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Electrochemical and surface characterization studies on Azathioprine drug as corrosion inhibitor for carbon steel in HCl Solutions

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ABSTRACT

The hindrance effect of pharmaceutical drug (Azathioprine) on metal corrosion in 2M hydrochloric acid was done by electrochemical (Tafel polarization curves, EFMEIS), and chemical (WL) methods. Polarization plots for compounds how that physical behavior for inhibitor. The temperature effect on inhibition corrosion have explained, the activation parameter was measured. Impedance Electrochemical work showed that the existence of this drug decreases the capacitance double layer(C_{dl}),and increment the resistance of charge transfer (R_{ct}). The drug absorption on metal surface was obeyed Temkin's isotherm. The morphology of surface on metal examples were evaluated using (EDX and SEM) analysis. The mechanism of inhibition process was explained for Azathioprine on the metal surface.

Keywords: C-steel, acid corrosion; Azathioprine drug; EFM; EIS; SEM.

INTRODUCTION

Corrosion is defined as a process act a main role on safety particularly and economics for alloys. Utilized of inhibitor is the greatest technique for hindrance corrosion, for example in acidic solution [1].C-steel an iron alloy utilized in chemical, metallurgical industries, petrochemical. whatever, it readily experience corrosion in different conditions for environmental [2-5].Solutions of acid are utilized in industry, acid cleaning, the biggest application role for acid pickling, oil well acidizing and acid decaling. Due to the common strong of acid solutions, inhibitors study for decrease the attack of corrosive on metallic alloys. Acidic inhibitors well-known as organic compounds contain triple bonds or aromatic ring with O, N, S, P. in recent year the efficiency of inhibition down: O<N<S<P[6-9]. Generally, organic compounds are effective inhibitor on corrosion aqueous solution for many alloys and metals. The lowering on corrosion rate processes of metal was utilized by chemical inhibitors [10-14].Also inhibition corrosion of iron organic has been used by copper [21] aluminum [22-24]heterocyclic compounds [15-20]and other metals [25-26] in varies media. The surface of metal was changes the corrosion- resisting particular of the metal by used the adsorption heterocyclic surfactant compounds [27-28] and explain the connection between the corrosion inhibition and adsorption is the most significant. Heterocyclic compounds are the greatest efficiency for inhibition of iron in H2SO4[29] and HCl [30]. Also, some authors used drugs as green inhibitors for corrosion on alloys and metals[31-39].

In present work, we explore the protection of corrosion by Azathioprine on metal were utilized surface examination, electrochemical and chemical technique. The drugs are utilized due to high solubility in water, safe use, containing electronegative atoms such as O & N and π-electrons in its compound. s

MATERIALS AND METHODS

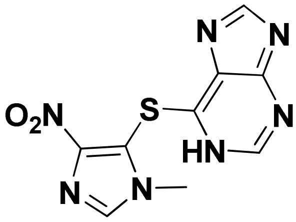
2.1. Composition of Material samples

Table (1). Chemical constituents and weight % of the metal

Constituents	Carbon	Si	Mn	P	Iron
Composition %	0.2	0.003	0.35	0.024	rest

2.2. Inhibitor

The Azathioprine drug has been imported from: International trading office, (Manufactured in India by RPG LIFE SCIENCES LIMITED) and used as received.



Chemical Formula: $C_9H_7N_7O_2S$
Exact Mass: 277.04

2.3. Solutions

2 M HCl was a BDH HCl (37 %) diluted with bidistilled water. The inhibitor concentrations used on experimental were50 to 250 ppm.

2.4. Technique for corrosion calculation

2.4.1. Mass reduction techniques

Square cones of size 2 x 2 x 2cm were utilized, then abraded with emery papers grit sizes (300, 900, 1200, 2000) degreased with acetone. The weight reduction estimations were completed to 100 ml measuring flask dipped in bath water thermostat. The samples were put in the test arrangement with or without drug. Triplicate samples were uncovered for every system and losses of weight were calculated.

The % IE and metal degree coverage (θ) have been measured using the relation[40]:

$$\%IE=\theta x100=[1-(\Delta W_{inh}/\Delta W_{free})]\ x100 \quad (1)$$

Where ΔW_{free} and ΔW_{inh} are the mass losses of C steel / unit area with and withoutinhibitorat specific time.

