Modazar as promising corrosion inhibitor of carbon steel in hydrochloric acid solution

A. S Fouda, G. El-Ewady and A. H. Ali

ABSTRACT

Modazar drug was tested as corrosion inhibitor for carbon steel in 1 M HCl solution using chemical (weight loss and gasometric) and electrochemical (open circuit potential, potentiodynamic polarization, electrochemical frequency modulation and electrochemical impedance spectroscopy) techniques. The results showed that the inhibitory efficiency increased with the increase in drug concentration reaching a maximum value of 92.3% at 300 ppm while it decreases with increasing the temperature. Polarization curves showed that Modazar drug is a mixed type inhibitor but the cathode is more polarized than the anode. The drug was adsorbed physically on the C-steel surface obeying Langmuir adsorption isotherm. The morphology of the surface of the specimens was analyzed using atomic force microscopy, energy dispersion spectroscopy and scanning electron microscopy. The results obtained from chemical and electrochemical techniques are in good agreement.

1. Introduction

Corrosion is a principal process assuming an important role in economics and safety especially for metals (1). The utilization of inhibitors is one of the best methods for protection corrosion of metals especially in acidic media (2). Most well-known acid inhibitors are organic compounds containing nitrogen (N-heterocyclic), sulfur, long carbon chain or aromatic and oxygen atoms. Organic heterocyclic compounds have been used for the corrosion inhibition of carbon steel (3–8), copper (9), aluminum (10–12) and other metals (13) in different aqueous media. A large number of organic compounds were studied as corrosion inhibitors; unfortunately most of these organic compounds are very expensive and health hazards. Their toxic properties limit their field of applications. Thus, it remains an important object to find cost-effective and non-hazardous inhibitors for the protection of metals against corrosion. In this connection, the influences of nontoxic organic compounds and drugs on the corrosion of metals in acid media were investigated by several authors (14–22). The use of drugs offers interesting possibilities for corrosion inhibition due to the presence of heteroatoms in their structures, and they are of particular interest because of their safe use, high solubility in water...
and high molecular structure size. The following table gives a comparison of % IE with different investigated drugs:

| Inhibitor (drug) | Sample | Medium | IE % | References |
|-----------------|--------|--------|------|------------|
| Modazar         | C-steel| 1 M HCl| 92.3 | This paper |
| Biopolymer      | Cu     | NaCl   | 86.0 | (23)       |
| Pyromellitic diimide linked to oxadiazole cycle | C-steel| 0.3 M HCl | 84.9 | (24)       |
| 2-mercaptobenzimidazole | C-steel| 1 M HCl | 82.0 | (25)       |
| Antidiabetic drug Janumet | Mild | 1 M HCl | 88.7 | (26)       |
| Januvia         | Zn     | 0.1–2.5 M HCl | 79.5 | (27)       |
| Cefuroxime axetil | Al     | 0.5 M HCl | 89.9 | (28)       |
| Phenotin sodium | C-steel| 1 M HCl | 79.0 | (29)       |
| Aspirin         | Mild   | 0.5 M H3SO4 | 71.0 | (30)       |
| Septazole       | Cu     | 0.1 M HCl | 84.8 | (31)       |
| Chloroquine diphosphate | Mild | 0.1 M HCl | 80.0 | (32)       |

Table 1. The composition of the carbon steel specimen.

| Constituent | C | Mn | P | Si | Iron |
|-------------|---|----|---|----|------|
| Composition (%) | 0.2 | 0.6 | 0.04 | 0.003 | Rest |

The objective of this work is to study the inhibitive action of Modazar drug for the corrosion of carbon steel in 1 M HCl by different techniques and at different temperatures. Also, a number of attempts have been made to understand different aspects of corrosion, such as mechanism, thermodynamics and kinetics of corrosion.

2. Experimental methods

2.1. Materials

The composition of the carbon steel specimen is listed in Table 1.

2.2. Inhibitors

Modazar drug is a mixed compound, which consists of two active ingredients: Hydrochlorothiazide (25 mg)/Losartan (100 mg), described in Table 2. This drug was purchased from **Egyptphar**, Pharmaceutical Company, Egypt. The drug is used to treat high blood pressure (hypertension) and diabetic nephropathy.

2.3. Solutions

The aggressive solution, 1 M HCl, was prepared by dilution of analytical grade (37%) HCl with bi-distilled water. The concentration range of the drug used was 50–300 ppm.

2.4. Weight loss measurements

Seven square carbon steel sheets of 2 × 2 × 2 cm were abraded using different grades of emery paper up to 1200 grit size and then washed with bi-distilled water and acetone. After accurate weighing, the specimens were dipped in a 100 ml beaker, which contained 100 ml of 1 M HCl with and without adding different concentrations of the investigated drug.

All aggressive acid solutions were opened to air. After three hours, the specimens were taken out, washed, dried and weighed accurately. The average weight loss for seven square C-steel specimens were obtained. The inhibition efficiency (% IE) and the degree of surface coverage (θ) of Modazar for the corrosion of C-steel were calculated as follows (22):

\[
\%IE = \theta \times 100 = \left[1 - \frac{W}{W^a}\right] \times 100, \tag{1}
\]

where \(W^a\) and \(W\) are the weight loss without and with adding different concentrations of investigate drug, respectively.

2.5. Gasometric measurements

Measurements of hydrogen evolution (HE) were estimated at 25°C, and the hydrogen volume developed...
every 15 minutes, degree of surface coverage (θ) and the efficiency of inhibition (% IE) were calculated by Equations (3) and (4).

\[ V = kt, \]  
where \( V \) is the volume of hydrogen in \( \text{cm}^3 \), \( k \) is the rate constant and \( t \) is the time in minutes.

\[ \Theta = 1 - \frac{k^o}{k}, \]  
where \( k^o \) and \( k \) are the rate constants of corrosion in the absence and presence of the drug, which were calculated by plotting \( V \) vs. \( t \) and \( k \) value is the slope.

\[ \%IE = \Theta \times 100. \]  

2.6. Electrochemical measurements

Electrochemical measurements including potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) were performed in a three-electrode cell at 25°C. The auxiliary electrode is a platinum sheet (1 cm²), saturated calomel electrode (SCE) coupled to a fine Luggin capillary as reference electrode and the working electrode was in the form of a square cut from C-steel embedded in epoxy resin of polytetrafluoroethylene (PTFE) so that the flat surface was the only surface of the electrode in 1 cm² area of the surface.

