



Cialis (Tadalafil) Drug as Save Corrosion Inhibitor for Zn in Hydrochloric Acid Solution

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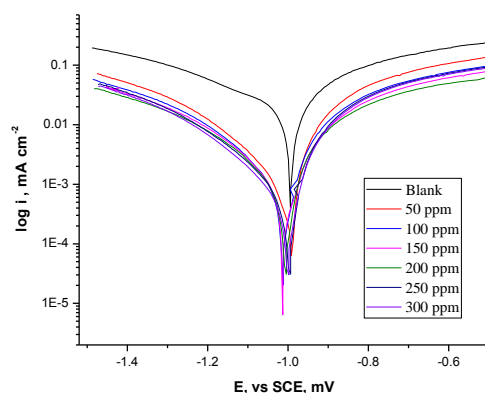
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ABSTRACT

The inhibiting effect of Cialis drug on the corrosion of Zn in 1 M HCl was studied by weight loss (WL), potentiodynamic polarization (PP), electrochemical frequency modulation (EFM) and electrochemical impedance spectroscopy (EIS) techniques. The adsorption isotherm of Cialis drug on the Zn surface follows Langmuir adsorption isotherm. Some thermodynamic parameters were calculated and discussed. The results indicated that the inhibition efficiency (IE) increases with increasing the concentration of the drug, while decreases with increasing the temperature. The morphology of inhibited Zn was analyzed by scanning electron microscope (SEM), the energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM). Polarization results showed that this drug is mixed type inhibitor. The results obtained from chemical and electrochemical techniques are in good agreement.

Graphical abstract:



Keywords: Adsorption, Corrosion inhibition, Zn, HCl, SEM, EDX, AFM, FTIR.

INTRODUCTION

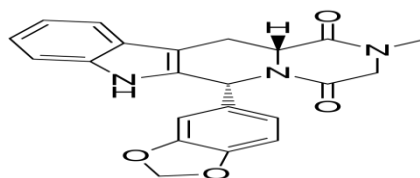
Corrosion is a fundamental process playing an important role in economics and safety, particularly for metals. Corrosion processes develop fast after disruption of the protective barrier and are accompanied by a number of reactions that change the composition and properties of both the metal surface and the local environment [1]. Zn corrosion causes short shelf life, safety issues (hydrogen gas evolution), self-discharge and loss of valuable capacity, to reduce these undesirable effects, Zn corrosion must be controlled [2]. Several inhibitors in use are either synthesized from cheap raw material or chosen from compounds having hetero atoms in their aromatic or long-chain carbon system [3]. Most of organic inhibitors are expensive, toxic and have negative effect on the environment these properties restrict its use to inhibit the metal corrosion. Thus it is important and necessary to develop low cost and environmentally safe corrosion inhibitors [4]. Organic heterocyclic compounds have been used for the corrosion inhibition of carbon steel [6-11], copper [12], aluminum [13-15], and other metals [16] in different aqueous medium. Adsorption of the drug facilitated to protect the metal surface [17]. A few medications such as tetracycline, cloxacillin, azithromycin, ampiclox, ampicillin and orphenadrine have been discovered great inhibition for corrosion of metal surface. The select of some medication for inhibitor of corrosion is taking in the following: (1) drug molecules contain oxygen, sulphur and nitrogen as active sites, (2) it is environmentally friendly furthermore vital in organic responses and (3) drugs can be easily produced and purified [18]. In recent years the drug's uses as corrosion inhibitors for various metals result to their nontoxic nature [19-20]. Adsorption of the drug molecules on the metal surface facilitates its inhibition [21]. A few medications have been discovered to be great corrosion inhibitors for metals such as: Biopolymer gave 86% IE for Cu in NaCl [22], pyromellitic diimide linked to oxadiazole cycle gave 84.6% IE for CS in HCl [23], 2-mercaptobenzimidazole gave 82% IE for CS in HCl [24], Antidiabetic Drug Janumet gave 88.7% IE for MS in HCl [25], Januvia gave 79.5% IE for Zn in HCl [26], Cefuroxime Axetil gave 89.9% IE for Al in HCl [27], Phenytoin sodium gave 79% for CS in HCl [28], Aspirin gave 71% IE for MS in H₂SO₄ [29], Septazole gave 84.8% IE for Cu in HCl [30] and Chloroquine diphosphate gave 80% IE for mild steel in HCl [31]. Tadalafil under the name of Cialis is used to treat erectile dysfunction (impotence) and symptoms of benign prostatic hypertrophy (enlarged prostate). Another brand of Cialis is Adcirca, which is used to treat pulmonary arterial hypertension and improve exercise capacity in men and women [32].

The objective of this study is to investigate the inhibitive behavior of Cialis towards the corrosion of Zn in 1M HCl using chemical and electrochemical techniques. The surface morphology of the Zn specimens was also analyzed.

MATERIALS AND METHODS

Metal sample: The composition of metal sample in weight % is: Cd 0.52, Fe 0.035, Mn 0.005, Pd 0.18, Sn 0.07 and Zn the rest

Chemicals: Inhibitor - Cialis (Tadalafil) is the investigated drug which has been used as inhibitor and purchased from Sandozn and Pfizer companies



Cialis (Tadalafil): (6R,12aR)-6-(1,3-benzodioxol-5-yl)-2-methyl-2,3,6,7,12,12a-hexahydropyrazino[1',2':1,6]pyrido[3,4-b]indole-1,4-dione

Mol. Formula = C₂₂H₁₉N₃O₄, Mol. Weight = 389.404

Solutions: The aggressive solutions, 1M HCl was prepared by dilution of analytical grade (%37) HCl with bidistilled water. The concentration range of the inhibitor which used was between 50 and 300 ppm

Weight loss technique: For weight loss measurements, square specimens of area surface (2 x 2 x 2 cm which exposed to the corrosive medium that used. The specimens were abraded with emery papers grit sizes (400,800 and 1200) and clean with acetone. Then rinsed several times with bi-distilled water, and finally dried by filter papers. The weight loss measurements were carried out in a 100 mL glass beaker placed in a water thermostat. The specimens were then immediately immersed in the test solution without and with different concentrations of the investigated compound. All aggressive acid solutions were opened to air. After three hour, the specimens were taken out, washed, dried, and weighted accurately per thirty minutes. The average weight loss for seven square Zn specimens will be obtained. The inhibition efficiency (% IE) and the degree of surface coverage (θ) of Cialis for the corrosion of Zn were calculated as follows [33]:

$$\% \text{ IE} = \theta \times 100 = [1 - (W/W^{\circ})] \times 100 \quad (1)$$

Where, W° and W are the weight losses, without and with adding various concentration of investigate inhibitor respectively.

Potentiodynamic polarization technique: Polarization experiments were carried out in a classical three-electrode cell with a platinum counter electrode and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode. The working electrode was in the form of a square cut from Zn sheet fixed in epoxy resin of poly tetrafluoroethylene so that the flat surface area was 1.0 cm². The working electrode was polisher with emery papers grit 1200 in size. Before measurement, the electrode was immersed in solution at natural potential for 30 min. until a steady state was reached. All experiments were carried out in freshly prepared solutions at room temperature and results were always repeated at least three times to check the validity results. Calculation of % IE and the θ as below [34]:

$$\text{IE \%} = \theta \times 100 = [1 - (i_{\text{corr(inh)}} / i_{\text{corr(free)}})] \times 100 \quad (5)$$

Where, $i_{\text{corr(free)}}$ and $i_{\text{corr(inh)}}$ are the corrosion current densities in the absence and presence of drug, respectively.

Electrochemical impedance spectroscopy (EIS) technique: All EIS measurements were performed at open circuit potential E_{ocp} at $25 \pm 1^{\circ}\text{C}$ over a wide frequency range of (1×10^5 Hz to x 0.1 Hz). The potential perturbation was 10 mV in abundance peak to peak. The obtained diameters of the capacitive loops increase in presence of inhibitors, and are indicated of the capacity of the extent of inhibition of corrosion process, contrary to the decrease of the capacity of double layer (C_{dl}) which is defined as:

$$C_{\text{dl}} = 1 / (2 \pi f_{\text{max}} R_p) \quad (6)$$

Where, f_{max} is the maximum frequency. The IE and the θ obtained from the impedance measurements were defined by the following relation:

$$\text{IE \%} = \theta \times 100 = [1 - (R_p^{\circ} / R_p)] \times 100 \quad (7)$$

Where, R_p° and R_p are the charge transfer resistance in the absence and presence of inhibitor, respectively.