2.4.2. Electrochemical technique

Estimations of electrochemical was including potentiodynamic polarization, EIS and EFM were performed in 3 electrodes cell at room temperature.

Electrochemical estimations utilizing by instrument Gamry which incorporates a Gamry frame work taking into account ESA400.From the curves of potentiodynamic we calculated%(IE) and (θ) were calculated as:

$$\%\ IE = \theta\ x\ 100 = [(i_{corr} - i_{corr(inh)}) / i_{corr}]\ x\ 100 \qquad (2)$$

Where$i_{corr(inh)}$= the current corrosion density data with drug and i_{corr} without drug, measured by Tafel lines technique. From spectra of impedance (EIS) data measured the surface coverage (θ) and % IE from the following relation:

$$\text{Inhibition efficiency} =[1-(R^{\circ}_{ct}/R_{ct})]\ x100 \qquad (3)$$

R^{o}_{ct}=resistance transfer charge without Azathioprine.

Rct = the resistance charge transfer presence of Azathioprine

EFM technique were utlized frequencies of 2 and 5Hz [20]. High peaks were study to calculateCF2,CF3, the density current of corrosion (i_{corr}), and Tafel slopes (β_c and β_a) [41].

*2.4.3.*Surface Examinations

The specimens of C-steel used for analysis of morphology surface was prepared in 2molarhydrochloric acid (blank) andwith250ppm of Azathioprineat room temperature for 2 days. The performed examinations used microscope electron scanning (JEOL JSM-5500, Japan).

RESULTS AND DISCUSSION

3.1. Weight loss methods

C-steel mass reduction-time plot with the addition of Azathioprine in 2 malar of acid at concentrations of different is shown in Figure (1).Corrosion hindrance is strengthens by the inhibitor concentration which appear in the Table(3).This trend may result formation of a film on its surface[42-43].

Table (3). %IE of Azathioprine drugimmersion in 2 M HCl with concentrations at 120 min

Inhibitor	Conc. ppm	CR mg cm^{-1} min^{-1}	%IE
Blank	2M HCl	0.076	------
Azathioprine	50	0.017	77.26
	100	0.012	83.83
	150	0.009	88.26
	200	0.006	92.05
	250	0.004	94.70

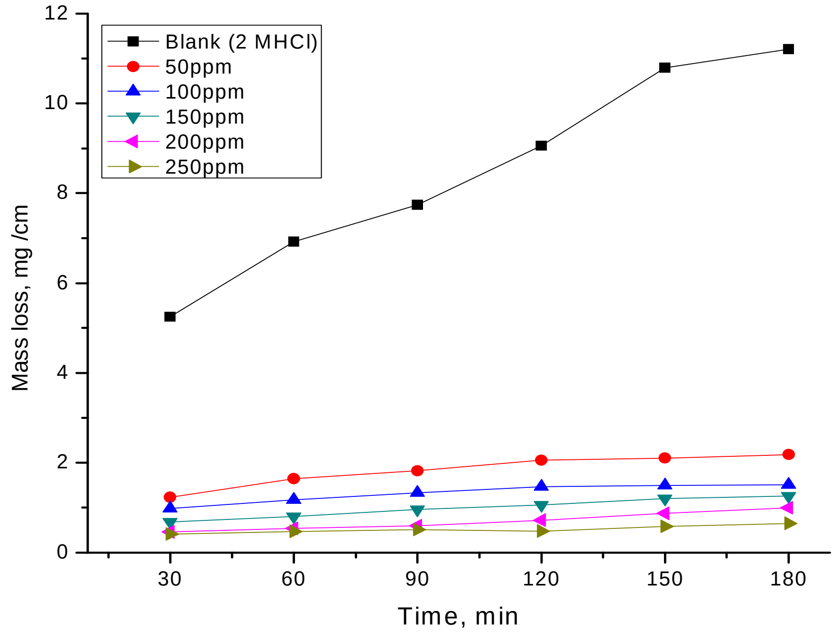


Figure (1).Mass loss and time curves for metal in 2M hydrochloric acidwith concentrations of Azathioprine at 25°C

3.1.1. Adsorption isotherms

The adsorption type of inhibitor on metal are discussed by (i) chemical inhibitor structure (ii) electrolyte type and (iii) the nature of the metal and charge.

