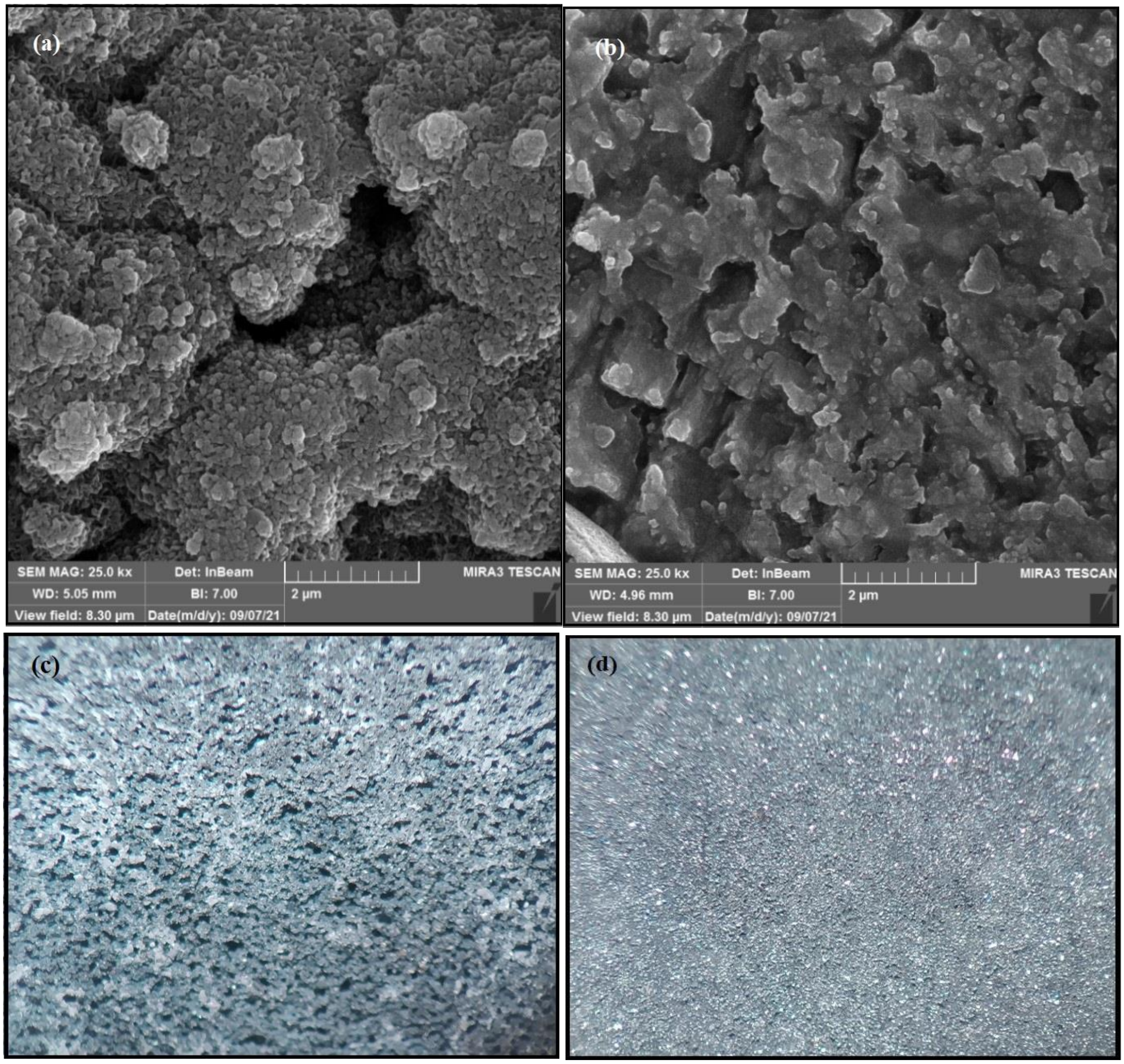

Figure 10: The images of ck45 alloy surface after 24 h immersion in 0.5 M H_3PO_4 solution in the (a) absence and (b) presence of 1000 ppm of *Tetracycline* drug using SEM and (c) without and (d) with 1000 ppm of *Tetracycline* drug using optical microscopy.

4. Conclusion

In this research, we have studied the anti-corrosion effect of Tetracycline drug on the carbon steel in 0.5 M H_3PO_4 solution using electrochemical methods, and the below conclusions were obtained:

1. Results derived from the Tafle polarization and EIS measurements show that the Tetracycline drug acts as an effective inhibitor of carbon steel corrosion in phosphoric acid solution.

2. The optimal inhibition efficiency of drug using the EIS technique (about 81 %) was in close agreement with that obtained using the Tafle technique (about 78 %).

3. Polarization curves indicate that Tetracycline acted as a mixed type inhibitor in 0.5 M H_3PO_4 solution.

4. The inhibition efficiency increased by increasing the temperature to a maximum of 95 % at 55±1 °C so that Tetracycline can be a suitable inhibitor for carbon steel at high temperatures.

6. The calculated positive values of ΔH_{ads} indicate that the inhibitor's adsorption on the carbon steel surface is endothermic behavior.

7. The SEM images showed a homogeneous surface of the alloy. It is suggested that with 1000 ppm concentration of inhibitor, the metal surface was covered by an excellent protective layer of compound molecules.

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