Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2019, 8 (5): 2188-2212

(International Peer Reviewed Journal)

Extract of the Green Corrosion Inhibitor for Carbon Steel in 1N and 2N HCl (An Experimental and Theoretical Study)

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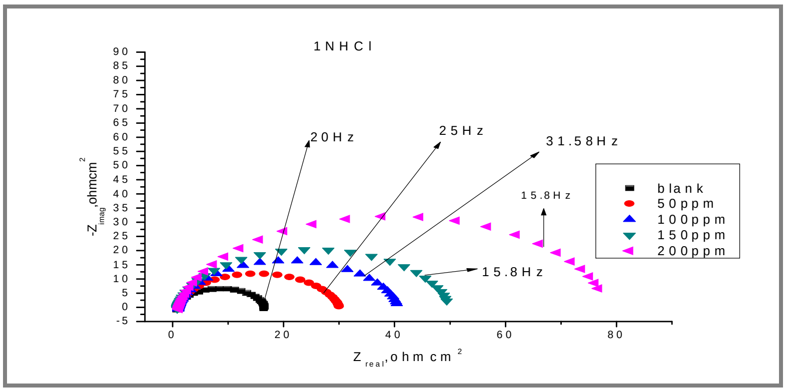
Accepted on 26th August, 2019

ABSTRACT

In our study the adsorption behavior of coffee husk extract and corrosion safeguard for carbon steel (C.S) in different concentrations from hydrochloric acid (1N and 2 N HCl solutions) have been examined using the gravimetric method, electrochemical methods [impendence spectroscopy (EIS), potentiodynamic polarization (pp), Electrochemical frequency modulation (EFM)], surface analysis [SEM, EDX, UV-Visible spectroscopy and FT-IR] and theoretical study. The electrochemical measurements and gravimetric method designated that the extract of coffee husk shows best protection productivity of up to 92.4% and 69.7% for C.S at 200 ppm from coffee husk extract in 1N and 2N HCl solutions at 25℃ respectively. The impact of temperature on protection efficiency, thermodynamic parameters, and adsorption isotherms for the coffee husk extract was studied. It was found that the adsorption occurred spontaneously, and the adsorption of coffee husk extract follows the Langmuir and Temkin adsorption isotherms. Potentiodynamic polarization measurements established that the extract of coffee husk performances as a mixed kind of inhibitor. The surface examination demonstrates the corrosion retardation of the coffee husk extract by the creation of a protective layer on the surface of C.S.

Graphical Abstract



Keywords: Coffee husk, Carbon steel, Corrosion, Electrochemical studies, Theoretical study.

INTRODUCTION

The damage by corrosion causes a high cost for inspection, repairing, replacement, and these give a public risk, so it is necessary to develop novel substances that behave as inhibitors for corrosion. However, most of the prepared inhibitors are toxic and expensive [1, 2]. So, the use of extracted from the plants is very important because these extracts are eco-friendly, non-toxic, cheap and effective inhibitors [3, 4]. In addition, plant extracts include altered organic assembled with hetero atoms (N, O) and conjugated bonds, are the best choice [5, 6]. The molecules of organic compounds are adsorbed on the surface metal among the hetero atoms and their conjugated structure. The adsorption for the organic molecules of the plant extracts can either be chemical, among covalent bond creation or physical, due to electrostatic interaction [7, 8]. Because of the low cost of carbon steel products, it's easy availability, and its excellent mechanical competency, it is used widely in the industry [9]. Hydrochloric acid consider is very important in many industries, and also used in washing procedures on surfaces of steel and this led to corrosion problems[10-15]. This research is intended to use coffee husk as a green and new inhibitor for corrosion inhibition for C.S in 1N and 2 N HCl by utilizing different techniques like gravimetric measurements, an electrochemical method, and analysis of the surface of C.S. In addition, the connection between the experimental data and the theoretical data has been shown.

MATERIALS AND METHODS

Materials and solutions: In present study, the utilized carbon steel has a chemical composition (in wt. %) 0.45% Mn, 0.11%C, 0.25% Si ,0.05% S, 0.04% P and Fe is the remained. The coupons of carbon steel which used have dimensions (20x20x1mm), the first step these coupons mechanically polished, after that by different grades of silicon carbide paper (320-1200), these coupons abraded, then washed with water bi-distilled, finally degreased by acetone, dried and put in desiccators. From stock (8 N HCl) the corrosive medium was prepared. This stock was prepared from a concentrated acid solution (37%, Merck) by liquefaction with water bi-distilled and checked by standard solution from sodium carbonate. The natural product, which used as an inhibitor is rich in organic compounds as, lignin, pectin cellulose, and hemicelluloses extract contain secondary compounds such as caffeine, polyphenol and tannin. Additionally, coffee husk extract contains chemical nutrients like nitrogen (N) and potassium (K) [16, 17]. From a powder of dried husk, we prepared the stock of inhibitor (1000 mg L^{-1}), firstly the coffee husk powder dripping in methanol for one week, and then the solution was filtered and distilled at 40 ^{0}C to eliminate the methanol from the extract, finally, the last step intense to dryness. 1g was obtained from the coffee husk extract, to liquefy in 1000 mL of water to obtain a dose of 1000 mg L^{-1}. In our measurements, new volumes were obtained from the solution stock of coffee husk to reedy altered dose of coffee husk with an aggressive solution (50-200 mg L^{-1}).

Gravimetric method: By means of glass hooks in beakers (100 mL) contain 100 mL from (1 or 2NHCl+ without and with differentconcentrations from coffee husk extract), the weighed specimens weresuspendedin triplicate, this step repeated at different temperatures(25-55°C). After that, the specimens taken out from the solution , rinsed and dried ,this step was applied conferring to the standard test [18] and the average weight loss was taken.By previously steps, and bythe altered in weight for an exposure period from 30 to180 min; the protection efficiency (%IE), the degree of surface coated (θ) and corrosion rate were calculated through the next equations:

$$\text{Inhibition efficiency (IE)}=100X(1-M_2/M_1)=100X\theta \quad (1)$$

$$\text{Corrosion rate(C.R)}=\Delta m/At \quad (2)$$

Where, M_2 = C.R in the existence of the coffee husk extract and M_1= C.R in the nonexistence of the coffee husk extract

Δm - loss in weight (mg), A - surface area of the coupons (cm^2), t - period of soaking (min)

Measurements by electrochemical techniques: In our investigation, we performed the electrochemical measurements utilizing the Gamry Instrument (PCI300/4) Potentiostat/Galvanostat/ ZRA, which contain a Gamry framework system established on the ESA400. Related to the potentiodynamic polarization measurements, the applications of Gamry included DC105 software, and for EIS and EFM, the applications, which used in the measurements, were EIS300 software and EFM 140 software respectively. Three electrodes were used as a standard in this method: a counter electrode, reference electrode (SCE) and the working electrode (WE). For plotting, graphically displaying, and fitting the value, utilizes E_{chem} Analyst 6.03 software. In Tafel polarization, we used scan rate 1 mVs^{-1} and related to potential range from -500to +500mV with respect to E_{ocp}.

EDX-SEM technique: The surface of carbon steel was accepted out by placing the specimen for 24 h immersing in 1NHCl and 2 N HCl in an existence and lack of higher dose of coffee husk extract (200 mg L^{-1}), SEM model HITACHI S-3000H combined to an analyzer EDAX-RONTEC were utilized to apply this experiment.

FTIR test: Fourier transform infrared spectrometer kind FT/IR-4100 type A, Serial Number B117761016was utilized to estimate the molecular structure and active groups of coffee husk extract.

UV-Visible spectroscopy: The result of coffee husk spectra, which obtained from UV spectroscopy technique, was a result of immersing the coupons of carbon steel 24 h in 1N and 2 N HCl in existence and non-existence of 200 mg L^{-1} coffee husk extract.

Molecular docking: This study mimics the real docking procedure in which the ligand–protein pair-wise interaction energies are measure utilizing Docking Server [19]. The MMFF94 Forcefield was for utilized minimization energy of ligand molecule utilizing Docking Server. Gasteiger charges partial were appending to the ligand atoms. Non-polar hydrogen atoms were combined, and rotatable bonds were definite. Calculations Docking were accepted on caffeine assembled protein model. Kollaman united atom type charges, Essential hydrogen atoms, and added parameters gotten from solvation with the aid of Auto Dock tools [20, 21]. Distance-dependent dielectric functions and parameter from AutoDock set- were utilized in the measure the electrostatic terms and the van der Waals, respectively.

Calculations of quantum chemistry: From the important compounds, which found in coffee husk extract is caffeine because it was used in many studies for corrosion inhibition of metals. So in our present study, the theoretical calculations were used for caffeine compound. The molecules investigated by using (Material Studio Version 7) Accelrys software to evaluate the chemical quantum parameters (electronegativity χ, chemical potential **Pi**, global hardness η andsoftnessσ**)** calculated by VAMP module (PM3 semi-empirical method) and DMol3 module as demonstrated in the next equations [22, 23]:

$$P_i = -\chi \qquad (3)$$

$$P_i=(E_{LUMO}+E_{HOMO})/2 \qquad (4)$$

$$\eta= \Delta E/2=(E_{LUMO}-E_{HOMO})/2 \qquad (5)$$

By the global hardness the softness is designated σ:

$$\sigma =1/\eta \qquad (6)$$

The electronegativity and global hardness were utilized to calculate the fraction of electrons transferred(ΔN) as shown from the next equation:

$$\Delta N=(\chi_{Fe}-\chi_{inh})/2(\eta_{Fe}-\eta_{inh}) \qquad (7)$$

Where $\chi_{Fe}$and χ_{in} giving the absolute electronegativity of copper and molecules of inhibitors, respectively.

According to Pearsons electronegativity scale, the electronegativity of iron is 7 and its hardness is 0 eV/mol [24].

RESULTS AND DISCUSSION

Gravimetric study: C.R (corrosion rate) and the inhibition efficiency of corrosion (IE) were obtained from the gravimetric study for carbon steel, existence and nonexistence of altered dose from the coffee husk in 1 and 2N HCl. The results were demonstrated in tables 1-4 and figures 1 and 2. It is clear that by increment the dose of coffee husk, the IE% increases and the C.R of carbon steel (C.S) lower dramatically. Theseoutcomesillustrate that the coffee husk adsorbed on C.S and the surface coverage increases [25]. The film of adsorption blocks the active sites, because of the molecules, which contain numbers of heteroatoms. This leads to the C.S surface isolates from the aggressive medium.