The adsorption on the surface of metal may regarded as a representation process adsorption between molecules of water adsorbed on metal surface (H_2O_{ads})and drug in aqueous phase (Org_{aq}) and the [44]:

$$x\,(H2O)ads \;+ Org\,(sol) \;\leftrightarrow\; x\,H2O(sol) \;+ Org(ads) \qquad (4)$$

x = ratio of size =adsorbed number water molecules exchange

The data of Azathioprine has a good fitted by adsorption Temkin isotherm. **Figure(2)** diagram obtains lines straight with unit slope realizing adsorption of Azathioprine on metal surface [45]:

Θ= (1/f) ln K_{ads}C (5)

Where C =inhibitor concentration, θ = surface coverage fractional and K_{ads}=constant equilibrium adsorption obeyed to the adsorption free energy ΔG^o_{ads} as [46]:

$K_{ads} = 1/\ 55.5\ e^{(-\Delta G^o ads/\ RT)}$ (6)

Where constant universal gas equal R and T =absolute temperature.

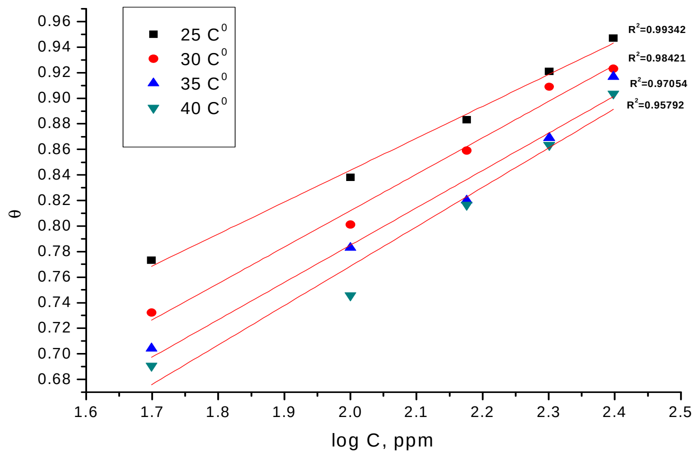


Figure (2).Temkin plotted (log Cof theAzathioprine against Θ)

The data of K_{ads} and $\Delta G\circ_{ads}$for Azathioprine were measured and write in **Table (4)**. The $\Delta G\circ_{ads}$ is large negative which indicate that this drug are strongly adsorbed and ensures that of the adsorption process is spontaneity[47].

Table (4).Free energy adsorption and Equilibrium constant for Azathioprineon surface at different temprature (25 to 40 °C).

Temp.°C	Temkin		
	f	K_{ads}, M^{-1}	$-\Delta G\circ_{ads}$, kJ mol^{-1}
25	0.24	5.31	14.09
30	0.30	19.09	17.55
35	0.29	28.53	18.86
40	0.30	107.73	22.63

3.1.2.Temperature Effect

The effect of temperature was examined by reduction of mass over different temperature from 25to 40°C.From data the corrosion rate higher as the temperature rise and lowering as the higher concentration for Azathioprine. Activation energy(E^*_a in kJ mol^{-1}) for the corrosion type was measured utilized Arrhenius equation:

$k=A\ exp\ (-E_a^*/\ RT)$ (7)

k = the rate of corrosion, T = temperature absolute, R = gas constant and A = Arrhenius constant.

E^*_a values obtained from the line slopes. **Table(5)**showed that the E^*_a value of drug is greater than uninhibiting solution which suggesting that dissolution of metal is slow with inhibitor and explain as physical adsorption[48]. The increasing E^*_a values lead to the decrease rate of corrosion because the formation of a film on the surface of metal serving as an energy barrier for metal corrosion[49].

