

Expired Paracetamol as Corrosion Inhibitor for Low Carbon Steel in Sulfuric Acid. Electrochemical, Kinetics and Thermodynamics Investigation

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Expired paracetamol is used as efficient inhibitor for the general and pitting corrosion of low carbon steel (LCS) in 1.0 mol L⁻¹ H₂SO₄ solution. Three electrochemical tests are used to measure the inhibition efficacy. The inhibition efficacy increases with increasing the concentration of the expired paracetamol and with lowering temperature. The outcomes indicate the values of corrosion current density and capacity of the double layer decrease while the charge transfer and the inhibition efficacy increase. The values of pitting potential are moved to more positive trend. These outcomes emphasize the inhibitory strength of expired paracetamol. The inhibition can be explicated in term of the spontaneous adsorption of the complex formed between iron (II) ion and paracetamol on the surface LCS. The adsorption followed Langmuir isotherm. The thermodynamics parameters for the activation and adsorption process were assessed from the study of impact temperature

Keywords: Low carbon steel, Expired paracetamol, Polarization, Adsorption, Corrosion inhibitor.

1. INTRODUCTION

Low carbon steel (LCS) is the one that has a carbon content of less than 0.25% by weight and is the most widely applied type of carbon steel in industry, for example car body components, body shapes, piping, building and bridge components, and food storage cans. When LCS is used in some industries, some unwanted scales and rust are formed. To clean the steel surface, we use an appropriate concentration of sulfuric acid, but the acid causes steel corrosion. An effective way to reduce this problem is to use corrosion inhibitors [1].

It has been observed from the published manuscripts that the organic compounds containing heterocyclic atoms give effective results in diminishing the corrosion rate of CS in acidic media [2-15].

The effectiveness of these compounds is due to their adsorption to the steel surface by displacing water from the surface of the steel. The strength of adsorption based on the type of steel used and its ability to resist corrosion, type of corrosive solution as well as its concentration, hydrogen ion concentration, chemical composition of the inhibitor, temperature and some other factors [16-20].

Despite the high inhibitory effectiveness, these compounds are harmful to health. Therefore, we try in this research to use compounds that are safe and their chemical composition contains more active centers for adsorption. Therefore, we used an expired drug. In previous studies, expired drugs were used and gave high efficacy in inhibiting the dissolution of iron alloys in acidic solutions [21-30].

The strategic goal of this work is to find a solution to the problem of LCS corrosion in sulfuric acid by using an expired drug like expired paracetamol. To avoid the economic and environmental problem of disposing of these drugs. We use it as a corrosion inhibitor for LCS in $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution using three methods of electrochemical tests. Moreover, the impact of high temperature on LCS corrosion and some activation and adsorption thermodynamic parameters was studied and interpreted.

2. EXPERIMENTAL MEASUREMENTS

2.1. Materials

Experiments were accomplished on LCS having the next chemical composition (weight%) C: 0.172; Mn: 0.441; Cu: 0.392; Ni: 0.092; Cr: 0.063; Si: 0.045; Co: 0.042 and the remainder was Fe. The test LCS electrode was performed in form rod embedded in Araldite so as to make the exposed bottom area to the solution is 0.36 cm^2 . Sulfuric acid employed in this research was obtained from Sigma-Aldrich. Twice distilled water was utilized to prepare all the solutions used in the manuscript. The tested expired paracetamol was sourced from the Egyptian International Pharmaceutical Industries Company (EIPICO). We use the expired drug after a month of expiration date, so that it does not lose its chemical effectiveness. The expired paracetamol was prepared by dissolving weighed samples in distilled water. Each experiment was run three times under identical conditions to ensure the accuracy of the outcomes.

2.2. Electrochemical tests

Three electrochemical tests were used in this research, namely, galvanostatic polarization (GP), potentiodynamic anodic polarization (PAP) and electrochemical impedance spectroscopy (EIS). Before any experiment, the electrode was sanded with different coarse and fine sandpapers, then washed with distilled water and finally with acetone. The electrolytic cell applied in the three tests contains three electrodes, LCS electrode as working electrode, Pt foil worked as auxiliary electrode. and a saturated calomel electrode (SCE) as reference electrode. All tests were performed at $300 \pm 0.1^\circ\text{K}$.

All these tests were carried out using a Metrohm Autolab PGSTAT30 potentiostat–galvanostat with a temperature-controlled routine. For GP tests the LCS electrode was put into the examined solution until steady state (corrosion potential) was attained. GP tests were performed at a sweep rate 2 mVs^{-1} . But in the case of PDP the scan rate was adjusted at 0.5 mVs^{-1} to determine the pitting potential (E_{pit}).

EIS tests were done in a frequency range of 100 kHz to 0.1 Hz with an amplitude of 4.0 mV via peak-to-peak amplitude utilizing AC signals at open circuit potential.

