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# Synthesized oxadiazole derivatives as benign agents for controlling mild steel dissolution: Experimental and theoretical approach



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# ABSTRACT

This study explains about the two newly synthesized oxadiazole derivatives, namely 5-benzyl-3-((4nitrophenylamino) methyl)-1,3,4-oxadiazole-2-(3H)-thione (B4NPAMOT) and 5-benzyl-3-((2nitrophenylamino) methyl)-1,3,4-oxadiazole-2-(3H)-thione (B2NPAMOT). The corrosion inhibition efficiency of both oxadiazole derivatives tested onto mild steel in 1.0 M hydrochloric acid solution through weight loss measurement, electrochemical impedance spectroscopy, and potentiodynamic polarization techniques. The weight loss measurement was conducted at different concentrations (50 ppm-300 ppm) and varying temperatures 298 K-318 K for immersion periods of 12.0 h. Weight loss results shown that 96.29% and 93.42% was maximized inhibition efficiency by B4NPAMOT and B2NPAMOT respectively at 300 ppm concentration at 298 K. EIS study defined that the charge transfer resistance shifted high at an enhanced concentration of each derivative. Polarization studies revealed a mixed type of inhibition and well obeyed through Langmuir adsorption isotherm by both the derivatives. Surface analysis of the steel sheet performed using a Scanning Electron Microscope (SEM) equipped with electron dispersive X-ray spectroscopy (EDX), respectively. Computational simulation (Fukui functions, DFT and molecular dynamics) was further analyzed to corroborate with the experimental techniques. © 2020 Elsevier B.V. All rights reserved.

## 1. Introduction

Due to the magnificent mechanical properties, easy availability and economic features, mild steel (MS) is used extensively in numerous industries like power production, petrochemical, oil-gas, manufacturing of different household goods, infrastructure and even more [1]. The nature of the solution (mostly the mineral acid solution) being used varies and depends upon the application like descaling, acid pickling and chemical cleaning for removing the undesirable scale and rust from the surfaces of metals in such industries. However, the major limitation is that when MS comes in contact with these solution environments as corrosive media, it becomes easily corroded [2-5]. Dilute hydrochloric acid, being more economical, productive and trouble-free in handling than other mineral acid, it is the most commonly used matrix for such purposes [6,7]. Hence, the corrosion process initiated by the acid is liable for the deterioration of useful properties of the metals like iron and also destroys the metal surface. Various methods are used to protect the metal surface against such corrosive attack; still one of the most adopted methods is the application of corrosion inhibitors especially in the acidic environments [8–10]. A large number of organic moieties

\* Corresponding author. *E-mail address:* hariom.chem@mdurohtak.ac.in (H. Dahiya). [11], inorganic compounds [12] and pharmaceutical drugs [12] are being used as corrosion inhibitors, out of these, use of the organic compounds is preferred as corrosion inhibitors that have pi-bonded structure, aromatic ring and contain hetero-atoms like nitrogen, sulphur and oxygen atoms. Generally, these compounds get adsorbed over the metal surface either by the formation of a partial bond through lone pair and pi orbital or electrostatic interactions and subsequently reduce the corrosion rate by blocking the aggressive cites in the acidic medium [13,14]. The effectiveness of such moieties is also related to their molecular size and structure of the compounds [15,16].

Oxadiazole derivatives account as important heterocyclic compounds, specifically as multipurpose drugs and researchers have studied different oxadiazole derivatives, even as corrosion inhibitors for MS in different acidic mediums [17–20]. Till date, no work is reported on the oxadiazole derivatives being synthesized herein, i.e. 5-benzyl-3-((4-nitrophenylamino) methyl)-1, 3, 4-oxadiazole-2-(3H)-thione (B4NPAMOT) and 5-benzyl-3-((2-nitrophenylamino) methyl)-1, 3, 4oxadiazole-2-(3H)-thione (B2NPAMOT) and tested as corrosion controlling agents for MS in 1.0 M HCl medium. Aim of the present work was to synthesize B4NPAMOT and B2NPAMOT and further, to study their anticorrosive impact on MS in 1.0 M HCl solution at different temperature and concentration. Herein, the studies were carried out through the techniques: electrochemical impedance, weight loss and



a) 5-benzyl-3-((4-nitrophenylamino) methyl)-1, 3, 4-oxadiazole-2-(3H)-thione

(B4NPAMOT)



b) 5-benzyl-3-((2-nitrophenylamino) methyl)-1, 3, 4-oxadiazole-2-(3H)- thione (B2NPAMOT)

Fig. 1. Structure of (a) B4NPAMOT and (b) B2NPAMOT.

polarization. In order to obtain the best insights into the adsorption process, thermodynamic parameters were deliberated and examined. MS surface was also analyzed using Scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (EDX). Additionally, the density functional theory (DFT), Fukui functions and molecular dynamics (MD) were used for both the structures to possess the theoretical calculation so that the impact of these molecular structures on corrosion inhibition may be analyzed satisfactorily.

# 2. Materials and method

# 2.1. Synthesis of the oxadiazole derivatives

Two oxadiazole derivatives were synthesized as per the literature reported elsewhere [21].

Step I: Synthesis of precursor (5-benzyl-1,3,4-oxadiazole-2(3H)-thione)

Phenylacetic hydrazide (0.1 mol) and  $CS_2$  (0.1 mol) were dissolved in ethanol and KOH (0.1 mol). The obtained mixture was added in a round bottom flask and stirred for 4.0 h until H<sub>2</sub>S evolution was stopped. After that, the precipitate filtered while the solution was cooled. The white crystals obtained were recrystallized using ethanol.

Step II: Synthesis of 5-benzyl-((4-nitrophenylamino)methyl)-1,3,4-oxadiazole-2-(3H)-thione

5-Benzyl-1,3,4-oxadiazole-2-(3H) -thione (0.1 mol) and 4-Nitroaniline (0.1 mol) in 1,4-Dioxane were grasped in a flat bottom flask and stirred for 6.0 h. The resulting mixture was cooled and thus the precipitates obtained were filtered, recrystallized using ethanol



Fig. 2. Graphical representation of variations in corrosion rate with increase concentration of a) B4NPAMOT and b) B2NPAMOT inhibitors at different temperatures.



Fig. 3. Variation in inhibition efficiency ( $\eta_w$  %) with the concentration of a) B4NPAMOT and b) B2NPAMOT.

to give yellowish crystals and characterized by spectral techniques namely nuclear magnetic resonance (NMR) and infra red spectroscopy (IR). Fig. 1(a) shows the structure of B4NPAMOT: Yield 89%, yellow solid, IR taken in KBr,  $v_{max}$  cm<sup>-1</sup>; 3423.90 (NH), 2929.05 (CH<sub>2</sub>), 3030.81 (aromatic stretching), 1525 and 1615 (NO<sub>2</sub>), 1247 and 1065 (Amines) and <sup>1</sup>H NMR taken in DMSO D<sub>6</sub>:  $\delta$  6.9–7.5 (m) 9H, 2.5 (d) 2H, 3.5 (t) 1H.

