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The effect of N-heterocyclic compound on corrosion inhibition of J55 steel in sweet corrosive medium

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Abstract

The corrosion inhibition behavior of naphthoxazinone derivative namely 1-Phenyl-1,2-dihydronaphtho[1,2-e][1,3]oxazin-3-one (PNO) on J55 steel in 3.5 wt.% NaCl solution saturated with carbon dioxide was evaluated using weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. The surface morphology on metal sample was analyzed using scanning electron microscopy (SEM) and Atomic force microscopy (AFM). The adsorption of PNO obeyed the Langmuir isotherm. The results of potentiodynamic polarization indicated that the PNO molecule behaved as a mixed type inhibitor by reducing both the anodic and the cathodic electrochemical reactions. The surface analysis showed that the metal surface is

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considerably smoother and with more uniform morphology in the presence of the inhibitor. The DFT based quantum chemical calculations and molecular dynamic (MD) simulation supported the experimentally obtained results.

Keywords: Carbon dioxide; Corrosion; DFT; MD

1. Introduction

In petroleum industry, carbon steels are commonly used for the manufacture of casing, tubing, transportation etc. Although carbon steel has limited corrosion resistance, but because of economic reasons they are given more preference than other materials [1]. In oil and gas industry carbon dioxide, which is a naturally occurring or intentionally injected constituent in presence of high chloride concentration is the most aggressive and frequent environment [2]. When carbon dioxide corrosion dissolves in aqueous, medium it produces carbonic acid, which undergoes interaction with carbon steel and causes its corrosion [3].

Organic compounds are the best and cost effective way to reduce the carbon dioxide corrosion during oil and gas production. The effective corrosion inhibitor are the organic compounds which contains heteroatoms like nitrogen, oxygen, phosphorous and sulphur, phenyl rings, lone pair of electrons and π -bonds conjugation in their molecular framework [4-8]. The adsorptions mechanism of inhibitors could be physical involving electrostatic interaction between the protonated inhibitor molecule and charged metal surface [9, 10] or chemical bond formation by transfer of electrons to the vacant metal d-orbitals or combination of both pathways. However, an additional route of inhibitor adsorption onto the metal surface known as back bonding, which is the ability of inhibitor molecules to accept the electrons from the filled metal orbitals into their antibonding orbitals [11]. All these mechanisms lead to the formation of

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 a protective inhibitor films and thereby resists the corrosive attack of the acid onto the metal surface.

Review of literature reveals that various imidazoline derivative has been reported as effective corrosion inhibitors due to their strong ability to adsorb onto the steel surface [12, 13]. Although, imidazolines in the form of cationic surfactants, can causes anodic dissolution by creating a number of micro anodes and thus leads to localized corrosion [14]. In fact, pitting corrosion is initiated in the pipelines [15].

In present time, corrosion scientists are interested to find environment friendly inhibitors [16]. Thus, Naphthoxazinone due to its antibacterial activity is categorized as green compound [17]. We herein report the synthesis and detailed investigation on the application of naphthoxazinone derivative for the corrosion inhibition study of J55 steel in 3.5% NaCl solution saturated with carbon dioxide. The techniques used for the analysis of corrosion inhibition includes weight loss and electrochemical. SEM and AFM analyzed the surface morphology of N80 steel specimen. Furthermore, the experimental results were validated by theoretical study i.e. density functional theory (DFT) and molecular dynamics (MD) simulation.

2. Experimental procedures

2.1. Inhibitor synthesis

The inhibitor was synthesized as per the literature procedure [18]. In a round bottom flask β -Naphthol (2mmol), benzaldehyde (2 mmol), urea (2mmol), and I₂ (0.1 g) were taken, stirred, and heated on a hot plate at 80 C for 5 min. The obtained contents were cooled to room temperature, then water was added, and finally the obtained solid precipitate was filtered and washed repeatedly with water to get the corresponding naphthoxazinones. Pure compound was obtained by recrystallization from ethanol. The molecular structure of the synthesized compound

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(PNO) is given in Fig.1. The inhibitor was characterized by ¹H NMR and ¹³C NMR spectra and are given in supplementary file S1and S2.



