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Corrosion Protection of Stainless Steel 201 in Acidic Media using Novel Hydrazine Derivatives as Corrosion Inhibitors

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This study aimed at the application of hydrazine derivatives (HZD) in acid media as corrosion inhibitors of stainless steel 201 (SS201). In the chemical and electrochemical technique, SS201 is the constructional material widely used. The various factors, which influence the corrosion inhibition efficiency of different HZD have been discussed. Different techniques were used to evaluate the corrosion inhibition. Atomic force microscopy (AFM) and FTIR were utilized to study the surface morphology of SS201which revealed that the inhibitors produce a thin film adsorbed on the surface of SS201.

Keywords: SS201, Hydrazine derivatives, HCl, Corrosion inhibition, AFM, FTIR

1. INTRODUCTION

Worldwide SS production drastically increased in the last decades. As costs of stainless steel increased by growth rate 5% with suppressing the growth rate of other materials because of its wide applications in industry as Kitchen utensils, Washing machine parts, automotive trim, and industrial tubes and pipes. Acid solutions have been commonly used in these industries as pickling agents to remove rust or any scale from the SS201 surface. SS has high resistance to corrosion due to the formation of a thin film of chromium ox-hydroxide which gives the protection to the alloy [1]. However, in an acidic medium as HCl, the passive film formed over the SS surface will be disappearing as chromium reacts with chloride producing chromium chloride, chromium will be gradually lost from SS leaving just iron [2-5]. The excessive dissolution of SS201 in such aggressive medium can be the best control by addition of suitable organic inhibitors. Therefore, using corrosion inhibitors is a very beneficial strategy for protecting SS against corrosion where the inhibitors are adsorbed on the surface of SS which protects it from the corrosive medium. Most inhibitors utilized in manufacturing are organic compounds

containing donor atoms like S, O and N. Inhibitors including triple or double bonds performance had a significant role in simplifying the adsorption of these compounds. A bond can be designed among the cloud π -electron and/or the electron pair of the donor atoms and the surface of metal, thus lowering the corrosive attack in an acidic solution [6-14], and utilized as corrosion protection and those including "N" have frequently mentioned to in the literature [15], pyrrole and its derivatives [16], Distyryl [17], 1,3-Thiazolidin-5-one [18], Pyrazolone [19], Pyrazolocarbothioamide [20]. The choices of these HZD have aimed to: a) They have high molecular sizes b) have high solubility in water, and c) have many donating atoms, which they can adsorb on the SS201 surface.

The scope of this paper is to study the inhibitory influence of HZD on the corrosion of SS 201 in 1.0 N HCl solutions utilizing mass loss (ML), potentiodynamic polarization (PP), electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) tests. Surface morphology characterized by AFM and FT-IR analysis.

2. EXPERIMENTAL

2.1 Materials and solution

The chemical composition of SS201 presents in this research is C 0.15%, Mn 5.5-7.5%, P 0.06%, Si 1%, Cr 16-18% and the reminder of the weight percentage is Fe. The specimens were mechanically cut into about 2 cm \times 2 cm \times 0.2 cm dimensions with for Mass loss, and 1cm \times 1cm \times 0.2 cm for electrochemical measurement techniques. These specimens were polished with sand paper 1000,1500 and 2000 to a metallic shine, degreased with absolute ethanol washed with bidistilled water and finally dried as previously. The hydrochloric acid was diluted to 1.0 M HCl as a corrosive medium. The inhibitors used with different concentrations ranged from (1 x10⁻⁶ - 21 x10⁻⁶M). 10⁻³ M stock solutions from the studied inhibitors were prepared by dissolving the convenient weights of the HZD in bidistilled water; the other concentrations of HZD (1 x10⁻⁶ - 21 x10⁻⁶M) were prepared by dilution with bidistilled water. All the materials used were of AR grade and used as received. The structure formulas of the examined inhibitors were given in Table 1.