Step III: Synthesis of 5-benzyl-((2-nitrophenylamino) methyl)-1,3,4-oxadiazole-2-(3H)-thione

5-Benzyl-1, 3, 4-oxadiazole-2-(3H)-thione (0.1 mol) and 2nitroaniline (0.1 mol) in 1,4-dioxane was grasped in a flat bottom flask and stirred for 6.0 h. The resulting mixture was cooled and precipitates, thus obtained were filtered, recrystallized using ethanol and characterized by spectral techniques, infra red (IR) and nuclear magnetic resonance (NMR) spectral techniques. Fig. 1(b) shows the structure of final product B2NPAMOT: Yield 83%, yellow solid, IR was taken in KBr, V<sub>max</sub> cm<sup>-1</sup>; 3416.12 (NH), 2929.57 (CH<sub>2</sub>), 3031.57 (aromatic stretching), 1486 and 1633 (NO<sub>2</sub>), 1246.74 and 1127.35 (amines). <sup>1</sup>H NMR employed in DMSO D<sub>6</sub>:  $\delta$  7.2–7.5 (m) 9H, 2.5 (d) 2H, 3.8–4.1 (t) 1H.

# 2.2. Materials

#### 2.2.1. Material preparation

Experimental tests were performed with MS specimens with chemical composition (wt%): C = 0.054, Si = 0.015, S = 0.017, P = 0.019, Cu = 0.010, Mo = 0.018, Mn = 0.26, Cr = 0.056, Ti = 0.002, Ni = 0.009 and remainder as iron were used for corrosion testing in aggressive environment. Prior, the MS sample was cut into pieces of 3 cm  $\times$  1.5 cm dimensions for weight loss measurement and into 3 cm  $\times$  1.5 cm dimensions used for electrochemical corrosion study. Then the samples were mechanically cleaned using emery paper by 220, 420, 800 and 1500 grades and chemically washed with bidistilled water and acetone, dried in hot air and finally placed in desiccators for experimental used.

#### 2.2.2. Solutions preparation

The stock solution of each derivative was prepared in ratio 10:1 in water and ethanol mixture by volume; to ensure solubility by using 1.0 M HCl solution. This stock solution of inhibitor was again diluted

#### Table 1

Weight loss data of B4NPAMOT and B2NPAMOT at different temperatures for MS in 1.0 M HCl.

Temperature (K)	Concentration (ppm)	<b>B4NPAMOT</b>			<b>B4NPAMOT</b>		
		CR (mm y <sup>-1</sup> ) (%)	η <sub>w</sub> (%)	θ	$CR (mm y^{-1})$	η <sub>w</sub> (%)	Θ
	Blank	16.25	-		16.85	-	
298	50	04.46	72.51	0.72	05.35	68.23	0.68
	100	03.54	78.16	0.78	04.18	75.18	0.75
	150	02.78	82.84	0.82	03.42	79.69	0.79
	200	01.73	89.35	0.89	02.21	86.88	0.86
	250	00.83	94.89	0.94	01.17	93.05	0.93
	300	00.60	96.29	0.96	01.10	93.42	0.93
	Blank	19.13	-	-	20.05	-	-
308	50	06.87	64.07	0.64	07.35	63.34	0.63
	100	05.76	69.86	0.69	06.27	68.72	0.68
	150	04.40	76.98	0.76	05.48	72.66	0.72
	200	03.67	80.79	0.80	04.15	79.30	0.79
	250	02.56	86.58	0.86	03.45	82.78	0.82
	300	02.37	87.58	0.87	03.10	84.51	0.84
	Blank	30.00	-		29.87	-	-
318	50	12.19	59.34	0.59	12.83	57.05	0.57
	100	10.42	65.25	0.65	11.59	61.18	0.61
	150	09.60	68.00	0.68	10.10	66.17	0.66
	200	08.99	70.01	0.70	09.03	69.77	0.69
	250	07.00	76.66	0.76	08.46	71.68	0.71
	300	07.63	74.55	0.74	07.63	74.44	0.74



Fig. 4. Arrhenius plots of (a) B4NPAMOT (b) B2NPAMOT in 1.0 M HCl.

with 1.0 M HCl to make desired concentrations ranging from (50 ppm-300 ppm).

# 2.3. Methods employed

#### 2.3.1. Weight loss measurement

The weight loss measurement was performed as per reported in the literature [29]. Prior to the experiment, the sample was weighed and then placed in test solution in a 100 mL beaker in 1.0 M HCl without and with various concentrations of inhibitor at different temperatures (298 K, 308 K and 318 K) for various time periods of 12.0 h. After completion of immersion time, the samples were withdrawn, cleaned using bidistilled water and acetone, dried between folds of filter paper then weighted again. This technique was experimented in triplicate measurements, thereafter; the average weight loss was recorded within limits  $\pm 0.01\%$ . Weight loss values were used to calculate percentage corrosion inhibition efficiency ( $\eta_w\%$ ) and surface coverage ( $\theta$ ) going through the following equations:

$$\eta_w\% = \frac{w_o - w_i}{w_o} \times 100 \tag{1}$$

$$\theta = \frac{w_o - w_i}{w_o} \tag{2}$$

where,  $w_o$  and  $w_i$  are weight loss of MS without and with various concentration of inhibitor, respectively. The corrosion rate of MS was calculated by the following equation:

$$C_{R}\left(mm\,y^{-1}\right) = \frac{87.6 \times W}{AtD} \tag{3}$$

where, w is weight loss of MS in mg, A is area of sample  $(cm^2)$ , t is exposure time (h) and D is density of MS  $(g cm^{-3})$  respectively [22].

# 2.3.2. Electrochemical measurement

A conventional three electrode cell assembly was used to perform the electrochemical study [31,32] where calomel was used as a reference electrode (RE), platinum wire as a counter electrode (CE) and MS sample with an exposed surface area of  $1.0 \times 1.0$  cm<sup>2</sup> was selected as working electrode at 298 K temperature. Open circuit potential (OCP) value was stabilized before performing the experiment by dipping electrodes in 100 mL test solution for about 30 min. Both the electrochemical studies were carried out using Princeton Applied Research parastat-4000.