Table 1. Outcome data gotten from WL (weight loss) of C.S in 1N HCl for an altered dose of coffee husk extract after 120 min., at (25, 35°C)

Conc., Ppm	**25°C**				**35°C**			
	Δm mg cm^{-2}	**ϴ**	**% IE**	**C.R.,** mg cm^{-2} min^{-1}	**Δm mg cm^{-2}**	**ϴ**	**% IE**	**C.R., mg cm^{-2} min^{-1}**
Blank	29.60	----	----	0.246	30.04	-----	-----	0.250
50	3.62	0.877	87.7	0.030	7.86	0.740	74.00	0.065
100	3.08	0.896	89.6	0.026	6.90	0.770	77.00	0.058
150	2.65	0.910	91.0	0.022	6.09	0.797	79.70	0.051
200	2.26	0.924	92.4	0.019	5.49	0.817	81.70	0.046

Table 2. Outcome data gotten from WL of C.S in 1N HCl for an altered dose of coffee husk extract after 120 min., at (45, 55°C)

Conc., ppm	**45°C**				**55°C**			
	Δm mg cm^{-2}	**ϴ**	**% IE**	**C.R., mg cm^{-2} min^{-1}**	**Δm** mg cm^{-2}	**ϴ**	**% IE**	**C.R., mg cm^{2}min^{-1}**
Blank	43.18	------	------	0.36	63.26	-----	-------	0.527
50	16.49	0.618	61.81	0.14	26.63	0.58	57.91	0.222
100	14.75	0.658	65.85	0.12	24.36	0.61	61.50	0.203
150	12.83	0.703	70.29	0.11	21.77	0.65	65.58	0.181
200	11.68	0.729	72.95	0.09	19.68	0.69	68.89	0.164

Table 3. Data from weight loss of carbon steel in 2N HCl for various concentrations of coffee husk extract after 120 min., at (25, 35°C)

Conc., ppm	**25°C**				**35°C**			
	Δm mg cm^{-2}	**ϴ**	**% IE**	**C.R.,** mg cm^{-2} min^{-1}	**Δm mg cm^{-2}**	**ϴ**	**% IE**	**C.R.,** mg cm^{-2} min^{-1}
Blank	36.249	----	-----	0.302	39.126	----	----	0.326
50	10.394	0.713	71.30	0.087	17.551	0.551	55.14	0.146
100	9.584	0.736	73.60	0.080	16.399	0.581	58.09	0.137
150	8.869	0.755	75.50	0.074	15.044	0.616	61.55	0.125
200	7.960	0.786	78.60	0.066	13.703	0.650	65.00	0.114

Table 4. Data from weight loss of carbon steel in 2M HCl for various concentrations of coffee husk extract after 120 min., at (45, 55°C)

Conc., Ppm	**45°C**				**55°C**			
	Δm mg cm^{-2}	**ϴ**	**% IE**	**C.R., mg cm^{-2} min^{-1}**	**Δm mg cm^{-2}**	**ϴ**	**% IE**	**C.R., mg cm^{-2} min^{-1}**
Blank	65.322	--	--	0.544	92.011	--	--	0.767
50	34.010	0.479	47.93	0.283	56.663	0.384	38.42	0.472
100	31.776	0.514	51.35	0.265	53.947	0.414	41.37	0.450
150	29.512	0.548	54.82	0.246	50.627	0.450	44.98	0.422
200	26.831	0.589	58.92	0.224	47.760	0.481	48.09	0.398

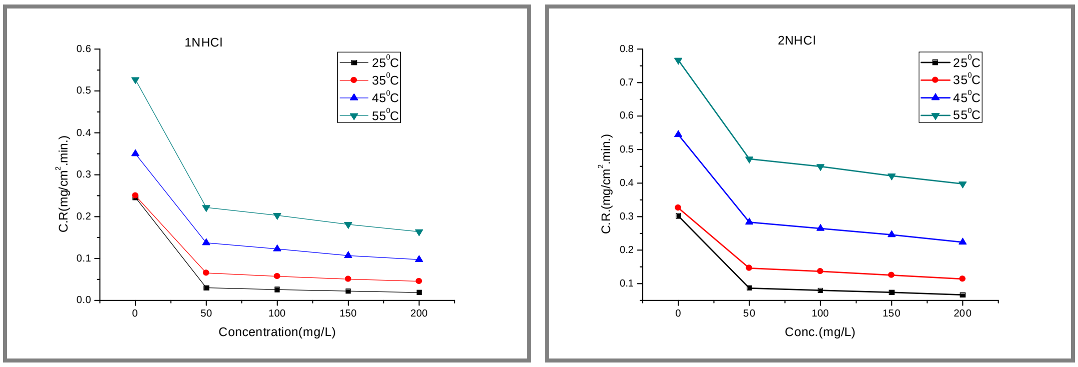


Figure 1. C. R for various dose from coffee husk extract on the surface of C.S in 1and 2 N HCl at 25 -55°C.

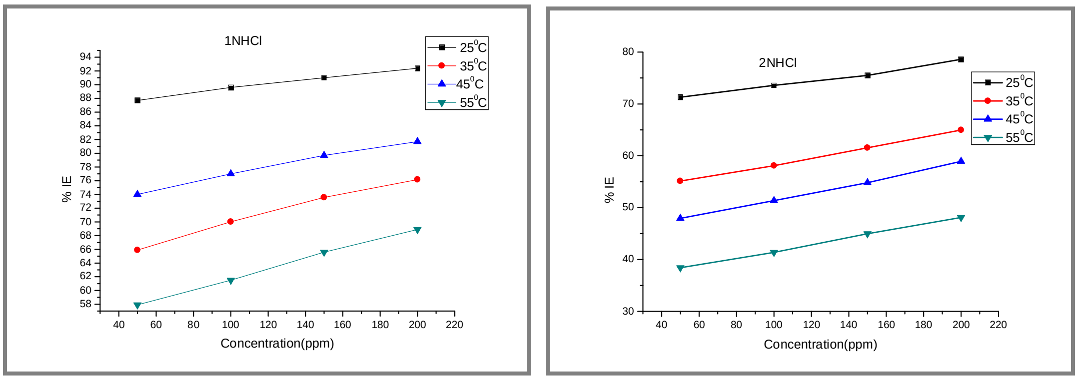


Figure 2. The dissimilarity of corrosion IE of C.S with different doses from coffee husk extract in 1and 2N HCl solutions at altered temperatures.

The temperature effect and calculations of activation parameters: From Figures1 and 2, and the data listed in Tables 1-4, the corrosion reaction accelerated by raising the temperature, so the C.R rises and IE decreases. As we know, on the C.S surface, different changes happened as rapid adsorption and desorption of coffee husk extract, also molecules of the extract may undergo decomposition, rearrangement and some chemical changes that happen to improve the efficiency of adsorption [26-28].

In our present study, we calculated the parameters gotten from thermodynamic of corrosion reaction (ΔS_a , E_a, and ΔH_a) by using an Arrhenius (Eq.8) and transition state theory (Eq.9) as shown:

$$C.R=A\exp(-E_a/RT) \quad (8)$$

$$C.R=RT/Nh\exp(\Delta S_a/R)\exp(-\Delta H_a/RT) \quad (9)$$

Where: A is the frequency factor and h Plank's constant.

In figure 3 we plotted log CR against 1/T .From the intercept and slope,we obtained the data of A and E_a. demonstrated the relation between log(CR/T) and1/T, slopes equal $(\Delta H_a/2.303R)$ and intercepts equal $(\log R/Nh + \Delta S_a/2.303R)$.Table 5 collects the values of activation parameters. Table 3 demonstrated that the values E_a for extract in 2NHCl less than the values of E_a for extract in 1NHCl and the activation energy increase by increasing the concentration of extract, so the corrosion rate in 2NHCl more than the corrosion rate in 1NHClat the surface of carbon steel. Therefore, the coffee husk extract is a good inhibitor and this concluded increment E_a of C.S liquefaction by creating a barrier to mass and charge transfer by its adsorption on C.S surface. The sign +ve of the ΔH_a demonstrated the endothermic type for carbon steel liquefaction. The ΔS^* data existence and nonexistence of the extract are maximum and –ve sign; i.e. the activated complex in the rate-determining step favors association rather than dissociation step, significance that a lesser in disordering obtain [29].

Table 5. The outcome data obtain from Kinetic-thermodynamic for C.S corrosion in the nonexistence and existence of an altered dose of coffee husk extract

Comp.	Conc., ppm	Ea, kJ mol^{-1}	ΔH, kJ mol^{-1}	-ΔS, J $mol^{-1}K^{-1}$
1N HCl	Blank	44.533	41.91	122.72
	50	54.980	52.36	97.98
	100	56.340	53.72	94.56
	150	57.538	54.91	91.88
	200	58.771	56.15	88.87
2N HCl	Blank	34.730	32.12	149.80
	50	46.587	43.97	117.84
	100	47.452	44.83	115.62
	150	47.914	45.29	114.78
	200	49.256	46.64	111.23

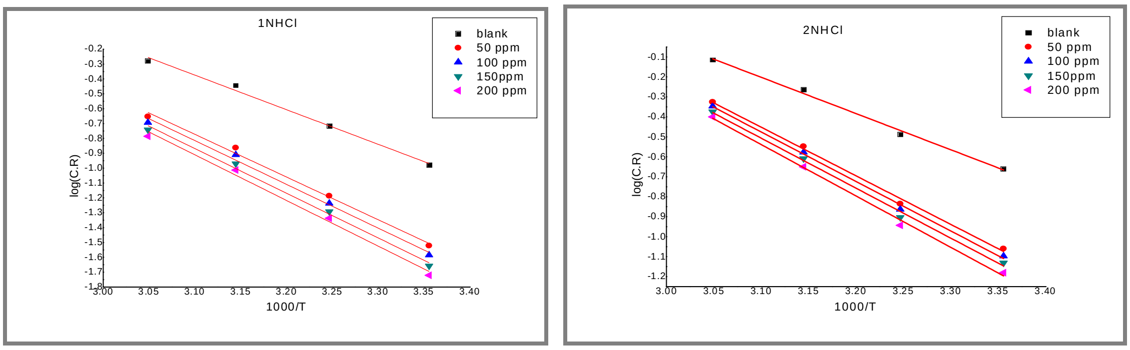


Figure 3. log C.R vs 1/T curves for C.S in 1 and 2N HCl solution in the presence and absence of altered dose of coffee husk extract using WL measurements.