Figure 1: Synthetic scheme and molecular structure inhibitor

2.2. Analytical data

1-Phenyl-1,2-dihydro-naphtho[1,2-e][1,3]oxazin-3-one: Mp: 230-232 °C; ¹H NMR (300 MHz, DMSO-d₆): δ= 6.34 (s, 1H, CH), 7.21-8.04 (m, 11H, Ar-H), 7.80 (d, 1H, NH)
¹³C NMR (100 MHz, DMSO-d₆): δ= 152.07, 145.05, 143.18, 141.12, 131.94, 130.97, 130.71, 129.07, 128.78, 128.73, 128.41, 127.77, 126.93, 126.35, 125.85, 123.05, 115.76, 52.01

2.3. Materials and specimens

In the present work J55 steel is used and its chemical composition is as follows: C (0.31), Mn (0.92), Si (0.19), P (0.01), Cr (0.2), S (0.008), and Fe in balance. The steel specimens used for weight loss experiment were cut into rectangular shape with the size of $2.5 \times 2.0 \times 0.2$ cm. For electrochemical experiments rectangular rod was used, which was sealed with epoxy resin, leaving an exposed face with an area of 1.0 cm². All the steel specimens were abraded with silicon carbide papers of 400 to 1200 grits. The samples were degreased with acetone, washed with ethanol, and finally dried in oven. An aggressive solution of 3.5 wt.% NaCl solution was prepared with analytical grade sodium chloride and double distilled water.

2.4. Weight loss measurements

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 Three identical steel coupons were used for weigh loss experiments and these coupons were weighted using an electric balance with precision of ± 0.1 mg. The inhibitor concentration is in the range of 50-500 mg/L. All the steel specimens were immersed into the aggressive solutions containing different concentrations of PNO. The the test solutions were purged with pure nitrogen gas for 1 h in order to remove the oxygen, after this carbon dioxide at the rate of 20 ml min⁻¹was introduced into the test solution throughout the experiment. The carbon dioxide containing brine solutions with the steel coupons were sealed using silicone sealants and incubated at 60 ± 1 °C for 72 h.

After the weight loss, the steel coupons were taken out, immersed in Clarke's solution for 5 min in order to clean the corrosion products, washed under running water, degreased in acetone, rinsed with ethanol, dried, and re-weighed accurately. The corrosion rate (v_{corr}) of J55 steel was calculated using the below equation:

$$\upsilon_{corr} = \frac{8.76 \times 10^4 \times \Delta m}{\rho A t} \tag{1}$$

where v_{corr} is corrosion rate (mm/y), Δm is weight loss (g), ρ is steel coupon density (g/cm³), A is exposed area of steel coupons (cm²) and t is exposure duration (h).

2.5. Electrochemical Analysis

Autolab Potentiostat device was used for electrochemical analysis. A three-electrode setup was attached to the potentiostat in which saturated calomel electrode (SCE) as reference electrode, a graphite rod as auxiliary electrode, and J55 steel as the working electrode. At first, working electrode was immersed in the test medium i.e. 3.5 % NaCl saturated with carbon dioxide for 30 min at 303 K before each experiment to maintain the steady state corrosion potential (E_{corr}).

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The electrochemical impedance spectroscopy (EIS) was performed in the range of frequency 100 kHz to 10 mHz at open circuit potential, by setting 10 mV as the AC sine wave amplitude frequencies per decade. Calculation of inhibitions efficiencies were done as follows:

$$\eta\% = \left(1 - \frac{R_{ct}}{R_{ct(i)}}\right) \times 100 \tag{2}$$

where R_{ct} and $R_{ct(i)}$ are the representative of resistance of charge transfer without and with the studied inhibitor respectively.