Impedance spectroscopy was performed with signal amplitude of 10 mV over a frequency range of 10 kHz to 0.01 Hz at its corrosion potential ( $-E_{corr}$ ). The experiments were conducted without and with varying concentrations of both the moieties and the impedance curves were obtained in the form of Nyquist plots. After EIS study, potentiodynamic polarization characteristics of MS specimens were studied in the absence and presence of both the inhibitors in 1.0 M HCl at a scan rate of 1.0 mV/s from an anodic potential range of +250 mV and cathodic potential range of -250 mV with respect to open circuit potential. The corrosion current densities ( $I_{corr}$ ) were obtained by extrapolating the Tafel slope of anodic and cathodic curves. Extrapolation of polarization plots, provided the polarization parameters such as  $-E_{corr}$ ,  $I_{corr}$ , cathodic ( $\beta_c$ ) and anodic ( $\beta_a$ ) Tafel constant.

# 2.3.3. SEM with EDX analysis

The surface morphology of samples immersed for 12 h in 1.0 M HCl solution and at higher concentration of both the inhibitors at temperatures of 298 K was analyzed through ZEISS Scanning Electronic Microscope.

# Table 2

Activation parameters at different concentrations of B4NPAMOT and B2NPAMOT.

<b>B4NPAMOT</b>				B2NPAMOT				
Conc. (ppm)	E <sub>a</sub> (kJ/mol)	$\Delta H^{\#} (kJ/mol)$	$\Delta S^{\#}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	E <sub>a</sub> (kJ/mol)	$\Delta H^{\#} (kJmol^{-1})$	$\Delta S^{\#}$ (J mol <sup>-1</sup> K <sup>-1</sup> )		
Blank	34.54	28.08	-129.16	30.36	25.13	-138.49		
50	39.57	37.01	-108.99	34.42	31.86	-124.49		
100	42.44	39.88	-101.18	40.17	37.61	-107.22		
150	48.70	46.14	-82.22	42.66	40.10	-100.57		
200	59.32	56.76	-49.38	51.81	49.42	-72.24		
250	73.74	71.18	-31.42	60.14	57.58	-47.36		
300	95.31	97.51	-22.19	69.37	65.09	-24.70		



Fig. 5. Plots of ln (CR/T) against 1000/T (a) B4NPAMOT (b) B2NPAMOT.

# 2.3.4. Quantum chemical calculations

The frontier molecular orbital approach was procured to measure the reactivity of inhibitor molecules and their respective interactions with the metal surface. Density functional theory and Fukui functions using atomic charge partitioning scheme i.e. Mulliken population analvsis were analyzed using Gaussian 09 [33] program with hybrid functional B3LYP [34] (Becke's three parameter Lee-Yang-Par correlation functional) and also with all electron Pople triple- $\zeta$  basis set including two polarization functions on heavier atoms 6-311G\*\*. Molecular Dynamics simulations carried out using the Forcite module of Material Studio software. In this simulation process, the iron crystal was imported from a Material Studio database and cleaved along (1 1 0) plane and a slab of 6 Å was employed. The Fe (1 1 0) chosen as a substrate because it possesses high stabilization energy and a highly packed structure. The Fe (1 1 0) surface was relaxed and then, enlarged to a  $(10 \times 10)$ supercell to provide a sufficient surface for the occurrence of the interaction by these derivatives with the iron surface. A vacuum slab that possesses zero thickness was also prepared. A simulation box of  $24.76 \times 24.76 \times 45.00$  Å<sup>3</sup> dimensions consisting of two layers generated using the layer builder module of the Material Studio to arrange the simulation closer to the real system as entirely as possible. The first layer at bottom composed of iron atoms and one layer above contained 500 H<sub>2</sub>O, 9H<sup>+</sup>, 9Cl<sup>-</sup> and 1 monomer of each inhibitor. All simulations were performed using COMPASSII Force Field, a time step of 1 fs, a simulation time of 2000 ps, and the canonical ensemble NVT at 303 K.

# 3. Result and discussion

#### 3.1. The weight loss measurement

#### 3.1.1. Effect of concentration

The inhibitive effect of B4NPAMOT and B2NPAMOT on the corrosion of the MS surface through weight loss experimentation is presented in Fig. 2 regarding the corrosion rate and Fig. 3 for efficiency where it was depicted that the values of corrosion inhibition efficiency ( $\eta_w$ %) increased but the corrosion rate declines on moving from lower to higher concentration for both the inhibitors (Table 1). That may be attributed to the fact that at higher inhibitor concentration, the adsorption coverage may go to the maturity level over the metal surface. In the present study, the maximum  $\eta_w$ % was raised up to 96.29% for B4NPAMOT and 93.42% for B2NPAMOT respectively only at quite a low concentration of 300 ppm for each derivative. Interestingly, it was also noticed that moving from 250 ppm to 300 ppm of each moiety, the rise in  $\eta_w$ % was not considerable and got optimized at 300 ppm for both compounds.

# 3.1.2. Effect of temperature

The effect of temperature for inhibitive properties at an entire range of concentration of B4NPAMOT and B2NPAMOT were found out by corrosion tests through weight loss at 298 K, 308 K and 318 K. After an investigation of Table 1, it was recognized that with a rise in temperature from 298 K to 318 K,  $\eta_W$ % value decreased but corrosion rate climbed at higher temperatures. This may happen due to the accelerated desorption and decay and/or rearrangement of inhibitor molecules at high temperature that may weaken the adsorption and it was the rationale behind high corrosion rate at elevated temperature [23,24].

#### 3.2. Activation and thermodynamic parameters

There is a significant role of activation and thermodynamic parameters during the corrosion inhibition mechanism. Arrhenius equation was used to calculate the activation energy ( $E_a$ ) for the disintegration of MS surface in 1.0 M HCl solution [25,26]:

#### Table 3

Adsorption parameters without and with various concentrations of B4NPAMOT and B2NPAMOT.

B4NPAMOT	тс					B2NPAMOT			
Temperature (K)	$\mathbb{R}^2$	$K_{ads}$ (g $L^{-1}$ )	Slope	$\Delta G^{\circ} (kJ/mol)$	$\mathbb{R}^2$	$K_{ads} (gL^{-1})$	Slope	$\Delta G^{\circ} (kJ/mol)$	
200	0.994	33.77	0.95	-25.83	0.994	30.78	0.98	-25.60	
298	0.996	28.89	1.03	-26.30	0.995	29.59	1.08	-26.36	
308	0.995	35.80	1.24	-27.72	0.997	29.92	1.25	-27.25	
318									



Fig. 6. Langmuir adsorption isotherms of a) B4NPAMOT and b) B2NPAMOT.

$$\ln CR = A - \frac{E_a}{RT}$$
(4)

where CR is corrosion rate, A is Arrhenius pre-exponential factor,  $E_a$  is activation energy (kJ/ mol), R is the molar gas constant (8.314 J K<sup>-1-</sup> mol<sup>-1</sup>) and T is the absolute temperature (K). The Arrhenius plot between ln CR against 1000/T for MS corrosion n 1.0 M HCl solution without and with the different concentrations of B4NPAMOT and B2NPAMOT are shown in Fig. 4(a, b) respectively.

