Journal for Electrochemistry and Plating Technology

JEPT

Edited by: DGO-Fachausschuss Forschung – Hilden / Germany

Corrosion Inhibition of Carbon Steel in hydrochloric acid medium using Gliclazide drug

The role of Gliclazide as corrosion drugs for CS in 1 M HCl have been studied by using weight loss (WL), Hydrogen evaluation (HE), potentiodynamic polarization (PP), electrochemical impedance spectroscopy (EIS) and Electrochemical frequency modulation (EFM) techniques. Weight loss (WL) studied at various temperatures between (25 – 45°C) but Hydrogen evaluation (HE), Open circuit potential (E_{OCP}) and all electrochemical studied at 25°C and seen that the gliclazide studied are mixed type drug. The effect of temperature on corrosion inhibition, the activation and the thermodynamic of adsorption parameters were determinate. Electrochemical impedance was utilizing to examine the inhibition of corrosion and the mechanism. The existence of...

Received: 2017-10-14
Received in revised form: 2017-11-22
Accepted: 2017-11-22

Keywords:
Adsorption, inhibition, SEM–EDX, AFM, CS, HCl

Authors:
A. S Fouda,
G. Y. El-Ewady, Adel H. Ali

DOI:
10.12850/ISSN2196-0267.JEPT5871

LEUZE VERLAG
seit 1902

Corrosion Inhibition of Carbon Steel in hydrochloric acid medium using Gliclazide drug

A. S. Fouda[1], G. Y. El-Ewady[1] and Adel H. Ali[1,2]

[1]*Department of Chemistry, Faculty of Science, El-Mansoura University, El-Mansoura-35516, Egypt, email:asfouda@hotmail.com, Fax: +2 050 2202271, Tel +2 050 2365730*

[2]*Department of medicinal chemistry, Faculty of medical Science, University of Taiz, Yemen*

Keywords: Adsorption, inhibition, SEM–EDX, AFM, CS, HCl **Paper:** Received: 2017-10-14 / Received in revised form: 2017-11-22 / Accepted: 2017-11-22
DOI: 10.12850/ISSN2196-0267.JEPT5871

The role of Gliclazide as corrosion drugs for CS in 1 M HCl have been studied by using weight loss (WL), Hydrogen evaluation (HE), potentiodynamic polarization (PP), electrochemical impedance spectroscopy (EIS) and Electrochemical frequency modulation (EFM) techniques. Weight loss (WL) studied at various temperatures between (25 – 45°C) but Hydrogen evaluation (HE), Open circuit potential (E_{OCP}) and all electrochemical studied at 25°C and seen that the gliclazide studied are mixed type drug. The effect of temperature on corrosion inhibition, the activation and the thermodynamic of adsorption parameters were determinate. Electrochemical impedance was utilizing to examine the inhibition of corrosion and the mechanism. The existence of the Gliclazide in the solution rise the charge transfer resistance and reducing the capacitance of the double layer. The adsorption of the Gliclazide on the surface of CS was found to obey with Langmuir adsorption isotherm and discussed the thermodynamic parameters (ΔG^o, ΔH^o and ΔS^o) that were determinate. The morphology of inhibition of Gliclazide on CS surface was analyzed by scanning electron microscope (SEM) technology, energy dispersive X-ray spectroscopy (EDX) and atomic force microscopy (AFM), all examine techniques illustrate the formation of thin film from Gliclazide inhibitor adsorbed on the metal surface.It was found the adsorption process is spontaneous and increases, with increasing of inhibition efficiency..

1. Introduction

Corrosion is a major process that assumes an important role in the economy, safe and especially for metals [1]. The usage of medications is a standout amongst the most strategies for safety versus to erosion particularly in acidic medium [2]. Most well-known acid drugs are organic compounds containing nitrogen (N-heterocyclic), sulfur, long carbon chain or aromatic and oxygen atoms. Among them, drugs have many advantages such as: high molecular size, highly soluble in water, availability, cheap, low toxicity, easy for using and easy production [3-5]. Natural heterocyclic mixes have been utilized for the erosion hindrance of CS [6-11], copper [12], aluminum [13-15], and various metals [16] in various watery medium. Adsorption of the drug molecules on the metal surface facilitates its inhibition [17]. A few medications have been discovered to be great corrosion inhibitors for metals such as: Biopolymer gave 86% IE for Cu in NaCl [18], pyromellitic diimide linked to oxadiazole cycle gave 84.6% IE for CS in HCl [19], 2-mercaptobenzimidazole gave

82% IE for CS in HCl [20], Antidiabetic Drug Janumet gave 88.7% IE for MS in HCl [21], Januvia gave 79.5% IE for Zn in HCl[22], Cefuroxime Axetil gave 89.9% IE for Al in HCl [23], Phenytoin sodium gave 79% for CS in HCl [24], Aspirin gave71% IE for MS in H2SO4 [25], Septazole gave 84.8% IE for Cu in HCl [26] and Chloroquine diphosphate gave 80% IE for MS in HCl [27].

Numerous authors for the most part concur that medications are drugs that can compete favorably with green inhibition of corrosion and that most medications can be synthesis from natural products. The select of some medication for drug of corrosion is taking in the following: 1) drug molecules contain oxygen, sulphur and nitrogen as active sites, 2) it is reportedly environmentally friendly furthermore vital in organic responses and 3) drugs can be easily produced and purified [28]. In recently years the drug's uses as corrosion drugs for various metals result to their nontoxic nature [29]. The investigation of the relations between the adsorption and consumption hindrance is of awesome important. Heterocyclic mixes have demonstrated more hindrance effectiveness for CS in both HCl [30] and H_2SO_4 [31] arrangements.

2. Experimental detail

2.1. Carbon steel sample (CS)

The composition of CS sample is recorded in the (*Tab. 1*):

Constituent	C	Mn	P	Si	Iron
Composition %	0.2	0.6	0.04	0.003	Rest

Tab. 1: Metal composition of the CS (weight %)

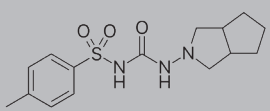
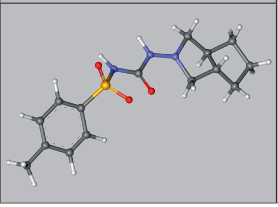
2.2. Chemicals

2.2.1. Drug

Gliclazide drug is used as an inhibitor which describing in (*Tab. 2*). It has been investigated purchased from Sandozinc and Pfizer inc. companies.

2.2.2. Solutions

The forceful arrangements, 1M HCl was set up by weakening of logical review (%37) HCl with distil water. The measurements scope of doses of the medication which utilized in the vicinity of or between (50 and 300 ppm).

Drug	Structure	IUPAC Name	Molecular weight	Active center	Chemical formula
Gliclazide	 Gliclazide 	Hexahydrocyclopenta[c] pyrrol-2(1H)-ylcarbamoyl)-4-methylbenzenesulfonamide	323.412 g/ mol	3O 3N S	$C_{15}H_{21}N_3O_3S$

Tab. 2: The Component and molecular structure of the investigated drug

2.3. Corrosion techniques

2.3.1. The (WL) technique

Collections data of the (WL) technique were taken by utilizing square coins samples. The area of surface is (2 cm x 2 cm) x 2 which exposed to the corrosive medium that used. The specimen coin polisher by SiC papers for different sizes (400, 600, 800, 1000 and 1200), clean with acetone, then clean with bi-distilled water and finally dried by filter paper. The (WL) data were achieves in a 100 ml glass beaker which put it in a thermostat water bath. The specimen coins were submersion in the investigate solution without and with different doses of the tested compound.