The potentiodynamic polarization study of the J55 steel without and with the inhibitor was conducted in the range of -250 mV to +250 mV potential and the sweep rate used was 0.2 mV/s. The below mentioned equation was used for inhibition efficiency calculation:

$$\eta\% = \left(1 - \frac{i_{\text{corr(i)}}}{i_{\text{corr}}}\right) \times 100 \tag{3}$$

where, i_{corr} and $i_{corr(i)}$ represents the values of corrosion current densities without and with inhibitor, respectively.

2.6. Computational details

2.6.1. Quantum chemical calculation

The molecular property of inhibitor molecule was explored using quantum chemical calculations. In the present time density functional theory (DFT) is the popular computational technique because it performed the calculation shorter time period with high accuracy. In the present paper all quantum chemical calculations were performed using ORCA programme package module version 2.7.0 [19]. The optimization of inhibitor molecule geometry was done hybrid B3LYP functional level of DFT [20-24]. In this calculation, a triple-ζ quality basis sets, TZV(P), along with one set of polarization functions on the O and N atoms have been employed

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[25]. Whereas, slightly smaller polarized split-valence SV(P) basis sets were used for atoms like carbon and hydrogen. Since, electrochemical corrosions take place in aqueous phase. So, it becomes important to consider the effects of solvent molecules. Here, COSMO model was used for incorporating solvent effect (water in present study) for all the calculations.

2.6.2. Molecular Dynamics simulation

The study of interaction between the inhibitor molecules and metal surface can be explored by molecular dynamics (MD) simulation. In the present analysis, the interaction of Fe (110) surface and inhibitor molecules was studied by Material StudioTM software (version 6.1) [26].

The preferential used of Fe (110) surface is based on the fact that it consists of packed and high stabile/low energy lattice crystal plane as compared to other iron lattice plane [27].

The investigation of the interactions between the Fe (110) surface and the concerned molecule have been performed in a modelled box (dimension: $39.85 \times 39.85 \times 76.46$ Å) under periodic boundary conditions. The number of layers of Fe atoms is to be selected in such a manner that the depth of the surface is higher than the non-bond cut-off radius used in the calculation. Herein, ten layers of Fe atoms have been chosen in order to maintain the surface depth and the related cutoff radius. The constructed simulation box comprises of the iron slab (lower most layer), solution slab (the middle layer) and the vacuum layer (upper most layer). The solution slab contains 1 inhibitor molecule, 150 H₂O molecules. After constructing the simulation box, an initial geometry optimization has been performed in order to minimize the energy of the whole system and dispose of unfavorable structures. All MD simulations were done at 298 K temperature and maintained constant by the Andersen thermostat, a time step of 0.1 fs, NVT (fixed atom number, system volume and temperature) ensemble and a simulation time of 2000 ps

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to reach simulation system under an equilibrium state. The energy minimization and MD calculation processes were performed using Condensed-phase Optimized Molecular Potential for Atomistic Simulation Studies (COMPASS) force field [28].

3. Results and discussion

3.1. Weight loss experiment

3.1.1. Concentration effect

The effect of inhibitor concentrations on the protection ability of metal surface is represented in the form of concentration vs. inhibition efficiency plot (Fig. 2).



C. **(mM) Figure 2:** Variation of inhibition efficiency (η %) with inhibitor concentration at 333 K

From figure, it is obvious that the inhibitory performance of inhibitor is going to increase with increase in inhibitor concentration and attain a maximum value of 90 % at 500 mg/L. The increase in inhibition efficiency is due to adsorption of inhibitor molecules onto the metal surface. In the present study, the molecular structure of inhibitor contains π electrons in the aromatic ring, non-bonding electrons on heteroatom's like oxygen and nitrogen, which help the inhibitor molecules to adsorb onto the J55 steel surface [29].

3.1.2. Adsorption isotherm of inhibitor on J55 steel

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Many adsorption isotherms like Langmuir, Frumkin, Flory Huggins and Temkin were investigated to find a good fitting with the experimental study. Out of these isotherms Langmuir isotherm i.e. C_{inh}/θ vs. the inhibitor concentration (C_{inh}) was found to be the best fit due to the slope and regression coefficient (R^2) values approaching towards unity (Fig. 3).