2.3. Additive used

The expired drug used in this research as corrosion inhibitor is paracetamol. The structural formula of paracetamol (acetaminophen) is given in Fig.1

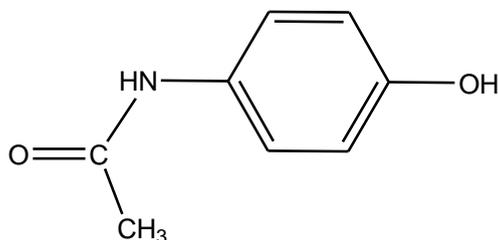


Figure 1. The structural formula of paracetamol

Chemical formula : $C_8H_9NO_2$

Molar mass : $151.165 \text{ g.mol}^{-1}$

3. RESULTS AND DISCUSSION

3.1. GP tests

The GP curves of LCS in blank $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution and with some concentrations of expired paracetamol are represented in Fig 2. Some corrosion parameters are extracted from this figure such as anodic (β_a), cathodic (β_c) Tafel slopes, corrosion potential (E_{corr}), corrosion current density (I_{corr}), surface coverage (Θ) and inhibition efficacy (%IE). These parameters are collected in Table 1.

The inhibition efficacy (% IE_{GP}) from GP tests was determined from I_{corr} values using the equation:

$$\%IE_{\text{GP}} = \left[1 - \frac{I_f}{I_{in}} \right] 100 \quad (1)$$

$$\Theta = \left[1 - \frac{I_f}{I_{in}} \right] \quad (2)$$

where, I_f and I_{in} are the corrosion current densities in free $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and in the existence of expired paracetamol.

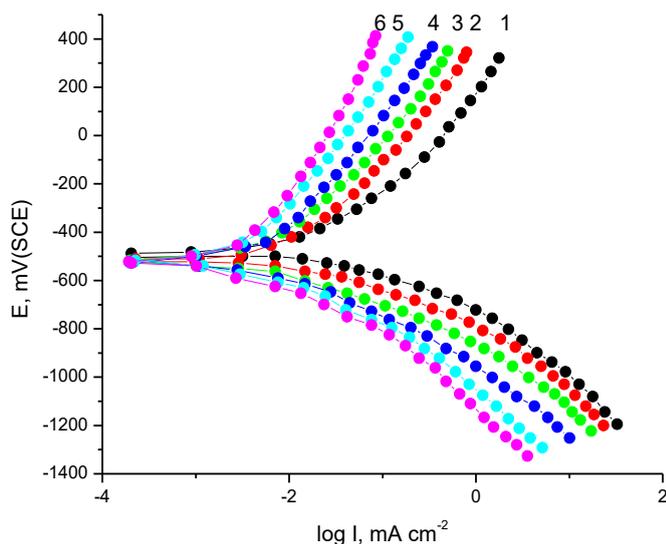


Figure 2. GP measurement of LCS in free 1.0 mol L⁻¹ H₂SO₄ solution and contains certain concentrations of contains expired paracetamol. 1) 1.0 mol L⁻¹ H₂SO₄; 2) 75 mg l⁻¹paracetamol; 3) 125mg l⁻¹ paracetamol; 4) 175 mg l⁻¹paracetamol; 5) 225 mg l⁻¹paracetamol; 6) 275 mg l⁻¹ paracetamol

From the Fig 2, it is evident that the existence of expired paracetamol in the H₂SO₄ solution led to retard the corrosion of LCS and the cathodic hydrogen evolution reaction and the retardation enhanced by increasing the concentration of expired paracetamol. Also, the Tafel lines are moved to the most negative and positive voltages with respect to the free curve and this confirms that the expired paracetamol acts as mixed inhibitor [31,32]. This is confirmed by the fact that the values β_a and β_c are almost unchanged or nearly constant about 12 mV in case of anodic polarization and 22mV in case of cathodic polarization. Also, the values of E_{corr.} are nearly constant. The transition between a free H₂SO₄ solution and the highest paracetamol concentration are low approximately 27 mV . This assertion that the expired paracetamol acts as mixed inhibitor. The values of I_{corr} are reduced, and the values of Θ and %IE_{GP} demonstrate the inhibitory strength of the investigated drug.

Table 1. Corrosion kinetics parameters from GP test for corrosion of LCS in blank 1.0 mol L⁻¹ H₂SO₄ solution and with some concentrations of paracetamol

Inh. Conc. (mg l ⁻¹)	-E _{corr} (mV (SCE))	β _a (mV/dec ⁻¹)	-β _c (mV/dec ⁻¹)	I _{corr} (μA/cm ²)	Θ	%IE _{GP}
0	495	86	116	1.812	-	--
75	502	88	120	0.372	0.79	79.5
125	512	90	125	0.275	0.85	84.8
175	515	92	132	0.212	0.88	88.3
225	519	94	136	0.154	0.92	91.5
275	522	98	138	0.106	0.94	94.2

3.2. Activation Kinetics parameters for LCS corrosion

The influence of high temperature on the dissolution of LCS in blank 1.0 mol L⁻¹ H₂SO₄ solution and with some concentrations of expired paracetamol at various temperatures (300, 310, 320 and 330 ,°K) was investigated using GP test. Analogous curves to the curves of Fig.1 but not shown. The corrosion parameters at various temperatures were collected in Table 2. From the Table 2, the values of I_{corr} increases and hence the values of Θ and % IE_{GP} decreases. This elucidate that, the adsorption expired paracetamol on the LCS surface is physical

The activation energy (E_a) values of dissolution of LCS in 1.0 mol L⁻¹ H₂SO₄ solution with certain concentrations of expired paracetamol were determined from the Arrhenius equation [33,34].

$$R_{corr} = A e^{(-E_a/RT)} \quad (3)$$

Where, R_{corr} represents the rate of corrosion and is directly related to I_{corr} [35], A, R and T are the constant, gas constant and the temperature respectively.