All test solutions are opened to air. Through 180 minutes, the specimens were taken out, washed, dried, and weighed accurately per half an hour. The mean (WL) for seven square CS coin samples will be obtained.

The degree of coverage (θ) and the (% IE) of Gliclazide inhibitor for the oxidation of CS were determinate as follows [32]:

$$\%\,IE = \theta \times 100 = \left[1 - \frac{W}{W^o}\right] \times 100 \qquad [1]$$

Where, Wº and W are (WL), in nonexistence and existence the different concentration of the investigate drug compound respectively.

2.3.2. Gasometric measurements

Measurements of hydrogen evolutions were estimation at 25ºC, and the hydrogen volume developed every 15 minutes, (Θ) and the (% IE) were determinate by (3) and (4).

$$V = K\,t \qquad [2]$$

Where, V is the volume of hydrogen in cm^3, K is rate constant and t is time in minute.

$$\Theta = 1 - K/K^o \qquad [3]$$

Where, K^o and K are the rate constant of corrosion in nonexistence and existence drug, which determinate by plotting V vs. t and K value is the slope.

$$\%\,IE = \Theta \times 100 \qquad [4]$$

2.3.3. Potentiodynamic polarization technique

The polarization cell comprise of three poles are (SCE) terminal that coupled to the fine Luggin hairlike as the reference pole, platinum counter pole and working anode pole. The working terminal is a square cut from CS sheet settled by epoxy pitch so that the level surface zone was 1.0 cm^2. The working electrode was polisher with SiC papers grit 1200 in size. The measurements were taken after the electrodes submersion in corrosive medium at natural potential for 10 minutes until reach the steady state. The (E_{ocp}) technique was started from - 533 to – 475.5 mV. All coin samples were achieves in new prepared solutions at 25ºC and data were always worked again to check the validity results. The (θ) and the (% IE) were determinate by the relation (5) [33]:

$$\%\,IE = \theta \times 100 = \left[1 - \frac{i_{corr(inh)}}{i_{corr(free)}}\right] \times 100 \qquad [5]$$

Where, $i_{corr(free)}$ and $i_{corr(inh)}$ are the current densities of corrosion in the nonexistence and existence of drug, respectively.

2.3.4. Electrochemical Impedance Spectroscopy (EIS) technique

They got distances or diameters across of the capacitive circles increment in nearness of medi-

cation, and are demonstrative of the capacitive of the degree of inhibits of erosion process, in spite of the decline or reduced of the limit of twofold layer (C_{dl}) which is characterized as:

$$C_{dl} = \frac{1}{(2\pi f_{max} R_p)} \quad [6]$$

Where, f_{max} is the maximum frequency.

The (%IE) and the (θ) given from the (EIS) data were determinate by the relation:

$$\%\, IE = \theta \times 100 = \left[1 - \frac{R_p^o}{R_p}\right] \times 100 \quad [7]$$

Where, R^o_p and R_p are the resistance of charge transfer in the nonexistence and existence of drug, sequence.

2.3.5. Electrochemical Frequency Modulation (EFM) technique

The measurements of (EFM) were achieved by implementation potential concerned signal with abundance 10 mV with two sine waves of 2 and 5 Hz. The frequencies that choice are 2 and 5Hz depend on three arguments [34]. The corrosion current density (i_{corr}) was determinate from the two larger peaks and the Tafel slopes (β_c and β_a) and the causality factors CF_2 and CF_3 [35]. The ($\%IE_{EFM}$) was determinate by applied the follows equation:

$$\%\, IE_{EFM} = \left[1 - \frac{i_{corr}}{i^o_{corr}}\right] \times 100 \quad [8]$$

Where, i^o_{corr} and i_{corr} are corrosion current densities in the nonexistence and existence of drug, respectively.

2.3.6. Surface Examinations

The CS coins used for analysis of morphology surface were prepared in 1M HCl acid (blank) and with 300 ppm of Gliclazide at 25°C for 24 hours after polisher mechanically by utilizing various emery papers up to 1000 and 1500 grit size. Then, after this submersion time, the coin samples were clean carefully by bi-distilled water, gently dried and achieves the coin samples examined by using scanning electron microscope (SEM), (EDX) and (AFM).

3. Results and discussion

3.1. (WL) measurement

The (WL) of CS in mg cm^{-2} relative to the surface area at different time periods in the nonexistence and existence of various doses (50 ppm -300 ppm) of the Gliclazide were determination. The obtained curve in the presence of various doses of drugs drown below that of free acid as seen in *Figure 1*. The (% IE) are recorded in (*Tab. 3*). In all state, the (% IE) of the drug increases with increasing doses of drug but the rate of corrosion were decreasing. These data indicated that, the Gliclazide as drugs under testing are good efficiency for CS oxidation in HCl medium.

Inhibitor	Conc. Ppm	k_{corr}x10^{-3} mg. cm^{-2} .min^{-1}	(% IE)
Blank	---	16.25	----
Gliclazide	50	4.17	74.4
	100	3.75	76.9
	150	3.33	79.5
	200	2.92	82.1
	250	2.50	84.6
	300	2.08	87.2

Tab. 3: The (% IE) variation of Gliclazide with various doses at 25°C from (WL) data at 120 minutes submersion in 1 M HCl medium

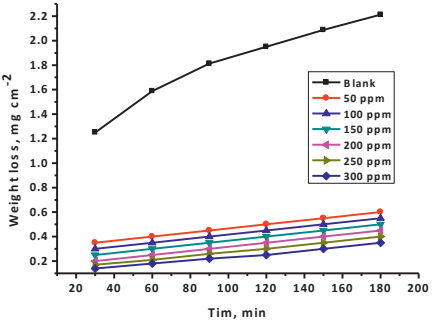


Fig. 1: The bends lines or curves of (WL)- time for the oxidation of CS in the nonexistence and existence of various dosages of gliclazide at 25°C

3.1.1. Effect of temperature

Using Arrhenius equation to study the influence of temperature and rate constant (k_{corr}) to determination of activation energy:

$$\log k_{corr} = A - \left[\frac{E_a}{2.303\,RT}\right] \qquad [9]$$

Where, R is the general gas constant, E_a is the activation energy, T is the (K°) and A is a Arrhenius pre-exponential constant based on electrolyte and the nature of metal. When plotting the log $k_{corr.}$ against (1/T) for CS in 1 M HCl in the nonexistence and existence of various doses of Gliclazide are seen in diagram in *Figure 2*. Gives straight lines that have slope ($-E_a/2.303R$) and the values of E_a were determinate and recorded in (*Tab. 4*). It is obvious that the drug behavior has the same of action mechanism. The activation energy (E_a) increases with the adding of various doses of drug, lead to, the increased of the energy barrier of the oxidation reaction and controlled the whole process by surface reaction, since the activation energy over 20 kJ mol^{-1} [36].