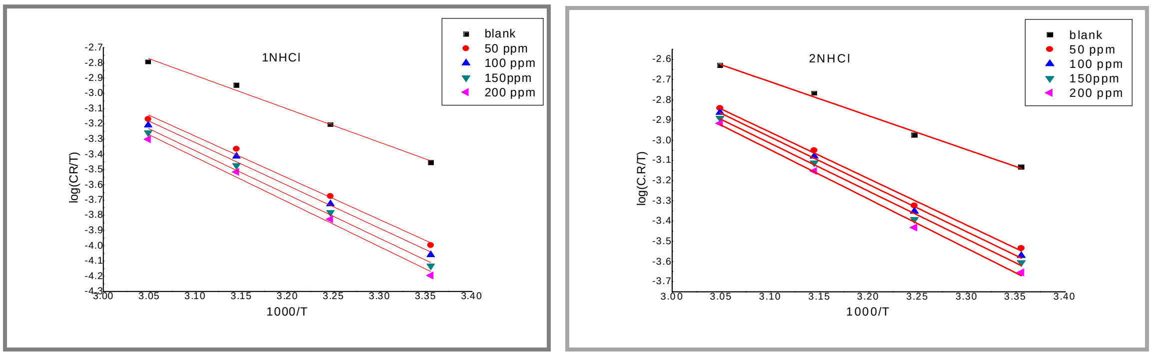


Figure 4. log C.R/T vs 1/T curves for C.S in 1 and 2N HCl solution in the presence and lack of altered dose of coffee husk extract using WL measurements.

Adsorption isotherms: The behavior of adsorption can be demonstrated by the isotherms of adsorption, it enables the elucidation of the investigated the mechanism of ionic liquid inhibition by understanding its behavior [30, 31]. The common adsorption isotherms fitting were used to analyze the data are Langmuir, Freundlich, Temkin, Flory–Huggins and Frumkin [32, 33]. In the present study, the data of our experiment, reveals to the best fitted for Langmuir isotherm and Temkin isotherm figures 5, 6 (Eq.10, Eq.11 respectively).

$$C_{inh.} / \theta = 1/K_{ads.} + C_{inh} \qquad (10)$$

$$a\theta = \ln K_{ads} + \ln C_{inh} \qquad .(11)$$

C_{inh}=inhibitor dose, K_{ads}= the adsorption constant equilibrium, and a = parameter of lateral interaction which describes the molecular interactions in the adsorbed layer and the degree of heterogeneity of the surface. From tables 4 and 5, the Langmuir isotherm was established to be a good explanation of the adsorption manner of the coffee husk extract on the surface of C.S than Temkin due to the accuracy R^2.The data of tables 4 and 5 designate to lower the data of K_{ads} by temperature raising. The high values of K_{ads} reveal to the adsorption ability of coffee husk on the surface of C.S [34]. The relation between K_{ads} and ΔG_{ads} of coffee husk extract on the C.S at altered temperatures were determined using the following relationship [35, 36]:

$$\Delta G_{ads} = -RT\ln(55.5K_{ads}) \qquad (12)$$

The previously relation was used to understand the adsorption type of coffee husk extract. The value of free energy designates that the adsorption is spontaneous because the data were negative [37]. The type of adsorption was physical adsorption because the valueswerearound–20 KJmol^{-1} (according to Langmuir adsorption) [38]. The heat of adsorption was calculated by Van't Hoff equation (13)[39]:

$$\text{Log } K_{ads} = (-\Delta H_{ads}/2.303RT) + (\Delta S_{ads}/ R) + \ln(1/55.5) \qquad (13)$$

And this by drawing log K_{ads}vs. 1/T (Figure 7); the values of ΔH_{ads} which obtained from the slopes (Tables 6, 7) were negative and smaller than the absolute value of physical adsorption(40KJmol^{-1}),so the adsorption of coffee husk extract is exothermic adsorption and physical adsorption [40].

From tables 6 and 7 the values of entropy were positive and this qualified to the rise of solvent entropy. That is, coffee husk extract was adsorbed on the surface of C.S as soon as the molecules of water get absorbed. It is reported that exothermic physisorption [41]. From our study, the values of K_{ads} when the corrosive medium is 1NHCl more than the values when the corrosive medium 2NHCl.

This indicates the ability of inhibition in the 1NHCl solution for coffee husk extract more than in 2NHCl solution.

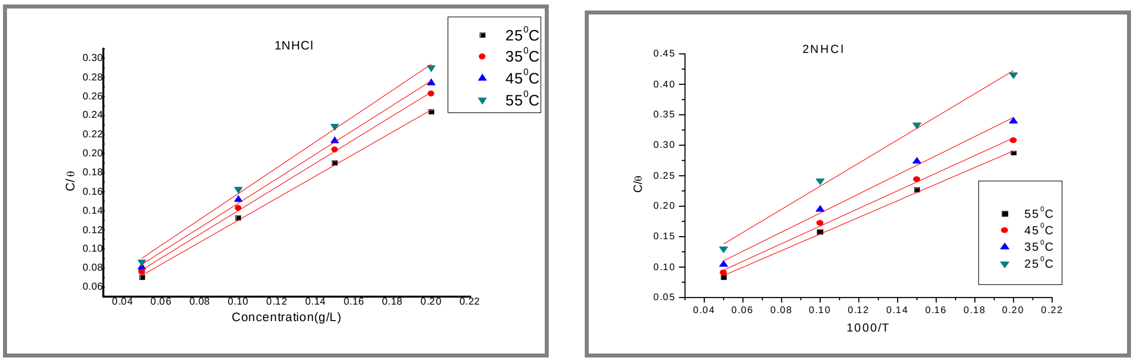


Figure 5. Langmuir isotherm for coffee husk extracts adsorbed on C.S in 1 and 2N HCl at altered temperatures after 120 min. soaking.

Table 6. Adsorption parameters on C.S corrosion inhibition by coffee husk extract obtained from Langmuir and Temkin adsorption isotherms in 1N HCl

Temp, °C	Langmuir isotherm					Temkin isotherm					
	K_{ads}	R^2	-ΔH, $KJ.mol^{-1}$	ΔS, $J\ mol^{-1}K^{-1}$	$ΔG^o_{ads}$, $KJ.mol^{-1}$	a	log K	R^2	-ΔH, KJ. mol^{-1}	ΔS, $J\ mol^{-1}K^{-1}$	$-ΔG^o_{ads}$, $KJ.mol^{-1}$
25	69.10	0.990	24.44	12.45	20.45	12.80	0.270	0.975	5.52	27.63	11.019
35	62.58	0.998			20.88	12.37	0.250	0.982			11.426
45	50.66	0.990			20.99	13.57	0.212	0.967			12.353
55	44.46	0.996			21.31	13.12	0.187	0.945			12.353

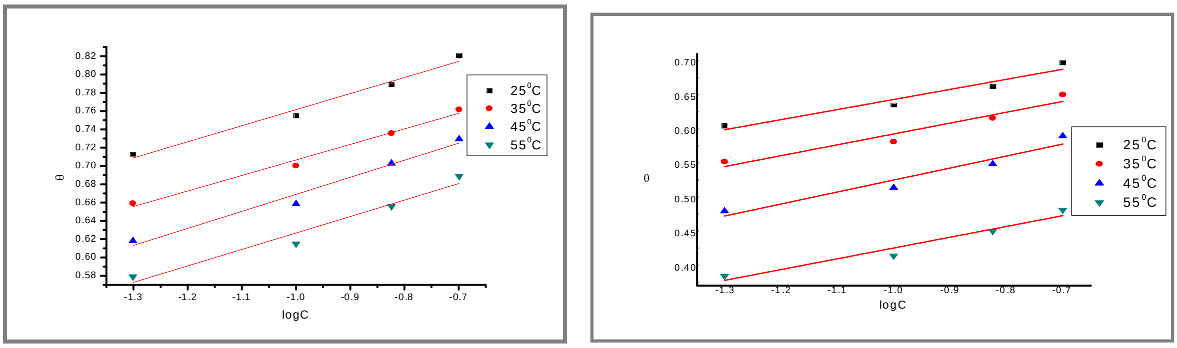


Figure 6. Temkin isotherm for coffee husk extracts adsorbed on C.S in 1 and 2N HCl at altered temperatures after 120 min. soaking.

Table 7. Adsorption parameters on C.S corrosion inhibition by coffee husk extract obtained from Langmuir and Temkin adsorption isotherms in 2N HCl.