Figure 3: Langmuir Isotherm plots for adsorption of inhibitor

The Langmuir isotherm is given by the following formula [30,31]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{4}$$

where C_{inh} is PNO concentration (mM), θ and K_{ads} represents the surface coverage and equilibrium adsorption constant respectively. Supplementary file (S3-S5) contains the Frumkin, Flory Huggins and Temkin isotherm plots. The K_{ads} value was determined from the intercept of the Langmuir plot and listed in Table 1.

Table 1

Parameter of Langmuir adsorption isotherm for the synthesized inhibitors				
Inhibitor	Slope	Regression Coefficient	K _{ads}	ΔG^{0}_{ads}
		(R ²)	$(10^{3}M^{-1})$	(kJ/mol)

TMI	0.996	0.997	4.56	-34.45

The strength of PNO molecules adsorption on J55 steel is represented by the values of K_{ads} . From the table it could be observed that the value of K_{ads} is large, which suggests its strongest adsorption onto the metal surface [32, 33]. The standard free energy of adsorption i.e. ΔG^{0}_{ads} could be correlated to K_{ads} according to the below mention equation [34].

$$\Delta G_{\rm ads}^{\rm o} = -2.303 RT \log(55.5 K_{\rm ads}) \tag{5}$$

where, absolute temperature and universal gas constant are represented by *T* and *R* respectively, 55.5 is magnitude of water molecules concentration. Table 1 reveals that the ΔG^0_{ads} values are negative, suggesting towards a spontaneous adsorption process [35]. Since, the value ΔG^0_{ads} is between -40 kJ/mol to -20 kJ/ mol, which confirms that the adsorption of inhibitor molecules on J55 steel surface is both physical and chemical [36-39].

3.2. Electrochemical Analysis

3.2.1. Electrochemical Impedance spectroscopy (EIS)

The fitted EIS results were presented in Figs. 4a in the form of Nyquist plots for J55 steel exposed to the 3.5 % solution of NaCl saturated with carbon dioxide at 308 K temperature with and without PNO.



Figure 4a: Nyquist plots in absence and presence of different concentration of inhibitor

The Nyquist plot, from high to low frequency consists a depressed semicircle with a small inductive loop at low frequency. The presence of capacitive semicircle in the Nuquist plots is attributed towards the presence of double layer capacitance and charge transfer resistance phenomenon. The adsorption of intermediate product (FeOH_{ads}) results in the appearance of inductive loop. The consecutive steps of the mechanism of intermediate formation can be written as follows [40]:

 $Fe + H_2O \rightarrow FeOH_{ads} + H^+ + e^-$

 $FeOH_{ads} \rightarrow FeOH++e^{-1}$

 $\rm FeOH^+ + H^+ {\rightarrow} Fe^{2+} + H_2O$

The equivalent circuit shown in Fig. 4b was used to simulate the capacitive and inductive process occurring during corrosion inhibition.



Figure 4b: Equivalent circuit used

The fitted values of impedance parameters are tabulated in Table 2. The roughness and inhomogeneities on the solid surfaces is responsible for the depressed semicircle in the

impedance spectra [41-43]. Thus, a constant phase element (CPE) was employed to describe the double layer capacitance, which has a non-integer power dependence on the frequency [44]. As can be observed from the figure that the diameter of the Nyquist plots are increasing with increasing the PNO concentration, which is due to the increase in the corrosion resistance property of metal surface because of adsorption of PNO moleculs. As per the table, the values of $R_{\rm ct}$ increases with the addition of PNO, while the values of Y^0 , which represents the double layer capacitance decreases. The increase of R_{ct} and decrease in Y^0 is attributed to the adsorption and finally inhibitor film formation over the metal surface. Also, the values of inhibition efficiency increases with increasing the inhibitor concentration, indicating that more metal surface is covered with increasing inhibitor concentration.