Table 1. Chemical structures of the prepared hydrazine derivatives



2.2 ML tests

The pretreated SS type 201 coins were dipped in 100 ml solution of 1.0 M HCl with and without different doses of HZD at 25-45°C for 3h. The range of HZD concentrations in test solutions has selected to be $(1 \times 10^{-6} - 21 \times 10^{-6} M)$. After indicated time the SS specimens had removed from corrosive solution, rinsed with bidistilled water, dried and weighted.

2.3 Electrochemical measurements

The behavior of HZD as inhibitors for corrosion of SS201 in 1.0 M HCl was further examined by PP and EIS. All electrochemical experiments were performed at 25°C using three-electrode cell setup consists of (SCE) saturated calomel electrode utilized as reference electrode, (Pt) platinum wire was utilized as counter electrode and SS430 as (WE) working electrode. The WE was prepared as follows at first one side of SS201 sheet (10 ml x 10 ml x 20 ml) has fused to a Cu wire for connection electrical. Subsequently, the Cu wire which attached to SS201 sheet was inserted into a glass tube and then fixed by epoxy resin to make the size of SS201 visible to the test solutions is 1 cm². Prior to measurements the sample was pretreated as mentioned before and the potential of electrode was permitted to stabilize for half hour in order to reach a steady state. For PP test the potential was initiated from -500 to 500 mV vs OCP with rate of scan 0.5 mVs⁻¹. EIS tests were done in a range of frequency from 0.1 Hz to 10^{-5} Hz with amplitude of 10 mV peak to peak under open circuit condition. However, polarization resistances R_p, were estimated from the altered among the intercepts of low- and high-frequency with the actual axis on the impedance spectra. EFM tests were performed utilizing two frequencies (2.0-5.0 Hz). 1.0 Hz was the base frequency of 32 cycles which means that the waveform repeats after 1s. The selection of the frequencies (2.0-5.0 Hz) was based on three principles [21-22].

2.4 Surface examination

Coins utilized for surface analysis were immersed in 1.0 M HCl in without and with 21 x10⁻⁶M of HZD solutions for 15 h. After this immersion time, the coins were removed, rinsed with bidistilled water many times to remove any residue and dried. The investigation was done by (AFM). FTIR analyses were tested for SS201 surface before and after immersion 15 h in 21 x10⁻⁶M of HZD and then compared to the spectra of HZD. Fourier transforms infra-red spectroscopy was utilized to investigate the film formed on the surface of SS201 by Thermo Fisher Nicolet IS10, USA in the spectral range of $400 - 4000 \text{ cm}^{-1}$.

2.5 Theoretical investigation

The quantum chemical parameter was found by M S D Mol [23] 4 4 0 which using efficient density theory DFT. The chemically quantum , E_{HOMO} (the highest occupied molecular orbital), E_{LUMO} (the lowest unoccupied molecular orbital), dipole moments (μ), energy gaping (ΔE), Hardness (η), Softness (σ),Ionization potentials (I), Electronegativity (X) of the created compound (I) were discussed.

3. RESULT AND DISCUSSION

3.1. ML measurements

Table (2) displays the mass loss values; (CR) corrosion rate, (%IE) inhibition efficiency, and (θ) surface of SS 201 coating in 1.0 M HCl in the absence and presence of different concentration of HZD which can be measure through the next equation (1).

$$\%\eta = \theta \times 100 = \left(1 - \frac{\Delta W_u}{\Delta W_i}\right) 100 \tag{1}$$

Where ΔW_u and ΔW_i are the ML's per unit area with and without the HZD, respectively. The addition of HZD accompanied by decreasing in ML and CR while, raising in %IE and θ . This ensures that efficiency of HZD as (%IE) at an optimum concentration 21×10^{-6} reach 87.1%. Fig (1) shows ML vs. time diagram of SS201 with and without various concentrations of HZD at 25°C. Alike plots done for other temperatures (not display).