The EIS measurements were carried out in the frequency range of 100 kHz–100 mHz at the open circuit potential by superimposing a sinusoidal AC signal of small amplitude, 5 mV, after immersion for 30 min in the corrosive media. The experimental impedance was analyzed and interpreted based on the equivalent circuit. The main parameters deduced from the analysis of the Nyquist diagram are the resistance of charge transfer \( R_p \) (diameter of high frequency loop) and the capacity of the double layer \( C_{dl} \).

The EFM technique is a technique that can directly determine corrosion current data without prior knowing of Tafel slopes. EFM was carried out using two frequencies, 2 and 5 Hz. The base frequency was 0.1 Hz. In this study, a perturbation signal with amplitude of 10 mV was used for both perturbation frequencies of 2 and 5 Hz. Equilibrium time leading to steady state of the specimens was 30 min. The inhibition efficiency (% IE) of EFM was calculated. Each experiment was repeated at least three times to check the reproducibility. The uncertainty for all measurements was found to be about 7%.

The electrode potential was allowed to stabilize 30 min before starting the measurements. All the experiments were conducted at 25 ± 1°C. Measurements were performed using Gamry (PCI 300/4) Instrument Potentiostat/Galvanostat/ZRA. This includes a Gamry framework system based on the ESA 400. Gamry applications include DC105 for corrosion measurements and EIS300 for EIS along with a computer for collecting data. Echem Analyst (5.58) software was used for plotting, graphing and fitting data.

2.7. Surface analysis by scanning electron microscopy (SEM)

The C-steel specimens used for analysis of the surface were abraded with different grades of emery papers and immersed in the corrosive solution with and without 300 ppm of Modazar at room temperature for one day and then examined by using SEM (JOEL 840, Japan). To observe the elements present on the carbon steel surface the same condition was carried out using an energy dispersive analyzer (EDAX) unit attached to the SEM.

2.8. Surface analysis by atomic force microscopy (AFM)

AFM is the most versatile and powerful microscopy whereby the sample surface was scanned by a fine tip to find out the surface morphology and properties to generate a 3D surface image. The surface morphology was calculated using an SPM 2100 AFM instrument operating in contact mode in air; the scan rate of all AFM images was 05 \( \mu \text{m} \times 05 \mu \text{m} \) areas at a scan speed of 6.68 \( \mu \text{m/s} \).

3. Results and discussion

3.1. Open circuit potential (\( E_{OCP} \))

Figure 1 shows the change of \( E_{OCP} \) with time obtained for C-steel in 1 M HCl in the absence and presence of various concentrations of Modazar drug at 25°C. The figure shows that \( E_{OCP} \) in the blank started at −533 mV and
then shifted anodically, and the steady state was reached after 600 s. This indicates that the initial dissolution of the air formed oxide film on C-steel and the begin of the attack of the bare metal attack on the bare metal. In the presence of Modazar drug, $E_{OCP}$ started at a relatively positive potential with respect to its absence, then shifted anodically. By increasing the concentration of the drug, the shift in $E_{OCP}$ increases in the positive direction, indicating that the drug might act mainly as an anodic inhibitor.

3.2. Weight loss measurements

The weight loss–time curves of C-steel without and with the addition of various concentrations of Modazar drug as an inhibitor in 1 M HCl are shown in Figure 2. The curves in the presence of the drug lie below those in its absence, and the weight loss decreased with increasing concentration of the drug. This indicated that this drug was adsorbed on the metal surface, forming a thin film (33) and preventing the metal surface from the aggressive solution. Table 3 shows the effect of corrosion rate and % IE for Modazar drug with the concentration.

3.2. Effect of temperature

To elucidate the mechanism of inhibition and to determine the activation energies of the corrosion process, weight loss tests were performed over a temperature range from 25°C to 45°C in the absence and presence of the investigated drug. Figure 3 represents the effect of temperature on the % IE. As shown in the figure, the % IE decreased with increasing the temperature of the medium. The activation energy ($E^*_{a}$) of the corrosion process was calculated using the Arrhenius Equation (5):

$$k_{corr.} = A \exp \left(\frac{-E^*_{a}}{RT}\right),$$

where $k$ is the rate of corrosion and $A$ is the Arrhenius constant or frequency factor, $R$ is universal gas constant and $T$ is the absolute temperature. Figure 4 represents

![Figure 3](image3.png)

**Figure 3.** The effect of temperature on the % IE of Modazar drug.

![Figure 4](image4.png)

**Figure 4.** Log $k_{corr.}$ vs. $1/T$ curves for carbon steel dissolution in 1 M HCl in the absence and presence of Modazar drug.

| Compound | Conc. (ppm) | $k_{corr.}$ (mg cm$^{-2}$ min$^{-1}$) | % IE |
|----------|-------------|---------------------------------|------|
| Blank    | –           | 16.25                           | –    |
| Modazar  | 50          | 3.33                            | 79.5 |
|          | 100         | 2.92                            | 82.1 |
|          | 150         | 2.50                            | 84.6 |
|          | 200         | 2.08                            | 87.2 |
|          | 250         | 1.67                            | 89.7 |
|          | 300         | 1.25                            | 92.3 |