The entropy and enthalpy of activation (ΔS^*, ΔH^*) are determinate from the theory of transition theory by applied the follows relation [37].

$$k_{corr} = \left[\frac{RT}{Nh}\right] \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{\Delta H^*}{RT}\right) \qquad [10]$$

Where, N is Avogadro's number h is Plank's constant. Draw log ($k_{corr.}$/T) vs. (1/T) also gave straight lines as seen in *Figure 3*, for CS that oxidation in 1M HCl in the nonexistence and existence of various doses of Gliclazide. The ($-\Delta H^*/2.303R$) are the slopes of these lines and the [log [RT/Nh] + ($\Delta S^*/2.303R$)] is intercept, that the values of (ΔH^*) and (ΔS^*) were determinate and recorded in (*Tab. 4*). From these data, it is obvious that

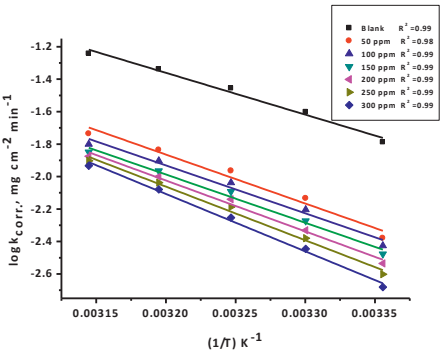


Fig. 2: Arrhenius draw (log k against 1/T) for corrosion of CS in 1M HCl in the nonexistence and existence of various doses measurements of Gliclazide

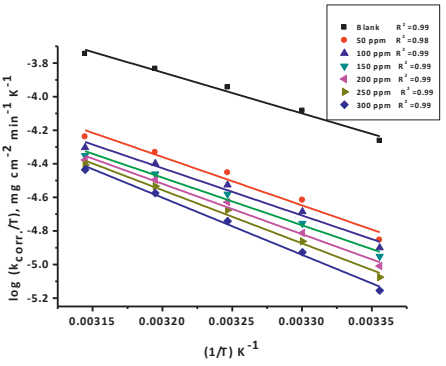


Fig. 3: Draw of (log$k_{corr.}$ / T) vs. (1/ T) for corrosion of CS in 1 M HCl in the nonexistence and existence of various doses measurements of Gliclazide at 25°C

the available of the test compound rising the values of (E_a) and follow reducing the rate of corrosion of the CS. From these data lead to the lest compound behavior as an inhibitor as a result the increasing E_a of CS oxidation by transfer of charge for their adsorption on the CS surface and making thin film barrier. The values of ΔH^* reflects the strong adsorption of Gliclazide compound on CS surface. The estimations of ΔS^* in nonexistence and existence of the investigation compound is negative and substantial esteem values, this prompt the rate-deciding of initiated complex represents to an collection step, instead of separation step, implying that a reductions in irregular happens and foreword from the enacted or activated complex of the reactants and put the actuated particles in more request state than that at the underlying or initial state [38].

Conc. Ppm	Thermodynamic parameters		
	E^*_a kJ. mol^{-1}	ΔH^* kJ. mol^{-1}	$-\Delta S^*$ J. mol^{-1} . K^{-1}
Blank	42.3	40.4	142.2
50	46.8	44.9	137.2
100	47.7	45.8	135.8
150	49.5	47.8	130.6
200	53.3	51.6	119.1
250	55.9	54.3	111.0
300	60.6	59.0	96.9

Tab. 4: Thermodynamic variables for the dissolution of CS in 1 M HCl in the nonexistence and existence of varied doses measurements of investigated drug

3.1.2. Adsorption isotherm

Assuming the inhibition of corrosion due to the adsorption of Gliclazide, and the values of (θ) for various doses of drug in 1 M HCl was determinate from (WL) data utilizing the follows relation:

$$\theta = \left[\frac{weight\ loss_{(pure)} - weight\ loss_{(inh)}}{weight\ loss_{(pure)}}\right] \quad [11]$$

The surface coverage (θ) increases with increasing the doses of the tested (Gliclazide) drug inhibitor. It's utilized in Langmuir adsorption isotherm that obeyed with experimental data that found fit on it. The mathematical expression of Langmuir is given as following [39].

$$\frac{C}{\theta} = \frac{1}{k_{ads}} + C \quad [12]$$

Where, $k_{ads.}$ is the equilibrium constant of adsorption. Plotting (C/Θ) vs. (C) of Gliclazide at various temperatures is introduced 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 ($1/k_{asd.}$) and slope similar the unity, the adsorption constant being result to the standard free energy of ΔG^o_{ads} adsorption by equation:

$$\Delta G^o_{ads} = -RT ln\,(55.5\,K_{ads}) \quad [13]$$

Where, R is the general gas constant, T is (K°) and 55.5 is the doses of water in M/L. The values of ΔG^o_{ads} at all studied temperatures which determinate by above equation (13) and recorded in

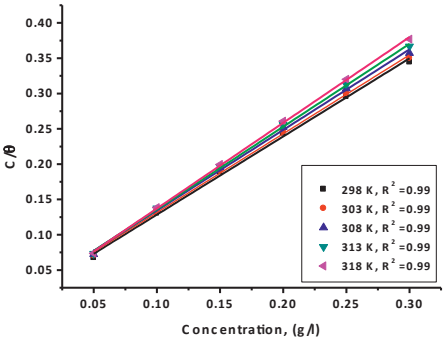


Fig. 4: Plotted the Langmuir adsorption isotherm as (log C) against (C/θ) of the tested drug for oxidation of CS in 1 M HCl solution from (WL) technique at various temperatures.

(*Tab. 5*). The heat of adsorption ($\Delta H^{o}_{ads.}$) was determinate according to the Van't Hoff relation [40].

$$\log k_{ads} = \left(\frac{-\Delta H^{*}_{ads}}{2.303RT}\right) + constant \quad [14]$$

Plotting ($\log k_{ads}$) versus (1/T) give straight line that seen in *Figure 5*, the straight line gives slope equal ($\Delta H^{o}_{ads.}$/2.303R), from this slope, the ΔH^{o}_{ads} were determinate and listing in (*Tab. 5*). Then in accordance with the basic equation (10):

$$\Delta G^{o}_{ads} = \Delta H^{o}_{ads.} - T\Delta S^{o}_{ads} \quad [15]$$

From introducing the values of ΔG^{o}_{ads} and $\Delta H^{o}_{ads.}$, the ΔS^{o}_{ads} was determinate at all studied temperatures by the above equation (15). All thermodynamic adsorption parameters for Gliclazide drug on CS from 1M HCl solution can be concluded that:

Temp. °C u	K_{ads} M^{-1}	$-\Delta G^{o}_{ads}$ kJ. mol^{-1}	ΔH^{o}_{ads} kJ. mol^{-1}	ΔS^{o}_{ads} J. mol^{-1}. K^{-1}
25	55.7	19.9		117.2
30	50.3	19.9		115.5
35	49.0	20.3	15	114.5
40	53.8	20.8		114.5
45	62.9	21.6		115.1

Tab. 5: The (K_{ads}) and free energy (ΔG^{*}_{ads}) for the adsorption of Gliclazide on CS in 1 M HCl from (WL) technique at various temperatures

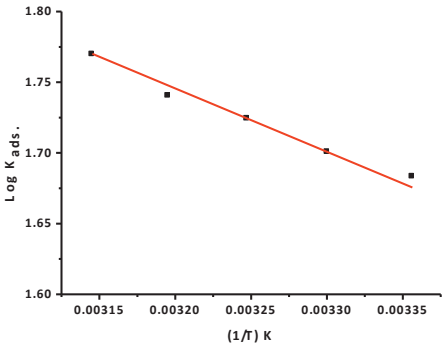


Fig. 5: ($\log k_{ads.}$) vs. (1/T) for the oxidation of CS in 1M HCl in the existence of Gliclazide at various absolute temperatures

1. The correlation coefficients between (0.99 - 0.98) reflected the experimental data which gives a good curves that exactly for the implementation adsorption isotherm.