Fig.3. displays the plot of $\log R_{corr}$ vs $1/T$ (Arrhenius relation). Straight lines were acquired with a slope equal $(-E_a/R)$. The E_a values at various concentrations of expired paracetamol were computed and recorded in Table 3. It is evident that the E_a values in the occurrence of expired paracetamol are more than the free 1.0 mol L⁻¹ H₂SO₄ solution confirming that the physical adsorption of the expired paracetamol on the surface of LCS. The presence of the expired paracetamol stimulates an energy barrier for the LCS corrosion and the barrier increases with increasing the concentration of paracetamol.

Table 2. The effect of increasing temperature on I_{corr} , θ and % P acquired from the dissolution of MS in blank 1.0 mol L⁻¹ H₂SO₄ and with some concentrations of paracetamol using GP tests.

T, °K	I_{corr} . ($\mu\text{A}/\text{cm}^2$)	% IE_{GP}	Θ
1.0 mol L ⁻¹ H ₂ SO ₄			
300	1.812	-	-
310	1.882	-	-
320	1.934	-	-
330	1.985	-	-
1.0 mol L ⁻¹ H ₂ SO ₄ +75 mg paracetamol			
300	0.372	79.5	0.79
310	0.435	76.9	0.77
320	0.496	74.4	0.74
330	0.564	71.6	0.72
1.0 mol L ⁻¹ H ₂ SO ₄ +125 mg l ⁻¹ paracetamol			
300	0.275	84.8	0.85
310	0.342	81.8	0.82
320	0.415	78.5	0.79
330	0.492	75.2	0.75
1.0 mol L ⁻¹ H ₂ SO ₄ +175 mg l ⁻¹ paracetamol			
300	0.212	88.3	0.88
310	0.256	86.4	0.86
320	0.315	83.7	0.84

330	0.412	79.2	0.79
1.0 mol L ⁻¹ H ₂ SO ₄ +225 mg l ⁻¹ paracetamol			
300	0.154	91.5	0.92
310	0.215	88.6	0.89
320	0.276	85.7	0.86
330	0.355	82.1	0.82
1.0 mol L ⁻¹ H ₂ SO ₄ +275 mg l ⁻¹ paracetamol			
300	0.106	94.2	0.94
310	0.168	91.1	0.91
320	0.243	87.4	0.87
330	0.313	84.2	0.84

Fig.3. displays the diagram of $\log R_{corr.}$ vs $1/T$ (Arrhenius relation). Straight lines were acquired with a slope equal $(-E_a/R)$. The E_a values at various concentrations of expired paracetamol were computed and recorded in Table 3. It is evident that the E_a values in the occurrence of expired paracetamol are more than the free 1.0 mol L⁻¹ H₂SO₄ solution, confirming that the physical adsorption of the expired paracetamol on the surface of LCS. The presence of the expired paracetamol stimulates an energy barrier for the LCS corrosion and the barrier increases with increasing the concentricity of paracetamol.

The values of enthalpy of activation(ΔH^*) and enthalpy of activation (ΔS^*) were computed from the subsequent equation[33,34]:

$$R_{corr.} = \frac{RT}{NH} \exp(\Delta S^* /R) \exp (-\Delta H^*/RT) \tag{4}$$

where, A, h and N are frequency factor, Planck’s constant and Avogadro’s number, respectively.

The plots of $(\log R_{corr.}/T)$ versus $(1000/T)$ for LCS in free 1.0 mol L⁻¹ H₂SO₄ and contains certain concentrations of contains expired paracetamol are represented in Fig.4. Straight lines were acquired from this plot and we can determine the values of ΔH^* from the slopes of straight lines and ΔS^* can be determined from the intercept and included in Table 3.