From Fig (2) by raising temperature, ML, increases indicating that the corrosion rate of SS201 increases while the protection efficiency (PE%) of the HZD decreases with the increase in the temperature. It can be clarified by the lower in the HZD adsorbed on the SS surface and acceleration of the dissolution process. The study revealed that, the inhibiting effect of compound (I) is higher than the inhibiting effect of compounds (II) and (III) at the same concentration.



Figure 1. ML &time diagrams of SS201 in 1.0 M HCl with and without various concentrations of the investigated compound (I) at 25°C

Fable 2 . CR and inhibitior	percent of SS201	in absence a	and existence	of various	concentrations	of the
studied HZD after	120 min immersion	at 25°C				

Comp]	[II		I	Π
Conc., x 10 ⁶ M	θ	% IE	θ	% IE	θ	% IE
1	0.773	77.3	0.762	76.2	0.735	73.5
5	0.794	79.4	0.779	77.9	0.763	76.3
9	0.808	80.8	0.797	79.7	0.782	78.2
13	0.829	82.9	0.814	81.4	0.803	80.3
17	0.845	84.5	0.839	83.9	0.821	82.1
21	0.871	87.1	0.856	85.6	0.845	84.5



Figure 2. Effect of temperature on the %IE of SS201 in presence of 21x10⁻⁶ M of compound (I)

3.2 Adsorption isotherm

Adsorption isotherms are commonly used to recognize the mechanism of protection on the metal surface [24]. The excellent fit was obeyed by Langmuir, which is signified in Fig (3) for HZD using equation (2):

$$\frac{C}{\theta} = \frac{1}{\kappa_{ads}} + C \tag{2}$$

Where C is the inhibitor concentration in the bulk of electrolyte (Mol L^{-1}) and K_{ads} is the equilibrium constant of adsorption and $\Delta G^o{}_{ads}$ is the free energy and can be calculated by:

 $K_{ads} = \frac{1}{55.5} \exp\left[\Delta G^{\circ}_{ads}\right] / RT]$ (3)

Where 55.5 is the molar concentration of water in the solution in M^{-1} , R is the constant gas, T is the absolute temperature. Thermodynamic parameters obtained from adsorption of the inhibitors on SS 201 surface in 1.0 M HCl at different temperatures was record in the Table (3). It was established that ΔG°_{ads} has –ve values among 19.5 to 22.1 kJ mol⁻¹ indicating that the HZD adsorption on SS 201 in 1.0 M HCl solution is a spontaneous process belong to physisorption mechanism [25].

The standard enthalpy ΔH°_{ads} and entropy ΔS°_{ads} obtained from adsorption can be measured using next eqs.(4) and (5)

$$Ln K_{ads} = \left[-\Delta H_{ads} / RT\right] + const$$

$$\Delta S_{ads} = \left(\Delta H_{ads} - \Delta G_{ads}\right) / T$$
(5)

The value of ΔH°_{ads} was evaluated from the slope of the lines of Ln K versus1/T see Fig (4). The –ve sign value of ΔH°_{ads} indicates that the process of adsorption is exothermic, and the –ve sign value of ΔS°_{ads} means that adsorption occurs spontaneously [26]. The investigated compounds have good inhibition efficiency as obtained from the values of K_{ads} where the high values of K_{ads} indicate there is strong electrical interaction between the adsorbed HZD molecules and the double-layer exist at the phase boundary. On the other hand, the small values of K_{ads} indicate that the interactions between the adsorbed molecules and the metal surface are weaker, and as a result, the HZD molecules are easily replaced by the solvent molecules from the metal surface [27].