2. $K_{ads.}$ values increases with increasing temperatures from 30 to 45°C except at 25°C.

3. The negative values of ΔG^{o}_{ads} reflected that the adsorption of gliclazide on CS surface in 1 M HCl medium is spontaneous process.

4. ΔG^{o}_{ads} slightly increases (becomes less negative) with increasing temperatures which indicated that the occurrence of endothermic process and the adsorption was unfavorable with increasing temperature of reaction due to decreasing the electrostatic attraction of the drug desorption with the surface of CS [41].

5. The ΔG^{o}_{ads} values are around -20 kJ mol^{-1} or less lead to the electrostatic attraction between positive charged of metal surface and the negative charge of organic molecules in the bulk of the medium i.e. physical adsorption.

6. The positive sign of ΔH^{o}_{ads} refer to the adsorption of drug compound is an endothermic process, lead to the physical adsorption. The unshared electron pairs in investigate molecule may attractive with positive center on the surface of CS by electrostatic attraction to provide a protective film prevent corrosion process [42].

7. The ΔS^{o}_{ads} values, in the existence of the investigate drug are positive and large that is

accompanied with endothermic adsorption process [43].

3.2. Hydrogen Evaluation (HE)

All information drowns from the volume of hydrogen which produces at versus time, for 50 – 300 ppm of Gliclazide focuses and exhibited in *Figure 6*. The slope of line evaluated the rate of corrosion. The great straight lines show the insoluble film on the metal surface. The certain of the rate of corrosion acquired from hydrogen evaluation individually at versus concentration are recorded in (*Tab. 6*). As shown, the rate of corrosion reduced with increasing of Gliclazide concentration, appearing diminishes conduct for the metal disintegration. This result is normal on the grounds that with increasing drug, both acidity and Cl^- ion focus are lessening. As indicated by chemical equation (11) pointed out that Fe dissociation in acid arrangements relies on hydrogen ion more than the chloride ion [44]. H^+ advancement and mass misfortune is delivered by the same response:

$$Fe_{(S)} + 2H^+ = Fe^+_2 + H_{2\,(g)} \qquad [16]$$

Conc. ppm	k_{corr} ml cm^{-2} min^{-1}	ϴ	% IE
Blank	0.158	----	----
50	0.059	0.627	62.7
100	0.055	0.652	65.2
150	0.052	0.671	67.1
200	0.048	0.696	69.6
250	0.045	0.715	71.5
300	0.041	0.741	74.1

Tab. 6: The rate of corrosion for metal at presence different concentration of Gliclazide drug

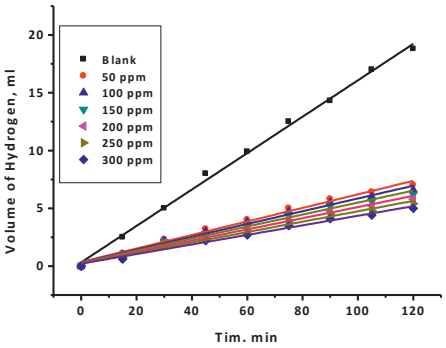


Fig. 6: Hydrogen volume produced versus time arrangements with distinctive centralization of drug at 25°C

3.3. Open circuit potential (E_{OCP})

From the *Figure 7* and (*Tab. 7*) is shown several interesting points:

1. The E_{OPC} in the blank solution is beginning from -533 mV then shifted anodically and reached the steady state after 300 S indicating that the initial dissolution process and formation oxide film on the surface of the metal.

2. The E_{OCP} is started in the existence of Gliclazide, at less negatively potential compared with that in the nonexistence of the drug and then shifted anodically that starting from 500.8, 495.3, 487.2, 479.4, 476.2 and 475.5 according to the increasing the concentration 50, 100, 150, 200, 250 and 300 respectively. The steady state is attained rapidly, with increasing the doses of the drug comparing with the blank, then the shift in the potential of E_{OCP} increasing in the active direction pointing and the drug might certain act mainly as an anodic inhibitor [45]. However, from *Figure 7*, the shifts in E_{OCP} on add Gliclazide inhibitor is 57.5 mV revealing that the existence drug acts as anodically drug.

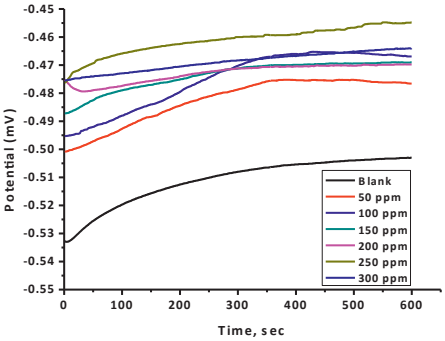


Fig. 7: The curves illustrated the of open circuit potential (E_{OCP}) for CS that submersion in 1M HCl in the nonexistence and existence of Gliclazide drug at 25°C

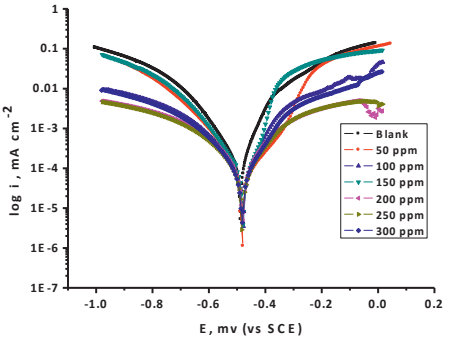


Fig. 8: The (PP) bend lines or curves for the oxidation of CS in 1 M HCl in the nonexistence and existence of varied doses of Gliclazide at 25°C

Conc.(ppm)	$-E_{Min}$ (mV)	$-E_{Max}$ (mV)
Blank	533	502
50	501	475
100	495	465
150	487	469
200	479	470
250	476.2	454.8
300	475.5	469

Tab. 7: Open circuit potential of the CS in nonexistence and in existence of Gliclazide drug at 25°C.

3.4. Potentiodynamic polarization (PP)

Anodic and cathodic polarizations were carried out potentiodynamic in 1 M HCl medium in the nonexistence and existence of different doses of Gliclazide at 25°C. The results are drowning in *Figure 8*. The obtained values of potentiodynamic polarization parameters are recorded in (*Tab. 8*). The cathodic and anodic bend lines or curves are acquired by Tafel-sort conduct. The type of the bend lines or curves are fundamentally the same and closed to gather, which lead to the mechanisms of CS oxidation and hydrogen reduction apparently remain in the existence Gliclazide drug. Both the cathodic and anodic current densities reduced when addition different concentration of Gliclazide and made chiefly parallel uprooting the more positive and negative values individually. This mean the existence of Gliclazide in medium inhibit both the anodic dissolution processes and the hydrogen evolution with overall shift of E_{corr} to more negative values.