Electrochemical frequency modulation (EFM) technique: EFM experiments were performed with applying potential perturbation signal with abundance 10 mV with two sine waves of 2 and 5 Hz. The choice for the frequencies of 2 and 5Hz was based on three arguments [35]. The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (β_c and β_a) and the causality factors CF_2 and CF_3 [36]. The % IE_{EFM} was calculated as follows:

$$\% \text{IE}_{\text{EFM}} = [1 - (i_{\text{corr}} / i_{\text{corr}}^{\circ})] \times 100 \quad (8)$$

Where, i_{corr}° and i_{corr} are corrosion current densities in the absence and presence of inhibitor, respectively.

All electrochemical experiments were carried out using Gamry instrument PCI300/4 Potentiostat/Galvanostat/Zra analyzer, DC105 Corrosion software, EIS300 Electrochemical Impedance

Spectroscopy software, EFM140 Electrochemical Frequency Modulation software and Echem Analyst 5.5 for results plotting, graphing, data fitting and calculating.

Surface Examinations: The Zn specimens used for analysis of morphology surface were prepared in 1M HCl acid (blank) and with 300 ppm of Cialis (Tadalafil) at room temperature for one day after abraded mechanically using different emery papers up to 1200 grit size. Then, after this immersion time, the specimens were cleaned gently with bidistilled water, carefully dried and mounted into the performed specimens examined by using scanning electron microscope (SEM), energy dispersive x-ray (EDX), Fourier transform infrared spectroscopy (FTIR) and atomic force microscope (AFM).

RESULTS AND DISCUSSION

Weight loss measurement: Weight loss of Zn, in mg cm^{-2} of the surface area, was determined at various time periods in the absence and presence of different concentrations (50 -300 ppm) of the Cialis. The curves obtained in the presence of different concentrations of drug fall significantly below that of free acid as shown in Figure 1. The % IE's are listed in Table 1. In all cases, the efficiency of the drug increases with increasing concentration of the drug but the rate of corrosion was decreased. These results indicated that, the Cialis under study are good efficient as inhibitor for Zn dissolution in HCl solution.

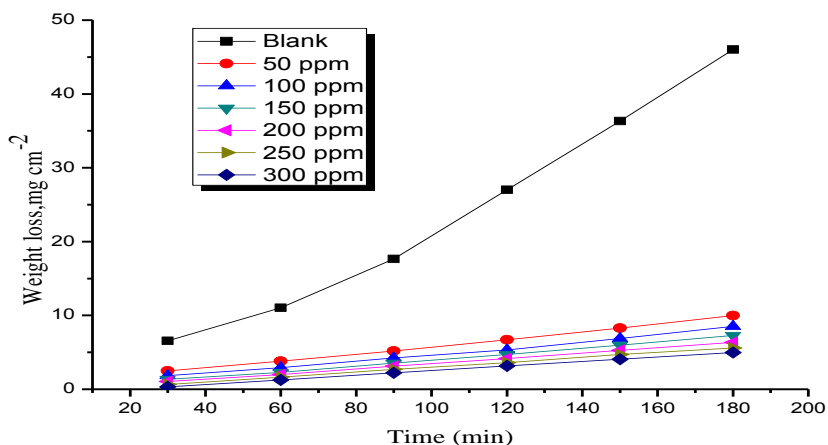


Fig. 1: Weight loss-time curves for the dissolution of Zn in the absence and presence of different concentrations of Cialis at 25°C

Table 1: Variation of % IE of the drug with its molar concentrations at 25°C from weight loss measurements at 120 min immersion in 1 M HCl

Compound	Conc., ppm	$k_{\text{corr.}}$ $\text{mg cm}^{-2} \text{min}^{-1}$	% IE
Blank	---	0.225	---
Cialis	50	0.055	75.2
	100	0.044	80.3
	150	0.039	82.6
	200	0.034	84.6
	250	0.032	85.6
	300	0.028	87.2

Effect of temperature: Corrosion reactions are usually regarded as Arrhenius processes and the rate constant (k_{corr}) can be expressed by the relation:

$$\text{Log } k_{\text{corr}} = A - (E_a^*/2.303RT) \quad (9)$$

Where, E_a^* is the activation energy of the corrosion process, R is the universal gas constant, T is the absolute temperature and A is a Arrhenius pre-exponential constant depends on the metal type and electrolyte. Arrhenius plots of $\log k_{\text{corr}}$ vs. $(1/T)$ for Zn in 1 M HCl in the absence and presence of different concentrations of Cialis is shown graphically in Figure 2. The variation of $\log k_{\text{corr}}$ vs. $(1/T)$ is a linear one and the values of E_a^* are obtained and summarized in Table 2. The increase in E_a^* with the addition of different concentrations of the drug, indicating that, the energy barrier for the corrosion reaction increased.

It is also indicated that the whole process is controlled by surface reaction, since the activation energy of the corrosion process is over 20 kJ mol^{-1} [37]. Enthalpy and entropy of activation (ΔH^* , ΔS^*) are calculated from transition state theory using the following equation [38].

$$k_{\text{corr}} = (RT/Nh) \exp(\Delta S^*/R) \exp(\Delta H^*/RT) \quad (10)$$

Where, h is Planck's constant, N is Avogadro's number. A plot of $\log(k_{\text{corr}}/T)$ vs. $(1/T)$ also gave straight lines as shown in Figure 3, for Zn dissolution in 1 M HCl in the absence and presence of different concentrations of Cialis. The slopes of these lines equal $-\Delta H^*/2.303R$ and the intercept equal $\log [RT/Nh] + (\Delta S^*/2.303R)$, that the value of ΔH^* and ΔS^* were calculated and listed in Table 2. From these results, it is clear that the presence of the tested compound increased the activation energy values and consequently decreased the rate of corrosion of the Zn. These results indicate that the tested compound acted as inhibitors through increasing activation energy of Zn dissolution by making a barrier to mass and charge transfer by their adsorption on Zn surface. The values of ΔS^* reflects the strong adsorption of these compounds on Zn surface. The values of ΔS^* in absence and presence of the tested compound is large and negative; this indicates that the activated complex in the rate-determining step represents an association rather than dissociation step, meaning that a decreases in disordering takes place on going from reactants to the activated complex and the activated molecules were in higher order state than that at the initial state [39].

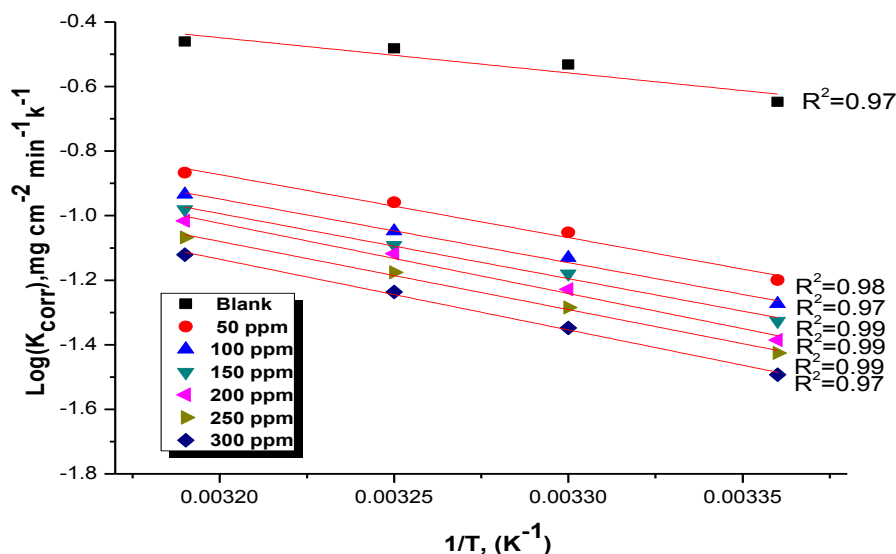


Fig. 2: Arrhenius plots ($\log k$ vs. $1/T$) for corrosion of Zn in 1 M HCl in the absence and presence of different concentrations of Cialis drug