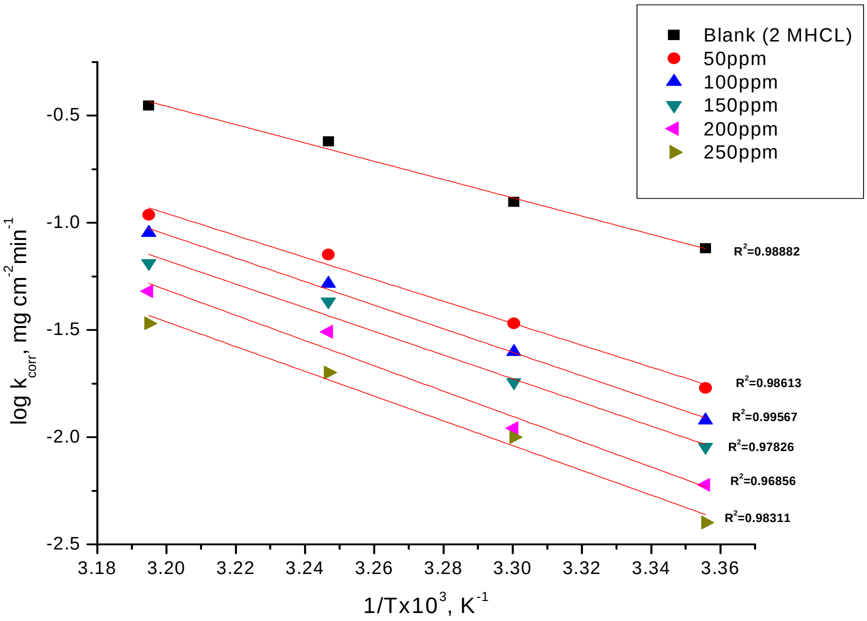


Figure (3).1/T againstLog k diagram for dissolution of metalwith and without Azathioprine

Entropy (ΔS^*in J mol^{-1} K^{-1}) and enthalpy(ΔH^*in kJ mol^{-1}) for process of corrosion were measured by theory of transition state **Table (5):**

$$\text{Rate} = (RT / Nh) \exp (\Delta S^*/R)\, e^{(-\Delta H^*/RT)} \qquad (8)$$

N =number Avogadro's and h = Planck's constant.

The positive enthalpy signs mirror the endothermic way of dissolution metal process. Vast and negative entropy estimations infer that the activated complex in the rate-determining step speaks to an association rather than dissociation step, implying decline in disordering occurred on heading from reactants to the activated complex [50-51]

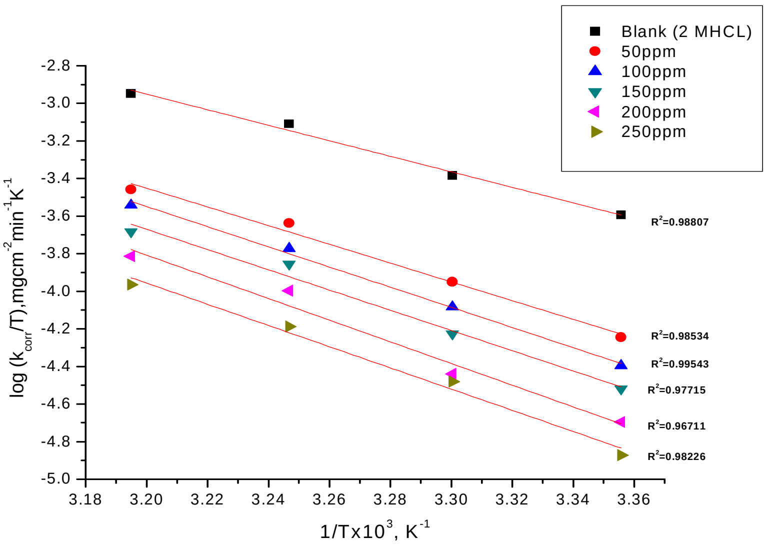


Figure (4).1/T vs log k/T digram for metal in hydrocholric acidwithout and withAzathioprine

Table(5). Activation parameters for Azathioprine on metal surface

Inhibitor	Conc., ppm	E_a^*	ΔH^*	ΔS^*
Free acid	------	81.9	34.3	-0.98
Azathioprine	50	98.0	41.5	41.8
	100	105.2	44.5	63.0
	150	105.6	44.7	62.0
	200	112.9	47.9	82.6
	250	110.5	46.8	72.2

3.2 polarization Tafel methods

It is clear From **Figure (5)**both reduction cathodic hydrogen reactions and dissolution anodic of metal were hindrance due to addition **Azathioprine** to 2molar hydrochloric acid, hindrance was pronounced with concentration large of inhibitor. The curves are direction to positive and negative potentials with appreciation to the blank band by expanding the drug concentration. The conduct demonstrates attempted added substances go about as mixed-type inhibitors [52]. The outcomes demonstrate that the increment in inhibitor focus prompts diminish the current density corrosion (i_{corr}), yet the Tafel inclines (β_a, β_c),are more or less consistent demonstrating that the lowering on two reactions (anodic metal disintegration and cathodic hydrogen diminished)was influenced without affecting the dissolution mechanism [53-54].