Table 2

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C _{inh} (mgL ⁻¹)	$R_{\rm s}$ (Ω)	$R_{\rm ct}$ ($\Omega \ {\rm cm}^2$)	Y ₀ (μF/cm²)	n	<i>L</i> (<i>H</i> cm ²)	R_L (Ω cm ²)	η (%)	
C _{inh} (mgL ⁻¹) Blank	R _s (Ω) 4.817	<i>R</i> _{ct} (Ω cm ²) 135.57	Y ₀ (μF/cm ²) 512.7	n 0.601	<i>L</i> (<i>H</i> cm ²) 8.04	<i>R_L</i> (Ω cm ²) 4.01	η (%)	homid
C _{inh} (mgL ⁻¹) Blank 100	R _s (Ω) 4.817 1.025	R _{ct} (Ω cm²) 135.57 471.87	Y ₀ (μF/cm ²) 512.7 208.12	<i>n</i> 0.601 0.728	<i>L</i> (<i>H</i> cm ²) 8.04 51.63	<i>R_L</i> (Ω cm ²) 4.01 31.54	η (%) 71.2	f Chomid
C _{inh} (mgL ⁻¹) Blank 100 200	Rs (Ω) 4.817 1.025 1.190	R _{ct} (Ω cm²) 135.57 471.87 711.21	Y ₀ (μF/cm ²) 512.7 208.12 175.34	<i>n</i> 0.601 0.728 0.801	<i>L</i> (<i>H</i> cm ²) 8.04 51.63 77.61	<i>R_L</i> (Ω cm ²) 4.01 31.54 65.82	η (%) 71.2 80.9	
C _{inh} (mgL ⁻¹) Blank 100 200 300	Rs (Ω) 4.817 1.025 1.190 1.262	R _{ct} (Ω cm²) 135.57 471.87 711.21 843.71	<i>Y</i> ₀ (μF/cm ²) 512.7 208.12 175.34 123.86	<i>n</i> 0.601 0.728 0.801 0.821	<i>L</i> (<i>H</i> cm ²) 8.04 51.63 77.61 61.63	R_L (Ω cm²) 4.01 31.54 65.82 45.82	η (%) 71.2 80.9 83.9	inroal of Chomic
C _{inh} (mgL ⁻¹) Blank 100 200 300 400	Rs (Ω) 4.817 1.025 1.190 1.262 1.101	R _{ct} (Ω cm²) 135.57 471.87 711.21 843.71 993.09	<i>Y</i> ₀ (μF/cm ²) 512.7 208.12 175.34 123.86 90.89	<i>n</i> 0.601 0.728 0.801 0.821 0.853	<i>L</i> (<i>H</i> cm ²) 8.04 51.63 77.61 61.63 116.26	R _L (Ω cm²) 4.01 31.54 65.82 45.82 85.12	η (%) 71.2 80.9 83.9 86.3	
C _{inh} (mgL ⁻¹) Blank 100 200 300 400 500	Rs (Ω) 4.817 1.025 1.190 1.262 1.101 1.028	R _{ct} (Ω cm²) 135.57 471.87 711.21 843.71 993.09 1297.38	Y₀ (µF/cm²) 512.7 208.12 175.34 123.86 90.89 62.52	 n 0.601 0.728 0.801 0.821 0.853 0.891 	<i>L</i> (<i>H</i> cm ²) 8.04 51.63 77.61 61.63 116.26 297.14	R _L (Ω cm²) 4.01 31.54 65.82 45.82 85.12 178.28	η (%) 71.2 80.9 83.9 86.3 89.5	w lournal of Chamie!

3.2.2. Potentiodynamic polarization

The corrosion kinetics of J55 steel immersed in 3.5% NaCl solution saturated with carbon dioxide without and with different concentration of PNO at 308 K is shown in Fig. 5.