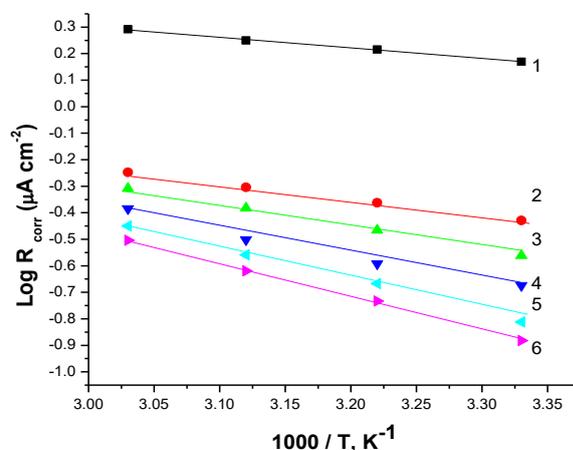


Figure 3. Relationship between $(\log R_{corr.})$ vs $(1000/T)$ for LCS in free 1.0 mol L⁻¹ H₂SO₄ solution and contains certain concentrations of expired paracetamol; 1)1.0 mol L⁻¹ H₂SO₄; 2) 75 mg l⁻¹paracetamol; 3) 125mg l⁻¹paracetamol; 4) 175 mg l⁻¹paracetamol; 5) 225 mg l⁻¹paracetamol; 6) 275 mg l⁻¹ paracetamol

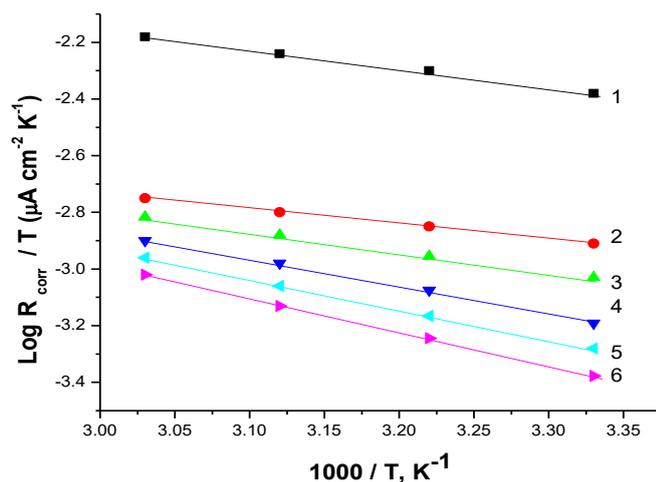


Figure 4. Plots of $(\log R_{\text{corr}}/T)$ vs $(1000/T)$ for LCS in free $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and contains certain concentrations of expired paracetamol; 1) $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$; 2) 75 mg l^{-1} paracetamol; 3) 125 mg l^{-1} paracetamol; 4) 175 mg l^{-1} paracetamol; 5) 225 mg l^{-1} paracetamol; 6) 275 mg l^{-1} paracetamol

The presence of expired paracetamol makes higher values of ΔH^* than those of blank $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution. Positive values of ΔH^* demonstrate the endothermic behavior of the corrosion process. This observation could be attributed to the presence of an energy barrier to the corrosion process due to the existence of expired paracetamol, that is, the adsorption process shows an increase in the entropy of the corrosion process. The negative sign of entropy of activation (ΔS^*), denotes that the transition state of the rate determining step symbolizes a binding rather than secession, reflecting the existence of further arrangement going from the reactant to the activated complex [35,36].

Table 3. Thermodynamic activation parameters for LCS in blank $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ in and with some concentrations of expired paracetamol

Conc.,ppm	$E_a(\text{kJ. mol}^{-1})$	$\Delta H^*(\text{kJ. mol}^{-1})$	$-\Delta S^*(\text{J. mol}^{-1}. \text{K}^{-1})$
$1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ +Expired paracetamol	15.3		
$1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$	16.3	19.8	378.4
75 mg l^{-1} paracetamol	20.2	22.6	402.2
125 mg l^{-1} paracetamol	22.6	27.3	428.9
175 mg l^{-1} paracetamol	27.5	30.5	476.5
225 mg l^{-1} paracetamol	29.7	32.8	492.3
275 mg l^{-1} paracetamol	30.6	34.9	509.2

3.3. Paracetamol as pitting inhibitor

Fig.5 displays the impact of increasing concentration of expired paracetamol ranged from the 75 to 275 mg l^{-1} on the PDP curves of LCS in $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ containing $0.5 \text{ mol L}^{-1} \text{ NaCl}$ solution at a sweep rate 0.5 mVs^{-1} . NaCl acted as pitting agent. It is observed from this figure the absence of any

dissolution peak. This behavior demonstrates the constancy of the film constructed on the surface of LCS. The current remains constant with increasing the potential until at certain potential the current increases abruptly. This elucidates that the broken of the film constructed and formation of the pitting attack. This potential is defined as the pitting potential ($E_{pitt.}$) [37,38]. The change in the value of the E_{pitt} gives an indication of the occurrence of pitting corrosion or its inhibition.