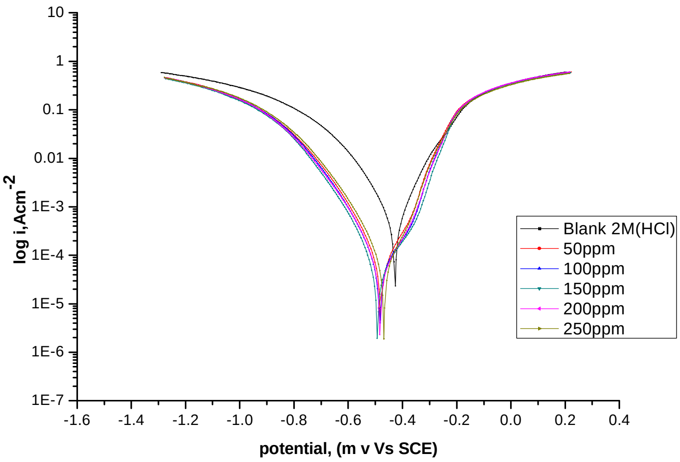


Figure (5).digrams of polarization for metalcorrosion on 2M hydrochloric acidfor the Azathioprine at room temprature

Table (6). Effect of Azathioprine concentrations on Tafel slopes (β_a& β_c), %IE, E_{corr}.and i_{corr}. on steel

Inhibitor	Conc., ppm	$i_{corr.}$	$-E_{corr.}$	β_a	β_c	% IE
B	2M HCl	1110.0	427.00	146.5	201.50	----
Azathioprine	50	109.0	469.00	110.9	163.40	90.2
	100	78.2	481.00	108.7	150.90	93.0
	150	68	482.00	112	144.00	93.3
	200	59.0	482.00	102.1	147.60	94.7
	250	41.0	491.00	105.9	138.10	96.3

3.3-Electrochemical impedance spectroscopy (EIS)

The metal corrosion in acid with and without Azathioprine was described by EIS technique at room temperature. Nyquist band in nonattendance and vicinity of Azathioprine are show in figure (5)lead to all Nyquist diagrams show a single capacitive loop with and without inhibitor. The EIS are explain in an equivalent circuit model. This includes the double layer capacitance C_{dl} and the solution resistance R_s by addition in parallel to the charge transfer resistance R_{ct}[55]. The capacity double layer (C_{dl}) can be measured from the following equation:

$C_{dl} = ½ \pi f_{max} R_{ct}$(9)

Wheref_{max}=frequency maximum. The results from impedance calculation are obtained in **Table (7** which shows that the data of R_{ct} increase with inhibitor concentration **[56]**. % IE rise with higher concentration inhibitor.

Impedance work utilized the inhibiting characters of this compound obtained from Tafel polarization with mass reduction technique. The (C_{dl}) values lead to lower while the concentration of this compound higher, this result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer **[57]**. The inhibiting effect of compound was credited to their adsorption parallel.