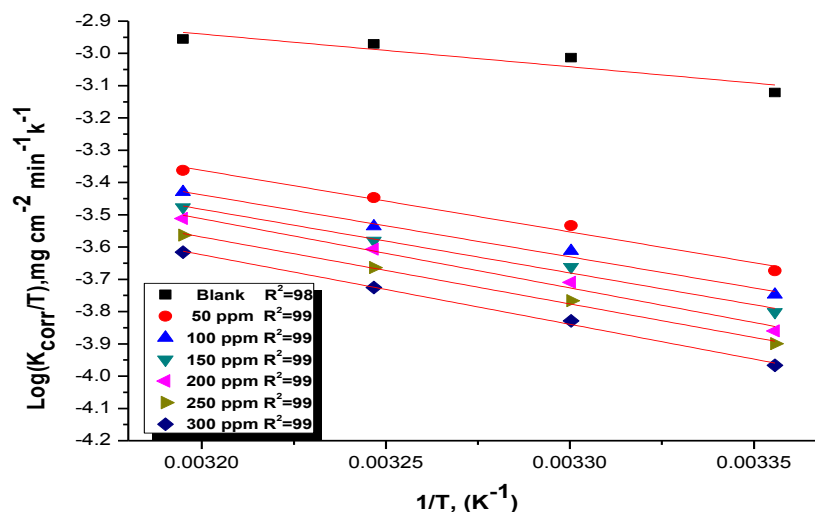


Fig. 3: Plots of $(\log k_{\text{corr.}} / T)$ vs. $(1/T)$ for corrosion of Zn in 1 M HCl in the absence and presence of different concentrations of Cialis at 25°C

Table 2: Thermodynamic activation parameters for the dissolution of Zn in 1 M HCl in the absence and presence of different concentrations of investigated drug

Conc. ppm	Activation parameters		
	E_a^* kJ mol ⁻¹	ΔH^* kJ mol ⁻¹	$-\Delta S^*$ J mol ⁻¹ K ⁻¹
Blank	20	19	191
50	36	34	148
100	37	36	145
150	39	37	143
200	40	38	140
250	41	39	138
300	45	41	134

Adsorption isotherm: Assuming the corrosion inhibition due to by the adsorption of Cialis, and the values of the degree of surface coverage for the different concentrations of the drug in 1 M HCl were evaluated from weight loss measurement using the following equation:

$$\theta = [\text{weight loss}_{(\text{pure})} - \text{weight loss}_{(\text{inh.})}] / \text{weight loss}_{(\text{pure})} \quad (11)$$

From the values of (Θ) , it is obvious that the values of (Θ) increased with increasing the concentration of Cialis. By using these values of surface coverage, for applied different adsorption isotherms to obey with experimental data. Langmuir adsorption isotherm was found to fit the experimental data. The mathematical expression of Langmuir is given as following [40].

$$C/\Theta = 1/k_{\text{ads}} + C \quad (12)$$

Where, k_{ads} is the adsorption equilibrium constant. Plotting (C/Θ) versus (C) of Cialis at various temperatures is shown in Figure 4 recommends that no forces repulsion or attraction between the atoms adsorbed, ever after relationship a linear is given with intercept equal to $(1/K_{\text{ads}})$ and slope similar the unity, the adsorption constant being result to the standard free energy of $\Delta G_{\text{ads}}^{\circ}$, by the following relation:

$$\Delta G_{\text{ads}}^{\circ} = -RT \ln (55.5 K_{\text{ads}}) \quad (13)$$

Where, R is the universal gas constant, T is the absolute temperature and 55.5 is the concentration of water in the solution in M/L. The $\Delta G_{\text{ads}}^{\circ}$ values at all studied at different temperatures which calculated by above

equation (13) and recorded in Table 3. The heat of adsorption ($\Delta H_{\text{ads}}^{\circ}$) was calculated according to the Van't Hoff equation [41].

$$\text{Log } K_{\text{ads.}} = (-\Delta H_{\text{ads.}}^{\circ} / 2.303RT) + \text{constant} \quad (14)$$

Plotting ($\log K_{\text{ads.}}$) against ($1/T$) give straight line that shown in Figure 5, the straight line gives slope equal ($\Delta H_{\text{ads.}}^{\circ} / 2.303R$), from this slope, the $\Delta H_{\text{ads.}}^{\circ}$ were calculated and listed in Table 3. Then by apply the following equation:

$$\Delta G_{\text{ads}}^{\circ} = \Delta H_{\text{ads.}}^{\circ} - T\Delta S_{\text{ads.}}^{\circ} \quad (15)$$

From introducing the values of $\Delta G_{\text{ads}}^{\circ}$ and $\Delta H_{\text{ads.}}^{\circ}$, the $\Delta S_{\text{ads.}}^{\circ}$ was calculated at all studied temperatures by the above equation (15). All thermodynamic adsorption parameters for Cialis inhibitor on Zn from 1M HCl solution can be concluded that:

1. The experimental data give good curves fitting for the applied adsorption isotherms as the correlation coefficients were in the range (0.99 - 0.98)
2. $K_{\text{ads.}}$ values increases with increasing temperatures from 25 to 40°C
3. The negative values of $\Delta G_{\text{ads}}^{\circ}$ reflected that the adsorption of Cialis on Zn surface in 1 M HCl solution is spontaneous process
4. $\Delta G_{\text{ads}}^{\circ}$ slightly increases (becomes less negative) with increasing temperatures which indicated the occurrence of endothermic process and the adsorption was unfavorable with increasing reaction temperature as a result of the inhibitor desorption from the steel surface [42]
5. The value of $\Delta G_{\text{ads}}^{\circ}$ around -20 kJ mol^{-1} or lower indicates the electrostatic interaction between charged metal surface and charge organic molecules in the bulk of the solution i.e. physisorption
6. The negative sign of $\Delta H_{\text{ads.}}^{\circ}$ refer to the adsorption of inhibitor molecules is an exothermic process, indicating that the adsorption is physical adsorption. The unshared electron pairs in investigate molecule may attractive with positive center on the surface of Zn by electrostatic attraction to provide a protective film prevent corrosion process [43]
7. The values of $\Delta S_{\text{ads.}}^{\circ}$ in the presence of investigate inhibitor are small and negative that is accompanied with endothermic adsorption process [44]

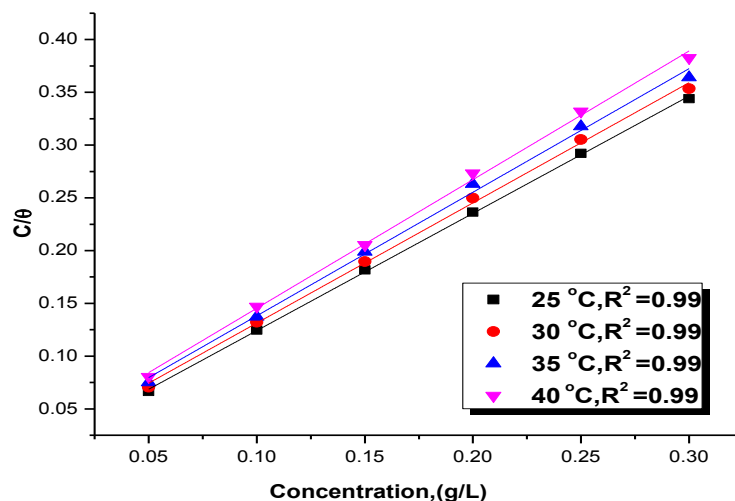
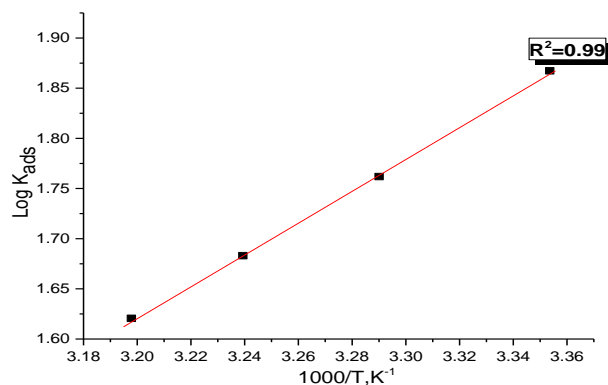


Fig. 4: Langmuir adsorption isotherm plotted as ($\log C$) vs (C/θ) of the investigated drug for corrosion of Zn in 1 M HCl solution

Table 3: Equilibrium constant (K_{ads}), adsorption free energy (ΔG°_{ads}) for the adsorption of drug on Zn in 1 M HCl.