Temp, °C	Langmuir isotherm					Temkin isotherm					
	$K_{ads.}$	R^2	-ΔH, KJ. mol^{-1}	-ΔS $J\ mol^{-1}K^{-1}$	$-ΔG^o_{ads}$, $KJ.mol^{-1}$	a	log K ads.	R^2	-ΔH $KJ.mol^{-1}$	-ΔS $J\ mol^{-1}$ K^{-1}	$-ΔG^o_{ads}$ $KJ.mol^{-1}$
25	55.52	0.996	12.41	70.47	19.91	14.6	0.223	0.929	2.45	88.67	12.65
35	43.76	0.995			19.96	13.1	0.217	0.916			12.15
45	31.29	0.992			19.73	14.5	0.193	0.918			11.53
55	23.22	0.992			19.53	15.6	0.186	0.926			11.02

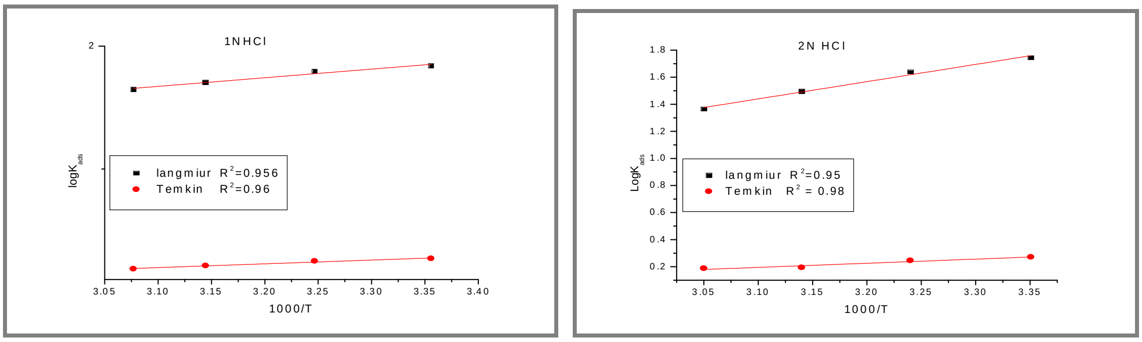


Figure 7. log K_{ads} vs. (1/T) diagrams for the C.S corrosion in1N and 2NHCl in existence and nonexistence of unlike dose of coffee husk extract at different temperatures.

OCP vs. Time study: The relation between the potential and the time is demonstrated in figure 8. After adding different concentrations from coffee husk extract at 25°C, this figure indicated to that, the blank solution is the most corrosive, it trends first to more negative values, after that itrises to a short step. By adding different concentrations from coffee husk extract, E_{corr} tends to move to a more noble direction and by the time, the values tend to stabilize. The stabilization by the time indicated to the adsorption and desorption of extract coffee husk shows dynamic stability, in the existence of altered dose from coffee husk [42-44].

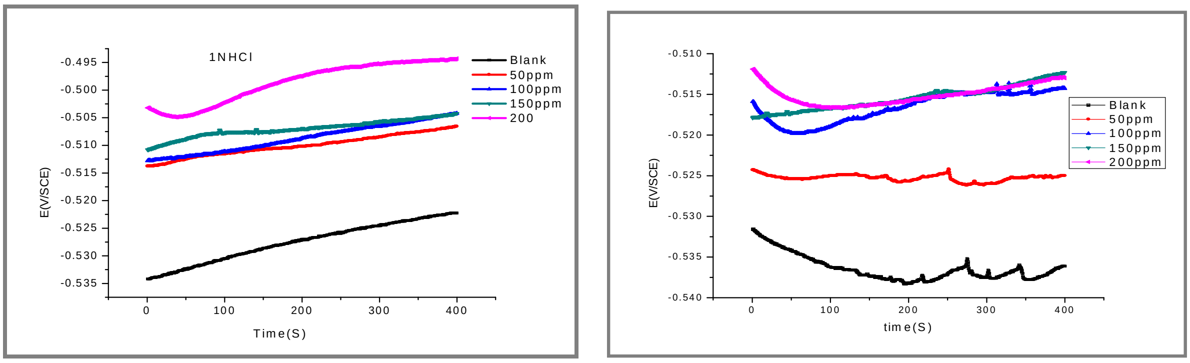


Figure 8. Variation of the OCP against the time of the C.S in 1 and 2 N HCl solutions and containing different concentrations from coffee husk extract at 25°C.

PP (potentiodynamic polarization) study: PP (potentiodynamic polarization) measurements are the other test was obtained to demonstrate the kinetic process of cathodic reactions and anodic. Figure 9 displays the Tafel diagrams of C.S in 1 and 2N HCl in nonexistence and the existence of an altered dose of coffee husk extract. The parameters of electrochemical kinetics [Tafel slopes(β_c,β_a), corrosion current (I_{corr}), corrosion potential and polarization resistance(R_p)] were presented in table 8. From table 8, by raising the concentration of coffee husk extract, the I_{corr} is decreased and the inhibition efficiency is increased and this because of the formation non-conductive layer when the coffee husk extract adsorbed on the surface of C.S [45, 46]. Also, the cathodic and anodic slopes had changed with the addition of coffee husk extract. So, this extract influences on the cathodic and anodic reaction [47]. The change of E_{corr} less than 85mV reveals the coffee husk extract is working as a mixed type inhibitor [48]. Figure 10 indicated to the polarization resistance increased by raising the dose of coffee husk extract as a result of adsorption this extract on the C.S surface [49]. The protection efficiency was obtained by the next equation:

$$I\% =(I^0_{corr} - I_{corr})/ I^0_{corr} \ x100=\theta x100 \qquad (14)$$

Where I^0_{corr} and I_{corr} are the currents of corrosion nonexistence and existence the coffee husk, correspondingly. The inhibition efficiency for coffee husk extracts in 1NHCl more than 2NHCl.

Table 8. PP parameters for C.S corrosion in 1and 2N HCl in the nonexistence and existence of altered dose of coffee husk extract at 25°C

Conc. of HCl	Inh.Conc, ppm	$-E_{corr}$, mV	I_{corr},A cm^{-2}	R_P, ohm	$-\beta_c$,mV dec^{-1}	β_a,mV dec^{-1}	Corrosion Rate, mpy	θ	I%
1N	blank	493	2.100	5.961	207.7	173.6	498.3	--	--
	50	486	0.317	6.673	205.9	113.4	327.8	0.849	84.90
	100	488	0.298	7.780	186.9	93	273.1	0.858	85.80
	150	478	0.201	7.892	179.5	85.7	183.2	0.904	90.04
	200	483	0.179	8.135	161.9	75.4	127.7	0.919	91.90
2N	blank	520	2.630	4.298	249.3	223.1	971.4	--	--
	50	513	0.770	6.081	223.7	148.0	701.3	0.707	70.70
	100	500	0.676	7.290	221.6	142.6	400.4	0.743	74.30
	150	501	0.653	7.350	219.0	125.5	380.7	0.752	75.20
	200	500	0.574	7.64	193.9	111.4	289.6	0.782	78.20

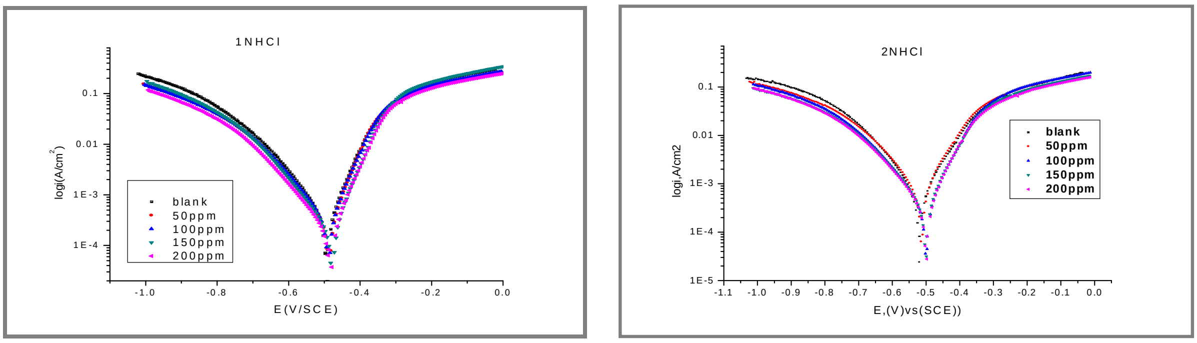


Figure. 9. Cathodic and anodic polarization diagrams for C.S in1 and 2N HCl in the nonexistence and existence of an altered dose of coffee husk at 25°C.

(EIS) Tests: In this investigation, we used EIS to study the mechanism of corrosion. The results of Nyquist and Bode plots are demonstrated in figures 11 and 12 respectively, and these figures showed a gradual increase in the semicircle diameter of the Nyquist diagrams by raising the dose of extract coffee husk. Therefore, the molecules of coffee husk extract retard the corrosion rate [**50**]. From figure 11 we noticed that the deviation from an ideal semicircle because of frequency dispersion due to the in homogeneity of the surface [**51**].

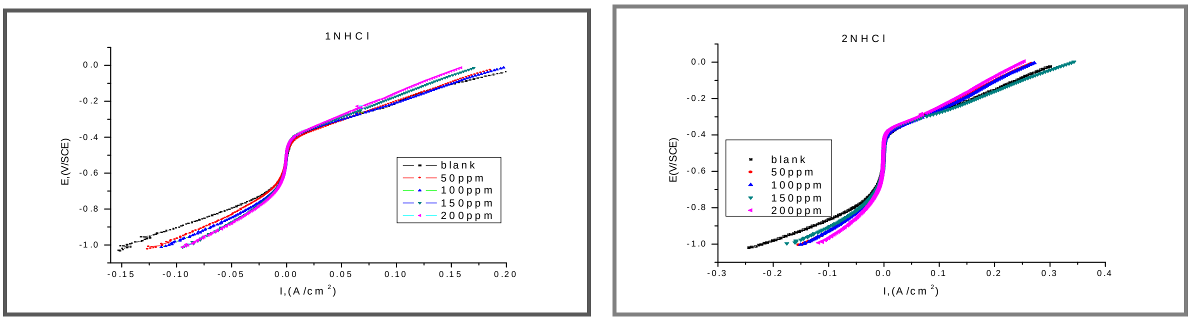


Figure 10. Linear sweep voltammetry plots of carbon in 1 and 2 N HCl with an altered dose of coffee husk.