The outcomes likewise are demonstrated that the anodic and the cathodic (β_a and β_c) marginally or slightly changed with expanding the dosages of the tested Gliclazide compound. This lead to there is no change of the mechanism of restraint in nearness and nonattendance of medications. In the fact the values of (β_c) are slightly more than the values of (β_a) refer to the cathodic action of the drug. It is obvious that an action of mixed drug control over the electrochemical semi-reactions. Clearly an activity of blended medication control over the electrochemical semi-responses. This implies the Gliclazide is blended sort medicate, yet the cathode is more specially spellbound than the anode. The higher estimations of Tafel incline line or slope can be identified with the surface motor or kinetic of surface process instead of the dispersion controlled process [46]. The cathodic inclines

Conc. ppm	$I_{corr.}$ mA cm^{-2}	$-E_{corr.}$ mV(SCE)	β_a mV dec^{-1}	β_c mV dec^{-1}	C. R. mpy	Θ	% IE
0.0	147	480	166	208	67.3	----	----
50	63.3	472	106	116	28.9	0.581	58.1
100	57.9	474	83.3	105	26.5	0.617	61.7
150	55.8	478	56.5	96.5	25.5	0.631	63.1
200	49.4	459	65.2	128	22.6	0.673	67.3
250	39.7	482	86.6	8.9	18.2	0.737	73.7
300	20	481	55.4	56.7	9.2	0.868	86.8

Tab. 8: The influence of concentration of Gliclazide on the (E_{corr}), (i_{corr}), Tafel inclines (β_a& β_c), (% IE) and (θ) of CS in 1 M HCl at 25°C

or slopes are gotten from the (PP) estimations demonstrate that the hydrogen advancement response was actuation controlled [47] and the expansion of the Gliclazide medicate did not alter the system of this procedure or mechanism. This outcome creates the impression that the inhibit method of the Gliclazide was utilized by straightforward follows of the surface by adsorption prepare.

3.5. Electrochemical Impedance Spectroscopy (EIS)

The (EIS) charts (Nyquist and bode) at frequencies extending from 0.1 Hz to 105 Hz with 10 mV plenitude motion at OCP for CS in 1 M HCl in the nonexistence and existence of varied measurements of Gliclazide doses are acquired. The identical circuit that depict for (CS) and electrolyte are found in *Figure 9*, where Rs, and Rp allude to arrangement resistance and charge exchange resistance, separately. EIS parameters and (% IE) were determinate and recorded in (*Tab. 9*).

The obtained Nyquist and bode plotting for Gliclazide is seen in *Figure 10*. Nyquist spectrum is characterized by a single full half-circle. These seen that the corrosion of CS is controlled by a charge exchange prepare [48]. The widths or diameter of the capacitance circle got that increments within the sight of Gliclazide were demonstrated that the increases or ascents the (% IE) of the consumption procedure [49].

Conc. ppm	R_p Ω cm^2	C_{dl} µF cm^2	Θ	% IE
0.0	64.7	594.2	-----	-----
50	231.2	50.82	0.720	72.0
100	255.6	43.49	0.747	74.7
150	257.9	30.2	0.749	74.9
200	281.0	29.39	0.769	76.9
250	301.1	23.47	0.785	78.5
300	328.0	20.4	0.803	80.3

Tab. 9: The variables that obtained by EIS method for CS in 1M HCl without and with varied doses of Gliclazide at 25 °C

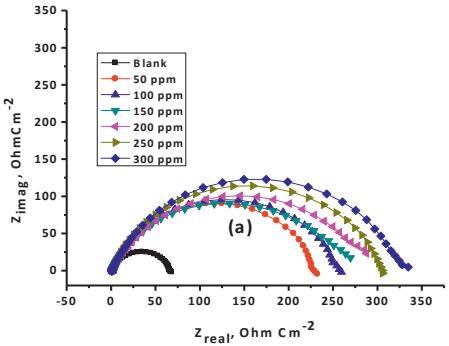


Fig. 9: The model of electrical equivalent circuit that used for the experimental results

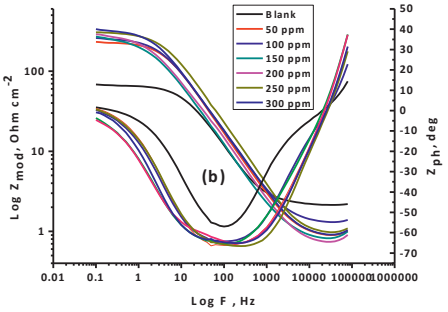
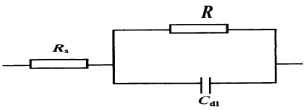


Fig. 10: The Nyquist (a) and Bode (b) curves for oxidation of CS in 1 M HCl in the nonexistence and existence of various doses of Gliclazide at 25 °C

From the results of (EIS) that obtained R_p rises and C_{dl} reducing with increasing of Gliclazide drug doses. The ascent or rise in Rp values improve the increases or ascents of the %IE because of the progressive substituent of water particles by the adsorption of the medication particles on the metal surface by an adherence film form on the metal surface. The formation film on the metal surface reduced the double layer thickness. Also, the decreasing of C_{dl} with rises the drug doses as result from reduce in local dielectric constant which indicating that, the drug was adsorbed on anodic sites and covered the cathodic sites on the surface of the metal [50].



3.6. Electrochemical Frequency Modulation technique (EFM)

The (EFM) technique is defined as a nondestructive corrosion measurement and a very good technique for determination corrosion information's [51].

The CF-2 and CF-3 are determinate or estimate from the range of the present spectrum of the reactions and the quality of the (EFM) is the causality components which fill in as an interior keep an eye on the good of EFM estimation. The EFM Inter-modulation spectrums of CS in 1 M HCl acid medium and in 1M HCl with containing (50 ppm – 300 ppm) of the Gliclazide are seen in Fig. 11. The intermodulation peaks and harmonic are obviously visible and are much larger than the background noise. The two high crests, with plenitude of about (<100 µA), are the reaction to the 100 mHz (2 and 5 Hz) excitation frequencies. It is essential to note that between the tops of crests there is almost no present reaction or current response (<100 µA). The information of (EFM) was dealt with by using two different models: the "activation" model demonstrates and finishes or completes dissemination control of the cathodic response. For the latter, a set of the solution of three nonlinear equations, suppose that the corrosion potential does not change as a result of the polarization of the working electrode [52]. The highest crests or pinnacles were usage to estimate (j_{corr}), the causality variables (CF-2 and CF-3) and Tafel inclines or slopes (βa and βc). At the same time, the electrochemical variables were assurance by Gamry EFM140 programming, and recorded in (*Tab. 10*). The data, obviously show that, add of investigated drug compound at a given doses to the acidic medium reducing the corrosion current density, lead to the Gliclazide frustrate or inhibit the corrosion of CS in 1 M HCl through adsorption. The causality components got under various trial conditions are approach equivalent to the hypothetical qualities (2 and 3) demonstrating that the estimation information are genuine and of good quality [53]. The $(\%\,IE)_{EFM}$ are increased by rises the doses of Gliclazide which determinate and recorded in (*Tab. 10*).