Figure 3. Plots fitting of corrosion value for SS201 in 1.0 M HCl with and without various concentrations of investigated compound (I)

Table 3. Adsorption parameters for HZD in 1.0 M HCl obtained from Langmuir at various temperatures

Comp	Temp., K	$-\Delta G^{\circ}_{ads}$ kJ mol ⁻¹	$-\Delta H^{\circ}_{ads}$ kJ mol ⁻¹	$-\Delta S^{ads}$ J mol ⁻ K ⁻¹
	298	22.1		98
	303	21.8		96
Ι	308	21.1	50	93
	313	20.9		91
	318	20.3		90
	298	21.9		78
	303	21.1		73
II	308	20.7	47	72
	313	20.1		71
	318	19.9		70
	298	21.1		76
	303	20.8		72
III	308	20.2	45	67
	313	19.8		64
	318	19.5		65



Figure 4. Ln K versus1/T plots for SS201 in 1.0 M HCl of the investigated compound (I)

3.3 Kinetic and thermodynamic parameters

The corrosion rate dependence on temperature can represent by Arrhenius equation:

 $k_{corr} = A \exp\left(-E^*_{a}/RT\right) \tag{6}$

Where A is the pre-exponential factor and Ea^* is the energy of activation for the corrosion process.

Enthalpy and entropy of activation (ΔH^* , ΔS^*) for the corrosion process were measured from the transition state equation:

 $k_{corr} = RT/Nh Exp(-\Delta H^*/RT)Exp(-\Delta S^*/R)$

(7)

Where N is the Avogadro's number and h is the Planck's constant.

Arrhenius plots (log (k_{corr}) of SS201 with and without various concentrations of HZD against 1/T) is presented in Fig (5). E_a^* can be measured from the slope of these lines, while ΔH^* and ΔS^* can be obtained through the intercept and slope of plots of log (k_{corr}/T) vs. (1/T) as shown in Fig (6). The data of E_a^* , ΔH^* , and ΔS^* are recorded in the Table (4)



Figure 5. Arrhenius plots of log(k_{corr}) vs 1/T of SS201 corrosion in 1.0.M HCl with and without various concentrations of inhibitor (I) at different temperatures



Figure 6. log k_{corr}/T vs 1/T plots for SS201 corrosion with and without the various concentrations of compound (I) in 1.0 M HCl

From Table (4) the E_a^* for inhibiting solution is greater than that for the uninhibited solution, indicating that SS201 dissolution decreases in the existence of HZD [28]. The higher E_a^* data lead to the minor k_{corr} , this is due to of the formation of an adsorbed a film on SS201 surface by HZD [29]. The -ve values of ΔS^* meaning that there is a decrease in disorder occur during progression of transition from reactants to the activated complex [30].

Comp	Conc., x 10 ⁶ M	E _a *, kJ mol ⁻¹	ΔH^* , kJ mol ⁻¹	$-\Delta S^*$, J mol ⁻¹ K ⁻¹
Blank	0.0	33.4	13.4	166.1
	1	70.79	27.6	51.9
	5	74.12	30.1	41.6
т	9	75.45	31.1	40.6
1	13	77.61	32.5	34.4
	17	82.78	34.8	18.1
	21	86.14	35.2	8.9
	1	70.1	26.5	53.1
	5	72.8	28.8	47.5
II	9	74.8	30.8	45.3
	13	76.4	32.1	38.8
	17	79.7	33.4	24.6
	21	82.5	34.7	10.7
III	1	69.5	24.2	55.7
	5	71.5	27.5	51.1
	9	73.2	29.8	48.6
	13	75.8	31.4	41.8
	17	78.7	32.4	27.1
	21	81.6	33.1	18.6

Table 4. Activation parameter for SS201 corrosion with and without various concentrations of investigated HZD in 1.0 M HCl

3.4 Electrochemical measurement

3.4.1 Potentiodynamic polarization (PP) technique



Figure 7. PP plots of dissolution of SS201 in 1.0 M HCl without and with different concentrations of inhibitor (I)

Table 5. The influence of inhibitor doses of investigated HZD on PP parameters (E_{corr}), (i_{corr}), ($\beta_a \& \beta_c$), % IE, and (Θ) for corrosion SS201 at 25°C