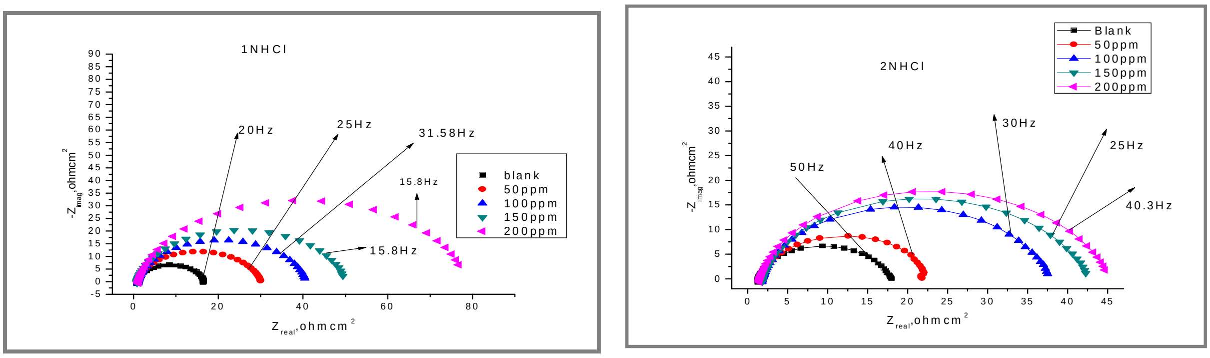


Figure 11. Nyquist plots of C.S in 1 and 2N HCl solutions in the existence and nonexistence of altered dose of coffee husk extract at 25°C.

Table 9 gives different parameters of impedance as, resistance charge transfer (R_{ct}), double layer capacitance (C_{dl}), protection efficiency (IE) and electrolyte resistance (Rs). The data of table 9 demonstrated that, the C_{dl} data lowered by raising the dose of coffee husk, this behavior because of molecules adsorption on the surface of carbon steel, and this demonstrated from Helmholtz model, where the capacitance of double layer was obtaining by the next relation [**52**].

$$C_{dl} = A(\varepsilon\varepsilon_0/\delta) \qquad (15)$$

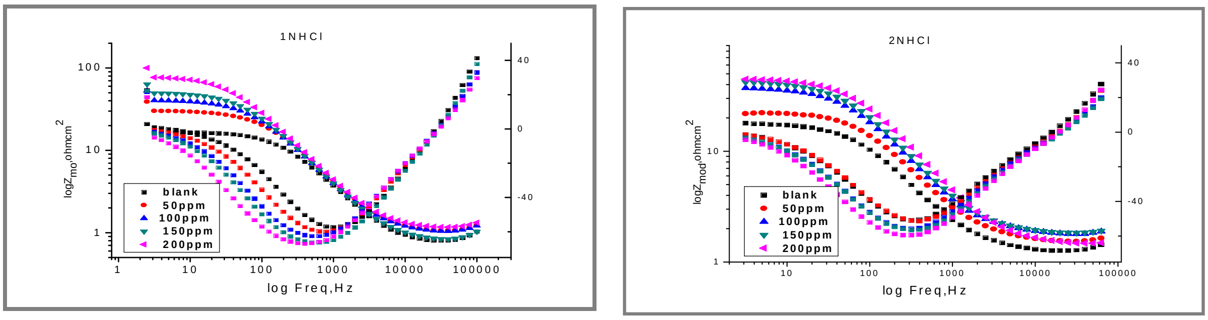


Figure 12. Bode diagrams for corrosion of C.S in 2N HCl in the existence and nonexistence of altered dose of coffee husk extract at 25°C.

Where A is the electrode area, ε is the dielectric constant of the solution, ε_0 the permittivity vacuum, and δ the thickness of the protective layer. From this equation, the data of double layer capacitance lower by raising the thickness of electric the double layer and/or because of decreasing local dielectric constant. The values of charge transfer resistance raise by increment the dose of coffee husk and this demonstrated the creation of a protective layer on the interface alloy/solution [53]. Figure 13 reveals to equivalent circuit, which used in our study [54]. The C.S impedance can be measure from the next relation [55]:

$$Z_{CPE}=Y_0^{-1}(j\omega)^{n-1} \qquad (16)$$

Where, (Y_0), $j^2 = -1$and ω are CPE coefficient, the imaginary number and sine wave modulation angular frequency respectively. The values of n between 0 and 1 in the real experimental study, and this because of different reasons, as dielectric constant, the roughness of the electrode and surface heterogeneity [56]. The data of double layer capacity were measured from the next relation [57]:

$$C_{dl}=Y_0\omega^{n-1}/\sin[n(\pi/2)] \qquad (17)$$

The data of inhibition efficiency, which found in table 6 were calculated from the following equation:

$$\%IE= 100X\theta =[1-(R^0_{ct}/R_{ct})] \qquad (18)$$

Where R^0_{ct} and R_{ct} are the charge transfer resistances existence and nonexistence addition different concentration from coffee husk extract. This investigation demonstrated that the coffee husk extract more effective in 1NHCl than in 2NHCl solutions.

Table 9. Impedance parameters recorded for C.S electrode in (1 and 2N HCl) solutions in the absence and attendance of altered dose of coffee husk at 25°C

Conc. of HCl	Conc, ppm	R_s, ohm cm^2	R_{ct}, ohm cm^2	Y° Ω^{-1}sn X10^6	n	C_{dl}, F cm^{-2} X10^5	θ	%IE
1N	Blank	0.981±0.004	6.2±0.011	55.95±0.24	0.983±0.005	5.55	--	--
	50	1.060±0.009	48.16±0.022	81.85±0.29	0.926±0.004	5.36	0.871	87.10
	100	1.058±0.009	58.79±0.032	93.55±0.30	0.921±0.004	4.89	0.895	89.50
	150	0.847±0.007	67.44±0.039	83.53±0.24	0.915±0.004	4.43	0.908	90.80
	200	1.17±0.009	79.41±0.066	85.14±0.66	0.914±0.003	4.33	0.921	92.10
2N	Blank	1.29±0.001	12.23±0.0133	146.1±6.4	0.997±0.005	7.69	--	--
	50	1.56±0.012	40.52±0.0165	110.8±4.9	0.998±0.005	5.55	0.698	69.80
	100	1.83±0.014	46.27±0.0293	95.5±3.64	0.994±0.005	5.29	0.736	73.60
	150	2.016±0.015	49.79±0.0328	86.19±3.19	0.892±0.005	4.88	0.754	75.40
	200	1.49±0.011	54.61±0.0357	96.90±3.26	0.981±0.004	4.86	0.776	77.60

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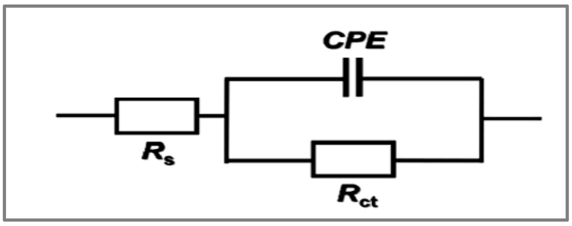


Figure 13. Equivalent circuit, which used to fit the EIS data.

(EFM) Tests: EFM has a small ac signal as EIS technique, and from the alteration between two tests, EFM has two sine waves (at varies frequencies) are applied to the cell at the same time. EFM test considers a nondestructive corrosion test because it gives the data of corrosion current directly without Tafel constants information. The data of this technique are collected in table 10 [Tafel constants (βa, -βc), inhibition efficiency, corrosion current density (mA cm^{-2}), and causality factors (CF-2, CF-3)].Causality factors give great strength to this technique because they are considered as an internal check on the validity of the EFM measurements [58].The data of causality factor which recorded in table 10 are good quality because these values close to theoretical values of CF-2 and CF-3 (2 and 3 correspondingly), this reveals that, there is a causal relationship among the response signal and the perturbation signal. Also, the value is presumed to be reliable [59]. Figure 14 gives the inter modulation spectra which gotten from EFM test for different concentration from coffee husk extract for 2NHCl (the other data not shown). It is clear from table 10 that, by increasing the concentration of coffee husk extract, the current density of corrosion decreases and the inhibition efficiency increases. We used the next equation to calculate the inhibition efficiency from this technique:

$$\%IE = 100X\theta = 100\ x[1-(i_{corr}/i^{0}_{corr})] \qquad (19)$$

Where i_{corr} and i^{0}_{corr} are the corrosion current in the presence and absence of different concentration of coffee husk extract. These techniques insured the results of other techniques, which demonstrated that, the inhibition of coffee husk extract on the surface of carbon steel in 1NHCl more than inhibition in the presence of 2NHCl.

From our study, we noticed that, the slight difference in the inhibition, which obtained through the different techniques used, and this because of the variation among the individual tests and the altered models, which utilized for the interpretation [60].

Table 10. Parameters obtained by EFM method for C.S in 1 and 2N HCl in the existence and lack of an altered dose of coffee husk

Conc. of HCl	Inh.Conc, ppm	i_{corr} , A cm^{-2}	β_a, mV dec^{-1}	$-\beta_c$, mV dec^{-1}	CF-2	CF-3	θ	%IE	R_{corr}, mpy^{-1}
1N	Blank	2.400	75.97	96.87	1.986	3.072	--	--	533.0
	50	0.308	75.09	94.86	1.955	2.985	0.872	87.20	278.0
	100	0.266	78.42	95.72	1.882	2.976	0.889	88.90	213.0
	150	0.208	75.87	95.32	1.970	2.809	0.913	91.30	172.0
	200	0.187	76.9	94.04	1.982	2.84	0.922	92.20	111.7
2N	Blank	2.700	83.94	94.13	1.884	3.213	--	--	464.2
	50	0.804	86.29	100.20	1.951	2.85	0.702	70.20	418.0
	100	0.725	83.54	95.43	1.916	2.553	0.731	73.10	196.6
	150	0.683	83.06	97.79	1.808	2.508	0.747	74.70	241.0
	200	0.577	82.12	96.67	1.967	2.543	0.786	78.60	208.9

EDX - SEM technique: Figures. 15 and 16 reveal images of SEM for the surface of carbon steel. Figurers15 and 16(a), the surface of carbon steel free from the product of corrosion but found scratches because of the grinding procedure. Figures15 and 16 (b) after one day from immersion in