The obtained slope  $(-E_a/R)$  from the plots shown in Fig. 4 for individual concentrations was adopted to calculate the respective activation energy (Table 2) for both the derivatives.

From Table 2, it can be examined that activation energy value uplifts as concentration of each B4NPAMOT and B2NPAMOT is shifted to higher values and found proportional to the inhibition efficiency and evidence that the corrosion control goes through physisorption with slight effects of chemisorption [27]. These findings represent the occurrence of physical adsorption taking place due to electrostatic interaction over the MS surface [28]. The enthalpy and entropy value for corrosion of MS were computed through transition state theory as Eq.5 [38]

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S^{\#}}{R}\right) \exp\left(\frac{-\Delta H^{\#}}{RT}\right)$$
 (5)



(a) B4NPAMOT

# (b) B2NPAMOT

Fig. 7. Nyquist plots of the MS of a) B4NPAMOT b) B2NPAMOT at 298 K.

 Table 4

 Impedance parameters of MS without and within the B4NPAMOT and B2NPAMOT.

Inhibitor	Conc. (ppm)	$R_{ct}$ ( $\Omega \cdot cm^{2}$ )	$\begin{array}{c} \text{CPE/Y}_0 \times 10^6 \\ (\text{S cm}^{-2} \ \text{S}^{n2}) \end{array}$	n	$\chi^2$	$\begin{array}{c} C_{dl} \\ (\mu F \ cm^{-2}) \end{array}$	η <sub>eis</sub> %
B4NPAMOT	Blank	12.19	164.0	0.998	0.896	150.40	-
	50	33.02	121.0	0.883	0.772	55.52	63.08
	100	38.05	108.7	0.937	0.796	48.18	67.96
	150	42.73	95.2	0.792	1.031	42.90	71.47
	200	47.18	89.5	0.870	0.793	38.86	74.16
	250	118.55	63.9	0.902	0.538	15.46	89.71
	300	156.41	44.2	0.929	0.494	11.72	92.20
B2NPAMOT	Blank	11.42	168.0	0.987	0.937	160.54	-
	50	29.08	129.2	0.915	0.846	63.04	60.72
	100	34.31	111.0	0.880	0.829	53.43	66.71
	150	37.34	96.1	0.825	0.778	49.10	69.41
	200	45.92	86.8	0.984	0.695	39.92	75.13
	250	105.14	68.6	0.847	0.520	17.43	89.13
	300	138.15	49.6	0.878	0.588	13.27	91.73

where h is Plank's constant and N is the Avogadro's number. A straight line graph between ln (CR/T) and 1000/T is shown in Fig. 5(a, b) respectively for B4NPAMOT and B2NPAMOT, from that the slope  $-\Delta H^{\#}/T$  and an intercept ln (R/Nh)  $+\Delta S^{\#}/R$  are obtained. All the calculated values of  $\Delta H^{\#}$  and  $\Delta S^{\#}$  are also listed in Table 2. From the table, it was found that enthalpy ( $\Delta H^{\#}$ ) of activation is positive which denotes that the dissolution of MS is endothermic in nature [29] and the value of enthalpy increase with increasing concentration of B4NPAMOT and B2NPAMOT in 1.0 M HCl solution. The entropy change ( $\Delta S^{\#}$ ) with a negative sign at activated conditions for both the derivatives represents the evolution of activated complex that may exist by the association instead of the dissociation which implies a decline in disorder (randomness) during the transition from reactant to activated complex [17].

# 3.3. Adsorption isotherm

An isotherm plays a vital role to find an adsorptive action of the compounds over the metal surfaces. It not only gives information about the interaction between metal surface and inhibitor but also offers additional information about the corrosion inhibition characteristics. In the current study, several isotherms such as Frumkin, Temkin, Langmuir, Freundlich and Flory-Huggins were tested to evaluate adsorption behaviour of the derivatives on MS surface, but among them, the present experimental data fitted well with Langmuir isotherm. The relation between degree of surface coverage ( $\theta$ ) and the derivative concentration observed through Langmuir isotherm is shown in the following Eq. (6) [23,30]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C \tag{6}$$

where,  $C_{inh}$  is a concentration of corrosion inhibitor,  $\theta$  is a degree of surface coverage and  $K_{ads}$  is the equilibrium constant for adsorption and is connected to the standard free energy of adsorption ( $\Delta G^0_{ads}$ ) through the following Eq. (7) [31,32]:

$$\Delta G^{0}_{ads} = -RT \ln \left( 1 \times 10^{6} \text{ K}_{ads} \right)$$
<sup>(7)</sup>

where, R is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), T is the absolute temperature and  $1 \times 10^6$  is the concentration of water expressed in mg L<sup>-1</sup>. The observed values of K<sub>ads</sub> from the graph and values of  $\Delta G^0_{ads}$  are placed in Table 3.

A straight line curve with strong correlation coefficient nearly equal to 1.0 was obtained by plotting  $C_{inh}/\theta$  against  $C_{inh}$  as at different temperatures i.e. 298 K–318 K for 12.0 h immersion time are shown in Fig. 6(a, b) [33].

Generally, the Free energy value of adsorption denoted as  $\Delta G_{ads}^0$  value lower than -20 kJ/mol represents physisorptions (physical

adsorption) between the metal surface and the molecule while the value higher than -40 kJ/mol represents chemisorptions (chemical adsorption) due to transfer of an electron from inhibitor molecule to a metal surface. A value observed between -20 kJ/mol and -40 kJ/mol shows a combination of both the adsorptions.  $\Delta G_{ads}^0$  values in work at different temperatures are accomplished and a higher negative value of  $\Delta G_{ads}^0$  indicates strong interactive behaviour of the derivative on metal surface. Table 3 shows that  $\Delta G_{ads}^0$  values obtained for B4NPAMOT range from -25.83 kJ/mol to -27.72 kJ/mol and for B2NPAMOT, it acquires the range of -25.60 kJ/mol to -27.25 kJ/mol at different temperatures and hence indicated physiochemical adsorption by both inhibitors [34].