Temp. °C	K_{ads} M^{-1}	$-\Delta G^{\circ}_{ads}$ $kJ\ mol^{-1}$	$-\Delta H^{\circ}_{ads}$ $kJ\ mol^{-1}$	$-\Delta S^{\circ}_{ads}$ $J\ mol^{-1}K^{-1}$
25	77	20.5	26	57.3
30	58	20.1		55.1
35	48	19.9		53.7
40	42	19.4		50.1

**Fig. 5:** ($\log k_{ads}$) vs ($1000/T$) for the corrosion of Zn in 1M HCl in the presence of Cialis at different temperatures

Potentiodynamic polarization: Anodic and cathodic polarizations were carried out potentiodynamic in 1 M HCl solution in the absence and presence of various concentrations of Cialis at 25°C. The results are drawing in Figure 6. The obtained potentiodynamic polarization parameters are listed in Table 4. These results indicating that the cathodic and anodic curves obtained according to Tafel-type behavior. The form of the curves is very similar either in the cathodic or in the anodic side, which indicates that the mechanisms of Zn dissolution and hydrogen reduction apparently remain in the presence of the inhibitor. Addition of Cialis decreased both the cathodic and anodic current densities and caused mainly parallel displacement to the more negative and positive values respectively, i.e. the presence of Cialis in solution inhibit both the hydrogen evolution and the anodic dissolution processes with overall shift of E_{corr} to slightly less negative values.

The results also show that the slopes of the anodic and the cathodic Tafel slopes (β_a and β_c) were slightly changed on increasing the concentration of the tested compound. This indicates that there is no change of the mechanism of inhibition in presence and absence of inhibitor. This means that the Cialis is mixed type inhibitor, but the cathode is more preferentially polarized than the anode. The higher values of Tafel slope can be related to the surface kinetic process rather the diffusion-controlled process [45]. The constancy and the cathodic slope obtained from the electrochemical measurements indicate that the hydrogen evolution reaction was activation controlled [46] and the addition of the inhibitor did not modify the mechanism of this process. This result appears that the inhibition mode of the Cialis was used by simple adheres of the surface by adsorption process.

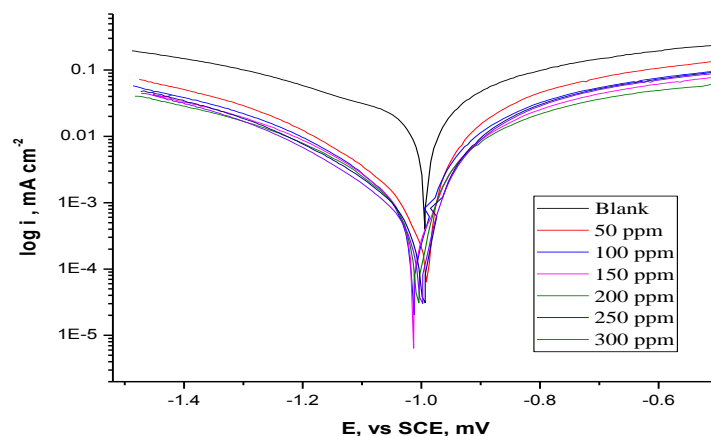


Fig. 6: Potentiodynamic polarization curves for the corrosion of Zn in 1 M HCl in the absence and presence of various concentrations of Cialis at 25°C

Table 4: The effect of concentration of Cialis on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_a & β_c), % IE, and (Θ) for the corrosion of Zn in 1 M HCl at 25°C

Conc. ppm	i_{corr} mA/cm ²	$-E_{\text{corr}}$ mV(SCE)	β_a mV dec ⁻¹	β_c mV dec ⁻¹	CR mpy	Θ	% IE
0.0	465	994	135	320	85	--	--
50	222	978	122	301	45	0.523	52.3
100	155	966	123	289	37	0.667	66.7
150	138	962	118	288	31	0.703	70.3
200	108	961	122	295	27	0.768	76.8
250	78	967	120	305	23	0.832	83.2
300	61	972	115	298	20	0.868	86.8

Electrochemical impedance spectroscopy (EIS) tests: Impedance diagrams (Nyquist and Bode) at frequencies ranging from 0.1 Hz to 10^5 Hz with 10 mV amplitude signal at OCP for Zn in 1 M HCl in the absence and presence of different concentrations of Cialis are obtained. The equivalent circuit that describe for metal and electrolyte are shown in Figure 7, where R_s and R_p refer to solution resistance and charge transfer resistance, respectively. EIS parameters and (% IE) were calculated and recorded in Table 5. The obtained Nyquist and Bode plotting for Cialis is shown in figure 8. Nyquist spectrum is characterized by a single full half-circle. These shows that the corrosion of Zn is controlled by a charge transfer process [47]. The diameters of the capacitive loop obtained increases in the presence of Cialis were indicated that the increasing the degree of inhibition of the corrosion process [48]. It was observed from the obtained EIS data that R_p increases and C_{dl} decreases with the increasing of inhibitor concentrations. The increase in R_p values gives increasing of the inhibition efficiency, due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface to form an adherence film on the metal surface. This suggests that the coverage of the metal surface by the film decreases the double layer thickness. Also, this decreasing of C_{dl} with increasing the inhibitor concentration can result from a decrease in local dielectric constant which indicating that, the inhibitor was adsorbed on the surface of both anodic and cathodic sites [49].

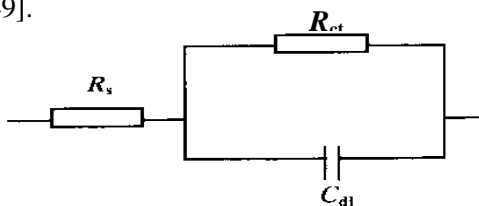


Fig 7: Electrical equivalent circuit model used to fit the experimental results

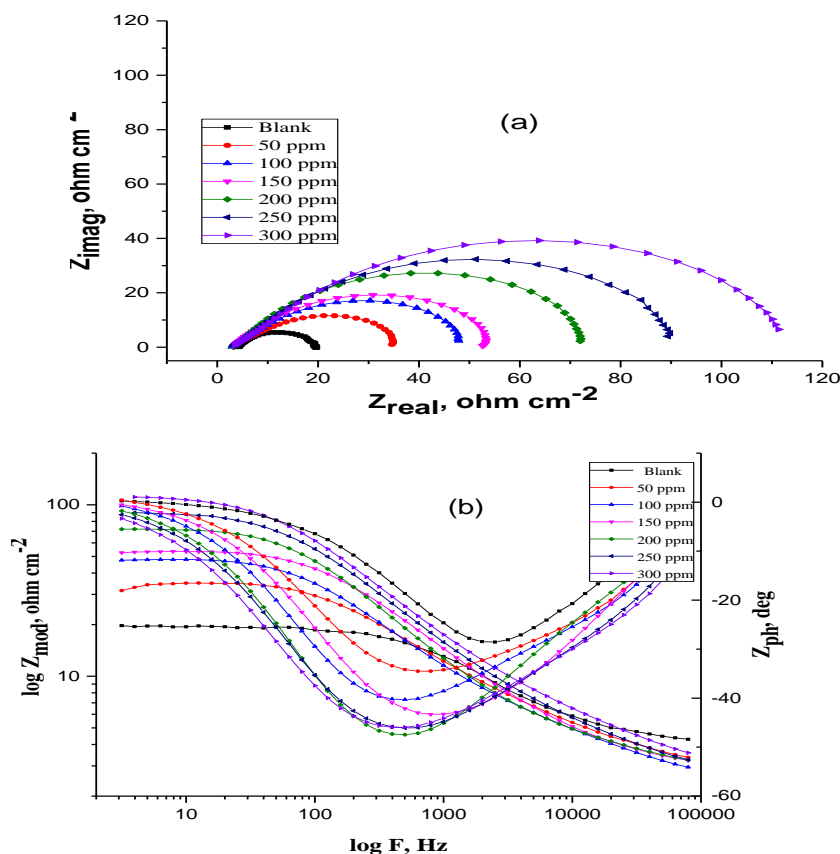


Fig. 8: The Nyquist (a) and Bode(b) plots for corrosion of Zn in 1 M HCl in the absence and presence of different concentrations of Cialis at 25°C