**Table 3.** Corrosion rates and inhibition efficiency (% IE) of different concentrations of Modazar at 25°C form weight loss measurements at 120 min immersion in 1 M HCl.
the Arrhenius plots in the presence and absence of the drug. $E^*_a$ values determined from the slopes of these linear plots are shown in Table 4. The linear regression ($R^2$) is close to unity, which indicates that the corrosion of C-steel in the 1 M HCl solution can be obvious using the kinetic model. The relationship between the temperature and both % IE and activation energy $E^*_a$ was given as follows (34): (a) Inhibitors whose % IE increases with temperature increase, the $E^*_a$ found was greater than that in the absence of inhibitors; (b) inhibitors whose % IE did not change with temperature. The $E^*_a$ did not change with and without inhibitor and (c) inhibitors whose % IE decreases with temperature, the $E^*_a$ found was less than that in the absence of the inhibitor. Table 4 shows that the value of $E^*_a$ for the inhibited solution is higher than that for the uninhibited solution, suggesting that the drug is adsorbed physically on the metal surface (35) and the dissolution of C-steel is slow in the presence of the drug. It is known from Equation (8) that the higher $E^*_a$ values lead to lower rate of corrosion. This is due to the formation of a film on the carbon steel surface serving as an energy barrier for the carbon steel corrosion (36). Enthalpy and entropy of activation ($\Delta H^*$, $\Delta S^*$) of the corrosion process were calculated from the transition state Equation (6) which listed in Table 4:

\[
\frac{k_{corr}}{T} = \frac{RT}{Nh} \exp \left( \frac{\Delta S^*}{R} \right) \exp \left( \frac{-\Delta H^*}{RT} \right),
\]

where $h$ is Planck’s constant and $N$ is Avogadro’s number. A plot of log ($k_{corr}/T$) vs. 1/$T$ for C-steel in 1 M HCl at different concentrations from the investigated drug gave straight lines as shown in Figure 5.

The positive signs of $\Delta H^*$ refer to the endothermic nature of the steel dissolution process. Large and negative values of $\Delta S^*$ imply that the activated complex in the rate-determining step represents an association rather than dissociation step, meaning that decrease in disordering takes place on going from reactants to the activated complex (37).

Table 4. Activation parameters for C-steel corrosion in the absence and presence of various concentrations of Modazar drug in 1 M HCl.

| Conc. (ppm) | $E^*_a$ (kJ mol$^{-1}$) | $\Delta H^*$ (kJ mol$^{-1}$) | $\Delta S^*$ (J mol$^{-1}$ K$^{-1}$) |
|---|---|---|---|
| Blank | 47.3 | 45.5 | 178.8 |
| 50 | 59.3 | 57.8 | 96.9 |
| 100 | 60.6 | 59.1 | 93.8 |
| 150 | 62.1 | 60.6 | 89.9 |
| 200 | 64.2 | 62.7 | 84.4 |
| 250 | 69.5 | 68.2 | 67.8 |
| 300 | 78.2 | 76.9 | 40.8 |

3.3. Adsorption isotherms

To explain the nature of the adsorption of the inhibitor, Temkin, Langmuir, Freundlich and Frumkin adsorption isotherms were studied. It is generally accepted that the studied drug inhibits the corrosion process by adsorbing at the metal/solution interface (38). In this case the plot of ($C/\Theta$) versus ($C$) of Modazar at various temperatures gave straight lines with correlation coefficients in the range 0.99–0.98, intercept of (1/$K_{ads}$) and with slope approximately equal to unity were obtained. The mathematical expression of Langmuir is given as follows (39).

\[
\frac{C}{\Theta} = \frac{1}{K_{ads}} + C,
\]

where $K_{ads}$ is the adsorption equilibrium constant. The small deviation from unity is generally attributed to the interaction of the adsorbed inhibitor molecules on the steel surface. This indicates that the adsorption of the drug on the steel surface in the 1 M HCl solution follows Langmuir’s adsorption isotherm, which is shown in Figure 6. Organic molecules having polar atoms or groups which are adsorbed on the metal
surface may interact by mutual repulsion or attraction and this may be advocated as the reason for the departure of the slope values from unity. The equilibrium adsorption constant is related to the standard free energy of adsorption \( \Delta G_{\text{ads}} \) by relation (8):

\[
\Delta G_{\text{ads}} = -RT \ln (55.5K_{\text{ads}}),
\]

where 55.5 is the concentration of water in the bulk of the solution in M\(^{-1}\). 

Plotting \( K_{\text{ads}} \) against \( 1/T \) gave a straight line as shown in Figure 7; the slope of the straight line gave \( \Delta H_{\text{ads}}/2.303R \); from this slope, \( \Delta H_{\text{ads}} \) values were calculated and are listed in Table 5. Then in accordance with the basic Equation (10):

\[
\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}}.
\]

By introducing the values of \( \Delta G_{\text{ads}} \) and \( \Delta H_{\text{ads}} \) in the above equation, the values of \( \Delta S_{\text{ads}} \) were calculated and are listed in Table 5. When the value of \( \Delta G_{\text{ads}} \) is around \(-20 \text{ kJ mol}^{-1}\) or lower, it indicated the electrostatic interaction between the charged metal surface and charged organic molecules in the bulk of the solution, that is, physisorption. The negative sign of \( \Delta H_{\text{ads}} \) refers to the adsorption of drug molecules is an exothermic process. The value of \( K_{\text{ads}} \) is not high and decreased with increasing the temperature (Table 5). This verifies the assumption that Modazar drug is physically adsorbed on a carbon steel surface in HCl solutions.

### 3.4. HE tests

The curves of Figure 8 represent the variation in the volume of hydrogen gas evolved on C-steel with immersion time without and with different concentrations of Modazar drug at 25°C. Inspection of these curves revealed that hydrogen gas evolution starts after the elapsing of a certain time from immersion. This time is identified as the incubation period which is the time needed by the acid to destruct the pre-immersion oxide film and start dissolution of C-steel. After this incubation period, the volume of hydrogen gas evolved increased linearly with time. The data of corrosion rate

---

**Table 5.** Thermodynamic parameters for the adsorption of Modazar drug on the carbon steel surface in 1 M HCl at different temperatures.

| Temp (°C) | \( K_{\text{ads}} \) (M\(^{-1}\)) | \( \Delta G_{\text{ads}} \) (kJ mol\(^{-1}\)) | \( \Delta H_{\text{ads}} \) (kJ mol\(^{-1}\)) | \( \Delta S_{\text{ads}} \) (J mol\(^{-1}\) K\(^{-1}\)) |
|----------|-----------------|----------------|-----------------|----------------|
| 25       | 62.5            | 20.2           | 9.62            | 100.1          |
| 30       | 50.0            | 20.0           | 9.76            | 97.76          |
| 35       | 52.6            | 20.4           | 9.74            | 97.47          |
| 40       | 58.8            | 21.0           | 9.78            | 97.83          |
| 45       | 58.8            | 21.4           | 9.75            | 97.55          |
(\(k_{\text{corr}}\)), surface coverage (\(\theta\)) and inhibition efficiency (% IE) are recorded in Table 6. As shown in the table, the rate of corrosion was decreases with increasing of Modazar concentration on the other hand, the surface coverage and % IE increase.