3.7. Scanning Electron Microscopy (SEM)

Figure 12, represents the micrograph obtained for CS specimens in nonexistence and existence

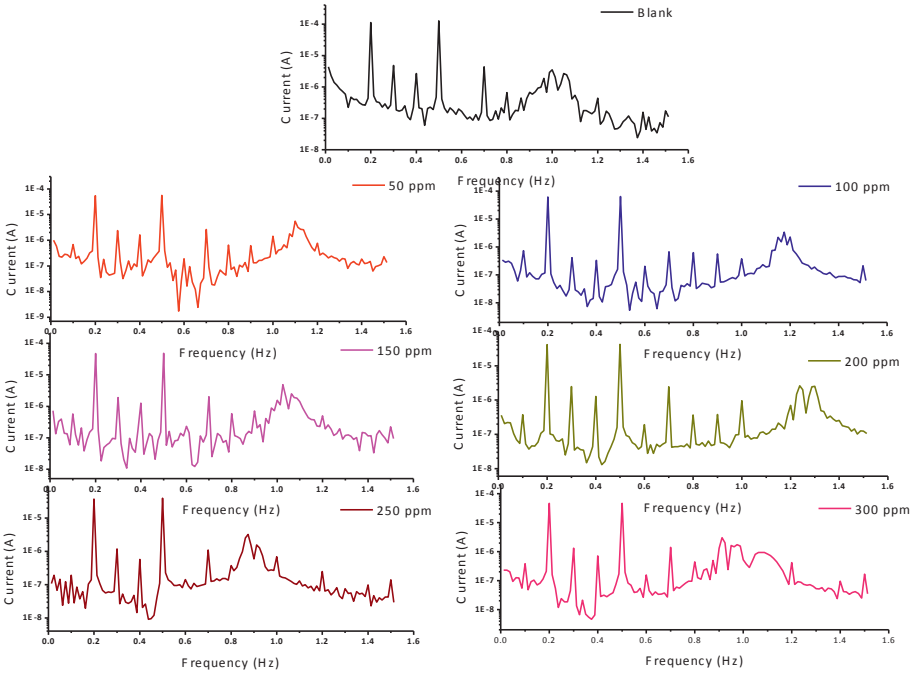


Fig. 11: EFM for meal in 1M HCl unlucky deficiency and vicinity of distinctive convergences of Gliclazide

Comp.	Conc. Ppm	$I_{corr.}$ μAcm^{-2}	$B_a \times 10^{-3}$ $mVdec^{-1}$	$B_c \times 10^{-3}$ $mVdec^{-1}$	CF (2)	CF (3)	CR Mpy	Θ	%IE
Blank	0.0	350.3	156.4	247.9	1.5	2.9	160.1	----	----
Gliclazide	50	89.9	92.7	125.3	1.6	3.2	41.1	0.743	74.3
	100	85.9	87.0	91.2	1.5	5.1	39.3	0.755	75.5
	150	79.3	94.3	123.0	1.4	2.6	36.3	0.774	77.4
	200	75.5	97.1	148.9	2.2	2.9	34.5	0.785	78.5
	250	72.8	110.6	138.3	1.8	2.5	33.3	0.792	79.2
	300	71.3	91.1	108.8	2.2	4	32.6	0.797	79.7

Tab. 10: EFM kinetic variables calculation from CS that submersion in 1 M HCl without and with various doses of Gliclazide at 25 °C

of 300 ppm of Gliclazide after exposure for 1 day submersion. It is obvious that CS surfaces help and facilitate corrosion attack in the blank sample.

It is significant to worry that when the compound is available in the solution, the morphology of CS surfaces is very unique in relation to the past one and the specimen coin surface was smoother. We noticed the make thin film which is circulated arbitrarily in general surface of the CS This might be thus the adsorption of the Gliclazide on the CS surface and make the inactive film keeping

in mind the end goal to hinder the dynamic site show on the CS surface. The drug molecule interaction with active sites of CS surface, that resulting the reducing in the contact between CS and the corrosive solution and sequentially exhibited excellent inhibition effect [54-55].

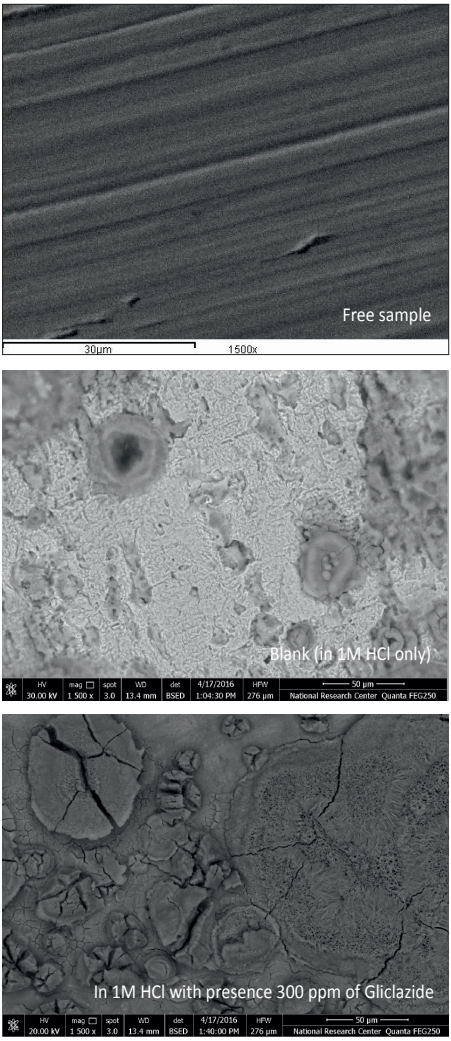


Fig. 12: SEM microstructures for CS in the nonexistence and existence of 300 ppm of Gliclazide after submersion for 1 day

3.8. Energy Dispersion Spectroscopy (EDX)

The EDX spectra were utilized to determine the elements existence on the surface of CS and after 1 day of immersion in acid with optimum concentration of drug. *Figure 13*, award to the EDX examination of CS in 1 M HCl with within the sight of 300 ppm of Gliclazide. The spectrum demonstrates extra lines, showing the existence of C (attributable to the carbon molecules of some Gliclazide). These data shows that the carbon, nitrogen, oxygen and sulfur atoms covered the specimen surface. The EDX analysis indicates that only nitrogen, carbon, oxygen and sulfur were detected, and show that the passivation film contained the chemical formula of Gliclazide drag adsorbed on the surface of CS. It is seen that, the percent weight of adsorb elements N, C, O and S were present in the spectra and recorded in (*Tab. 11*).