Figure 5: Potentidynamic polarization curves in absence and presence of different

concentration of inhibitor

It could be observed from figure that the addition of PNO reduces both the anodic and

cathodic current densities. The obtained kinetic parameters like corrosion potential (E_{corr}),

corrosion current density (i_{corr}), anodic and cathodic Tafel slope (β_a , β_c) are tabulated in Table 3.

Table 3

Electrochemical polarization parameters in absence and presence of different concentrations of inhibitor at 308K

Inhibitor	E _{corr} (mV/SCE)	i _{corr} (μA/cm ²)	β _a (mV/dec)	- β _c (mV/dec)	η (%)
Blank	-703	104.4	154	590	
100	-714	34	192	583	67.4
200	-734	21	184	543	79.8
300	-743	18	183	599	82.7
400	-776	14	164	582	86.5
500	-826	10	171	574	90.4

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The values of corrosion potentials (E_{corr}) shifts towards the cathodic direction with the addition of PNO and this shifts depends upon the concentration of PNO. The reduction of both anodic and cathodic current density slows down the corrosion rate, along with the slight negative shift in corrosion potential, indicating towards the mixed-type inhibitor inhibition action. From Table 3, it is reveals that the value of inhibition efficiency increases with increase in PNO concentration, which suggests that PNO, inhibits the corrosion of J55 steel. In addition, the values of cathodic (β_c) and anodic (β_a) Tafel slopes were not considerably affected, thus revealing that the mechanism of corrosion reactions are not changed with the addition of PNO.

In the anodic polarization curves there was an increase of corrosion current density occurs as the polarization potential approach a relatively positive value. This was due to the anodic desorption of inhibitor [45]. The increase of polarization potential accelerates metal dissolution not only on the surface without adsorbed species but also with adsorbed inhibitive species because they become unstable at a high polarization potential [46]. Thus, at positive potential the equilibrium between adsorption-desorption process gets disturbed due to the slower adsorption process than desorption one, which causes a reduction in the surface coverage and finally enhance the metal dissolution.

3.3. Surface analysis: SEM and AFM

3.3.1. Scanning electron microscopy (SEM)

The morphological changes on the J55 steel surface without and with optimum concentration of PNO were shown in Fig. 6(a, b). Fig. 6a represents that in absence of PNO the surface was highly corroded. However, with the addition of PNO the morphology of J55 steel

 surface becomes smooth (Fig. 6b). This is due to the adsorption of PNO on the J55 steel surface. These results are in good agreement with the weight loss and electrochemical measurement.



Figure 6: SEM images (a) In absence of inhibitor (b) In presence of inhibitor

3.3.2. Atomic force microscopy (AFM)

The AFM images in three-dimensional form for uninhibited and inhibited surface were shown in Fig. 7(a, b). J55 steel surface was strongly damaged for uninhibited system, and achieved an average roughness value to 700 nm (Fig. 7a). However, for inhibited system, the J55 steel surface appears to be smooth and homogeneous morphology with an average roughness value of 20 nm (Fig. 7b) due to the adsorption of PNO on the J55 steel surface.



Figure 7: AFM images (a) In absence of inhibitor (b) In presence of inhibitor

3.4. Quantum chemical calculations

3.4.1. Optimized geometrical structure

The optimized structure, HOMO and LUMO of the inhibitor molecule (PNO) are shown in Fig. 8a-c.



(a) Figure 8a: Optimized geometry of inhibitor





The optimized parameters like bond lengths, bond angles and torsion angles are tabulated

in Table 4.