### 3.5. Tafel polarization studies

Polarization measurement was carried out to obtain Tafel plots in the absence and presence of various concentrations of the drug. Figure 9 shows the potentiostatic polarization curves for C-steel corrosion in 1 M HCl solution with and without various concentrations of Modazar drug at 25°C. From the graph, it was observed that Modazar drug behaved like a mixed type inhibitor (41). The inhibition efficiency (% IE) and surface coverage (\(\theta\)) were calculated using Equation (11)

\[
\% \text{IE} = \theta \times 100 = \left[ 1 - \left( \frac{i_{\text{corr(inh)}}}{i_{\text{corr(free)}}} \right) \right] \times 100, \quad (11)
\]

where \(i_{\text{corr(free)}}\) and \(i_{\text{corr(inh)}}\) are the corrosion current densities in the absence and presence of the drug, respectively. The electrochemical kinetic parameters such as the corrosion current density \(i_{\text{corr}}\), the corrosion potential \(E_{\text{corr}}\), the anodic Tafel slope \(\beta_a\), the cathodic Tafel slope \(\beta_c\), degree of surface coverage (\(\theta\)) and the inhibition efficiency (% IE) at different concentrations of Modazar drug are listed in Table 7. It was observed that both the cathodic and anodic reactions are suppressed with the addition of the drug, which suggests that the studied drug reduced anodic dissolution and retarded the HE reaction. It follows from Table 6 that the values of \(\beta_c\) changed with increasing drug concentration, indicating the influence of the drug on the kinetics of HE. The shift in the \(\beta_a\) may be due to the chloride ions/or inhibitor molecules adsorbed onto the steel surface. In addition, cathodic and anodic current densities decrease by adding the drug while \(E_{\text{corr}}\) values have not considerably changed (maximum change in \(E_{\text{corr}}\) is 23 mV). Therefore, the studied drug acts as a mixed type inhibitor at 25°C. The results obtained from potentiostatic polarization showed good agreement with the results obtained from weight loss and HE methods.

### 3.6. EIS studies

Electrochemical impedance spectra for C-steel in 1 M HCl without and with different concentrations of Modazar drug at 25°C are presented as Nyquist plot and Bode plots in Figure 10(a, b). An equivalent circuit model (Figure 11) was proposed to fit and analyze EIS data.

![Figure 9. Potentiostatic polarization curves for corrosion of carbon steel in 1 M HCl in the absence and presence of different concentrations of Modazar drug at 25°C.](image)

| Conc. (ppm) | \(k_{\text{corr}}\) (ml cm\(^{-2}\) min\(^{-1}\)) | \(\theta\) | % IE |
|------------|-----------------|-------|-----|
| Blank      | 0.155           | –     | –   |
| 50         | 0.050           | 0.677 | 67.7|
| 100        | 0.040           | 0.742 | 74.2|
| 150        | 0.039           | 0.748 | 74.8|
| 200        | 0.035           | 0.774 | 77.4|
| 250        | 0.033           | 0.787 | 78.7|
| 300        | 0.029           | 0.813 | 81.3|

![Table 6. The corrosion rate and % IE of carbon steel in 1 M HCl with and without different concentrations of Modazar drug.](table)

![Figure 10. The Nyquist (a) and Bode (b) plots for corrosion of C-steel in 1 M HCl in the absence and presence of different concentrations of Modazar drug at 25°C.](image)
EIS parameters calculated in accordance with equivalent circuit are listed in Table 8. Nyquist plots are depressed into real axis and not perfect semi-circles as a result of the roughness and other inhomogeneity of the metal surface (42, 43). This kind of phenomenon is known as the dispersing effect. The capacity of double layer ($C_{dl}$) is defined as:

$$C_{dl} = \frac{1}{(2\pi f_{\text{max}} R_p)^n},$$

where $f_{\text{max}}$ is the maximum frequency. The inhibition efficiencies and the surface coverage ($\Theta$) obtained from the impedance measurements were defined by the following relation:

$$\% \text{IE} = \Theta \times 100 = \left[1 - \frac{R_p}{R_p'}\right] \times 100,$$

where $R_p$ and $R_p'$ are the charge transfer resistance in the absence and presence of the inhibitor, respectively. The capacitive loop corresponds to the polarization resistance ($R_p$); the sum of the charge transfer resistance ($R_c$), diffuse layer resistance ($R_d$) and double layer formation on the bare CS surface (44) and $n$ shows the phase shift which can be explained as the degree of surface inhomogeneity (45). The value of $n$ is between 0 and 1 ($0 < n < 1$). This is related to the deviation from the ideal capacitive behavior. Capacitance phase element (CPE) represents a constant phase element to replace a double layer capacitance ($C_{dl}$) in order to give a more accurate fit to the experimental results (46). Data indicated that increasing $R_p$ is associated with a decrease in the CPE. It has been reported that the adsorption of the organic inhibitor on the metal surface is characterized by a decrease in CPE and increase in $R_p$ value. The value of CPE was found to decrease, while the $R_p$ value increased, which may be due to the replacement of water molecules at the electrode interface by Modazar drug through adsorption (Table 8), suggesting that the drug was taken up by adsorption at the metal–solution interface (47). The value of CPE determines the characterization of the adsorption, desorption and film formation on the metal surface. The obtained Bodes plot for Modazar is shown in Figure 10(b).