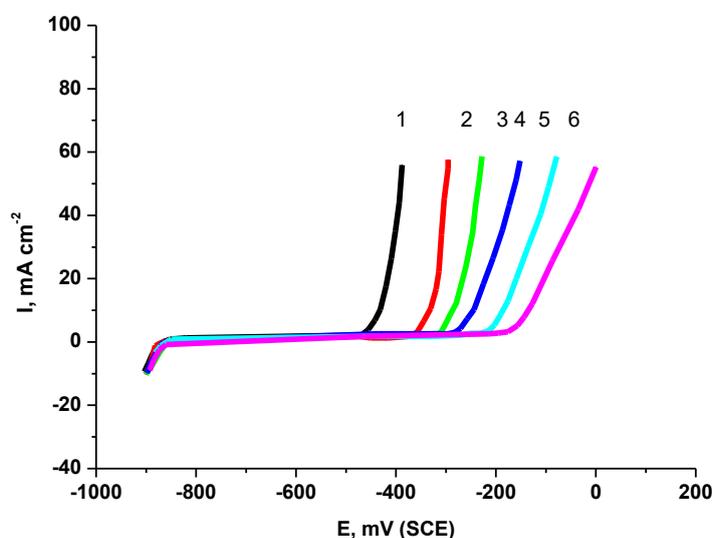


Figure 5. PDP curves of LCS in free 1.0 mol L⁻¹ H₂SO₄+ 0.5 mol L⁻¹ NaCl and contains certain concentrations of contain expired paracetamol; 1)0.0 mg l⁻¹paracetamol; 2) 75 mg l⁻¹paracetamol; 3) 125mg l⁻¹paracetamol; 4) 175 mg l⁻¹paracetamol; 5) 225 mg l⁻¹paracetamol; 6) 275 mg l⁻¹ paracetamol

Obviously from the curves of Fig 5 that, when the concentration of the expired paracetamol rises, we note the values of $E_{pitt.}$ is being moved in a more noble direction. The relation between the $E_{pitt.}$ and the logarithmic concentration of expired paracetamol is displayed in Fig.6. From this figure, it is evident that the values of $E_{pitt.}$ is moved to more positive trend. This demonstrates that the pitting attack was retarded by the existence of paracetamol which satisfies satisfying the subsequent equation [39,40]:

$$E_{pitt} = c + d \log C_{inh} \tag{5}$$

where, c and d are constants relies on the chemical composition of the electrode utilized and the additives applied. A straight line relationship was acquired demonstrating that as the higher the paracetamol concentration, the more E_{pitt} moves into positive trend. This confirms that the expired paracetamol increases the resistance to a pitting attack of LCS.

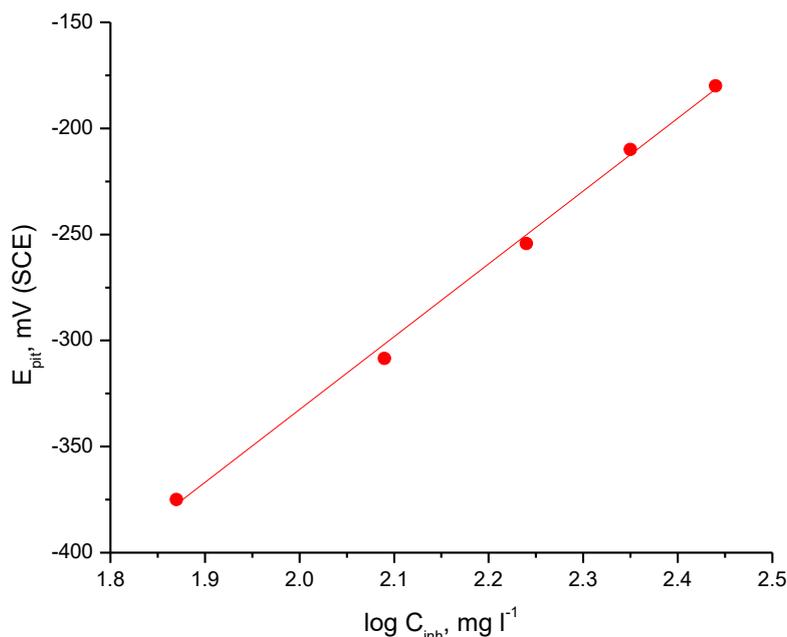


Figure 6. The relation between (E_{pit}. vs log C inh.)

3.3. EIS technique

The Nyquist diagram of LCS in free 1.0 mol L⁻¹ H₂SO₄ and with some concentrations of expired paracetamol at 300 °K are displayed in Fig 7. It is evident from this figure, the EIS diagram the shows one semicircle but not perfect. The deviation of ideal behavior owing to the frequency dispersion as a result of the coarseness and heterogeneity of the LCS surface [41]. As the concentricity of the expired paracetamol increases, the radius of semicircles increases. This demonstrate that the characteristics of the coating film on the surface of the LCS increased.

The equivalent circuit utilized to the analysis of the data extracted from the impedance diagram are represented in Fig.8. This circuit composed of the solution resistance (R_s), the charge-transfer resistance of the interfacial corrosion reaction (R_{ct}) and the double layer capacitance (C_{dl}).