#### 3.4. Electrochemical study

# 3.4.1. Electrochemical impedance spectroscopy measurement

Electrochemical impedance behaviour of MS sample in 1.0 M HCl without and with various concentrations of B4NPAMOT and B2NPAMOT was carried out at 298 K. Fig. 7(a, b) represents the effect of these inhibitors on impedance behaviour in the form of the Nyquist plot. From the inspection of Fig. 7, it can be seen that the impedance diameter of MS for an inhibited sample was higher enough than that of uninhibited sample and further with a higher concentration of each corrosion inhibitor, the diameter of the loop further increases.

One capacitive loop shown in Fig. 7 represents that the corrosion process is related to double layer capacitance and charge transfer resistance behaviour [30]. Considerably, impedance spectra were not found as perfect semicircles but depressed in nature which is the consequence of frequency dispersion that showed the rough and non-homogeneous nature of MS surface.

In the Nyquist plot, the value of charge transfer resistance ( $R_{ct}$ ) obtained from difference in real impedance value at lower to higher frequency. Charge transfer values were used for calculating the inhibition efficiency ( $\eta_{eis}$ %) by adopting the following equation.

$$\eta_{eis}\% = \frac{R_{ct (inh)} - R_{ct}}{R_{ct (inh)}} \times 100$$
(8)

where,  $R_{ct}$  and  $R_{ct (inh)}$  indicate the charge transfer resistance in without and with different concentrations of inhibitor.

All the calculated electrochemical parameters are introduced in Table 4 and it was observed that the values of both, charge transfer resistance and inhibition efficiencies increase but there is a decline in double layer capacitance as the concentration of both inhibitors increases. This behaviour may be the consequence of the evolution of inhibitive layer on to the MS surface which may decrease the interaction between the metal surface and the corrosive environment. The decreased value of double layer capacitance ( $C_{dl}$ ) with increasing inhibitors concentration might be referred due to enhancement in the thickness of electric double layer or reduction in local dielectric constant which suggests that each inhibitor molecule works via adsorption over the MS surface or solution interface [35]. The result also showed that the charge transfer resistance process is generally the corrosion controlling process,  $C_{dl}$  values were calculated using the equation:

$$C_{dl} = \frac{1}{2\pi f_{max}} \times \frac{1}{R_{ct}}$$
(9)

where,  $f_{max}$  is the frequency that is midway of  $Z_{real}$  and also where  $Z_{image}$  component is maximal. Fig. 8(a–d) represents the plots of Bode Phase and Bode modulus for MS without and with various concentrations of B4NPAMOT and B2NPAMOT in 1.0 M HCl at 298 K. The figures represent that the phase angle gets enhanced at a higher concentration for each of the inhibitors and subsequently evidences the effective interaction at metal/solution interface [36]. Fig. 8(e) shows Equivalent circuit diagram, which is used to fit electrochemical impedance measurement data. The equivalent circuit has three



Fig. 8. (a), (c) Bode phase and (b), (d) Bode modulus of B4NPAMOT and B2NPAMOT respectively, (e) equivalent circuit fit.

essential elements, namely, solution resistance ( $R_s$ ), constant phase element (CPE) and charge transfer resistance ( $R_{ct}$ ). The CPE is used to provide the information about the formation of double layer at electrode (metal)/electrolyte (solution) interface. Moreover, the n

value which is exponential of CPE equal to 0, 0.5, 1, and -1 linked with resistance, Warburg impedance, capacitance and inductance, respectively [30]. The CPE impedance can be calculated by following Eq. (10) [30]:

8



Fig. 9. Polarization curves of MS in 1.0 M HCl without and with various concentrations of (a) B4NPAMOT (b) B2NPAMOT at 298 K.

$$Z_{CPE} = \left(\frac{1}{Y^0}\right) \left[(j\omega)n\right]^{-1} \tag{10}$$

where  $Y^0 = CPE$  constant,  $\omega =$  angular frequency, and j = imaginary number respectively. The observed value of CPE, n and Chi square ( $\chi^2$ ) also summarised in Table 4. Hence these inspections indicate that the MS surface is smoother in the presence of corrosion inhibitors may be due to the formation of a protective layer by B4NPAMOT and B2NPAMOT molecules.

# 3.4.2. Potentiodynamic polarization measurement

Polarization curve for corrosion behaviour of MS in 1.0 M HCl without and with different concentration of B4NPAMOT and B2NPAMOT are shown in Fig. 9(a) and (b) respectively. The potentiodynamic parameters such as  $-E_{corr}$ , polarization resistance ( $R_p$ ),  $I_{corr}$  (corrosion current densities),  $\beta_a$  anodic Tafel slope and  $\beta_c$ , cathodic Tafel slope are extracted from extrapolation of anodic and cathodic Tafel lines and percentage inhibition efficiency ( $\eta_{pol}$ %) are indexed in Table 5.

As can be seen from Fig. 9(a) and (b), both cathodic and anodic curves are affected by adding B4NPAMOT and B2NPAMOT and curves shifted towards the lower current density value with increasing inhibitors concentration in 1.0 M HCl solution which represents that the investigated inhibitors significantly resist both the reactions such as anodic dissolution and cathodic hydrogen evolution at MS surface [37], and suggests that both compounds act as mixed type inhibitors

Table 5

Polarization data at various concentrations of B4NPAMOT and B2NPA	MOT.
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without changing the basic corrosion mechanism. This also proposed that the investigated inhibitors reduced the corrosion process through surface blocking and thus resulted in adsorption activity on MS surface.

Further, data from Table 5 indicates that the value of I<sub>corr</sub> declines and percentage inhibition efficiency ( $\eta_{pol}$ %) increases with the presence of inhibitors in corrosive media that may be attributed to the fact that active centres of corrosion reaction on the metal surface are blocked by the inhibitor molecules adsorbed on the MS surface. Additionally, both  $\beta_c$  and  $\beta_a$  Tafel constant values slightly change with inhibitor concentration, which indicated that the studied compounds controlled both cathodic as well as an anodic reaction on the metal surface and act as mixed type inhibitors. The I<sub>corr</sub> calculated by adopting the Stern-Geary equation given as follows.

$$I_{corr} = \frac{\beta_a \times \beta_c}{2.303(\beta_a + \beta_c)} \times \frac{1}{R_p}$$
(11)

where,  $R_p$  is polarization resistance,  $\beta_a$  anodic and  $\beta_c$  cathodic Tafel constant respectively.

The  $\eta_{\text{pol}}$  % was calculated by using the following equation:

$$\eta_{\text{pol}}\% = \left(1 - \frac{I_{\text{corr}^i}}{I_{\text{corr}^0}}\right) \times 100 \tag{12}$$

where, I<sub>corr<sup>o</sup></sub> and I<sub>corr<sup>i</sup></sub> are the corrosion current density without and with different concentrations of B4NPAMOT and B2NPAMOT, respectively.