### 3.7. Electron frequency modulation (EFM) studies

EFM is a nondestructive corrosion measurement technique that can directly and quickly determine the corrosion current value without prior knowledge of Tafel slopes, and with only a small polarizing signal. These advantages of the EFM technique make it an ideal candidate for online corrosion monitoring (48).

The high strength of the EFM is the causality factors which serve as an internal check on the validity of EFM measurement. The EFM Intermodulation spectrums of carbon steel in 1 M HCl acid solution containing different concentrations of the Modazar drug are shown in Figure 12. The large peaks were utilized to calculate

### Table 7. Potentiostatic polarization parameters for the corrosion of C-steel in 1 M HCl in the absence and presence of various concentrations of Modazar at 25°C.

| Conc. (ppm) | $\iota_{\text{corr}}$ (mA cm$^{-2}$) | $-\iota_{\text{corr}}$ (mV) vs SCE | $\beta_{\text{p}}$ (mV dec$^{-1}$) | $\beta_{\text{c}}$ (mV dec$^{-1}$) | C. R. mpy | $\Theta$ | % IE |
|------------|-------------------------------|---------------------------------|-------------------------------|-------------------------------|-----------|--------|------|
| 0.0        | 147                           | 480                             | 166                           | 208                           | 67.3      | –      | –    |
| 50         | 58.5                          | 467                             | 88                            | 150                           | 26.74     | 0.613  | 61.3 |
| 100        | 48.8                          | 459                             | 64                            | 128                           | 22.28     | 0.677  | 67.7 |
| 150        | 40                            | 482                             | 88                            | 88                            | 18.3      | 0.735  | 73.5 |
| 200        | 30.7                          | 459                             | 35                            | 72                            | 14.03     | 0.797  | 79.7 |
| 250        | 27.1                          | 459                             | 32                            | 64                            | 12.37     | 0.821  | 82.1 |
| 300        | 19.8                          | 479                             | 75                            | 59                            | 9.07      | 0.869  | 86.9 |

### Table 8. EIS data of C-steel in 1 M HCl and in the absence and presence of different concentrations of the investigated drug at 25°C.

| Conc. (ppm) | $R_p$ (Ω cm$^2$) | $C_{dl}$ (µF cm$^2$) | $\Theta$ | % IE |
|------------|-----------------|---------------------|---------|------|
| 0.0        | 64.7            | 594                 | –       | –    |
| 50         | 231.5           | 52.0                | 0.720   | 72.0 |
| 100        | 255.5           | 45.0                | 0.747   | 74.7 |
| 150        | 301             | 37.8                | 0.785   | 78.5 |
| 200        | 303.8           | 35.4                | 0.787   | 78.7 |
| 250        | 327.7           | 30.5                | 0.802   | 80.2 |
| 300        | 350.1           | 26.0                | 0.815   | 81.5 |
the corrosion current density ($i_{corr}$), the Tafel slopes ($\beta_a$ and $\beta_c$) and the causality factors (CF-2 and CF-3). These electrochemical parameters are listed in Table 9. The inhibition efficiencies % $\text{IE}_{\text{EFM}}$ increase by increasing the studied inhibitor concentrations and can be calculated as follows:

$$\%\text{IE}_{\text{EFM}} = \left(1 - \frac{i_{corr}}{i_{Wcorr}}\right) \times 100,$$

where $i_{corr}$ and $i_{Wcorr}$ are corrosion current densities without and with different concentrations of inhibitors, respectively. It was observed that by increasing the Modazar concentration the corrosion current density decreased and the % IE increased. The causality factors obtained under different experimental conditions are approximately equal to the theoretical values (2 and 3) indicating that the measured data are valid and of good quality (49).

**Table 9.** Electrochemical dynamic parameter by the EFM method for meal in the absence and presence of different concentrations of Modazar in 1 M HCl at 25°C.

| Comp. | Conc. (ppm) | $i_{corr}$ (µA cm$^{-2}$) | $\beta_a$ (mV dec$^{-1}$) | $\beta_c$ (mV dec$^{-1}$) | CF (2) | CF (3) | CR mpy | $\Theta$ | % IE |
|-------|-------------|-----------------|----------------|----------------|--------|--------|--------|--------|------|
| Blank | 0.0         | 350.3           | 156            | 248            | 1.5    | 2.9    | 160.1  | –      | –    |
| Modazar | 50        | 85.5            | 87             | 119            | 2      | 2.5    | 39.1   | 0.756  | 75.6 |
|        | 100        | 80.7            | 107            | 115            | 1.9    | 4      | 36.9   | 0.769  | 76.9 |
|        | 150        | 78.5            | 95             | 101            | 1.9    | 4      | 35.9   | 0.776  | 77.6 |
|        | 200        | 75.6            | 90             | 123            | 1.8    | 3.5    | 34.6   | 0.784  | 78.4 |
|        | 250        | 72.0            | 95             | 139            | 1.8    | 2.5    | 32.9   | 0.794  | 79.4 |
|        | 300        | 61.0            | 86             | 130            | 1.9    | 3.0    | 30.1   | 0.826  | 82.6 |

**Figure 12.** EFM spectra for C-steel in 1 M HCl in the absence and presence of various concentrations of Modazar drug at 25°C.
3.8. Energy dispersion spectroscopy (EDX) studies

The EDX spectra were used to determine the elements present on the surface of carbon steel and after one day of exposure to the uninhibited and inhibited 1 M HCl. Figure 13 shows the EDX analysis of carbon steel with 300 ppm of the drug. The EDX analysis indicates that only Fe and oxygen were detected, which shows that the passive film contained only Fe₂O₃.

The spectra show additional lines indicating the existence of C (owing to the carbon atoms of Modazar). These data showed that the carbon, oxygen, sulfur and N atoms covered the specimen surface. This layer is entirely owing to the inhibitor, because the carbon, oxygen, sulfur and N signals are absent on the specimen surface exposed to uninhibited HCl. It is shown that, in addition to N, C, O and S were present in the spectra. A comparable elemental distribution is shown in Table 10.