Table 5: Electrochemical kinetic parameters obtained by EIS technique for Zn in M HCl without and with various concentrations of Cialis at 25°C

Conc. ppm	R_p $\Omega \text{ cm}^2$	C_{dl} $\mu\text{F cm}^2$	Θ	% IE
0.0	13.5	97	--	--
50	29	25	0.532	53.2
100	42	22	0.679	67.9
150	48	19	0.719	71.9
200	65	17	0.791	79.1
250	85	16	0.840	84.0
300	105	14	0.871	87.1

Electrochemical frequency modulation technique (EFM) tests: 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 EFM technique make it a very good technique for determination corrosion information's [50]. The strength of the EFM is the causality factors which serve as an internal check on the validity of EFM measurement. The causality factors CF-2 and CF-3 are calculated from the frequency spectrum of the current responses. The EFM Inter-modulation spectrums of Zn in 1 M HCl acid solution and in 1M HCl with containing (50 – 300 ppm) of the Cialis are shown in Figure 9. The harmonic and Inter-modulation peaks are clearly visible and are much larger than the background noise. The experimental EFM–data were treated using two different models: complete diffusion control of the cathodic reaction and the “activation” model. For the latter, a set of three non-linear equations had been solved, assuming that the corrosion potential does not change due to

the polarization of the working electrode [51]. The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (β_a and β_c) and the causality factors (CF-2 and CF-3). These electrochemical parameters were simultaneously determined by Gamry EFM140 software and recorded in Table 6. The data obviously show that, the addition of tested compound at a given concentration to the acidic solution decreases the corrosion current density, indicating that the Cialis inhibit the corrosion of Zn in 1 M HCl through adsorption. The causality factors obtained under different experimental conditions are approximately equal to the theoretical values (2 and 3) indicating that the measurement data are real and of good quality [52]. The inhibition efficiencies (% IE_{EFM}) increases by increasing the concentration of Cialis which calculated and recorded in Table 6.

Table 6: Electrochemical kinetic parameters obtained by EFM technique for Zn in M HCl without and with various concentrations of Cialis at 25 °C

Comp.	Conc. M	$i_{\text{corr.}}$ μAcm^{-2}	β_a mVdec ⁻¹	β_c mVdec ⁻¹	CF (2)	CF (3)	CR mpy	θ	%IE
Blank	0.0	13.3	139	427	2.1	2.8	14.8	--	--
Cialis	50	5.1	98	401	1.9	3.1	4.1	0.617	61.7
	100	4.2	90	398	1.9	2.9	3.9	0.684	68.4
	150	3.6	88	390	1.8	3.1	3.5	0.729	72.9
	200	2.7	97	388	2.1	3.0	3.1	0.797	79.7
	250	2.1	86	386	2.0	3.1	2.9	0.842	84.2
	300	1.7	81	380	2.0	2.9	2.7	0.872	87.2

Scanning electron microscopy (SEM): Figure 10, represents the micrograph obtained for Zn samples in presence and in absence of 300 ppm of Cialis after exposure for 1 day immersion. It is clear that Zn surfaces help and severe corrosion attack in the blank sample. It is important to stress out that when the compound is present in the solution, the morphology of Zn surfaces is quite different from the previous one, and the specimen surface was smoother. We are obvious that the formation of a film which is distributed in a order way on the whole surface of the Zn. This may be due to the adsorption of the Cialis on the Zn surface and make the passive film in order to block the active site present on the Zn surface. The inhibitor molecule interaction with active sites of Zn surface, resulting in a decrease in the contact between Zn and the corrosive medium and sequentially exhibited excellent inhibition effect [53-54].

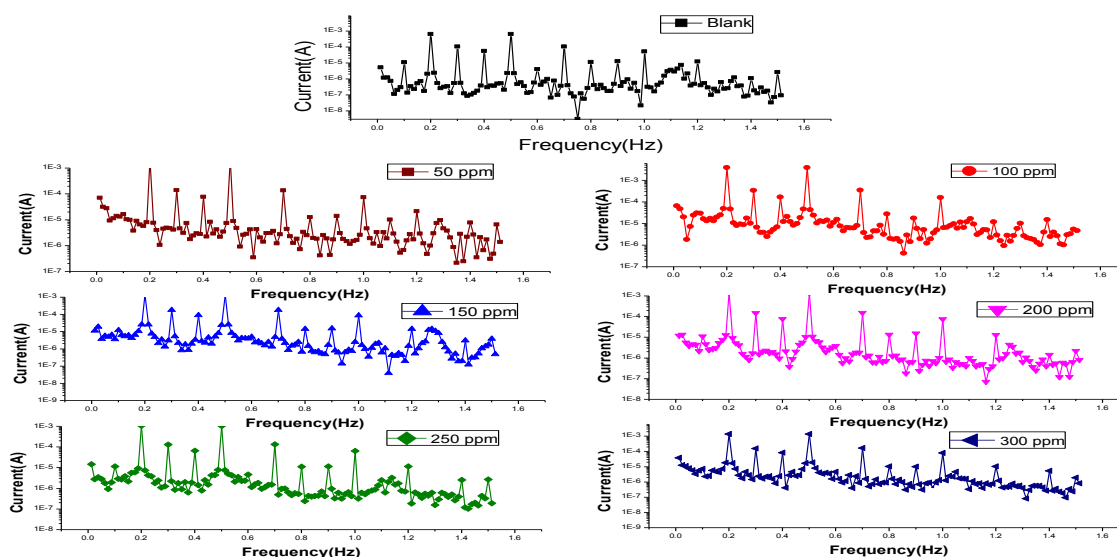
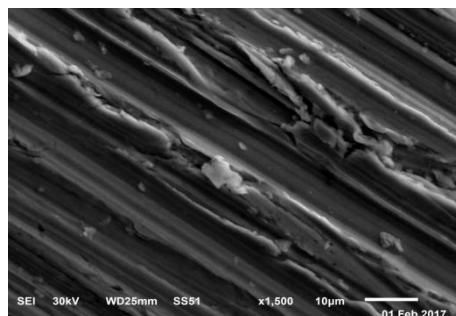
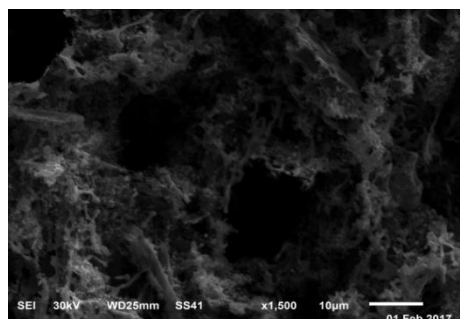


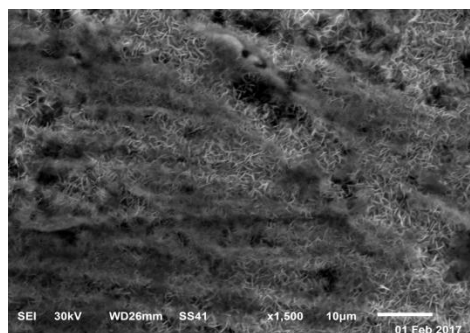
Fig 9: EFM for Zn metal in 1 M HCl in presence and absence of various concentrations of Cialis



Free sample



Blank (in 1M HCl only)



In 1M HCl with presence 300 ppm of Cialis

Fig 10: SEM micrographs for Zn in the absence and presence of 300 ppm of Cialis after immersion for 1 day

Energy dispersion spectroscopy (EDX): The EDX spectra were used to determine the elements present on the surface of Zn and after 1 day of exposure in 1 M HCl acid with optimum concentration of inhibitor. Figure 11, gives the EDX analysis of Zn in 1 M HCl with in the presence of 300 ppm of Cialis. The spectra show additional lines, demonstrating the existence of C (owing to the carbon atoms of some Cialis). These data shows that the carbon and oxygen atoms covered the specimen surface. The EDX analysis indicates that only, carbon and oxygen was detected, and shows that the passivation film contained the chemical formula of Cialis drag adsorbed on the surface of Zn. It is seen that, the percent weight of adsorb elements C and O were present in the spectra and recorded in Table 7.