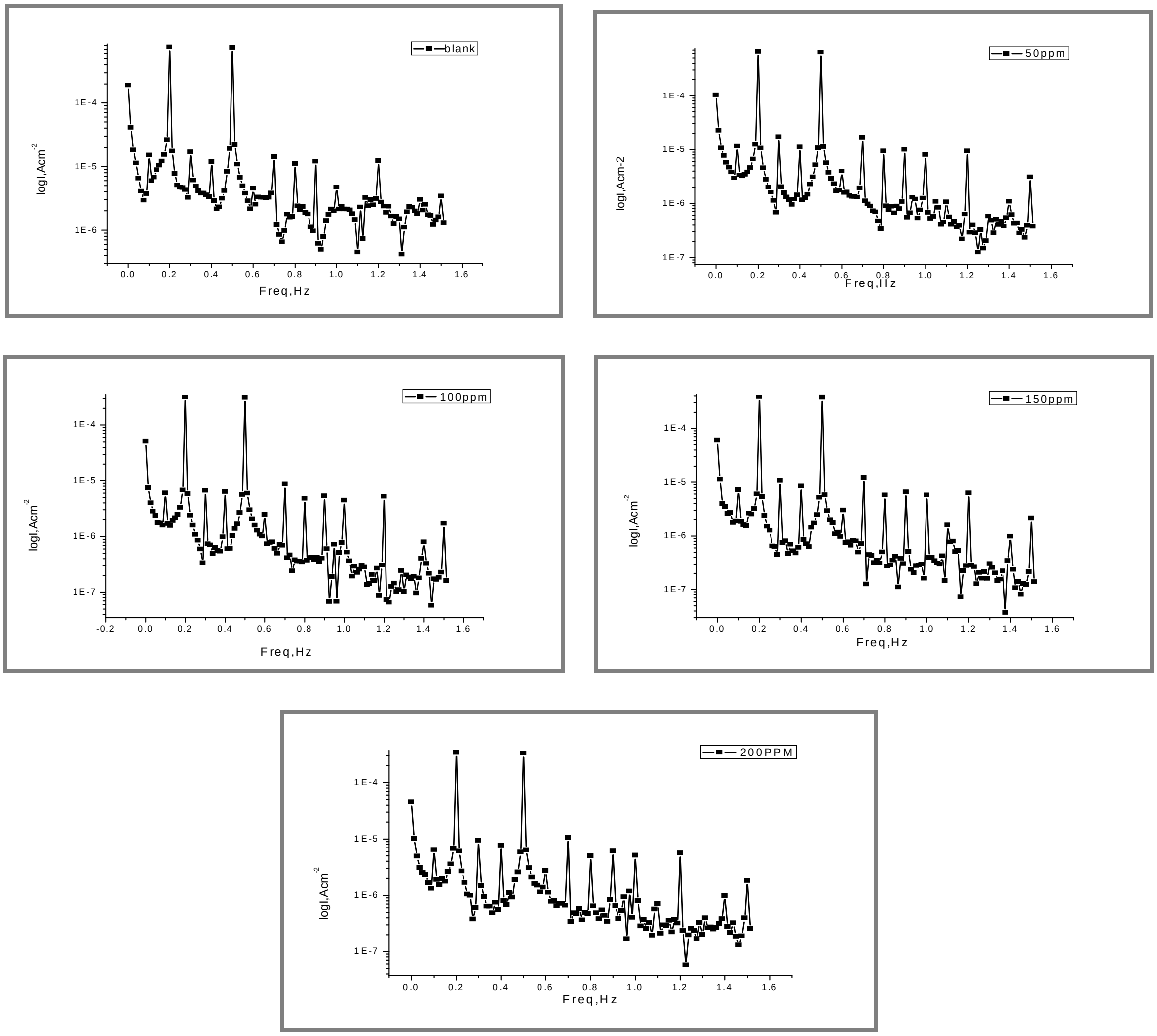
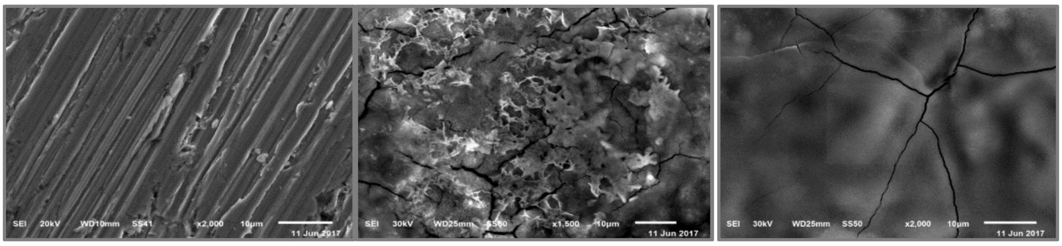


Figure 14. EFM diagrams for C.S in 2N HCl solutions in the existence and lack of altered dose of coffee husk.

1 and 2N HCl and indicated torise degree of attack with the corrosion product which precipitated on the surface of C.S. Figures. 15 and16(c), after immersion in1N and 2N HCl for 24h in presence of 200mg L^{-1} of coffee husk extract. Which, demonstrated that the creation of protective layer randomly distributed on the surface, so the contact between the surface and aggressive medium decrease; this because of the adsorption of molecules of coffee husk on the surface of C.Swhich gives passive film block the existence of the active side on the C.S surface [61, 62].



(a) (b) (c)

Figure 15. Scanning electron microgram of carbon steel (a) alone (b) after soaking in 1 N HCl (c) after soaking in 2 N HCl containing 200 ppm of inhibitor.

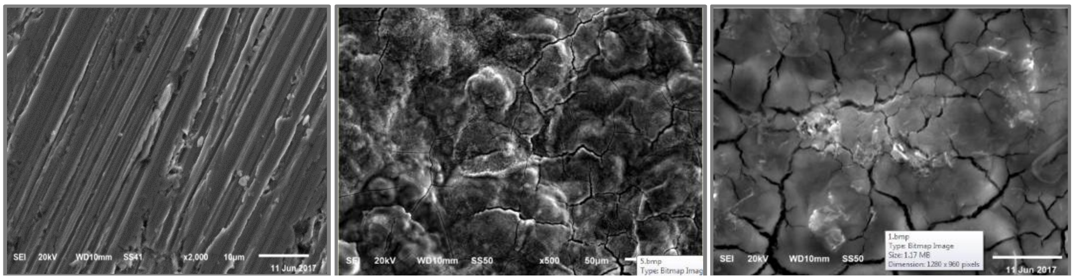


Figure 16. Scanning electron microgram of carbon steel (a) alone (b) after soaking in 2N HCl (c) after soaking in 2N HCl containing 200 ppm of inhibitor.

In our study, EDX spectra were utilized to demonstrate the type of elements, which found in the C.S surface after soaking it 24 h in1 and 2N HCl at nonexistence and existence 200ppm of coffee husk extract. The surface of carbon steel without any exposure to acid or coffee husk extract solution is demonstrated in figures 17 and 18(a), which demonstrated the elements constituting a sample of carbon steel, in addition to oxygen signal as a result of formation oxide film through the air [63]. Figures 17 and 18 (b) indicate to the spectra of C.S surface after soaking 24 h in 1and 2N HCl, which these, contain spectra of Cl and O atoms. Figures.17 and 18(c) illustrate the spectra of C.S surface

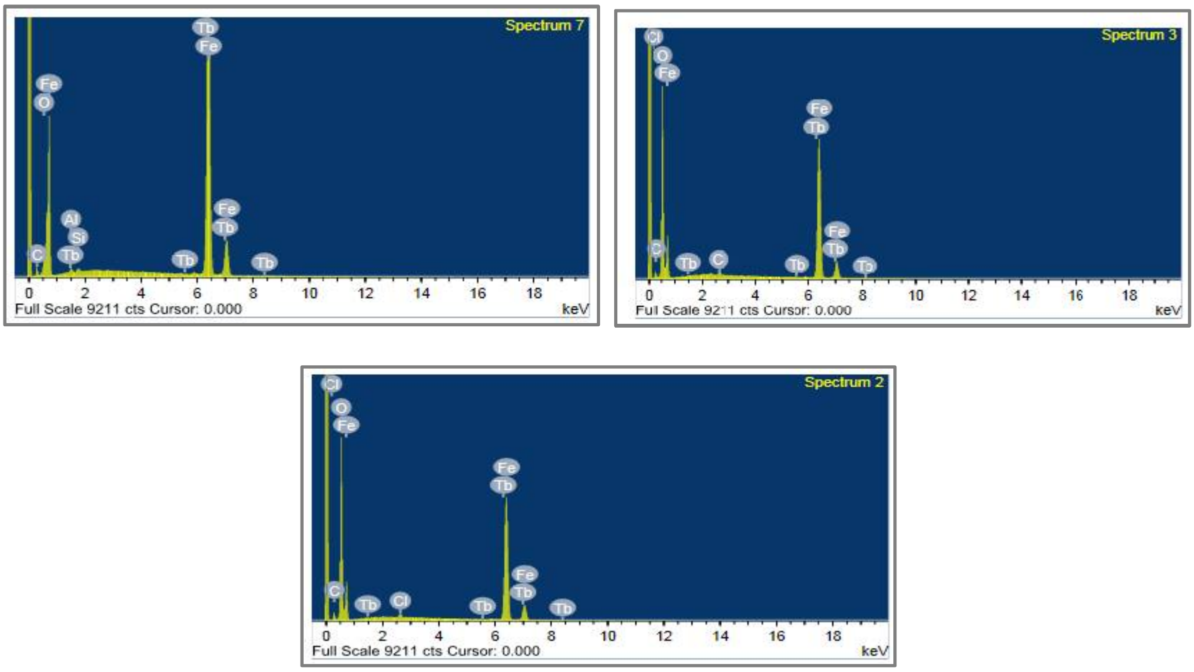


Figure 17. EDX spectra of C.S: (a) before of soaking in 1 N HCl, (b) after 24 h of soaking in 2 N HCl and (c) after 24h of soaking in 1 N HCl + 200 ppm coffee husk at 25°C.