(Mass %)	Fe	C	O	N	S	Cl
Pure	98.28	0.78	--	--	--	--
Blank	72.1	9.23	17	--	--	0.35
Gliclazide	61.23	15.3	1.1	21.36	0.09	--

Tab. 11: Surface composition (% weight) of CS after one day of submersion in 1M HCl nonexistence and existence the 300 ppm of Gliclazide

3.9. 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 drugs 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 drug under study. Among the roughness take a role in explanation about the nature of the adsorbed film on the surface [45-46]. *Figure 14*, shows the 3D images as well as eleva-

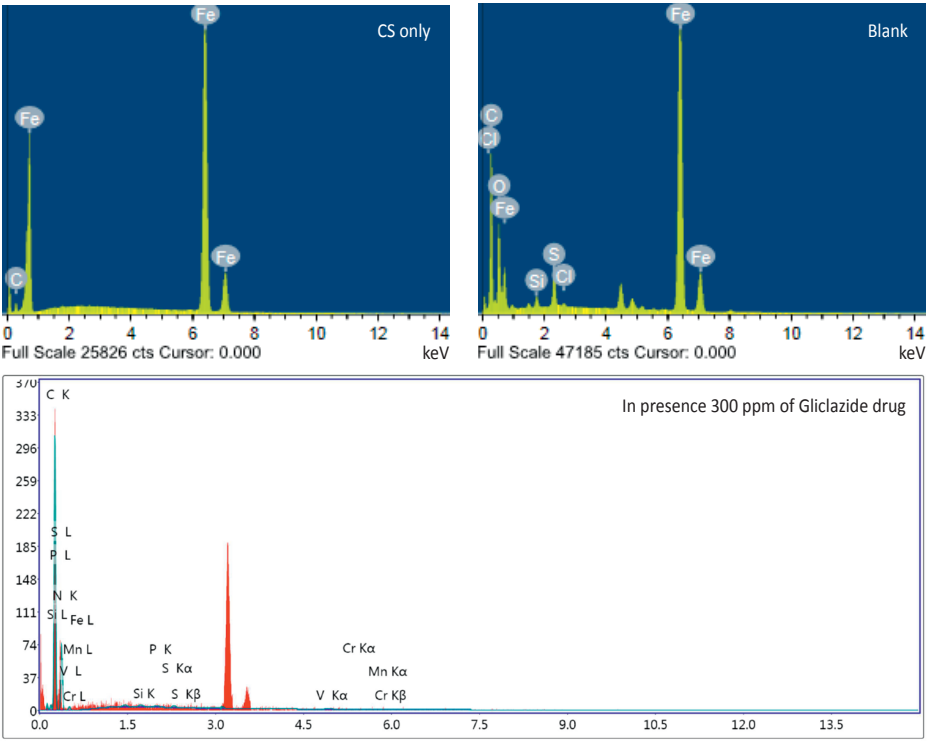


Fig. 13: EDX analysis on CS in the existence and nonexistence of Gliclazide for 1 day submersion.

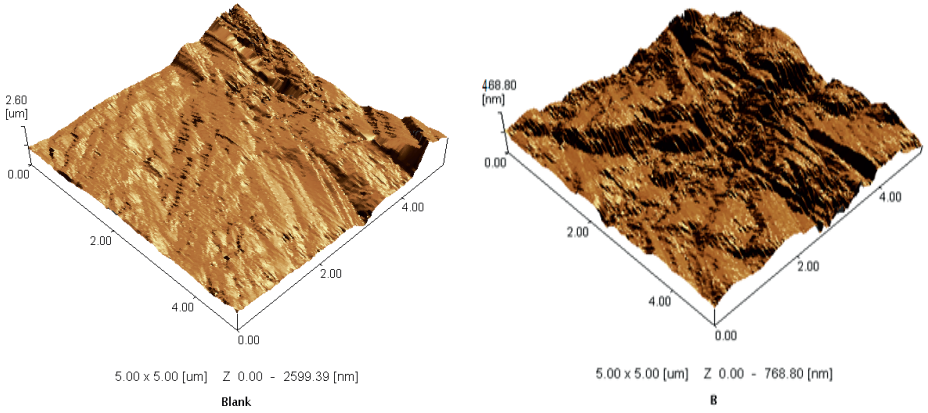


Fig. 14: The 3D of optical images of AFM in absence (a) and presence (b) of Gliclazide drug

tion profiles of polished of CS in absence and present Gliclazide as drug. It observed in *Figure 14*, the surface of CS 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 (2.60 µm) for the blank in acid solution which placed in 1M HCl one dye and analyzed. The observation of the metal surface which immersed in 1M HCl in existence of 300 ppm of Gliclazide drug possess roughness (468.80 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 to the adsorption of drug molecule on metal surface thereby reducing the rate of corrosion.

4. References

[1] Trabanelli G., drugs - an old remedy for a new challenge Corrosion, 1991, 47, 410 - 419.

[2] Singh D.N. and 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. and 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. and 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] Hajjaji N., Ricco I., Srhiri A., Lattes A., Soufiaoui M., Benbachir A., Effect of N-Alkylbetaines on the Corrosion of Iron in 1 M HCl Solution, Corrosion, 1993,49, 326-334.

[7] Elachouri M., Hajji M.S., Salem M., Kertit S., Coudert R., Essassi E.M., Some surfactants in the series of 2-(alkyldimethylammonio) alkanol bromides as drugs of the corrosion of iron in acid chloride solution Corros.Sci., 1995, 37, 381-389.

[8] Luo H., Guan Y.C., Han K.N., Inhibition of mild steel corrosion by sodium dodecyl benzene sulfonate ... and Sodium Oleate in Acidic Solutions, Corrosion, 1998, 54, 619-627.

[9] 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.

[10] 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.

[11] 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.

[12] Villamil R.F.V., Corio P., Rubim J.C., Siliva Agostinho M.L., Effect of sodium dodecylsulfate on copper corrosion in sulfuric acid media in the nonexistence and existence of benzotriazole, J.Electroanal.Chem., 1999, 472 ,112-119.

[13] 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.

[14] 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.

[15] 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.

[16] 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.

[17] Branzoi V., Golgovici F., Branzoi F., Aluminium corrosion in hydrochloric acid solutions and the effect of some organic drugs, Mater.Chem.Phys., 2002, 78, 122-131.

[18] Oukhrib R., El Ibrahimi 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.

[19] Al-Azzawi A. M. and Hammud K. K., Newly antibacterial / anti-rusting oxadiazoleporomellitic di-imids of carbon steel / hydrochloric acid interface: Temkin isother model, IJRPC, 2016, 6(3): 391-402.

[20] El Ouasif L., Merimi I., Zarrok H., El ghoul M., Achour R., Guenbour M., Oudda H., El-Hajjaji F. and 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.

[21] Sani U. M. and Usman U.; Electrochemical Corrosion Inhibition of Mild Steel in Hydrochloric Acid Medium Using the Antidiabetic Drug Janumet as Drug , International Journal of Novel Research in Physics Chemistry & Mathematics, 2016, 3(3): 30-37.

[22] Kolo A.M., Sani U.M., Kutama U. and Usman U.; The Pharmaceutical and Chemical Journal, 2016, 3(1):109-119.

[23] Ameh P. O. and Sani U. M.; Cefuroxime Axetil: A Commercially Available Pro-Drug as Corrosion Drug for Aluminum in Hydrochloric Acid Solution ,Journal of Heterocyclics, 2015, 1(1): 2 – 6.

[24] Al-Shafey H. I., Abdel Hameed R. S., Ali F. A., Aboul-Magd A. S., Salah M.; 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.

[25] Kushwah R. and Pathak R. K.; 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.

[26] Fouda A. S., EL-Haddad M.N. and Abdallah Y.M.; Septazole: Antibacterial Drug as a Green Corrosion Drug for Copper in Hydrochloric Acid Solutions,IJIRSET, 2013, 2 (12): 7073-7085.

[27] Ofoegbu S. U. and Ofoegbu P. U.; 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.

[28] Bentiss Traisnel F., Lagrenee M., The substituted 1,3,4-oxadiazoles: a new class of corrosion drugs of mild steel in acidic media, Corros.Sci., 2000, 42, 127-146.