Inhibitor	Concentration (ppm)	$\beta_a (mV  dec^{-1})$	$-\beta_c(mV\;dec^{-1})$	$R_p (\mu \cdot cm^2)$	$-E_{corr}$ (mV vs. SCE)	$I_{corr}(\mu A~cm^{-2})$	$\eta_{\text{pol}}\%$
B4NPAMOT	Blank	336	144	15.08	412.29	2.90	-
	50	238	132	31.78	446.28	1.16	60.01
	100	170	136	34.61	454.42	0.94	67.33
	150	215	140	40.46	469.47	0.90	68.64
	200	159	101	44.68	479.76	0.60	79.30
	250	109	122	63.47	478.37	0.39	86.42
	300	126	89	70.32	491.42	0.32	88.89
B2NPAMOT	Blank	249	198	16.98	414.74	2.82	-
	50	191	146	29.01	459.64	1.23	56.08
	100	362	100	36.15	455.40	0.94	66.63
	150	174	133	38.92	479.76	0.84	70.18
	200	213	87	42.36	491.73	0.63	77.55
	250	131	99	54.89	493.73	0.44	84.18
	300	112	83	61.03	495.29	0.33	87.97



Fig. 10. Surface morphology of MS (a) polished surface and after immersion in (b) 1.0 M HCI (c) B4NPAMOT (d) B2NPAMOT at 298 K.

The highest inhibition efficiency value was found to be 88.89% for B4NPAMOT and 87.97% for B2NPAMOT molecule at 300 ppm concentration.

It is also clear from Table 5 that the presence of both inhibitors concentration caused changed in -Ecorr value. It is reported in the literature [30] that if the amount of deviation in the corrosion potential  $(-E_{corr})$  is higher than 85 mV in the presence of inhibitor with respect to  $(-E_{corr})$ in the absence of inhibitor, indicates the inhibitor could act as anodic or cathodic type inhibitor whereas the value of deviation in  $(-E_{corr})$  is lower than 85 mV, the inhibitor could be seen as mixed type controlling both cathodic and anodic type reactions. In the present study, the maximum deviation in corrosion potential (-Ecorr) is 79 mV for B4NPAMOT and 80 mV for B2NPAMOT, which clearly indicates that these oxadiazole derivatives act as mixed type inhibitors. The inhibition efficiency of these two inhibitors from polarization measurement follows the order B4NPAMOT > B2NPAMOT and the same trend is followed as accordance with the results accessed from weight loss measurement and impedance measurement. Hence corrosion inhibition efficiencies obtained from weight loss measurement  $(\eta_{w\%})$  electrochemical; impedance spectroscopy (neis%) and potentiodynamic polarization measurement  $(\eta_{\text{pol}} \%)$  are in good agreement with each other.

#### 3.5. Scanning electron microscopy and energy dispersive X-ray analysis

The morphological characteristic of MS samples before and after dipping in 1.0 M HCl solution in the absence and presence of B4NPAMOT and B2NPAMOT after 12.0 h immersion at 298 K is represented in Fig. 10(a-d). Fig. 10(a) showed the polished MS surface before immersion, which appears smooth and uniform Fig. 10(b) shows that after immersion in 1.0 M HCl solution without inhibitor, the MS surface is very rough and/or there is an attack of a corrosive environment that damaged the surface. Fig. 10(c and d) shows that in the presence of B4NPAMOT and B2NPAMOT at 300 ppm concentration, the corrosion rate decreases on to the surface and surface seems smoother. EDX spectroscopy analysis was performed in order to recognize the composition of species formed over the MS surface in 1.0 M HCl solution in the absence and presence of 300 ppm concentration of B4NPAMOT and B2NPAMOT after 12.0 h exposure. The selected areas of SEM images were chosen for the EDX spectroscopy analyses that are shown in Fig. 11 (a) for corrosive medium alone, (b) for B4NPAMOT and (c) for B2NPAMOT.

The atomic percentage of species found through the EDX study for MS in 1.0 M HCl solution is 53.71% O, 32.12% Fe and 14.55% C. This result indicates that corrosion of MS surface is attributed to the formation of oxide layer onto the surface. Identically, the species composition obtained in the 300 ppm concentration of B4NPAMOT (14.91% O, 1.70% N, 0.10% S and 67.49% Fe) and that of in B2NPAMOT (20.92% O, 1.33% N, 0.06% S and 60.89% Fe) proves that there is the formation of protective layer over the steel surface where iron percentage goes almost two-fold than its amount present in the corrosive medium alone in the form of iron compounds. The findings strengthen the observed experimental output by all the three techniques and also support that B4NPAMOT performs even better than B2NPAMOT.

#### 3.6. Theoretical calculation and proposed action

# 3.6.1. Quantum chemical measurements

The study of quantum chemical measurements was performed to identify the role of the molecular structure of each inhibitor towards percentage inhibition efficiency [38]. The optimized structure,  $E_{HOMO}$  and  $E_{LUMO}$  related to electron density [39] surface of investigated inhibitors are given in Fig. 12. Various quantum chemical factors such as the value of the energy of highest occupied molecular orbital ( $E_{HOMO}$ ), that of the lowest unoccupied molecular orbital ( $E_{LUMO}$ ), ionization energy (I), dipole moment ( $\mu$ ), energy gap ( $\Delta E$ ), electron affinity (Y), electronegativity ( $\chi$ ), chemical hardness ( $\eta$ ) and chemical softness ( $\sigma$ ) were calculated and listed in Table 6.







Fig. 11. EDX spectra of MS in (a) 1.0 M HCl solution (b) B4NPAMOT (c) B2NPAMOT.

According to FMO (frontier molecular orbital) theory, the reactivity of a compound depends on the distribution of molecular orbitals (HOMO and LUMO) and interaction between these orbitals that are stronger for smaller energy gap ( $\Delta E$ ) [40]. From Table 6, we get various energy parameters, the ionization potential (I) and electron affinity (Y) that are computed as [41,9]:

$$\mathbf{I} = -\mathbf{E}_{\mathsf{HOMO}} \tag{13}$$

$$Y = -E_{LUMO}$$
(14)

Further, the value of electronegativity ( $\chi$ ), chemical hardness ( $\eta$ ) and softness ( $\sigma$ ) of each compound are also important reactivity parameters. These parameters were calculated by using following equations:

$$\chi = -\frac{1}{2} \left( E_{HOMO} + E_{LUMO} \right) \tag{15}$$

$$\eta = -\frac{1}{2} \left( E_{\text{HOMO}} - E_{\text{LUMO}} \right) \tag{16}$$

The above mentioned parameters i.e. electro-negativity ( $\chi$ ), chemical hardness ( $\eta$ ), chemical softness ( $\sigma$ ) and dipole moment ( $\mu$ ) are also related to inhibition efficiency of any inhibitor. Higher value of the dipole moment ( $\mu$ ), comparatively high softness as well as electro-negativity are responsible for enhanced inhibition efficiency of a compound. Presently, almost all the parameters got through DFT study favour the experimental findings and more importantly, these



Fig. 12. Optimized structures, HOMO and LUMO images of the derivatives.