Comp	Conc., x10 ⁶ M	i _{corr,} μA cm ⁻²	- E _{corr,} mV vs SCE	β_a mV dec ⁻¹	β_c mV dec ⁻¹	C.R mpy	θ	% IE
Blank	0.0	5310	448	120.3	152	25.4		
	1	1251	445	116	146	21	0.764	76.4
	5	1110	458	120	141	13.8	0.791	79.1
т	9	989	456	128	140	10.1	0.814	81.4
1	13	897	460	118	154	9.7	0.831	83.1
	17	730	461	116	165	8.1	0.863	86.3
	21	570	452	121	155	7.8	0.892	89.2
	1	1361	49	111	163	22.2	0.744	74.4
	5	1217	450	112	144	20.7	0.771	77.1
п	9	989	451	124	156	19.6	0.814	81.4
11	13	918	456	101	150	17.3	0.827	82.7
	17	776	461	98	148	13	0.854	85.4
	21	689	468	94	157	9.7	0.870	87.0
	1	1640	470	113	149	24.3	0.691	69.1
	5	1310	469	125	147	21.8	0.753	75.3
	9	1100	461	111	156	20.7	0.793	79.3
111	13	890	460	116	164	18.7	0.832	83.2
	17	839	459	103	144	16.1	0.842	84.2
	21	710	453	96	139	12.3	0.866	86.6

Anodic and cathodic polarization curves were obtained in 1M HCl solution with and without various concentrations of HZD at 298 °K. In Fig (7) Tafel curves for compound (I) is presented. The area among line obtained from cathodic and anodic curves come to be wider by adding the inhibitor to the free solution (HCl) [31]. It is clear from the Tafel polarization curves that the presence of investigated compounds to the corrosive media shifts both cathodic and anodic lines to lower values of i_{corr} and hence, there is a decrease in the k_{corr} . The parameters obtained from PP diagrams are recorded in Table (5). The (% IE) can be calculated using the (i_{corr}) values determined by Tafel extrapolation as follows:

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

where i_{corr}^{o} and i_{corr} are the current densities of uninhibited and inhibited solution, respectively.

A slight change was observed on Tafel slopes (β_a and β_c) upon the addition of investigated compounds confirming that the mechanism of the corrosion process was maintained even with the existence of the tested compounds. It is generally, known that HZD can be ordered as mixed kind if the shift of E_{corr} in the presence of HZD is less than 85 mV with respect to the absence of the HZD [32]. In our research, the higher shift in E_{corr} was 27 mV which lead to that these compounds are mixed kind inhibitors

3.4.2 EIS method

EIS was known as a great method for the corrosion analysis [33]. Fig (8-9) displays the Nyquist and Bode plots obtained at OCP both with and without raising the concentration of HZD at 25°C. Similar curves for another inhibitor was obtained but not display. The increase in the area of the loop by examining compound, which displayed that a barrier has formed progressively on the surface of SS201, improve in the capacitive loop area Fig (8) expands, at a constant inhibitor dose, obey the order: I > II >III compounds. Bode diagrams Fig (9), indicated that the total impedance improves with raising HZD inhibitor dose, also Bode diagrams displayed correlating among the continuous improvement in the phase angle move and the rise of adsorbed HZD compound on the surface of SS201. The Nyquist diagrams don't produce perfect semicircles as predictable from the EIS theory due to the dispersion of a frequency [34] in addition to inhomogeneity of SS surface. The double layer capacitance (C_{dl}) and % η are calculated from the following equations:

$$2\pi f_{max}R_c$$

(7)

(6)

Where, f_{max} refers to the maximum frequency at which the imaginary constituent of the impedance (Z_{im}) is higher.

$$\%\eta = \frac{R_{ct} - R_{ct}^0}{R_{ct}}$$

(8)

Where, R_{ct} and R^o_{ct} are the resistances in absence and presence of inhibitor