The capacity of double layer (C_{dl}) can be determined from the angular frequency(f). (Ω = 2 π f) at the maximum imaginary component and R_{ct} according to the next equation:

$$C_{dl} = \left[\frac{1}{\Omega_{max} \cdot R_{ct}} \right] = \left[\frac{1}{2\pi \cdot f_{max} R_{ct}} \right] \tag{6}$$

The inhibition efficacy (%IE_{EIS}) from EIS tests was computed from the values of R_{ct} the using the equation.

$$\%IE_{GP} = \left[1 - \frac{(R_{ct})_f}{(R_{ct})_{in}} \right] 100 \tag{7}$$

where, $(R_{ct})_f$ and $(R_{ct})_{in}$ are the charge transfer resistance in free $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution and with the presence of expired paracetamol. The electrochemical parameters obtained from EIS tests such as R_{ct} , C_{dl} and $\%IE_{EIS}$ are collected in Table 4.

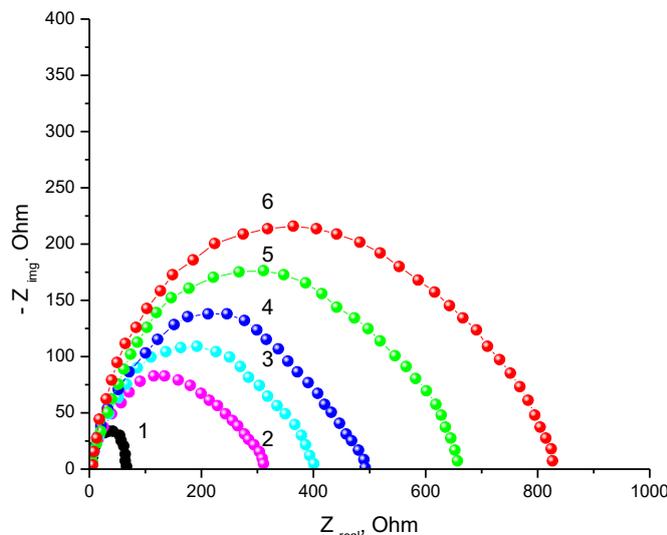


Figure 7. Nyquist plot of LCS in free $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution and with some concentrations of expired paracetamol; 1) $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$; 2) 75 mg l^{-1} paracetamol; 3) 125 mg l^{-1} paracetamol; 4) 175 mg l^{-1} paracetamol; 5) 225 mg l^{-1} paracetamol; 6) 275 mg l^{-1} paracetamol

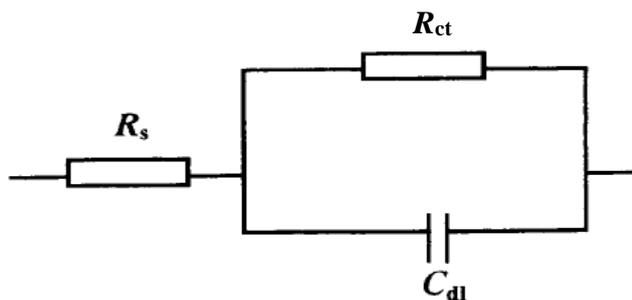


Figure 8. The equivalent circuit fit the experimental outcomes

It is concluded that from Table 4, with increasing concentration expired paracetamol, the R_{ct} values increased and this in turn led to a reduce in the corrosion rate of LCS in $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution. This owing to the building of covering layer on the surface of the LCS [42]. The semicircle profile of Nyquist diagram demonstrates that the corrosion of LCS is mainly controlled by a charge transfer reaction. The C_{dl} values diminished due to the exchange of the water molecule on the surface of the LCS with paracetamol molecules with low dielectric constant through adsorption. The $\% IE_{EIS}$ increases and is approximately equal to that derived from GP test

Table 5. Electrochemical data obtained from the EIS tests LCS in free 1.0 mol L⁻¹ H₂SO₄ solution and with some concentrations of expired paracetamol

Inh. Conc. (ppm)	C _{dl} , μF cm ⁻²	R _{ct} , Ω cm ⁻²	%I _{EIS}
0	192	65	--
75	162	305	78.7
125	152	390	83.3
175	142	486	86.6
225	136	652	90.0
275	128	826	92.1

3.4. Adsorption isotherm and interpretation of inhibition

The outcomes obtained from the three electrochemical technique used indicates the expired paracetamol inhibits the corrosion of LCS in 1.0 mol L⁻¹ H₂SO₄ solution. The inhibition efficacy of this drug is mainly due to its adsorption on the surface of LCS. The effectiveness of adsorption depends on some factors such as the chemical structure of the drug used, the nature and chemical composition of the type the steel, the concentration of corrosive electrolyte, the concentration of hydrogen ion, temperature and other factors. The adsorption of expired paracetamol on the surface of LCS is considered an exchange process between the expired paracetamol in the aqueous phase and the number of water molecules (z) adsorbed on the LCS surface. Hence the expired paracetamol is adsorbed on the surface of LCS according to the subsequent equation:



To find a suitable isotherm, the values of θ are applied in many isotherms and we choose to which our results apply. We found that the appropriate adsorption isotherm is Langmuir isotherm according to the next equation:

$$\frac{C_{inh}}{\theta} - \frac{1}{K_{ads}} = C_{inh} \tag{9}$$

where, C_{inh} is the concentration of paracetamol, K_{ads} is the equilibrium constant of adsorption.