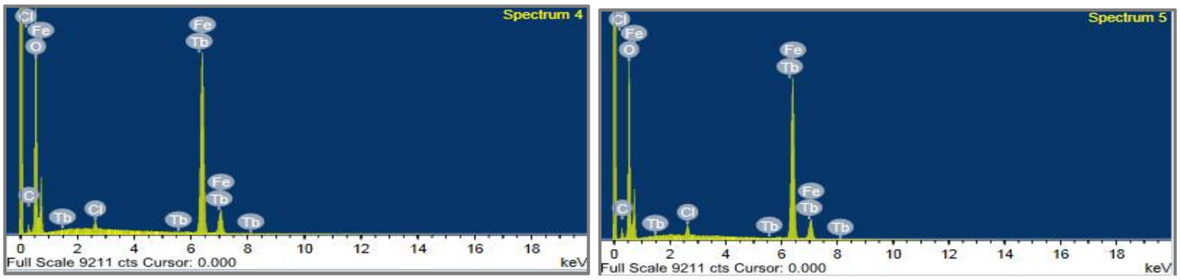


Figure 18. EDX spectra of C.S: (a) after 24 h of soaking in 2N HCl and (b) after 24h of soaking in 2N HCl + 200 ppm coffee husk at 25°C.

after soaking one day at 1 and 2N HCl with 200ppm of coffee husk extract. This spectrum shows that more carbon atoms and appearance of O, because of the extract contains the carbon and oxygen atoms. The peaks of iron considerably suppressed in the presence of coffee husk extract and this because of the overlying inhibitor film [**64**].

FT-IR analysis: Another technique was utilized in our study is FT-IR, this technique demonstrates the interaction among the surface of C.S and organic compounds which found in coffee husk extract [**65**]. Figures 19 and 20 shows the spectrum of coffee husk previously and later soaking the coupon of carbon steel for one day. These figures demonstrated that before immersion of carbon steel at 1 and 2N HCl +200pm from extract display that broad peaks seemed at 3346, 2966, 2221, 1650, 1083 and 566 cm^{-1} for 1NHCl and 3367, 2980, 1640, 1042 and 591 cm^{-1} for 2NHCl, which resemble the O–H, aliphatic C–H , C=O, C-O and Fe Stretching vibration, correspondingly. Thus, coffee husk extract was described by IR spectra [**66-68**]. After immersion of carbon steel, the wavelength was shifted, these variations and shifts illustrate the interaction among the surface of carbon steel and molecules of coffee husk extract [**69**]. Therefore, it can be confirmed that the functional groups of coffee husk extract have coordinated with the surface of carbon steel to give Fe-complex of extract to promote the inhibition.

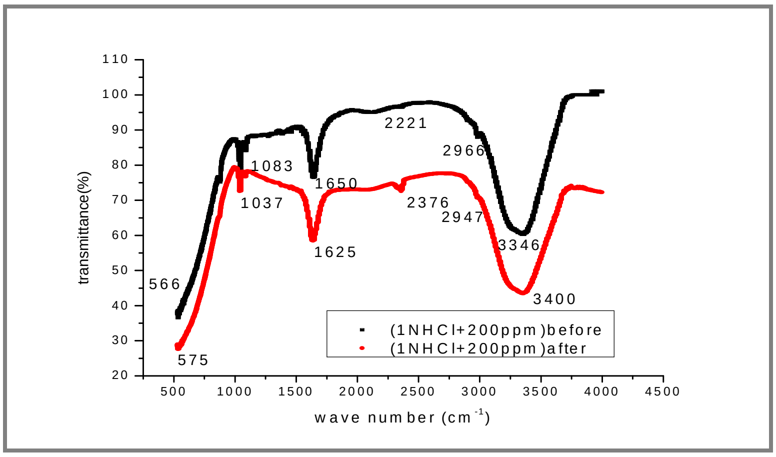


Figure 19. The FT-IR spectrum of extract in 1N HCl before and after adsorption on a carbon steel surface.

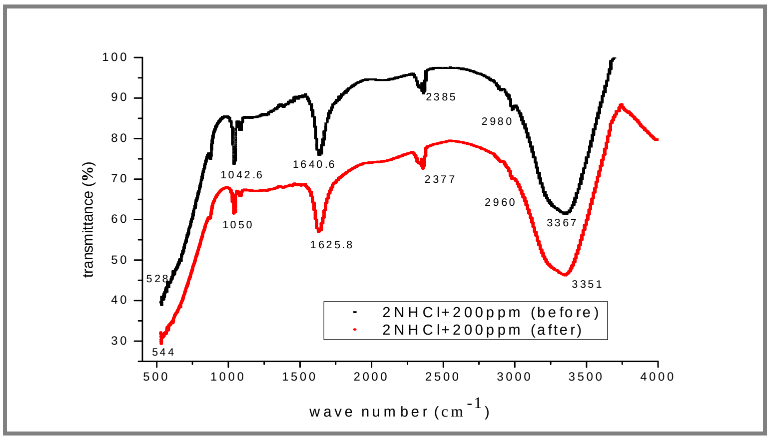


Figure 20. The FT-IR spectrum of extract in 2N HCl before and after adsorption on a carbon steel surface.

UV-Visible spectroscopy: Another technique was used in addition to the FT- IR technique for known the interaction between the organic molecules, which found in coffee husk extract and the surface of carbon steel, is UV-Visible spectroscopy. Figures 21 and 22 demonstrates UV-visible absorption, which measured for 1 and 2N HCl solutions with 200ppm from coffee husk extract previously and later soaking the coupons of C.S for one day. From these figures, we notice that the alteration in the value of absorbance and change in the position of absorbance maximum. This means the creation of Fe-extract complex [70, 71]. Also, Figures 21 and 22 reveal to no alteration in the form of absorption spectra.

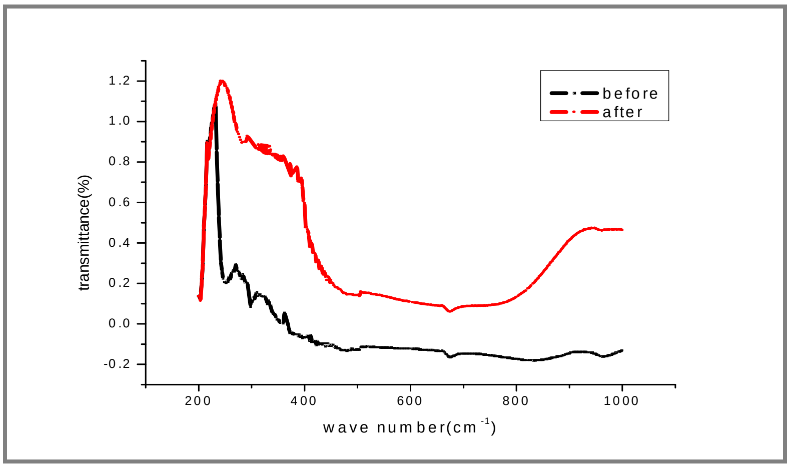


Figure 21. UV–Visible absorption spectra of 1N HCl solutions previously and later dipping of steel for one day in the existence and nonexistence of 200 ppm from coffee husk extract.

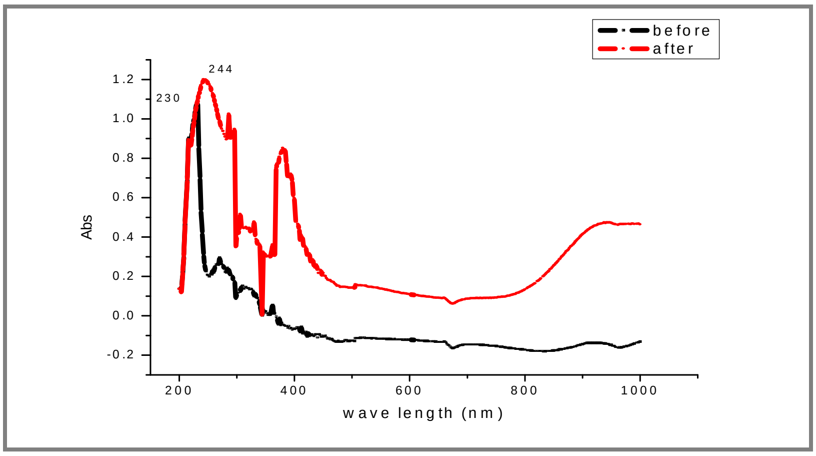


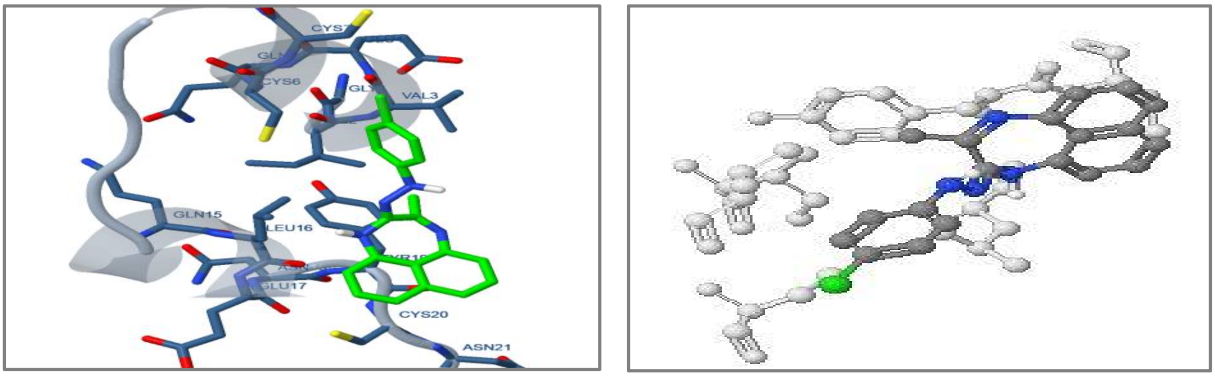
Figure 22. UV–visible absorption spectra of 2NHClsolutionspreviously and later dipping of steel for one day in the existence and nonexistence of 200 ppm from coffee husk extract.

Molecular docking: The docking study showed a favorable interaction between caffeine compound and the receptor of 3tt8-hormone of crystal structure analysis of Fe Human Insulin Derivative. The calculated energy is listed in table 11 and figure 23. According to the results obtained in this study, HB plot curve indicated that the caffeine compound binds to the proteins hydrogen bond and decomposed interactions energies in kcal mol^{-1} existed between the caffeine compound and 3tt8

Table 11. Parameters got from docking of caffeine compound with the 3tt8 receptor

Compound	Est. free energy of binding (kcal mol^{-1})	Est. inhibition constant (K_i) (μM)	vdW+ bond+ desolve energy (kcal mol^{-1})	Electrostatic Energy (kcal mol^{-1})	Total intercooled Energy (kcal mol^{-1})	Interact surface
Caffeine	-5.51	91.73	-6.11	+0.00	-6.11	523.681

receptor as shown in figure 24. The calculated productivity is favorable where K_i data assessed by AutoDock was likened with experimental K_i data, when available, and the -ve sign Gibbs free energy [72]. In addition, established on this value, it can propose that interaction among the 3tt8 receptor and the caffeine compound is probable. 2D plot bends of docking with caffeine compound are displayed in figure 25.