EIS values recorded in Table (6) showed that R_{ct} values increased by raising the concentration of the inhibitors and this lead to improvements in % IE_{EIS}, which agrees with the obtained data from PP. Actually, the existence of inhibitors improves the values of R_{ct} and decreases both the C_{dl} and i_{corr} values, signifying that HZD hindrance the CS corrosion by adsorption among acid/metal. The %IE was calculated from the R_{ct} values from eq.3 [35]:



Figure 8. EIS Nyquist diagrams for SS201 in1.0 M HCl without and with various concentrations of compound (I)



Figure 9. EIS Bode diagrams of SS201 in 1 M HCl with and without different concentrations of compound (I)

Table 6. EIS data of SS201 corrosion in 1 M HCl with various concentrations of HZD at 25°C

Comp	Conc., x 10 ⁶ M	$R_{ct},$ Ω cm^2	$C_{dl},\ \mu Fcm^{-2}$	θ	%IE
Blank	0	23	393		
	1	98	134	0.765	76.5
	5	111	122	0.793	79.3
т	9	132	118	0.826	82.6
1	13	151	112	0.848	84.8
	17	172	105	0.866	86.6
	21	198	97	0.884	88.4
	1	88	139	0.739	73.9

	5	105	127	0.781	78.1
Π	9	126	116	0.817	81.7
	13	135	114	0.830	83.0
	17	159	111	0.855	85.5
	21	180	101	0.872	87.2
	1	76	142	0.697	69.7
	5	80	132	0.713	71.3
III	9	102	123	0.775	77.5
111	13	138	118	0.833	83.3
	17	145	115	0.841	84.1
	21	167	110	0.862	86.2



Figure 10. Equivalent circuit utilized to fit the EIS data

3.4.3 EFM method



Figure 11. EFM data for SS201 dissolution in 1 M HCl with and without various concentrations of compound (I) at 25°C

EFM is a non-degradation corrosion technique that has characterized by rapid and accurate in calculating the current data from the absence of Tafel slopes [36-40]. The higher power of the EFM is the causality factors (CF) [41]. Fig (11) represents the EFM diagrams of SS201 in HCl solution which include various doses of compounds HZD. The greater peaks have used to calculate the (i_{corr}), (CF-2 and

CF-3) and (β_c and β_a). EFM data were recorded in Table (7). The obtained values in Table (7) clearly indicated that the adding of any one of HZD tested compounds in the acidic solution lowers i_{corr}, indicates that these compounds prevent the corrosion of SS201 among adsorption. The %IE_{EFM} improves by raising the inhibitor concentration and was calculated from Eq. (6). The %IE_{EFM} obtained from this test is in the order: I > II > III at all concentrations. The IE obtained from EFM technique is similar to those calculated by ML, PP and EIS techniques.

Table 7. Parameters obtained from EFM for	SS201 dissolution	in 1 M HCl with and	without various
concentrations of investigated HZD a	ıt 25°C		

Comp	Conc., x 10 ⁶ M	$i_{corr,}$ $\mu A \ cm^{-2}$	$eta_{a,}$ mVde c^{-1}	$eta_{c},\ mVdec^{-1}$	C.R , mpy	CF- 2	CF-3	θ	%IE
Blank	0.0	3788	103.2	116.0	173	2.1	3.1		
	1	837	101	121	135	2.8	3.1	0.779	77.9
	5	765	104	120	120	1.80	2.9	0.798	79.8
т	9	640	106	112	119	2.0	2.9	0.831	83.1
1	13	566	104	118	112	1.9	3.0	0.851	85.1
	17	467	98	115	106	1.90	2.9	0.877	87.7
	21	393	102	117.2	89	2.2	3.0	0.896	89.6
	1	901	103	133	145	2.1	2.9	0.762	76.2
	5	814	101	128	133	1.7	3.1	0.785	78.5
T	9	667	94	125	120	2.2	2.7	0.824	82.4
11	13	578	95	123	118	2.0	3.1	0.847	84.7
	17	547	88	118	115	1.9	2.9	0.856	85.6
	21	477	98	121	110	1.8	2.7	0.874	87.4
	1	974	102	110	148	1.9	3.3	0.743	74.3
	5	886	89	117	151	1.8	3.1	0.766	76.6
ш	9	687	95	116	143	2.1	2.9	0.819	81.9
111	13	623	85	121	132	2.0	2.7	0.836	83.6
	17	590	96	119	127	2.1	2.8	0.844	84.4
	21	501	94	105	123	2.2	3.1	0.868	86.8