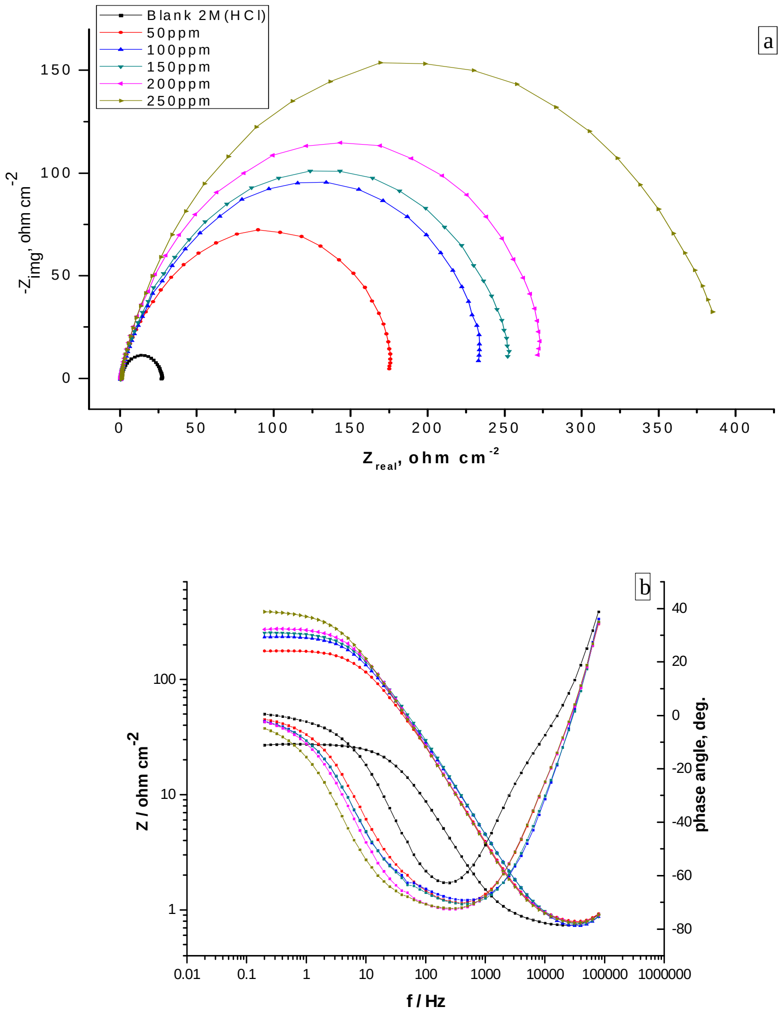


Figure (6).The Nyquist (a) and Bode (b) curves for metalcorrosion in 2M HCl onnonattendance and vicinity of various concentrations of Azathioprine at room temprature

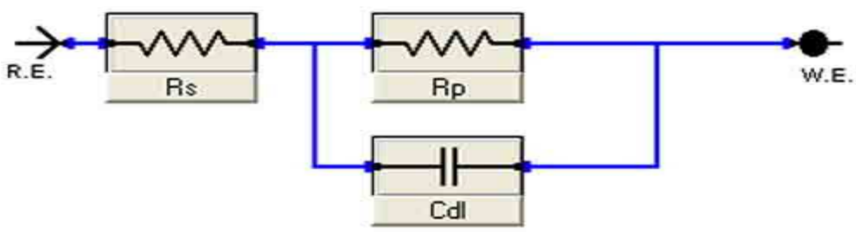


Figure (7). Electrical circuit equivalent model utlized to fit impedanceresults

Table (7). parameters reslut from EIS for Azathioprine at room temprature

Inhibitor	Conc., ppm	C_{dl}, Ohm cm^{-2}	R_{ct}, ohm cm^2	θ	IE%
Blank	2M HCl	230	27.50	------	------
	50	93.6	175.90	0.844	84.4
	100	81.5	235.80	0.883	88.3
Azathioprine	150	81.2	250.40	0.890	89.0
	200	80.6	274.60	0.900	90.0
	250	75.5	379.50	0.928	92.8

3.4. Electrochemical frequency modulation technique (EFM)

"These technique EFM make it a perfect competitor for online corrosion monitoring [58]. Figure (8) shows EFM (current vs frequency) of steel in acid solution containing different concentrations of drug. The harmonic intermodulation peaks are clearly visible which are much larger than the background noise. The experimental EFM data were treated using two different models: complete diffusion control of the cathodic reaction the activation model, 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 [59-60]. The peaks larger were utilized the current corrosion density (i_{corr}), (CF-2 and CF-3)the causality factors and the Tafel slopes (β_c and β_a). All parameters were listed in Table (8).The data presented in Table (8) the addition of drug at a given concentration to the acidic solution down the corrosion density current this lead to these compounds ac as corrosion inhibition of metal in acidic medium through adsorption. The causality factors obtained under different conditions are approximately equal to the values theoretical (2 and 3) demonstrating that the deliberate information is verified a good quality". The inhibition efficiencies %IE EFM increase by increasing the inhibitor concentrations and was measured as from equation 10:

$$\%IE = [1-(i_{corr}/i^{\circ}_{corr})] \times 100 \qquad (10)$$

Where i°_{corr} and i_{corr} are corrosion densities current in with and without of inhibitor, respectively. Figure (8) shows the EFM Intermodulation spectra of carbon steel in Hydrochloric acid solution containing concentrations different of drug. Larger peaks were used to measured (β_c and β_a), (i_{corr}), and (CF-2 and CF-3) these electrochemical parameters were listed in Table (8). The data presented in Table (8) show the addition of any one of tested compound at a given concentration to the acidic solution decreases the corrosion current density which indicating that compound corrosion inhibition of metal in acid through adsorption.