[29] Christopher M.A.B., Isabel Jenny A.R.G., The electrochemical behaviour and corrosion of aluminium in chloride media. The effect of drug anions, Corros.Sci., 1994, 36, 915-923.

[30] Elachouri M., Hajji M.S., Salem M., Kertit S., Aride J., Coudert R., Essassi E., Some Nonionic Surfactants as Drugs of the Corrosion of Iron in Acid Chloride Solutions, Corrosion, 1996, 52,103-108.

[31] Algaber A.S., El-Nemma E.M., Saleh M.M., Effect of octylphenol polyethylene oxide on the corrosion inhibition of steel in 0.5 M H2SO4, Mater.Chem.Phys., 2004, 86, 26-32.

[32] 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 Sci., 1996, 52, 853-856.

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

[34] Da Costa S. L. F. A. and Agostinho S. M. L., Electrochemical studies of cu-Al Alloys in Sulphate – SciELO, Corrosion, 1989, 45, 472 – 477.

[35] Aljourani J., Raeissi K., Golozar M.A., Benzimidazole and its derivatives as corrosion drugs for mild steel in 1M HCl solution, Corros. Sci., 2009, 51 ,1836-1843.

[36] Amar H., Tounsi A., Makayssi A., Derja A., Benzakour J., Outzourhit A., Corrosion inhibition of Armco iron by 2-mercaptobenzimidazole in sodium chloride 3% media Corros. Sci., 2007, 49, 2936-2945.

[37] Migahed M.A., 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.

[38] Bllglc S., Caliskan N., An investigation of some Schiff bases as corrosion drugs for austenitic chromium-nikel steel in H_2SO_4, Applied Electro-chemistry, 2001, 31, 79-83.

[39] Ashassi-Sorkhabi H., , Ghalebsaz-Jeddi N., Inhibition effect of polyethylene glycol on the corrosion of carbon steel in sulphuric acid , Mater.Chem.Phys., 2005, 92, 480-486

[40] El Maghraby A., Soror T. Y., Efficient surfactant as corrosion drug for carbon steel in hydrochloric acid solutions, Adv. App. Scie., 2010, 1, 156 – 168.

[41] Khalifa O. R., Abdallah S. M., Corrosion inhibition of some organic compounds on low carbon steel in Hydrochloric acid solution, Portugaliae Electrochemica Acta, 2011, 29, 47-56.

[42] Al-shafey I., Abass M. A., Hassan A. A., Sadeek S. A., Corrosion inhibition of carbon steel in 1M HCl Solution by Schiff base compound obtained from 1,3-Diaminopropane, IJABC, 2014, 3, 1004-1015.

[43] Fouda A. S., Gouda M. M., and Abd El-Rahman S. I., Benzaldehyde, 2-Hydroxybenzoyl Hydrazone Derivatives as Drugs of the corrosion of Aluminium in hydrochloric Acid, Chem. Pharm. Bull., 2000, 48 (5), 636- 640.

[44] Fouda A, S., El-Wakeel A. M., Shalabi K., El-Hossiany A., Corrosion inhibition for carbon Steel by Levofloxacin Drug in Acidic Medium, Elixir Corrosion &Day, 2015, 83, 33086-33094.

[45] Hazazi O. A., Fawzy A., Awad M.; Synergistic Effect of Halides on the Corrosion Inhibition of Mild Steel in H2SO4 by a Triazole Derivative: Kinetics and Thermodynamic Studies, Int. J. Electrochem. Sci., 2014, 9, 4086 – 4103.

[46] Fouda A. S., El- Defrawy A. M. and El-Sherbeni M. W., Pharmaceutical compounds as save corrosion drugs for carbon steel in 1M H_2SO_4 solution, Reprint form the Mansoura, J, Chemistry, 2012, 39(2) 1-27.

[47] Fouda A.S., , Al-Sarawy A.A., El-Katori E.E., Pyrazolone derivatives as corrosion drugs for Mild steel HCl solution, Desalination, 2006, 201 ,1-13.

[48] Farag A. A., Ibrahim I. M., Influence of Nonionic Surfactant on the Carbon Steel Corrosion in Hydrochloric Acid Solution, IJSR, 2014, 3, 1087-1091.

[49] Benalli O., Larabi L., Traisnel M., Gengembra L., Harek Y., Electrochemical, theoretical and XPS studies of 2-mercapto-1-methylimidazole adsorption on mild steelin 1 M $HClO_4$, Appl. Surf. Sci., 2007, 253, 6130-6139.

[50] Kshama Shetty S., Nityananda A., Shetty, Ionic Liquid as an Effective Corrosion drug on 6061Al-15 Vol.PCT.$SIC_{(p)}$ Composite in 0.1M H_2SO_4 Medium, An Ecofriendly Approach, 2015, 3, 41-64.

[51] Kus E., Mansfeld F.,an Evalation of the Electrochemical Frequency Modulation (EFM) Technique, Corros. Sci. 2006, 48, 965-979.

[52] Caigman G. A., Metcalf S. K., Holt E. M., Thiophene substituted dihydropyridines, J.Chem. Cryst. 2000, 30, 415-422,

[53] Bosch Hubrecht R.W. J., Bogaerts W.F., B Syrett.C., Electrochemical Frequency Modulation: A New Electrochemical Technique for Online Corrosion Monitoring, Corros. Sci., 2001, 57 ,60-70.

[54] Fouda A. S., Abdallah Y. M., Nabil D., Dimethyl pyrimidine Derivative as Corrosion drugs for Carbon Steel in Hydrochloric Acid solutions, IJIRSET, 2014, 3,12965-12982.

[55] Yelri Y., Enriadi, Jamarun N., Gunawarman, Corrosion Inhibition Efficiency of mild Steel in Hydrochloric Acid by Adding theobroma Cacao Feel Extract, BCES, 2014, 14, 15-19.

[56] Otmocic Curkovic H., Marusic K., Stupnisek-Lisac E., and Telegdi J., Electrchemical and AFM study of Corrosion Iinhibition with Respect to Application Method, Chem. Biochem. Eng. Q. , 2009, 23 (1) 61- 66.

[57] Pralhibha S. B., Kotteeswaran P., Bheema Raju V., Study on the inhibition of MU steel Corrosion by Cationic Surfactant in HCl Medium, IOSR Journal of Applied Chemistry (IOSR-JAC), 2012, 2, 45-53.

Authors

Dr. Adel H. Ali
Department of medicinal chemistry,
Faculty of medical Science,
University of Taiz, Yemen
E-mail: Adelchemst22@Gmail.com
Phone: +201015586443

Prof. Dr. G. Y. El-Ewady
Department of Chemistry, Faculty of Science,
El-Mansoura University
El-Mansoura-35516, Egypt

Prof. Dr. A. S. Fouda
Department of Chemistry, Faculty of Science,
El-Mansoura University
El-Mansoura-35516, Egypt
Email: asfouda@hotmail.com
Phone: +2 050 2365730
Fax: +2 050 2202271

CONTACT:

EUGEN G. LEUZE VERLAG KG
Ralf Schattmaier
Karlstraße 4
88348 Bad Saulgau
Germany

Email: ralf.schattmaier@leuze-verlag.de
Phone: +49 0 7581 4801-12
Fax: +49 0 7581 4801-10