3.5 Surface Examinations

3.5.1 AFM examination

AFM is a remarkable technique used for measuring the surface roughness with high resolution [42]. Many details about SS201 surface morphology can be obtained from AFM measurements which help to explain the corrosion process. The three dimensional AFM images represented in Fig (12).







Figure 12. (a) 3D AFM image of SS201 immersed 1.0 M HCl for 1day, (b) 3D AFM image of SS201 immersed in 1.0 M HCl+21x10⁻⁶M of compound (I) for 1 day, (c) 3D AFM image of SS201 immersed in 1.0 M HCl+21x10⁻⁶M of compound (II) for 1 day, (d) 3D AFM image of SS201 immersed in 1.0 M HCl+21x10⁻⁶M of compound (III) for 1 day.

Table 8. AFM parameters of investigated hydrazine derivatives (I, II and III) at 25°C

Sample	Roughness average (Sa), nm
Blank	512
Ι	203
II	221
III	291

The roughness calculated from AFM image are summarized in Table (8). The values showed that the roughness increases with adding HCl due to the corrosion occurs on the SS201 surface but decreased with adding the prepared [43].

3.5.2 FTIR analysis



Figure 13. FTIR spectra of inhibitor (I) stock solution (black line) and a layer of inhibitor (I) adsorbed on SS 201 surface (red)

Functional groups and characterizing covalent bonding knowledge had been identified by FT-IR which is an influential analytical device [44]. The fingerprint spectra of the HZD (I) and the SS 201 surface after inundation in 1.0N HCl + 21x10⁻⁶ to (I) for 180 min has achieved and compared to each other. (The same diagrams have achieved in the presence of the other OC, (not shown). FTIR spectroscopy demonstrations, exciting features, for example, power peak to noise ratio, great selectivity and little quantity of sample needed for the examination. Fig (13a and 13b) signify the IR spectrum of HZD and the film produced on the SS201. The FTIR of pure HZD had shown Fig (13a) The -OH-frequency seems at 3407 cm⁻¹, the C=O seems at 1646 cm⁻¹, Aromatic ring seems at 744 cm⁻¹, the –SH frequency seems at 2101 cm⁻¹. The FTIR of the film coated on the SS201 is displayed in Fig (13b). The -OH is stretching frequency moves from 3407 cm⁻¹ to 3416 cm⁻¹. The –SH is stretching moves from 2101 cm⁻¹ to 2093 cm⁻¹.

3.6. Quantum chemical and statistical parameters

Quantum chemical factors, expecting the relationship of molecular structure for inhibitors (A) particles and its action against corrosion and corrosion of SS201, the important influence directly on an electronic interfering metal SS201 / inhibitor solution, were given in Table (9). The HOMO and LUMO the distributions of electron concentrations of the new surfactants that signify in Fig (14). Higher E_{HOMO} of elements with electrons providing (lager adsorption) had an affinity to donate unoccupied d-orbital by electrons. Low E_{LUMO} lead particles have a propensity to abstract electrons. ($\Delta E = E_{LUMO}$ - E_{HOMO}) estimated throw away of electron densities to higher complete level [45]. Hardness (η) and softness (σ) Table (9) shows the data of molecular stability and reactivity. The hardness of the surface displays the resistance of the distortions or deviation from the cloud of electrons, the atoms with slight perturbations in the reactions [46]. Generally, the huge values (σ) and small values (η) have good action. The dipole

moment (μ) denotes the covalent bonding of the polarities of the surfactants, reliant on the distributions of electrons cloudy. Also, (η) and (σ) are very vital factors for determining the stability's and reactivity's molecules. The hard molecules have large (ΔE) of the materials, and soft and smooth molecules have small (ΔE).