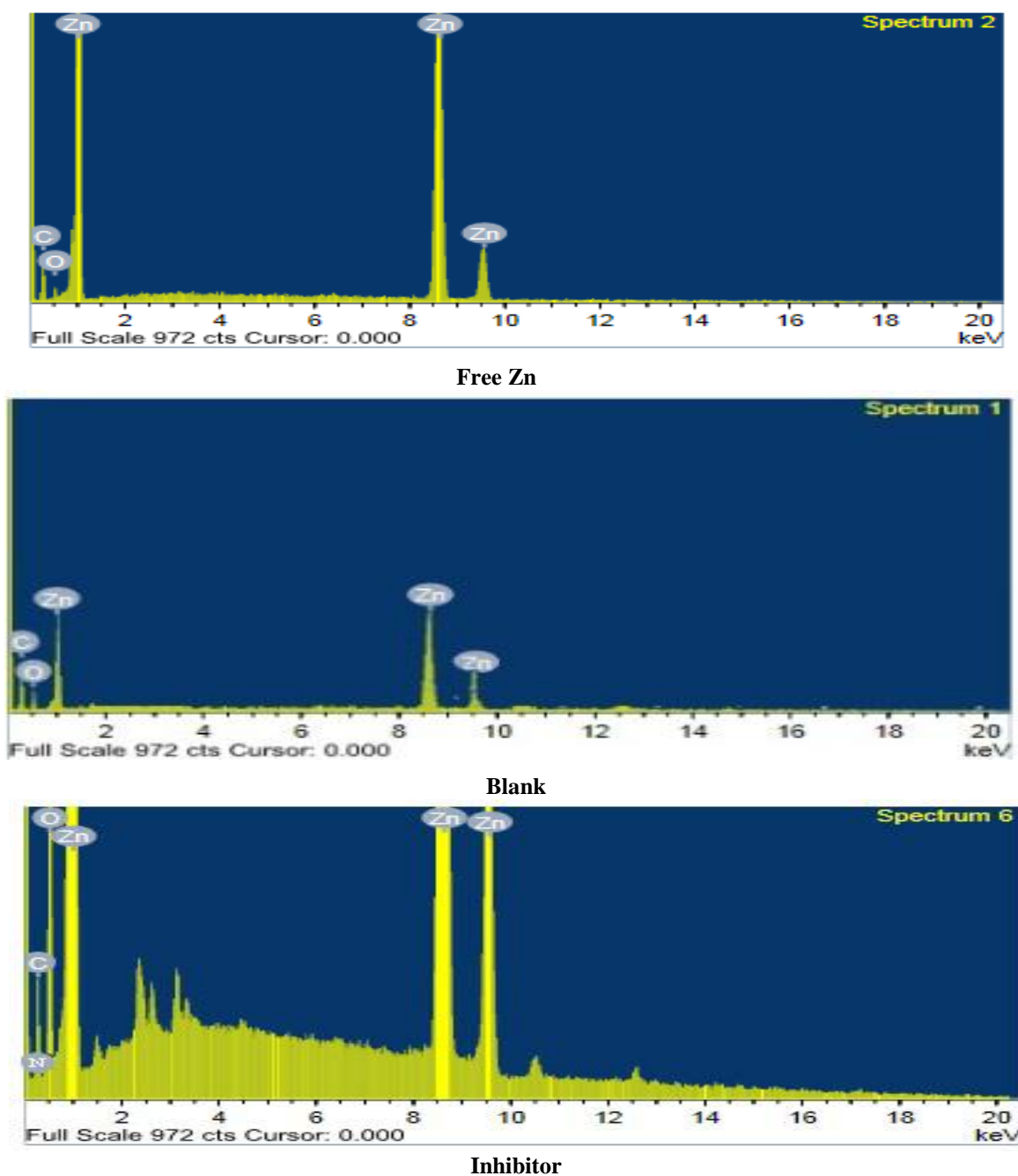


Fig. 11: EDX analysis on Zn in the presence and absence of Cialis for 1 day immersion

Table 7: Surface composition (% wt) of Zn after one day of immersion in 1M HCl without and with the 300 ppm of Cialis

(Mass %)	Zn	C	O	N
Free	94.8	0.3	4.9	-
1 M HCl	81.5	6.3	12.2	-
drug	70.1	11.0	16.6	2.3

Atomic force microscopy (AFM): AFM is a powerful tool to investigate the surface morphology of various samples at nano- micro scale that is currently used to study the influence of corrosion inhibitors on

metal solution interface. From the analysis, it can be gained regarding the roughness on the surface. The roughness profile values play an important role in identifying and report the efficiency of the inhibitor under study. Among the roughness take a role in explanation about the nature of the adsorbed film on the surface [55-56]. Figure 12, shows the 3D images as well as elevation profiles of polished of Zn in absence and present Cialis as an inhibitor. It observed in figure 12, the surface of Zn specimen (a) exposed to corroded solution affected vales structure with large and deep crack but the surface (b) reveal that is covering film adsorbed on the metal surface. The conclusion, that the adsorption film can protect the surface of the metal from corrosion process. Analysis of the values indicated higher the values of roughness parameter reached. The mean roughness is found to be (553 nm) for the blank in acid solution which placed in 1M HCl one day and analyzed. The observation of the metal surface which immersed in 1M HCl in presence of 300 ppm of Cialis inhibitor possess roughness (332 nm) compared to the blank solution. It can be noted that the value is lower than that of the blank value. The decrease in the roughness value reflected the adsorption of inhibitor molecule on metal surface thereby reducing the rate of corrosion.

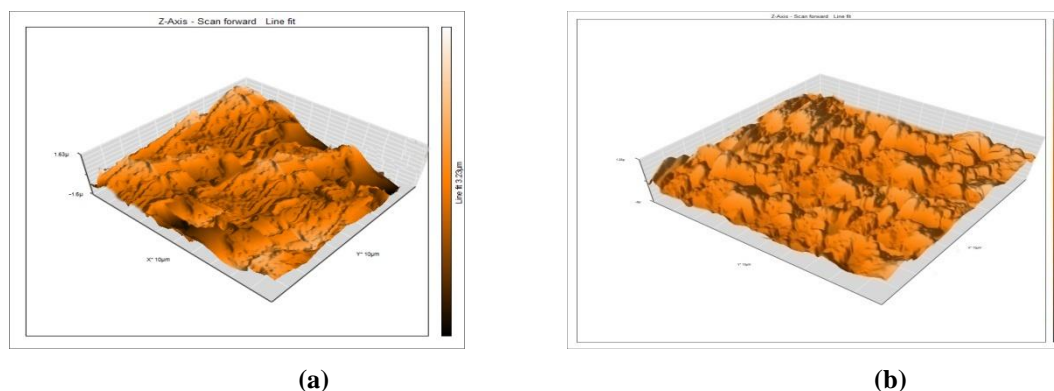


Fig 12: The 3D of optical images of AFM in absence (a) and presence (b) of Cialis inhibitor

FTIR analysis: FTIR spectroscopy displays interesting features such as high signal to noise ratio, high sensitivity and selectivity, accuracy, mechanical simplicity, short analysis time and small amount of sample required for the analysis. Figure 13 shows the FTIR spectra of the Cialis inhibitor. The finger print spectra of the drug and the Zn surface after immersion in 1M HCl + 300 ppm of Cialis was obtained and compared to each other it was obviously clear that the same finger print of Cialis stock solution present on Zn surface except the absence of some functional group and it suggested to be due to reaction with HCl. From Figure there are small shift in the peaks at Zn surface from the original peak of the stock inhibitor solution, these shifts indicate that there is interaction between Zn and some of the inhibitor's molecules.