3.9. SEM analysis

Figure 14 represents the micrographs obtained for the C-steel sample surface before and after immersion in 1 M HCl solution with and without the inhibitor, after exposure to one day of immersion. Figure 14(a) shows the surface of the carbon steel specimen before immersion in HCl while Figure 14(b) shows the surface of carbon steel after immersion in 1 M HCl for one day in the absence of the drug. Figure 14(c) shows the surface of the carbon steel specimen after immersion in the corrosive solution in the presence of 300 ppm of drug for the same period of time. The SEM micrograph revealed that the surface morphology was strongly damaged in the absence of the inhibitor, but in the presence of 300 ppm of the inhibitor the damage was considerably diminished and the surface became smooth, which confirmed the high efficiency of Modazar at this concentration.

3.10. AFM analysis

AFM is a powerful tool to investigate the surface morphology of various samples at nano-micro scale, currently used to study the influence of a corrosion inhibitor on the generation and the progress of corrosion at the metal/solution interface (50). Analysis of the images allowed quantification of surface roughness over area scale of 5 μm. The three dimensional AFM images of the carbon steel surface without and with the inhibitor are shown in Figure 15(a, b). The surface roughness of the carbon steel surface after immersion in 1 M HCl is up to 2600 nm (Figure 15(a)), while in the presence of the drug, the roughness decreases to 365.28 nm (Figure 15(b)). It shows that the carbon steel surface in the presence of the drug is more compact and uniform, so it can efficiently protect the carbon steel surface from corrosion. This confirms that the inhibited surface is smoother than the uninhibited surface. The smoothness of the surface is due to the formation of a protective film on the metal surface.

Table 10. Surface composition (weight %) of the carbon steel after 24 h of immersion in 1 M HCl with 300 ppm of Modazar drug.

| (Mass %) | Fe | N | Cl | C | O | S | Mn |
|----------|----|----|----|---|---|---|----|
| Blank    | 55.83 | – | 0.32 | 2.12 | 39.24 | – | 0.31 |
| Inhibitor (Modazar) | 60.37 | 6.17 | – | 26.51 | 6.49 | 0.83 | – |

Figure 13. EDX analysis on carbon steel in the presence of Modazar for one day of immersion.
3.11. Mechanism of inhibition

Modazar drug is a mixture of Losartan (C_{22}H_{23}N_{6}O) with molecular weight 422.9 and hydrochlorothiazide (C_{7}H_{8}N_{3}O_{4}S_{2}) with molecular weight 297.7. These compounds were adsorbed on the C-steel surface in their neutral form through their donor atoms N, O, S atoms and π-electrons in the benzene rings. The high % IE is due to the synergistic effect of the two compounds that exists in the drug. Corrosion inhibition of C-steel in 1 N HCl by Modazar drug can be explained on the basis of molecular adsorption. This compound inhibits corrosion by controlling both the anodic and cathodic reactions.

Another mode of inhibition is, in acidic solutions the Modazar molecules can exist as protonated species. These protonated species adsorb on the cathodic sites of the C-steel and decrease the evolution of hydrogen. The adsorption on anodic sites occurs through the π-electron of the aromatic ring and lone pair of electrons of nitrogen, oxygen and sulfur atoms which decrease anodic dissolution of C-steel. Corrosion inhibition of Modazar drug is attributed to the presence of π electrons, oxygen, sulfur and nitrogen atoms and the larger molecular size. The SEM study confirms the presence of N, O, C and S atoms on the C-steel surface. Also, AFM analysis confirms the presence of the deposited film on the metal surface (this was confirmed by the very lower values of roughness in the presence of drug than in its absence). This indicates that the investigated drug is involved in film formation on the metal surface.

4. Conclusions

From every study (chemical or electrochemical) it could said that Modazar drug is a good corrosion inhibitor for carbon steel in 1 M HCl. A polarization study shows
References

[1] Trabanelli, G. 1991 Whitney Award Lecture: Inhibitors – An Old Remedy for a New Challenge. Corrosion 1991, 47, 410–419.

[2] Singh, D.N.; Dey, A.K. Synergistic Effects of Inorganic and Organic Cations on Inhibitive Performance of Propargyl Alcohol on Steel Dissolution in Boiling Hydrochloric Acid Solution. Corrosion 1993, 49, 594–600.

[3] Banerjee, G.; Malhotra, S.N. Contribution to the Adsorption of Aromatic Amines on Mild Steel Surfaces from HCl Solutions by Impedance, UV and Raman Spectroscopy. Corrosion-NACE 1992, 48, 10–15.

[4] Arab, S.T.; Noor, E.A. Inhibition of Acid Corrosion of Steel by Some S-Alkylisothiouronium Iodides. Corrosion 1993, 49, 122–129.

[5] Raspini, I.A. Influence of Sodium Salts of Organic Acids as Additives on Localized Corrosion of Aluminum and Its Alloys. Corrosion 1993, 49, 821–828.

[6] Migahed, M.A.; Azzam, E.M.S.; Al-Sabagh, A.M. Corrosion Inhibition of Mild Steel in 1 M Sulfuric Acid Solution Using Anionic Surfactant. Mater. Chem. Phys. 2004, 85, 273–279.

[7] Osman, M.M.; Omar, A.M.; Al-Sabagh, A.M. Corrosion Inhibition of Benzyl Triethanol Ammonium Chloride and Its Ethoxylate on Steel in Sulphuric Acid Solution. Mater. Chem. Phys. 1997, 50, 271–274.

[8] Zucchi, F.; Trabanelli, G.; Brunoro, G. The Influence of the Chromium Content on the Inhibitive Efficiency of Some Organic Compounds. Corros. Sci. 1992, 33, 1135–1139.

[9] Villamil, R.F.; Corio, P.; Rubim, J.C.; Siliva Agostinho, M.L. Effect of Sodium Dodecysulfate on Copper Corrosion in Sulfuric Acid Media in the Absence and Presence of Benzotriazole. J. Electroanal. Chem. 1999, 472, 112–119.