#### Table 6

Ouantum chemical	parameters for E	34NPAMOT and	<b>B2NPAMOT i</b>	using hybrid	functional B3LYP/6-311G.
<u> </u>				0 3	

Molecule	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)	$\Delta E (eV)$	I (eV)	A (eV)	μ(D)	χ (eV)	η (eV)	$\sigma(\text{eV}^{-1})$
B4NPAMOT	-6.486	-2.274	4.212	6.486	2.274	6.263	4.380	2.106	0.474
B2NPAMOT	-6.368	-2.563	3.805	6.368	2.563	5.599	4.465	1.902	0.525

values are not much deviated for the two derivatives. This supports that the adsorption extent followed by the two derivatives over MS surface is more or less similar and directly associated with inhibition efficiency except that it is more inclined to B4NPAMOT than B2NPAMOT [40,36,42,43].

# 3.6.2. Fukui functions

The Fukui functions help to locate electrophilic and nucleophilic sites [44]. These functions (Table 7) inform about the local reactivity of atoms and are calculated as:

 $f_k^+ = \mathbf{q}_k(\mathbf{N}+1) - \mathbf{q}_k(\mathbf{N}) \tag{17}$ 

$$f_k^- = \mathbf{q}_k(\mathbf{N}) - \mathbf{q}_k(\mathbf{N} - 1) \tag{18}$$

where qk (N + 1), qk (N - 1) and qk (N) are the charge of the cationic, anionic and neutral species of the kth atom, respectively. Fig. 13 exposes the Fukui indices as locally reactive locations for B4NPAMOT and B2NPAMOT moieties.

Table 7 indicates that in B4NPAMOT moiety, the most available local reactive sites for the electrophilic attack are positioned on C (7), C (11) and C (13), S (24), N (14) while high values of  $\Delta f$  are located on S (24), N (14), N (9), N (10), O (12), C (16) and C (20) and shows the highly preferred sites for nucleophilic attack. The inspection about  $\Delta f$  for B2NPAMOT indicates that O (22), C (18), C (20) S (24) and N (14) are the local active centres while for an electrophilic attack, herein these are located at S (24) and N (14) and that for nucleophilic attack at C (7), C (11) and C (13). Overall, it can be concluded that B4NPAMOT and B2NPAMOT, both the inhibitors hold the electron donation capability that carries the corrosion inhibition pathway over the metal surface.

3.6.3. MD simulations

The initial and final views of both the inhibitor molecules with their maximum adsorptive tendency are shown in Fig. 14. The energy

# **Table 7**Fukui indices for a) B4NPAMOT and b) B2NPAMOT.

B4NPAMOT	$\mathbf{f}_k^+$	$f_k^-$	$\Delta f(k)$	B2NPAMOT	$f_k^+$	$f_k^-$	$\Delta f(k)$
C(1)	0.0	-0.5	0.5	C(1)	-0.4	-0.9	0.5
C(2)	-0.6	-0.3	-0.3	C(2)	-0.5	-0.3	-0.2
C (3)	-1.6	-1.2	-0.4	C (3)	-0.9	-1.2	0.3
C (4)	0.1	-0.7	0.8	C (4)	-0.1	-0.9	0.8
C(5)	-1.0	-0.1	-0.9	C(5)	-0.6	-0.4	-0.2
C (6)	-0.2	0.2	-0.4	C (6)	-0.2	0.1	-0.3
C(7)	1.3	0.5	0.8	C(7)	0.8	0.5	0.3
C (8)	-3.6	-1.7	-1.9	C (8)	-2.2	-1.7	-0.5
N (9)	-2.3	-2.0	-0.3	N (9)	0.2	-2.2	2.4
N (10)	0.9	-0.8	1.7	N (10)	0.9	-1.1	2.0
C(11)	0.4	0.7	-0.3	C(11)	1.0	0.9	0.1
0(12)	-1.8	-2.3	0.5	0(12)	-1.4	-2.3	0.9
C (13)	1.2	1.8	-0.6	C (13)	1.4	1.8	-0.4
N (14)	-0.7	-5.2	4.5	N (14)	-0.3	-5.1	4.8
C(15)	-3.3	-0.2	-3.1	C (15)	-4.5	-0.5	-4.0
C (16)	-0.6	-2.7	2.1	C (16)	-1.6	-2.7	1.1
C(17)	-3.0	-1.5	-1.5	C(17)	-3.7	-0.5	-3.2
C(18)	0.0	-3.7	3.7	C (18)	0.2	-3.5	3.7
C (19)	-2.5	-1.5	-1.0	C (19)	-3.8	-1.6	-2.2
C (20)	-0.7	-2.6	1.9	C (20)	0.0	-3.2	3.2
N (21)	-4.9	-0.4	-4.5	N (21)	-5.8	-0.8	-5.0
0 (22)	-11.8	-4.9	-6.9	0 (22)	-13	-2.1	-10.9
O (23)	-11.8	-4.9	-6.9	0 (23)	-14.4	-5.4	-9.0
S (24)	-8.6	-21.1	12.5	S (24)	-6.5	-20.8	14.3



Fig. 13. Fukui indices location represented for a) B4NPAMOT and b) B2NPAMOT compounds.

parameters calculated are calculated as [24] using the following equations and are given in Table 8.

 $E_{\text{adsorption}} = E_{\text{interaction}} = E_{\text{total}} - (E_{\text{surface+solution}} + E_{\text{inhibitor}})$ (19)

$$E_{\rm Binding} = -E_{\rm adsorption} = -E_{\rm interaction} \tag{20}$$

where  $E_{\text{total}}$  means, the total energy of the whole system;  $E_{\text{surface+solution}}$  assigned as the total energy of (110) surface of iron and solution leaving out the inhibitor and  $E_{\text{inhibitor+solution}}$  denotes the combined energy of solution and inhibitor while  $E_{\text{solution}}$  as the whole energy of the water molecules [46]. In the present work, a high value of B4NPAMOT than B2NPAMOT molecule lucidly strengthened the protection to a great extent and that accord with the experimental results. Moreover, the binding as well as the interaction energies for both the derivatives are comparable with slightly more inclined to the B4NPAMOT than B2NPAMOT molecules and again supports the experimental findings for each value of inhibition efficiency.