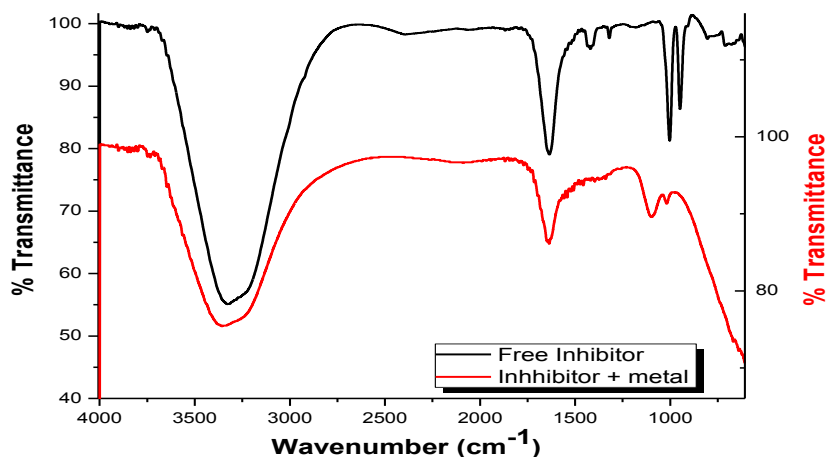


Fig 13: IR spectrum of pure Cialis at 25 °C

Inhibition mode of action: We noted the formation of a film which is distributed in a random way on the whole surface of the Zn. Due to the adsorption of the drug molecules on the metal surface and block the active site present on the surface. Also may be due to the involvement of drug molecules in the interaction with the reaction sites of Zn surface, lead to a decrease in the contact between Zn and the aggressive medium (1M HCl) and hence, exhibited excellent inhibition effect [57-58]. This compound can be adsorbed on the metal surface through the lone pair of electrons of nitrogen, oxygen atoms and delocalized π -electrons of heterocyclic ring. The %IE of this investigated compound can be explained on the basis of his molecular structure. Cialis, Contains seven active centers (4 O atoms and 3 N atoms) and this compound lies flat on the Zn surface, so, more surface area was covered and hence, more IE was observed. Other mode of adsorption is the electrostatic interaction between the negatively charged Zn surface [59] and the protonated drug molecule in acidic medium.

CONCLUSIONS

The tested drug establish a very good inhibition for Zn corrosion in HCl solution, where IE% increased by increasing in Cialis concentration. The decrease in corrosion inhibition with increasing temperature indicates that desorption of the adsorbed inhibitor Cialis molecules takes place. Cialis inhibits Zn corrosion by adsorption on its surface and follow Langmuir adsorption isotherm. Polarization curves show that Cialis is mixed-type inhibitor. Double layer capacitances (C_{dl}) decrease with increasing the inhibitor concentration added. While the charge-transfer resistance (R_{ct}) increases. The values of inhibition efficiencies obtained from the different techniques used are compatible with each.

Highlights:

- * Effect of Cialis (Tadalafil) on the corrosion of Zn was studied
- * Adsorption of Cialis (Tadalafil) clearly decreased E_{corr} and i_{corr}
- * Inhibition efficiency is over 86.8 % at 300 ppm
- * Chemical and electrochemical corrosion kinetics in HCl was identified

REFERENCES

- [1] G. Trabanelli, Inhibitors - an old remedy for a new challenge, *Corrosion*, **1991**, 47(6): 410-419.
- [2] F. Suedile, F. Robert, C. Roos, M. Lebrini, Corrosion inhibition of Zn by Mansoa alliacea plant extract in sodium chloride media: Extraction, Characterization and Electrochemical Studies, *Electrochimica Acta*, **2014**, 133: 631-638.
- [3] RT Loto, CA Loto, API Popoola, Corrosion inhibition of thiourea and thiazole derivatives: a review, *Journal of Materials and Environmental Science*, **2012**, 3:885-894.
- [4] DG Ladha, UJ Naik, NK Shah, Investigation of cumin (Cuminum Cyminum) extract as an eco-friendly green corrosion inhibitor for pure Aluminum in acid medium", *Journal of Materials and Environmental Science*, **2013**, 4:701-708.
- [5] IA Raspini, Influence of Sodium Salts of Organic Acids as Additives on Localized Corrosion of Aluminum and Its Alloys, *Corrosion* **1993**, 49: 821-828.
- [6] N Hajjaji, I Ricco, A Srhiri, A Lattes, Soufiaoui M, Benbachir A Effect of N-Alkylbetaines on the Corrosion of Iron in 1 M HCl Solution, *Corrosion*, **1993**, 49: 326-334.
- [7] M. Elachouri, MS Hajji, M. Salem, S Kertit, R. Coudert, EM Essassi, Some surfactants in the series of 2-(alkyldimethylammonio) alkanol bromides as inhibitors of the corrosion of iron in acid chloride solution, *Corros Sci*, **1995**, 37:381-389.
- [8] H Luo, YC Guan, KN Han, Inhibition of mild steel corrosion by sodium dodecyl benzene sulfonate and Sodium Oleate in Acidic Solutions, *Corrosion*, **1998**, 54: 619-627.
- [9] MA Migahed, EMS Azzam, AM Al-Sabagh, Corrosion inhibition of mild steel in 1 M sulfuric acid solution using anionic surfactant, *Mater. Chem. Phys*, **2004**, 85: 273-279.

- [10] MM Osman, AM Omar, AM Al-Sabagh, Corrosion inhibition of benzyl triethanol ammonium chloride and its ethoxylate on steel in sulphuric acid solution, *Mater Chem Phys*, **1997**, 50: 271-274.
- [11] F Zucchi, G Trabanelli, G Brunoro, The influence of the chromium content on the inhibitive efficiency of some organic compounds, *Corros Sci.*, **1992**, 33: 1135-1139.
- [12] RFV Villamil, P Corio, JC Rubim, ML Siliva Agostinho, Effect of sodium dodecylsulfate on copper corrosion in sulfuric acid media in the absence and presence of benzotriazole, *J Electroanal Chem*, **1999**, 472:112-119.
- [13] TP Zhao, GN Mu, The adsorption and corrosion inhibition of anion surfactants on aluminium surface in hydrochloric acid, *Corros Sci.*, **1999**, 41:1937-1944.
- [14] SS Abd El Rehim, H.Hassan, MA Amin, Corrosion inhibition of aluminum by 1,1(lauryl amido)propyl ammonium chloride in HCl solution, *Mater Chem Phys.*, **2001**, 70: 64-72.
- [15] SS Abd El Rehim, H.Hassan, MA Amin, 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.
- [16] R.Guo, T. Liu, X Wei, Effects of SDS and some alcohols on the inhibition efficiency of corrosion for nickel, *Colloids Surf*, **2002**, 209: 37-45.
- [17] V Branzoi, F.Golgovici, F.Branzoi, Aluminium corrosion in hydrochloric acid solutions and the effect of some organic inhibitors, *Mater Chem Phys*, **2002**, 78: 122-131.
- [18] TF Bentiss, M Lagrenee, The substituted 1,3,4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media, *Corros Sci.*, **2000**, 42:127-146.
- [19] MAB Christopher, AR Isabel Jenny, The electrochemical behavior and corrosion of aluminium in chloride media. The effect of inhibitor anions, *Corros Sci.*, **1994**, 36:915-923.
- [20] M Elachouri, M Hajji, M Salem, S Kertit, J Aride, R Coudert, E Essassi, Some Nonionic Surfactants as Inhibitors of the Corrosion of Iron in Acid Chloride Solutions, *Corrosion*, **1996**, 52:103-108.
- [21] AS Algaber, EM El-Nemma, MM Saleh, Effect of octylphenol polyethylene oxide on the corrosion inhibition of steel in 0.5 M H₂SO₄, *Mater Chem Phys*, **2004**, 86: 26-32.
- [22] R Oukhrib, B El Ibrahimy, H Bourzi, K El Mouaden, A Jmiai, S.El Issami, L Bammou, L Bazzi, Quantum chemical calculations and corrosion inhibition efficiency of biopolymer "chitosan" on copper surface in 3%NaCl, *JMES*, **2017**, 8 (1): 195-208.
- [23] AM Al-Azzawi, KK Hammud, Newly antibacterial / anti-rusting oxadiazoleporomellitic di-imids of carbon steel / hydrochloric acid interface: Temkin isother model, *IJRPC*, **2016**, 6(3): 391-402.
- [24] L El Ouasif, I. Merimi, H Zarrok, M El ghou, R Achour, M Guenbour, H Oudda, F El-Hajjaji, B Hammouti, 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.
- [25] UM Sani, U Usman, Electrochemical Corrosion Inhibition of Mild Steel in Hydrochloric Acid Medium Using the Antidiabetic Drug Janumet as Drug, *CInternational Journal of Novel Research in Physics Chemistry & Mathematics*, **2016**, 3(3): 30-37.
- [26] AM Kolo, UM Sani, U Kutama, U Usman, Adsorption and Inhibitive Properties of Januvia for the Corrosion of Zn in 0.1 M HCl, *The Pharmaceutical and Chemical Journal*, **2016**, 3(1):109-119.
- [27] PO Ameh, UM Sani, Cefuroxime Axetil: A Commercially Available Pro-Drug as Corrosion Drug for Aluminum in Hydrochloric Acid Solution, *Journal of Heterocyclics*, **2015**, 1(1): 2-6.
- [28] HI Al-Shafey, RS Abdel Hameed, FA Ali, AS Aboul-Magd, M Salah, Effect of Expired Drugs as Corrosion Drugs for Carbon Steel in 1M HCL Solution, *Int J Pharm Sci Rev Res.*, **2014** 27(1):146-152.
- [29] R Kushwah, RK Pathak, Inhibition of Mild Steel Corrosion in 0.5 M Sulphuric Acid Solution by Aspirin Drug, *International Journal of Emerging Technology and Advanced Engineering*, **2014**, 4(7): 880-884.
- [30] AS Fouda, MN EL-Haddad, YM Abdallah, Septazole: Antibacterial Drug as a Green Corrosion Drug for Copper in Hydrochloric Acid Solutions, *IJIRSET* **2013**, 2(12):7073-7085.