[10] Zhao, T.P.; Mu, G.N. The Adsorption and Corrosion Inhibition of Anion Surfactants on Aluminium Surface in Hydrochloric Acid. Corros. Sci. 1999, 41, 1937–1944.

[11] Abd El Rehim, S.S.; Hassan, H.; Amin, M.A. Corrosion Inhibition of Aluminum by 1,1(lauryl amido)propyl Ammonium Chloride in HCl Solution. Mater. Chem. Phys. 2001, 70, 64–72.

[12] Abd El Rehim, S.S.; Hassan, H.; Amin, M.A. The Corrosion Inhibition Study of Sodium Dodecyl Benzene Sulphonate to Aluminium and Its Alloys in 1.0 M HCl Solution. Mater. Chem. Phys. 2003, 78, 337–348.

[13] Guo, R.; Liu, T.; Wei, X. Effects of SDS and Some Alcohols on the Inhibition Efficiency of Corrosion for Nickel. Colloids Surf. A 2002, 209, 37–45.

[14] Li, X.; Deng, S.; Fu, H.; Li, T. Adsorption and Inhibition Effect of 6-benzylaminopurine on Cold Rolled Steel in 1.0M HCl. Electrochim. Acta 2009, 54, 4089–4098.

[15] Moretti, G.; Guidi, F.; Grion, G. Tryptamine as a Green Iron Corrosion Inhibitor in 0.5 M Deaerated Sulphuric Acid. Corros. Sci. 2004, 46, 387–403.

[16] Ferreira, E.S.; Giancomelli, C.; Giacomelli, F.C.; Spinelli, A. Evaluation of the Inhibitor Effect of L-ascorbic Acid on the Corrosion of Mild Steel. Mater. Chem. Phys. 2004, 83, 129–134.

[17] Morad, M.S. Inhibition of Iron Corrosion in Acid Solutions by Cefatrexyl: Behaviour Near and at the Corrosion Potential. Corros. Sci. 2008, 50, 436–448.

[18] Singh, A.K.; Quraishi, M.A. Effect of Cefazolin on the Corrosion of Mild Steel in HCl Solution. Corros. Sci. 2010, 52, 152–160.

[19] Shukla, S.K.; Singh, A.K.; Ahamad, I.; Quraishi, M.A. Streptomycin: A Commercially Available Drug as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution. Mater. Lett. 2009, 63, 819–822.

[20] El-Naggar, M.M. Corrosion Inhibition of Mild Steel in Acidic Medium by Some Sulfa Drugs Compounds. Corros. Sci. 2007, 49, 2226–2236.

[21] Abdallah, M. Antibacterial Drugs as Corrosion Inhibitors for Corrosion of Aluminium in Hydrochloric Solution. Corros. Sci. 2004, 46, 1981–1996.

[22] Mu, G.N.; Zhao, T.P.; Liu, M. Gu, T. Effect of Metallic Cations on Corrosion Inhibition of an Anionic Surfactant for Mild Steel. Corrosion 1996, 52, 853–856.

[23] Oukhrib, R.; El Ibrahim, B.; Bourzi, H.; El Mouaden, K.; Jmiai, A.; El Issami, S.; Bammou, L.; Bazzi, L. Quantum Chemical Calculations and Corrosion Inhibition Efficiency of Biopolymer “Chitosan” on Copper Surface in 3%NaCl. JMES 2017, 8 (1), 195–208.

Disclosure statement

No potential conflict of interest was reported by the authors.

Notes on contributors

A. S Fouda received his Ph.D. in Physical Chemistry from El-Mansoura University, Egypt, 1979, 1988, Prof. of Physical Chemistry, D.Sc in Chemistry 2013. He granted the Chemical Engineering Department and Material Science, Minnesota University, USA 1982–1983 and Institute, Bonn Univ. Germany 1989. He is an international reviewer for a huge number of thesis, journals and projects. He has published more than 300 papers in international journals, especially electrochemistry (corrosion and corrosion inhibition in all media for metals and alloys, fuel cells, electrode position of metals and oxides).

G. El-Ewady. She is an associate prof. of physical chemistry, Faculty of Science, Mansoura University, Egypt. She has published papers in corrosion and electrochemistry fields, focusing on plant extracts, drugs, hetero cyclic compounds and other organic compounds.

A. H. Alia is a Ph.D. researcher student, working on corrosion field. He uses some drugs as corrosion inhibitor for some metals in different media. He has published three papers in international journals. He works in Chemistry Department, Faculty of Science, Mansoura University, Egypt.

that Modazar drug is a mixed type inhibitor. Modazar drug obeyed the Langmuir adsorption isotherm. ΔG_ads values revealed that the adsorption of Modazar drug is physical. AFM micrographs show the carbon steel surface protection in the presence of the drug. The values of inhibition efficiency obtained from the different independent techniques used showed the validity of the obtained results.
[24] Al-Azzawi, A.M.; Hammud, K.K. Newly Antibacterial/Anti-rusting oxadiazoleporomellitic di-imids of Carbon Steel/ Hydrochloric Acid Interface: Temkin Isother Model. *URPC 2016*, 6 (3), 391–402.

[25] El Ouaif, L.; Merimi, I.; Zarok, H.; El ghoul, M.; Achour, R.; Guenbour, M.; Oudda, H.; El-Hajjaji, F.; Hammouti, B. Synthesis and Inhibition Study of Carbon Steel Corrosion in Hydrochloric Acid of a New Surfactant Derived from 2-mercaptobenzimidazole. *J. Mater. Environ. Sci. 2016*, 7 (8), 2718–2730.

[26] Sani, U.M.; Usman, U. Electrochemical Corrosion Inhibition of Mild Steel in Hydrochloric Acid Medium Using the Antidiabetic Drug Janumet as Inhibitor. *Int. J. Novel Res. Phys. Chem. Mathemat. 2016*, 3(3), 30–37.

[27] Kolo, A.M.; Sani, U.M.; Kutama, U.; Usman, U. *Pharmac. Chem. J. 2016*, 3(1), 109–119.