Table 4

Bond lengths (Å), bond angles (°) and torsion angles of the optimized forms of inhibitor in aqueous phase

Bond lengths		
C1-C2	1.4250	
C2-C3	1.4378	
C3-C4	1.4230	
C4-C5	1.3812	
C5-C6	1.4170	
C6-C1	1.3829	

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C2-C7	1.4350
C7-C8	1.3790
C8-C9	1.4161
C9-C10	1.3748
C10-C3	1.4258
C7-C14	1.5142
C14-C18	1.5323
C18-C21	1.4045
C21-C20	1.3982
C20-C19	1 4014
C19-C16	1 3990
C16-C17	1 4005
C17-C18	1 4029
C14-N15	1 4740
C12-N15	1 3477
C12-O11	1 3713
C8-011	1 3934
C12-O13	1 2214
	1,2211
Bond angles	
C1-C2-C3	118 16
C2-C3-C4	119 39
C3-C4-C5	120.97
C4-C5-C6	119.80
C5-C6-C1	120.66
C6-C1-C2	121.03
C2-C7-C8	118.66
C7-C8-C9	122.91
C8-C9-C10	119.09
C9-C10-C3	120.90
C10-C3-C2	119.35
C3-C2-C7	119.08
C7-C14-C18	114.50
C18-C21-20	120.52
C21-C20-C19	120.14
C20-C19-C16	119.72
C19-C16-C17	120.01
C16-C17-C18	120.63
C17-C18-C21	118.98
C18-C21-C20	120.52
Torsion angles	
C7-C14-C18-C21	45 32
N15-C14-C18-C17	99.84

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C7-C14-C18-C17	-137.03
N15-C14-C18-C21	-77.81
C7-C14-C18-C21	45.32
C2-C7-C14-C18	74.00
C2-C7-C14-N15	-161.61

Table 4 reflects that the carbon-carbon (C-C) bond lengths in the benzene ring are in the range of 1.398-1.402 Å. Thus, in benzene ring the bonds are shorter than C-C bond lengths as compared to the normal C-C single bond length and also it is longer than the C=C double bond length [47]. The obtained bond length in the present study reveals that there exists a π -bonds conjugation in the benzene ring. It is important to find out that the optimized structure of inhibitor molecule possessed an ideal geometrical structure or not. So, it becomes important to study the other bond lengths present in the inhibitor molecules.

In the heterocyclic ring, the bond length values of C14-N15 and C12-N15 are 1.474 and 1.347 Å respectively. These bond lengths are close to C-N bond length reported in the literature [48]. Furthermore, the obtained bond length of C-O (C12-O13) is 1.2063 Å, which is also coming in the range of C-O double bond length as per the literature [49]. Therefore, finally it is concluded that the geometrical structure of inhibitor molecule is ideal.

Inhibitor molecule must process planar structure in order to achieve stronger adsorption on the iron surface. Therefore, it becomes important to analyze all the bond angles and torsion angles of the inhibitor molecule. The values of the bond angles are given in Table 4. It can be observed that the bond angle values for heterocyclic and phenyl rings are lying in the range of 114.50°-122.91°. The values of bond angles are very much close to 120°, revealing that benzene, heterocycle rings atoms are sp² hybridized, and thus they have planar orientation. Therefore, inhibitor molecules possessed an ideal planar structure.

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 It is important to analyze wither both the heterocyclic ring and phenyl ring participate in adsorption on the iron surface or one participate in adsorption and other remains free. In order to answer these questions, it becomes necessary to analyze the torsion angles values.

The values of torsion angles listed in the Table 4. It is observed from table that the values torsion angles formed by the planes of atoms C7-C14-C18-C2, N15-C14-C18-C17, C7-C14-C18-C21, C7-C14-C18-C21, C2-C7-C14-C18, C2-C7-C14-N15 are 45.32°,99.84°, -137.03, -77.81°,45.32°, 74.00° and -161.61° respectively. Here none of the torsion angles lie nearby to either 0° or 180°. Thus, the deviation in the torsion angle confirmed that the orientation of the heterocyclic ring and phenyl ring are non-planar to each other i.e. their position exists in different plane position. This deviation in planarity reveals that only one participate in adsorption process and other will do not. Review of literature suggests that adsorption of heterocyclic ring is dominated as compared to phenyl ring because of the presence of heteroatoms in their molecular framework.