#### 3.6.4. Proposed action of inhibition

Herein, appreciable protection was obtained by the synthesized oxadiazole derivatives termed as B4NPAMOT and B2NPAMOT at low dosage (50 ppm to 300 ppm) and even for longer exposure timing of 12.0 h during weight loss study of mild steel in 1.0 M HCl solution. This may be justified due to the fact that the presence of a variety of high electron density sites like multi hetero atoms (N, S and O) in addition to  $\pi$ -bonds and delocalized  $\pi$  electron clouds adequately distributed over the entire structure may effectively donate electron density to the metal substrate. That is why both the compounds provide better efficiency even for longer immersions at their low concentration. Furthermore, synthesized B4NPAMOT provided slightly better inhibition in comparison to that of B2NPAMOT. This may be described due to the reason that B4NPAMOT has more symmetry in its structure with proper positioning of all the electron rich centres or heteroatoms in comparison to that of B2NPAMOT. So, as a matter of fact, both the molecules possess well-distributed density with a negative charge that the adsorption occurs with high impact presenting the structures as designer molecules



Fig. 14. Initial and final views of adsorption of a) B4NPAMOT b) B2NPAMOT.

# 14

 Table 8

 Energy parameters for B4NPAMOT and B2NPAMOT obtained from MD simulation.

Inhibitor	E <sub>total</sub> kcal/mol	E <sub>surface+solution</sub> kcal/mol	E <sub>inhibitor</sub> kcal/mol	E <sub>interaction</sub> kcal/mol	Ebinding kcal/mol
B4NPAMOT	-17,257.39		-21.29	2593.11	-2593.11
B2NPAMOT	-17,185.01		-28.34	2672.55	-2672.55

for controlling corrosion with persistence. One more point to be noted that the data obtained by all the adopted experimental methods herein agree well with the computational observations and provide justified inhibition via physiochemical adsorption. Table 9 indicates the inhibition efficiency of some reported oxadiazole derivatives and compares the findings of the present work. Subsequently, the two oxadiazole derivatives studied here can be approached to get better protection for mild steel in 1.0 M HCl electrolyte.

# 4. Conclusion

Both the synthesized and characterized oxadiazole derivatives i.e. B4NPAMOT and B2NPAMOT were found to be efficient corrosion controlling agents even at low dosage (300 ppm) for immersion at 12.0 h for mild steel (MS) in 1.0 M HCl solution. Corrosion inhibition efficiency is directly related with concentration of both the molecules with the order: B4NPAMOT > B2NPAMOT but behaves inversely at higher temperatures. EIS spectra show one capacitive loop and results indicate that charge transfer resistance  $(R_{ct})$  gets enhanced with the addition of each inhibitor dose. The potentiodynamic polarization data suggested that both the agents follow mixed-type inhibition. The adsorption of B4NPAMOT and B2NPAMOT obey the Langmuir adsorption isotherm. The study of quantum chemical computation (MD, Fukui and DFT) revealed that the parameters supported the experimental findings with slightly dominating control by the symmetrical structure of B4NPAMOT in 1.0 M HCl. SEM and EDX analysis of MS surface indicated that a controlling barrier is formed by both the designer inhibitors over the surface, providing functional inhibition against corrosion.

# **CRediT authorship contribution statement**

Vikas Kalia: Conceptualization, Data curation, Funding acquisition, Methodology, Project administration, Investigation, Writing - original draft. **Pradeep Kumar:** Formal analysis, Writing - review & editing.

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**Suresh Kumar:** Formal analysis, Writing - review & editing. **Priti Pahuja:** Data curation, Writing - review & editing. **Gaurav Jhaa:** Software. **Suman Lata:** Writing - review & editing, Validation. **Hariom Dahiya:** Conceptualization, Methodology, Investigation, Resources, Supervision, Validation, Visualization.

# Declaration of competing interest

Authors declare no conflict of interest.

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#### Table 9

unparative performance of some oxadiazore derivatives.					
Oxadiazole derivatives	Steel	Corrosive medium	Concentration	% inhibition efficiency	References
2,5-Bis(4-methoxyphenyl)-1,3,4-oxadiazole (4-MOX)	MS	0.5 M H <sub>2</sub> SO <sub>4</sub>	$8\times 10^{-4}\;\text{M}$	96	[27]
3,5-Bis(2-pyridyl)-1,3,4-oxadiazole (2-POX), 3,5-bis(3-pyridyl)-1,3,4-oxadiazole (3-POX) and 3,5-bis (4-pyridyl)-1,3,4-oxadiazole (4-POX)	MS	1 m HClO4	12 × 10 <sup>-4</sup> M 2-POX 3-POX 4-POX	85 92 76	[47]
2,5-Bis(4-dimethylaminophenyl)-1,3,4-oxadiazole ( <b>DAPO</b> ) 2-Methyl-4H-benzo[d][1,3]oxazin-4-one ( <b>BZ1</b> ) and 3-amino-2-methylquinazolin-4(3H)-one ( <b>BZ2</b> )	CS MS	1 M HCl 1.0 M HCl	1.0 mM 800 ppm <b>BZ1</b> <b>BZ2</b>	91 65 89	[48] [49]
5-((2-ethyl-1Hbenzo[ <i>d</i> ]imidazol-1-yl)methyl)-1,3,4-oxadiazole-2-thiol ( <b>EBIMOT</b> ) 1,3,4-Oxadiazole derivatives viz 5-((2-methl-1H-benzo[ <i>d</i> ]imidazol-1-yl) methyl)-13, 4-oxadiazole-2-thiol ( <b>MBIMOT</b> ), 5-((2-ethyl-1H-benzo[ <i>d</i> ]imidazol-1-yl) methyl)-1, 3, 4-oxadiazole-2-thiol ( <b>EBIMOT</b> ) and 5-((2-propyl-1H-benzo[ <i>d</i> ]imidazol-1-yl) methyl)-1, 3, 4-oxadiazole-2-thiol ( <b>PBIMOT</b> )	MS MS	0.5 M HCl 0.5 M H <sub>2</sub> SO <sub>4</sub>	760 μM 760 μM MBIMOT EBIMOT PBIMOT	95 85 88 92	[50] [51]
5-Benzyl-3-((4-nitrophenylamino) methyl)-1,3,4-oxadiazole-2-(3H)-thione ( <b>B4NPAMOT</b> ) and 5-benzyl-3-((2-nitrophenylamino) methyl)-1,3,4-oxadiazole-2-(3H)-thione ( <b>B2NPAMOT</b> )	MS	1.0 M HCl	300 ppm B4NPAMOT B4NPAMOT	96 93	Present study

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