Figure 9. displays the relationship between C_{inh}/θ vs. C_{inh} for LCS in free 1.0 mol L⁻¹ H₂SO₄ solution and with some concentrations of expired paracetamol at various temperatures ranging from 300 °K to 330 °K. A straight line was acquired with slope equal to nearly equal unit. This clarifies that the adsorption of expired paracetamol on the LCS is subjected to Langmuir isotherm. This indicates that zero interaction between adsorbed particles. We can determine the values of K_{ads}. From the intercept of Langmuir plots. The variation in Gibbs free energy for adsorption (ΔG_{ads}) can be computed from the next equation applying the following equation:

$$55.5 K_{ads} = \exp(-\Delta G_{ads}^{\circ} / RT) \tag{10}$$

where 55.5 the concentration of water in mol. L⁻¹, R is the gas constant. The computed values of K_{ads} were equal to 13.3, 11.7, 9.5, and 8.3 × 10⁻³ at 300, 310, 320, and 330 °K, respectively. From the

values of K_{ads} , we compute the values of ΔG_{ads} and equal; -31.32, -32.24, -33.53, and -34.96 kJ. mol⁻¹ at the tested temperatures of 300, 310, 320, and 330 °K, respectively.

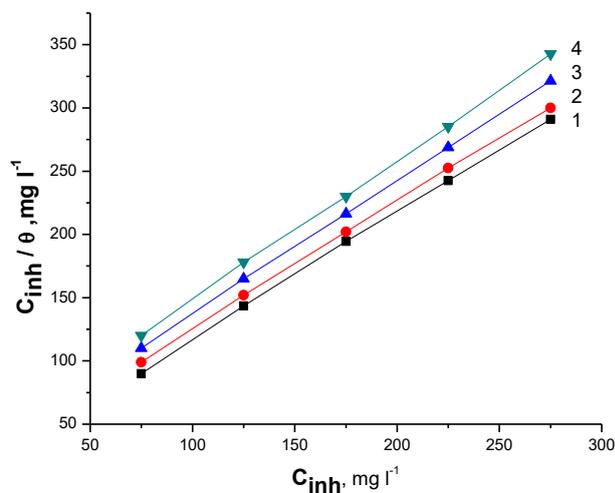


Figure 9. Langmuir isotherm plots of LCS in 1.0 mol L⁻¹ H₂SO₄ solution containing certain concentrations of expired paracetamol at various temperature; 1)300 °K; 2) 310 °K; 3)320 °K; 4)330 °K

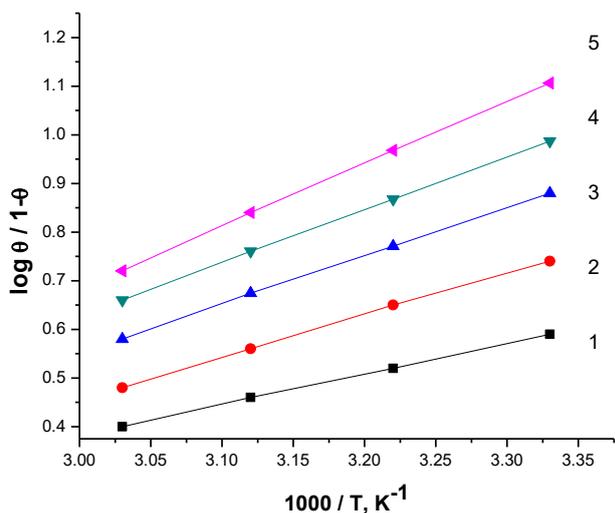


Figure 10. The plots between $\log(\theta / 1 - \theta)$ vs $1/T$ for LCS in 1.0 mol L⁻¹ H₂SO₄ solution including certain concentrations of paracetamol.; 1) 75 mg l⁻¹paracetamol; 2) 125mg l⁻¹paracetamol; 3) 175 mg l⁻¹paracetamol; 4) 225 mg l⁻¹paracetamol; 5) 275 mg l⁻¹ paracetamol

Obviously, when the temperature rises the values of K_{ads} and ΔG_{ads} are reduced temperatures. This coincides with the lower inhibition efficacy at elevated temperature due to the removal of the adsorbent film on the surface of the LCS. From the values of K_{ads} and ΔG_{ads} reveals that the adsorption of paracetamol on the surface of LCS surface is spontaneous. It is known previously when the value of ΔG_{ads} is less than -40 KJ Mol⁻¹, it indicates the presence of chemical adsorption of inhibitors [43]. But

when it is greater than -20 kJ mol^{-1} , it gives an indication of the occurrence of the physical adsorption of the inhibitors. Therefore, we conclude that from the determined values of ΔG_{ads} , the adsorption of paracetamol on the LCS surface is a mixed between physical and chemical adsorption [44,45].