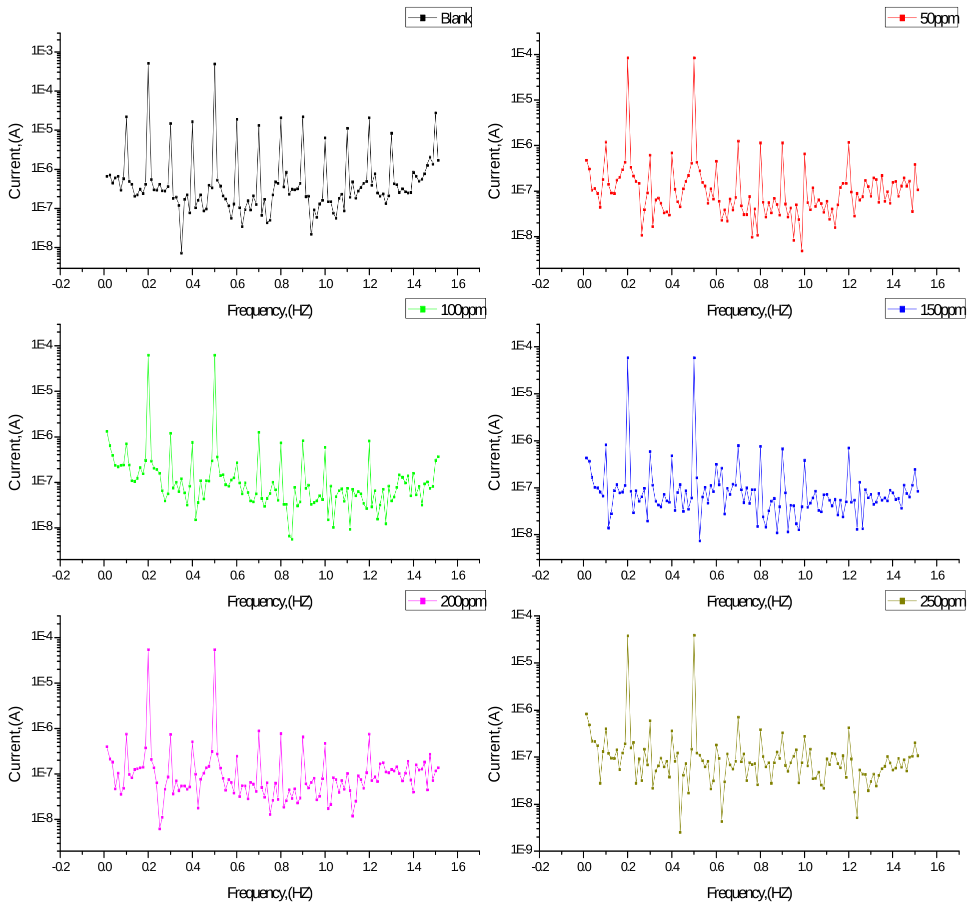


Figure (8).EFM for meal in 2 M Hydrochloric acid unlucky deficiency and vicinity of distinctive convergances of drug

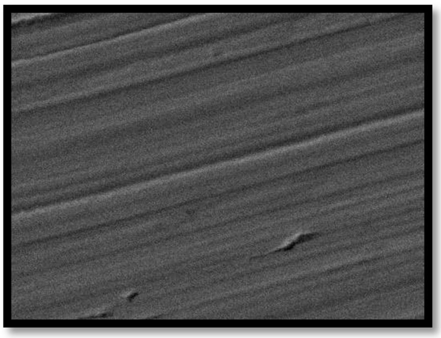
Table (8).Electrochemical dynamic parameters got by EFM method for meal in the unlucky deficiency and vicinity of different amassings of Levofloxacin in 2M hydrochloric acid at 25oC