[28] Ameh, P.O.; Sani, U.M. Cefuroxime Axetil: A Commercially Available Pro-Drug as Corrosion Inhibitor for Aluminum in Hydrochloric Acid Solution. *J. Heterocycles 2015*, 1(1), 2–6.

[29] Al-Shafeey, H.J.; Abdel Hameed, R.S.; Ali, F.A.; Aboul-Magd, A.S.; Salah, M. Effect of Expired Drugs as Corrosion Inhibitors for Carbon Steel in 1M HCL Solution. *Int. J. Pharm. Sci. Res. 2014*, 27 (1), 146–152.

[30] Kushwah, R., Pathak, R.K. Inhibition of Mild Steel Corrosion in 0.5 M Sulphuric Acid Solution by Aspirin Drug. *Int. J. Emerging Technol. Adv. Eng. 2014*, 4 (7), 880–884.

[31] Fouda, A.S., El-Haddad, M.N.; Abdallah, Y.M. Septazole: Antibioclastic Drug as a Green Corrosion Inhibitor for Copper in Hydrochloric Acid Solutions. *IJIRSET 2013*, 2 (12), 7073–7085.

[32] Ofoegbu, S.U.; Ofoegbu, P.U. Corrosion Inhibition of Mild Steel in 0.1 M Hydrochloric Acid Media by Chloroquine Diphosphate. *ARPN J. Eng. Appl. Sci. 2012*, 7 (3), 272–276.

[33] Lipkowski, J.; Ross, P.N., Eds. *Adsorption of Molecules at Metal Electrodes*; VCH: New York, 1992.

[34] Dehri, I.; Özcan, M. The Effect of Temperature on the Corrosion of Mild Steel in Acidic Media in the Presence of Some Sulphur-containing Organic Compounds. *Mater. Chem. Phys. 2006*, 98, 316–323.

[35] Umoren, S.A. Inhibition of Aluminium and Mild Steel Corrosion in Acidic Medium Using Gum Arabic. *Cellulose 2008*, 15, 751–761.

[36] Da Costa, S.L.F.A.; Agostinho, S.M.L. Electrochemical Behavior of Copper in 0.5 M H2SO4 Solutions in the Absence and Presence of Fe(III) and Benzotriazole. *Corrosion 1989*, 45, 472–477.

[37] Aljourani, J.; Raeissi, K.; Golozar, M.A. Benzimidazole and Its Derivatives as Corrosion Inhibitors for Mild Steel in 1M HCl Solution. *Corros. Sci. 2009*, 51, 1836–1843.

[38] El-Etre, A.Y.; Abdallah, M.; El-Tantawy, Z.E. Corrosion Inhibition of Some Metals Using Lawsonia Extract. *Corros. Sci. 2005*, 47, 385–395.

[39] Migahed, M.; Azzam, E.M.S.; Morsy, S.M.I. Electrochemical Behaviour of Carbon Steel in Acid Chloride Solution in the Presence of Dodecyl Cysteine Hydrochloride Self-assembled on Gold Nanoparticles. *Corros. Sci. 2009*, 51, 1636–1644.

[40] Bilgic, S.; Caliskan, N. An Investigation of Some Schiff Bases as Corrosion Inhibitors for Austenitic Chromium-Nickel Steel in H2SO4. *J. Appl. Electrochem. 2001*, 31, 79–83.

[41] Kasthuri, P.K.; Arulanantham, A.; Natesan, M. The Effect of *Acalypha indica* Extract as Corrosion Inhibitor on the Mild Steel in 1 m Sulphuric Acid. *J. Metall. Mater. Sci. 2006*, 48 (2), 109–116.

[42] Li, W.H.; He, Q.; Zhang, S.-t.; Pei, C.L.; Hou, B.R. Some New Triazole Derivatives as Inhibitors for Mild Steel Corrosion in Acidic Medium. *J. Appl. Electrochem. 2008*, 38, 289–295.

[43] Fouda, A.S.; Al-Sarawy, A.A.; El-Katori, E.E. Pyrazolone Derivatives as Corrosion Inhibitors for C-steel in Hydrochloric Acid Solution. *Desalination 2006*, 201, 1–13.

[44] Farag, A.A.; Ibrahim, I.M. Influence of Nonionic Surfactant on the Carbon Steel Corrosion in Hydrochloric Acid Solution. *USR 2014*, 3, 1087–1091.

[45] Solmaz, R.; Kardas, G.; Çulha, M.; Yazici, B.; Erbil, M. Investigation of Adsorption and Inhibitive Effect of 2-Mercaptothiazoline on Corrosion of Mild Steel in Hydrochloric Acid Media. *Electrochim. Acta 2008*, 53, 5941–5952.

[46] Özcan, M.; Karadag, E.; Dehri, I. Investigation of Adsorption Characteristics of Methionine at Mild Steel/Sulfuric Acid Interface: An Experimental and Theoretical Study. *Colloids Surf. A Physicochem. Eng. Aspects 2008*, 316, 55–61.

[47] Behpour, M.; Ghoreishi, S.M.; Soltani, N.; Salavati-Niasari, M. The Inhibitive Effect of Some bis-N,S-bidentate Schiff Bases on Corrosion Behaviour of 304 Stainless Steel in Hydrochloric Acid Solution. *Corros. Sci. 2009*, 51, 1073–1082.

[48] Yıldız, R.; Dogan, T.; Dehri, I. Evaluation of Corrosion Inhibition of Mild Steel in 0.1M HCl by 4-amino-3-Hydroxynaphthalene-1-sulphonic acid. *Corros. Sci. 2014*, 85, 215.

[49] Ashassi-Sorkhabi, H.; Shaabani, B.; Seifzadeh, D. Corrosion Inhibition of Mild Steel by Some Schiff Base Compounds in Hydrochloric Acid. *Appl. Surf. Sci. 2005*, 239, 154–164.

[50] Danaee, I.; Niknejad Khomami, M.; Atan, A.A. Corrosion Behavior of AISI 4130 Steel Alloy in Ethylene Glycol–Water Mixture in Presence of Molybdate. *Mater. Chem. Phys. 2012*, 135, 658–667.