The enthalpy of adsorption, ΔH_{ads} , was computed by applying the Langmuir equation [46]:

$$\theta = (1 - \theta)A C_{\text{inh}} \exp\left(\frac{-\Delta H_{\text{ads}}}{RT}\right) \quad (11)$$

where A is a constant and C is the concentration of expired paracetamol. Figure 10 displays plots between $(\theta/1 - \theta)$ and $1/T$ for for LCS in a $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution including specific concentrations of paracetamol. These plots give straight lines with a slope equal to $-\Delta H_{\text{ads}}/2.303R$. The values of ΔH_{ads} can be determined from the slope of the straight lines and are equal to -11.48 , -13.40 , 15.32 , -17.23 and $-19.52 \text{ kJ mol}^{-1}$ at paracetamol concentration 75 mg l^{-1} , 125 mg l^{-1} , 175 mg l^{-1} , 225 mg l^{-1} and 275 mg l^{-1} respectively. The negative values for the ΔH_{ads} demonstrate that the adsorption of paracetamol on the surface of LCS surface is an exothermic process.

The entropy of adsorption (ΔS_{ads}) is computed from the next equation [46]:

$$\Delta S_{\text{ads}} = (\Delta G_{\text{ads}} - \Delta H_{\text{ads}}) / T \quad (20)$$

The determined values of ΔS_{ads} are equal -0.062 , -0.066 , -0.068 , and $-0.071 \text{ kJ mol}^{-1}$ at the studied temperatures of 300 , 310 , 320 , and $330 \text{ }^\circ\text{K}$, respectively.

The negative values for ΔS_{ads} demonstrate the decreased of perturbation on the transition from the reactant to the adsorbed metal. This confirms the vigour of adsorption paracetamol on the surface of LCS.

3.5. Explanation of inhibition

The efficacy of paracetamol inhibition against the corrosion of LCS in a $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution was evaluated by electrochemical tests. Addition of certain concentrations of paracetamol reduced the values of I_{corr} , C_{dl} and increase the values of R_{ct} , θ and %IE. Also, the values of E_{pitt} is transferred to a more noble direction. These outcomes confirm the inhibitory activity of paracetamol. The inhibition strength of paracetamol depends mainly on its adsorption on the surface of LCS by construction of a barrier film between the LCS and the corrosive electrolyte. This film prevents the mass and charge transformation between the LCS and its surrounding. From ΔG_{ads} values, the adsorption is mixed between the physical and chemical adsorption. The effectiveness of the inhibition depends on some factors such as the nature and the chemical composition of the steel used, the temperature, the concentration of paracetamol, the ability to form complex agents and other factors.

The inhibitory effect of the investigated expired paracetamol can be interpreted by the formation of the insoluble complex. Expired paracetamol can be interacted with iron (II) ion, according to the suggested complex formed (Fig. 11). As seen from Fig., the iron (II) ion was binding to two molecules of paracetamol through the lone pairs localized on nitrogen atom and oxygen atom of the carbonyl group. The paracetamol as illustrated formed a (2:1) [paracetamol: iron (II) ion] complex. The complex formed is adsorbed on the surface of LCS and increase the inhibition efficacy.

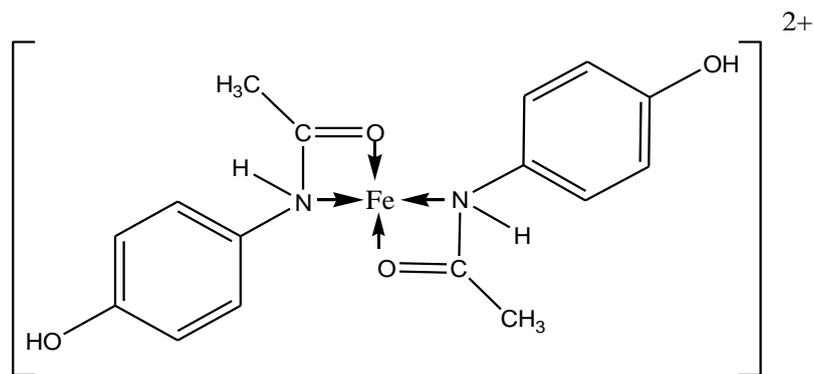


Figure 11. The suggested complex formed between iron (II) ion and expired paracetamol.

The inhibition of pitting corrosion of LCS by the investigated expired paracetamol as demonstrated by PDP assay may be due to the occurrence of competitive adsorption of between the expired paracetamol and the Cl⁻ ions so that the expired paracetamol is faster than chloride ions. Therefore, the expired paracetamol is rapidly adsorbed than Cl⁻ ions onto the surface of the LCS, and thus the pitting corrosion is inhibited by shifting the values of E_{pitt} into noble trend.

4. CONCLSIONS

1. Expired paracetamol acted as a good efficacious inhibitor for LCS in $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$
2. The inhibition efficacy increases with increasing the concentricity of expired paracetamol and at lower temperature.
3. The inhibitory effect was explicated by spontaneous adsorption of the complex formed between the expired paracetamol and iron (II) ion.
4. The adsorption of expired paracetamol on the surface of LCS followed Langmuir isotherm
5. EIS tests have demonstrated that the charge transfer process controls the corrosion reaction.
6. Expired paracetamol inhibits the pitting corrosion of LCS

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