Inhibitor	Conc., ppm	$i_{corr.}$ μA cm^{-2}	β_c , mV decc^{-1}	$\beta_{,a}$, mV dec^{-1}	CF(2)	CF(3)	θ	% IE
B	2 M HCl	426.4	58.5	53.200	1.21	2.98	----	----
Azathioprine	50	128.1	101.6	95.030	1.39	2.82	0.700	70.0
	100	102.7	112.3	99.000	1.80	2.70	0.759	75.9
	150	90.43	105.3	98.300	1.60	2.70	0.788	78.8
	200	84.83	105.8	95.400	1.60	3.00	0.801	80.1
	250	68.63	122.3	109.000	2.03	3.02	0.839	83.9

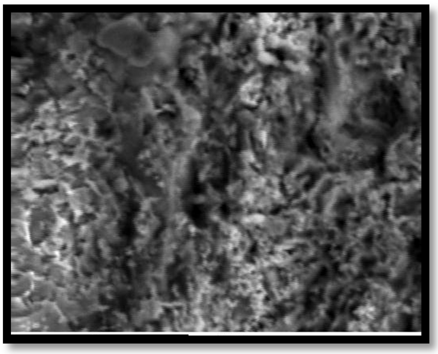
3.5- Scanning electron microscopy (SEM)studies

Figure (9)sthat the micrographs obtained for steel samples with and without250ppm of azathioprine immersion in 2 days. It is clear that surfaces of carbon steel suffer from severe corrosion attack in the blank sample.

Pure sample



Blank



Inhibitor

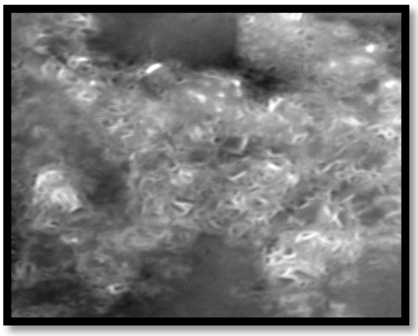


Figure (9). SEM micrographs for carbon steel in absence and presence of 250 ppm of Azathioprine

We noticed the arrangement of a film which is dispersed in an arbitrary manner in general surface of the carbon steel. This may be translated as because of the adsorption of the Azathioprine on the carbon steel surface joining into the aloof film so as to square the dynamic site exhibit on the carbon steel surface. Alternately because of the association of inhibitor particles in the connection with the response destinations of carbon steel surface, bringing about a lessening in the contact between carbon steel and the forceful medium and successively displayed fantastic restraint impact [61].

4. Corrosion inhibition mechanism

The adsorption of medication particles can be ascribed to the presence of polar unit having iotas of nitrogen and oxygen and fragrant/heterocyclic rings. In this way, the conceivable response focuses are unshared pair of electron hetero-atom and л-electrons of sweet-smelling ring [62]. The adsorption and hindrance impact of medication particles in 2 M HCl arrangement can be clarified as takes after: In fluid acidic arrangements drug atoms exist either as unbiased particles or as protonated particles and may adsorb on the metal in corrosive arrangement interface by one and a greater amount of the accompanying ways: (i) electrostatic collaboration of protonated particles with effectively adsorbed chloride particles, (ii) communication between unshared electron sets of hetero-iotas and empty d-orbital of iron surface molecules. The conceivable clarification of the hindrance is because of adsorption procedure which is considered as the key of the instrument of restraint activity. It may be recommended that the medication particles stick to the steel surface. This prompts a reduction of the surface zone at which cathodic and anodic responses occur. Restraint productivity of the medication particles relies on upon numerous factors[63], which incorporate the quantity of adsorption dynamic focuses in the atom and their charge thickness, atomic size, and method of cooperation with metal surface[64- 65]**.** The transition of metal in solution interface with a state of active dissolution to the passive state of great interest. The inhibition effect is attributed to the adsorption of the inhibitor molecules via their functional group onto the metal surface, so drug can be adsorbed in the form of negatively charged species on the metal surface which can interact electrostatically with positively charged metal surface given increase the surface coverage and consequently protect efficiency controlling the anodic metal dissolution and cathodic evolution hydrogen. The adsorption rate is usually rapid due to the reactive metal is shielded from the aggressive environment.

CONCLUSION

1) The Azathioprine establish a very good inhibition for metal corrosion in HCl solution
2) Azathioprine inhibit corrosion ofC-steel by adsorption on its surface and act better than the passive oxide film
3) The inhibition efficiencies of the compound increment with expanding of their concentrations
4) Capacitances double layer lower with respect to blank solution when added the drug.
5) The adsorption of Azathioprine follows adsorption Temkin isotherm

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