The inhibitor adsorption onto the metal surface depends upon the position of the frontier orbital energy level between the inhibitor molecules and the Fermi level of the iron metal [50]. The optimized geometry and frontier orbital energy of inhibitor are shown in Fig. 9.



Figure 9: Interaction of molecular orbital's of inhibitor and iron

The frontier orbital energies of inhibitor molecules and the Fermi level of iron are shown in Fig. 9. Figure 9 shows that the E_{HOMO} energy level of inhibitor is at -6.160 eV, which is very close to the iron Fermi level i.e., -5.177 eV. However, the E_{LUMO} energy level of inhibitor is at -1.510 eV eV, which is far away from the iron Fermi level. Therefore, the electron transfer from the HOMO energy level of inhibitor to the iron surface is possible. While, the energy gap between the LUMO of inhibitor and iron Fermi level is quite large. Therefore, the electron transfer from the iron surface to the LUMO orbital of the inhibitor molecule is difficult.

3.4.2. Molecular dynamics simulation

In the modern time, the interaction between the inhibitor and metal surface can be analyzed using molecular dynamics (MD) simulation. Literature survey supports in recent times the use of MD simulation in the corrosion inhibition study is well-recognized [51-53]. Thus, in the present study MD simulation has been performed in order to explore the inhibitor-metal interaction and to understand the mechanism of inhibitor molecules adsorption onto metal surface.

 In MD simulation, initially inhibitor molecules were optimized by applying 'smart' algorithm. In this first step is steepest decent path, followed by conjugate gradient path and lastly completed with Newton's method [26]. When the total energy of inhibitor molecules approach at the minimum energy level, then the inhibitor molecules atomic coordinates were adjusted using COMPASS force field [54]. After completing this, a simulation box was constructed and within this simulated box inhibitor and water molecules were incorporated. Figs. 10 and 11 represents the minimum energy state of the inhibitor in the midway of simulation processes.



Figure 10: Temperature equilibrium curve obtained from molecular dynamics simulation for inhibitor

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Figure 11: Energy fluctuation curves obtained from molecular dynamics simulation for inhibitor

The equilibrium configurations of adsorbed inhibitor molecule on the metal surface are represented in Fig. 12. The close observation of Fig. 12 reveals a flat/parallel adsorption of inhibitor molecule on the metal surface. This kind of parallel adsorption of inhibitor molecules confirmed that it occupies maximum area of metal surface and provide stronger adsorption.



Figure 12: Side and top views of the final adsorption of inhibitor molecule on the Fe (110) surface in solution (a) Side view (b) Top view

The values of interaction and binding energies is useful in determining the adsorption potential ability of the inhibitor molecules onto the metal surface.

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Table 5

Selected energy parameters obtained from MD simulations for adsorption of inhibitors on Fe (110) surface

Systems	E _{interaction} (kjoule/mol)	E _{binding} (kjoule/mol)
Fe + PNO	-606.855	606.855

Inspection of Table 5 reveals that the interaction and binding energies values are -

606.855 kJ/mol and 606.855 kJ/mol respectively. The negative value of interaction energy suggests that inhibitor adsorption on metal surface (Fe110) is spontaneous. The values of interaction and binding energies in the present case is higher than presents in the literature. This confirmed the stronger adsorption of the studied inhibitor on the metal surface [55-57].

4. Conclusions

- 1. The corrosion inhibition performance of PNO increased with increase in concentration and achieved maximum value of inhibition efficiency of 90.4 at 500 mg/L concentration.
- 2. The adsorption of PNO obeyed the Langmuir isotherm.
- 3. The ΔG_{ads}^0 values showed spontaneous adsorption of PNO on the metal surface involving both the physical and chemical interaction.
- 4. In EIS, study charge transfer resistance values increases with increase in the concentration of PNO.
- 5. Potentiodynamic polarization studies suggests the mixed mode of PNO action.
- 6. The quantum chemical calculations showed the planar structure of PNO.
- 7. MD study reveals that PNO can interact strongly with the metal surface.

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