(A) **(B)**

Figure 23. Caffeine compound (green in (A) and gray in (B)) in interaction with the 3tt8 receptor.

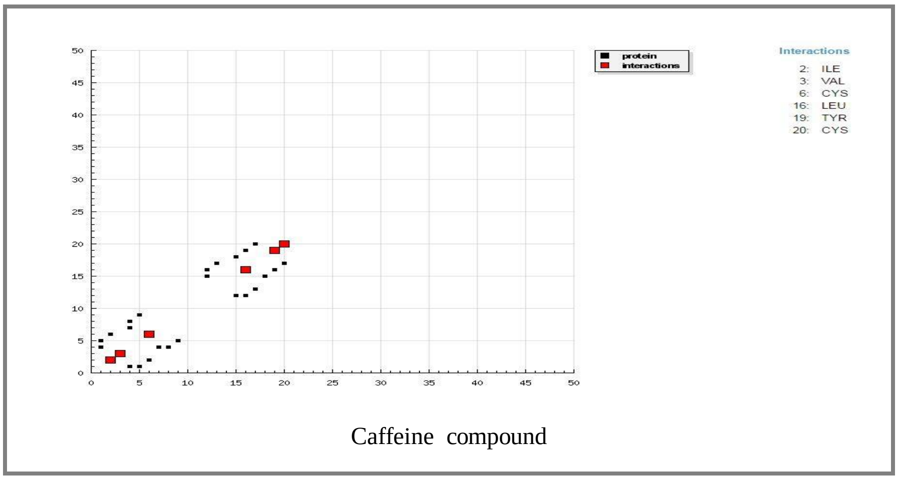


Figure 24. HB bends of interaction among caffeine compound and the receptor of the breast the cancer mutant 3tt8.

Calculations of quantum chemistry: Calculations of quantum chemistry are performed to model the adsorption structure of caffeine to know the interaction between it and the C.S surface. The data of table 12 give the parameters of quantum chemical calculation, which obtained from $DMol^3$ and VAMP modules. The values of E_{HOMO} designates to the capacity of the molecule to give electrons to suitable acceptor has empty molecular orbitals and the data of E_{LUMO} demonstrated the molecule ability for accepting electrons. When the value of E_{HOMO} high this means the compound has the ability to offer electrons to unoccupied d-orbital of the metal surface and the protection productivity becomes high [73, 74]. The lesser data of E_{LUMO} means the molecules of the inhibitor likely accept electrons. ΔE is the significant parameter because it demonstrated the reactivity of the caffeine molecule to adsorption on the C.S surface. By decreasing the value of the energy gap (ΔE), the reactivity of molecule increases. In this case, the ionization energy, which required eliminating an electron from an outer shell orbital, will be low and the molecules give more corrosion inhibition for metal [75]. In our study, the energy gap can be considered as a low value compared to other values for other researches [76-78]. Another important parameter is the dipole moment, μ that utilized to discuss and rationalize the structure [79]. The molecule which has a high value of μ give strong dipole-dipole interaction with the surface of C.S, so the more protection occurs as a result of adsorption on the surface of C.S [**80**]. The dipole moment in our case considers high related to other researches [**81**]. From the important properties of the molecule are softness (σ) and absolute hardness (η), because they measure the molecule reactivity and stability. The molecule, which has a low energy gap more softly than the molecule, which has a high-energy gap. The soft molecule more reactive than hard ones, so it can easily offer electrons to an acceptor and the adsorption occurs [**82**]. That is demonstrated in our study because caffeine consider has low hardness related to other values from other researches [**83**]. The high value of chemical potential gives good inhibition efficiency because it enhances the releasing power of the caffeine molecule. We used caffeine molecule in our theoretical study because it used in many types of research as an inhibitor for many alloys and metals[**84, 85**] and in our study the inhibition was high compared to other studies because of the presence of other compounds in our extract which have high molecular weight [**73, 86, 87**].

Table 12. The parameters got from a quantum chemical of caffeine compound

	Parameter	Caffeine		Parameter	Caffeine
PM3	E_{HOMO}(eV)	-9.151	$Dmol^3$/ GGA / BOP	E_{HOMO}(eV)	-5.199
	E_{LUMO} (eV)	-0.526		E_{LUMO} (eV)	-1.617
	ΔE (eV)	8.62		ΔE (eV)	3.58
	μ (debyes)	5.942		μ (debyes)	5.32
	η(eV)	4.31		η(eV)	1.79
	σ(eV^{-1})	0.232		σ(eV^{-1})	0.558
	Pi (eV)	-4.84		Pi (eV)	-3.408
	χ (eV)	4.84		χ (eV)	3.408
	Molecular area ($A^{\circ\,2}$)	211.379		Molecular area ($A^{\circ\,2}$)	207.750

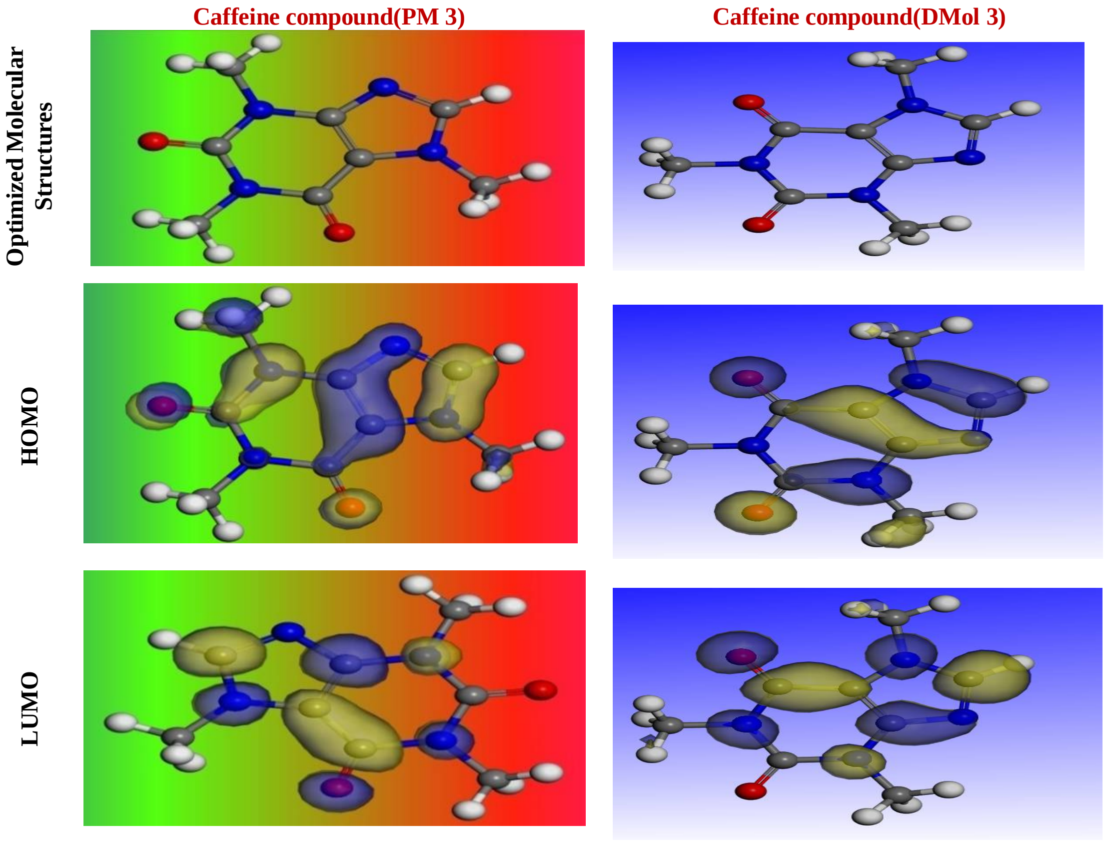


Figure 26. The optimized molecular structures, HOMO, LUMO for caffeine compound using PM3 and Dmol3 module.

APPLICATION

The coffee husk extract exhibit excellent corrosion resistance to the carbon steel in HCl medium. The coffee husk inhibitor that has little or no impact on the environment i.e this extract is safe, Ecofriendly and give good corrosion resistance with temperature. Therefore, coffee husk extract can be used for the corrosion protection of carbon steel in acid medium for numerous industries.

CONCLUSION

Our study assesses the corrosion protection of coffee husk extract on the surface of C.S in 1 and 2N HCl. The important deductions are as next:

1. The gravimetric method showed that the inhibition effect rises by raising the concentration of coffee husk extract and lower by raising the temperature.
2. The data of Polarization method demonstrates that the type of inhibition is a mixed type because the coffee husk extract hindered both the anodic and cathodic process.
3. The adsorption of coffee husk extract on the surface of C.S in 1 and 2N HCl solutions is mainly physical adsorption and obeys Temkin and Langmuir adsorption.
4. The measurements of the EIS technique illustrate that relationship between the concentration of coffee husk extract and R_{ct} and the relation between the concentration and C_{dl}. The charge transfer resistance rises by raising the dose of coffee husk extract, also the capacitance of double layer decreases, because of the adsorption of molecules of coffee husk extract on the C.S surface.
5. The adsorption of molecules of coffee husk extract on the surface of C.S was confirmed by surface analysis (SEM, EDX, UV, and FT-IR).
6. The calculations of quantum chemistry illustrate the relation between parameters of the structure for caffeine compound and its inhibition efficiency for the corrosion process.
7. Molecular docking and binding energy calculations of caffeine compound with the receptor of 3tt8-hormone of crystal structure analysis of Fe Human Insulin Derivative indicated that the compound is an efficient inhibitor of the receptor of 3tt8-hormone.
8. The inhibition efficiency in 1N HCl is more than the inhibition efficiency in 2N HCl.

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