Figure 14. HOMO and LUMO electronic densities distributions of compounds (I, II and III) in the liquid phase.

Table 9. Quantum chemical parameters for compounds (I, II and III) in liquid phase.

13	parameter	Comp.(I)	Comp.(II)	Comp.(III)
DO	E _{HOMO} (eV)	-9.08	-8.97	-8.92
D	E _{LUMO} (eV)	-0.6	-0.46	-0.35
	$\Delta E (eV)$	8.480	8.510	8.570
	η(eV)	4.240	4.255	4.285
	σ(eV ⁻¹)	0.236	0.235	0.233
	Pi (eV)	-4.840	-4.715	-4.635
	χ (eV)	4.840	4.715	4.635
	μ (debyes)	1.650	1.280	1.020

The soft molecule is more active and lowers pitting due to easily donate for electrons to acceptors. In solution, the inhibitors act as a Lewis base (donor) but SS201 (vacant d- orbital) work as a Lewis acid (acceptor). The SS201 atoms are the soft acids then soft base inhibitor are more efficient in corrosive solution.

3.7. The mechanism of inhibition

Studying the effect of inhibition performance for the corrosion of SS201 in 1.0 M HCl, as destructive media, was investigated by using the HZD derivatives. The inhibition process base on many factors such as concentration, the numbers of active sites for their charges densities, molecular mass and their stability in its environments [47]. Actually, the electrons and charge quantities of heteroatoms (N, O, and S atom) which give the tendency to decrease or inhibit the corrosion of the metal surface. The inhibition process depends on the interface of the compounds (I, II, III) on the SS201, depress in active sites of the metal surface and reduce the dissolution. Surface-activities of inhibitors (HZD), organic compounds, can be used as inhibitors, due to large tendency to be adsorbed on the SS201 of the adsorption film of the HZD particles [48].

The sequence of IE is at I > II > III. This order of the lowering in the IE of the tested compounds can be accounted for in terms of the polar effect. I > II > III, this may be due to: the greater molecular size of (I) then (II) and (III), the existence of the number of $-CH_3$ and -OH group in the molecules (HZD) which adsorbed and form film on the SS201 by blocking the active site and reduce the dissolution SS201 in high concentration of HZD than lower as shown below.



Table (10) gives a comparison of %IE with a different investigated organic compound. The present HZD gives considerably significant corrosion %IE compared to another compound. Thus, the present HZD can utilize as a corrosion inhibitor with promising results

Inhibitor	Structure	sample	IE%	Referenc es
Ethyl-2-(m- tolyldiazenyl) acetate		SS 316L	71	49
(E)-3-oxo-2- (phenyldiazenyl) pentanenitrile		SS 316L	70	49
1,8- Octanediamine	H ₂ NCH ₂ (CH ₂) ₆ CH ₂	SS 304	58	50
4-Hydroxy coumarin	OH OH OH	Mild steel	61	51
Cetylpyridinium chloride	CI - CI - CH ₂ (CH ₂) ₁₄ CH	Carbon steel	81	52
HZD	present work	SS 201	89.6	This study

Table 10. Some organic compound as corrosion inhibitors by other authors for steel in HCl and in this study

4. CONCLUSIONS

The investigated hydrazine derivatives (I, II, III) is the best inhibitor for corrosion of SS201 in 1.0N HCl. From all experiments, the inhibition increase with raising HZD concentration and decrease with an elevation of temperature. Adsorption of HZD on SS201 surface obeys Langmuir isotherm. From thermodynamic value addition of HZD extract increase activation energy the negative data of (ΔG^{o}_{ads}), and $\Delta H^{o}ads$ indicate that adsorption spontaneous and exothermic. Potentiodynamic polarization technique suggests that HZD can use as an additive in anodic and cathodic protection.

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