- [31] SU Ofoegbu, PU Ofoegbu, Corrosion inhibition of mild steel in 0.1 M hydrochloric acid media by chloroquine diphosphate, *ARPN Journal of Engineering and Applied Sciences*, **2012**, 7 (3):272-276.
- [32] M. Saeedi, MR Rafati, KM Semnani, AY Rostam, HR Kelidari, Evaluation of effect of tween 80 on characteristics of Cialis 0.1% suspension, *Mazums-pbr*, **2015**, 1(2):35-43.
- [33] GN Mu, TP Zhao, M Liu, T Gu, Effect of Metallic Cations on Corrosion Inhibition of an Anionic Surfactant for Mild Steel, *Corrosion*, **1996**, 52:853-856.
- [34] J Lipkowski, PN Ross, Adsorption of Molecules at Metal Electrodes, VCH, **1992**, New York.
- [35] SLFA Da Costa, SML Agostinho, Electrochemical studies of cu-Al Alloys in Sulphate – SciELO, *Corrosion*, **1989**, 45:472-477.
- [36] J. Aljourani, K. Raeissi, MA Golozar, Benzimidazole and its derivatives as corrosion inhibitors for mild steel in 1M HCl solution, *Corros Sci.*, **2009**, 51:1836-1843.
- [37] H. Amar, A. Tounsi, A.Makayssi, A Derja, J Benzakour, Outzourhit, A Corrosion inhibition of Armco iron by 2-mercaptobenzimidazole in sodium chloride 3% media, *Corros Sci.*, **2007**, 49:2936-2945.
- [38] MA Migahed, EMS Azzam, SMI Morsy, 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.
- [39] S Bllglc, N Caliskan, An investigation of some Schiff bases as corrosion inhibitors for austenitic chromium-nikel steel in H₂SO₄, *Applied Electro-chemistry*, **2001**, 31:79-83 .
- [40] H. Ashassi-Sorkhabi, N. Ghalebsaz-Jeddi, Inhibition effect of polyethylene glycol on the corrosion of carbon steel in sulphuric acid, *Mater Chem Phys*, **2005**, 92:480-486.
- [41] A. El Maghraby, TY Soror, Efficient surfactant as corrosion inhibitor for carbon steel in hydrochloric acid solutions, *Adv App Scie.*, **2010**, 1:156-168.
- [42] OR Khalifa, SM Abdallah, Corrosion inhibition of some organic compounds on low carbon steel in Hydrochloric acid solution, *Portugaliae Electrochemica Acta*, **2011**, 29:47-56.
- [43] I Al-shafey, MA Abass, AA Hassan, SA Sadeek, Corrosion inhibition of carbon steel in 1M HCl Solution by Schiff base compound obtained from 1,3-Diaminopropane, *IJABC*, **2014**, 3:1004-1015.
- [44] AS Fouda, AM El-Wakeel, K Shalabi, A El-Hossiany, Corrosion inhibition for carbon Steel by Levofloxacin Drug in Acidic Medium, *Elixir Corrosion &Day*, **2015**, 83:33086-33094.
- [45] AS Fouda, AM El- Defrawy, MW El-Sherbeni, Pharmaceutical compounds as save corrosion inhibitors for carbon steel in 1M H₂SO₄ solution, Reprint form the Mansoura, *J Chemistry*, **2012**, 39(2):1-27.
- [46] AS Fouda, AA Al-Sarawy, EE El-Katori, Pyrazolone derivatives as corrosion inhibitors for Mild steel HCl solution, *Desalination*, **2006**, 201:1-13.
- [47] AA Farag, IM Ibrahim, Influence of Nonionic Surfactant on the Carbon Steel Corrosion in Hydrochloric Acid Solution, *IJSR*, **2014**, 3: 1087-1091.
- [48] O. Benalli, L Larabi, M Traisnel, L Gengembra, Y Harek, Electrochemical, theoretical and XPS studies of 2-mercapto-1-methylimidazole adsorption on mild steel in 1 M HClO₄, *Appl Surf Sci.*, **2007**, 253:6130-6139.
- [49] SK Shetty, A Nityananda, Ionic Liquid as an Effective Corrosion inhibitor on 6061Al-15 Vol.PCT.SIC_(p) Composite in 0.1M H₂SO₄ Medium, *An Ecofriendly Approach*, **2015**, 3:41-64.
- [50] E Kus, F.Mansfeld, an evaluation of the Electrochemical Frequency Modulation (EFM) Technique, *Corros Sci.*, **2006**, 48:965-979.
- [51] GA Caignan, SK Metcalf, EM Holt, Thiophene substituted dihydropyridines, *J Chem Cryst*, **2000**, 30:415-422.
- [52] RWJ Bosch Hubrecht, WF Bogaerts, BC Syrett, Electrochemical Frequency Modulation: A New Electrochemical Technique for Online Corrosion Monitoring, *Corros Sci.*, **2001**, 57:60-70.
- [53] AS Fouda, YM Abdallah, D Nabil, Dimethyl pyrimidine Derivative as Corrosion inhibitors for Carbon Steel in Hydrochloric Acid solutions, *IJRSET*, **2014**, 3:12965-12982.

- [54] YY Enriadi, NJ Gunawarman, Corrosion Inhibition Efficiency of mild Steel in Hydrochloric Acid by Adding theobroma Cacao Feel Extract, *BCEs*, **2014**, 14:15-19.
- [55] HO Curkovic, K Marusic, E Stupnisek-Lisac, J Telegdi, Electrochemical and AFM study of Corrosion Inhibition with Respect to Application Method, *Chem Biochem Eng Q*, **2009**, 23(1):61-66.
- [56] SB Pralhibha, P Kotteeswaran, V Bheema Raju, Study on the inhibition of MU steel Corrosion by Cationic Surfactant in HCl Medium, *IOSR Journal of Applied Chemistry (IOSRJAC)*, **2012**, 2:45-53.
- [57] S Muralidharan, KLN Phani, S Pitchumani, S Ravichandran, SKJ Iyer, Electrochemical Probing of Internal vs external species in microporous materials: application to zeolites, *Electrochem Soc.*, **1995**, 142:1478-1486.
- [58] E. Samiento-Bustos, JGG Rodriguez, J Uruchurtu, G Dominguez-Patino, VM Salinas-Bravo, Effect of inorganic inhibitors on the corrosion behavior of 1018 carbon steel in the LiBr + ethylene glycol + H₂O mixture, *Corros Sci.*, **2008**, 50:2296-2303.
- [59] LT Antropov, A correlation between kinetics of corrosion and the mechanism of inhibition by organic compounds, *Corros.Sci.*, **1967**, 7(9): 607-620.

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