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# **Corrosion Inhibition of Carbon Steel in 1 M HCl by Carbendazim: Experimental and Theoretical Study**

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**Abstract**- The effect of the benzimidazole-2-ylcarbamate methyl (Carbendazim) in corrosion inhibition for carbon steel has been studied using stationary and transient electrochemical techniques. The potentiodynamic curves show that Carbendazim acts as a mixed-type inhibitor. The electrochemical impedance diagrams show a capacitive response of carbon steel with and without inhibitors at different concentrations in 1M HCl. The polarization resistance increases with increasing inhibitor concentration. Consequently, the inhibition efficiency increases and reaches 84% at 10<sup>-2</sup>M and its adsorption follows the Langmuir isotherm. This shows that the protective effect of Carbendazim is significant in an acidic medium. The study of the synergistic effect with KI shows that an equimolar mixture of KI and Carbendazim compound enhances the inhibition efficiency. The theoretical investigation of the tested compound ability to inhibit corrosion using DFT shows that the HOMO, LUMO, and electrostatic potential maps

surfaces can qualitatively identify the most nucleophilic and electrophilic centers, this will enable us to give an adsorption mechanism for the inhibitor studied on the metal surface.

**Keywords-** Carbendazim; Corrosion; Inhibitor; Electrochemical technics; Monte Carlo; Density Functional Theory

# **1. INTRODUCTION**

Three to four percent of the gross domestic product in developed nations is spent on corrosion-related expenses [1,2]. In addition to being a source of energy and raw material waste, corrosion can also result in accidents [3,4] that have grave repercussions and, in certain situations, lead to environmental degradation [5].

Corrosion is a problem with the surface, or more specifically, the interface, which results in the deterioration of metallic materials [6–9]. Due to the widespread usage of metals and alloys in contemporary life, this problem has become significantly more significant [10].

Some authors have used organic compounds as corrosion inhibitors [11–13]. High inhibition efficiency, low cost, and non-toxicity are requirements for an efficient corrosion inhibitor [14].

In this paper, we employed Carbendazim noted as CBDZ (Figure 1), a heterocyclic organic chemical, to protect carbon steel against corrosion in an acidic medium. The choice of this compound is justified by the fact that the heterocyclic organic compounds act by forming an inhibitor film on the metal surface [15,16].

The protective effect of CBDZ has been studied using the electrochemical measurements completed by theoretical techniques such as DFT and Monte Carlo.

The electrochemical results show that the inhibition efficiency increases with increasing inhibitor concentrations and reaches its maximum value of 84% at a concentration of  $10^{-2}$  M.

The electrical properties and reactivity of CBDZ molecules with steel surfaces were investigated by computational investigations.

#### 2. EXPERIMENTAL SECTION

# 2.1. Materials

Carbon steel (E24) is the resource consulted for this study. Table 1 provides the chemical composition information.

Element	С	Р	S	Ν	Fe
Content (%)	0.2	0.005	0.05	0.07	99.675

Table 1. Chemical composition of carbon steel used

Each test begins with a pre-treatment that entails polishing the surface with abrasive paper of progressively finer granulometry (400, 600, 1500, and 2000), followed by acetone degreasing, distilled water rinsing, and air-lime pulsation drying.

## 2.2. Corrosive medium

Solution of 1 M HCl, which is prepared from commercial 37% HCl by dilution with bidistilled water.

## 2.3. Inhibitor

Carbendazim, an organic molecule having the general formula  $C_9H_9N_3O_2$  and the following structure, was employed in this investigation as an inhibitor.



Figure 1. Chemical structure of Carbendazim

## 2.4. Electrochemical potentiodynamic curves

Plots of the polarization curves were in potentiodynamic mode with a scanning speed of 1 mV/s, the polarization curves were recorded in the potential range of -0.8 to 0 V. The inhibition efficiency was calculated using the following formula [17]:

$$\%E = \frac{\dot{i_{corr}} - i_{corr}}{\dot{i_{corr}}} X100$$

i°<sub>corr</sub> : current density in the absence of inhibitor.
i<sub>corr</sub> : current density in the presence of inhibitor.

# 2.5. Electrochemical impedance spectroscopy

A Biologic SP150 potentiostat connected to the corrosion analysis program EC-LAB was used to plot the electrochemical impedance curves under static conditions. Three electrodes made up the electrochemical cell: An Ag/AgCl as the reference electrode, a platinum electrode as the auxiliary electrode, and carbon steel as a working electrode with a surface area of 1 cm<sup>2</sup>. Before each measurement, the working electrode was submerged in the test solution for 30 minutes to obtain the open circuit potential stability Eocp. At 298K, impedance measurements (EIS) were made in the 100 kHz to 10 mHz frequency band. The Nyquist mode is used to depict these curves [18].

The following relation [19] was used to calculate the inhibition efficiency of the inhibitor:

$$\%E = \frac{R_t - R_t^\circ}{R_t} X100$$

 $R_t^{\circ}$ : polarization resistance of blank solution HCl 1M  $R_t$ : polarization resistance of corrosion inhibitor

# 2.6. Quantum chemical calculations

#### 2.6.1. Computational details

# 2.6.1.1. DFT Details

The molecular geometries of all studied molecules were optimized in their ground states employing the hybrid method (DFT/B3LYP) [20,21] in conjonction with the 6-311+G(d,p) basis set. This optimisation process was conducted in an aqueous solution, utilising the polarized continuum solvation model (PCM) [22]. Frequencies were also computed at the same theoretical level to ensure that the structure is at a minimum with respect to the potential energy surface, devoid of any imaginary frequencies. These computations were executed using the Gaussian 16 software package [23]. The energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), denoted as EH and EL, respectively, were extracted by examining the output file with the Gaussview program [24]. The energy gap ( $\Delta E$ =EL-EH) of the molecule was then calculated as a measure of the structural stability. Additionally, chemical reactivity desciptors for MB were determined, including the vertical ionisation potential (VIP) and the vertical electron affinity (VEA). These descriptors were computed using the following equations:

$$VIP = E_0^+ - E_0$$
 and  $VEA = E_0^- - E_0$ 

where;

 $E_0$ : represents the total energies of the optimized structure

 $E_0^+$ : denotes the energies of cationic radical of the optimized stucture of neutral species  $E_0^-$ : corresponds to the energies of anionic radical of the optimized structure of the neutral species

The chemical reactivity was determined by several descriptors such as absolute electronegativity ( $\chi$ ), overall hardness ( $\eta$ ), softness ( $\sigma$ ), electrophilicity ( $\omega$ ), overall nucleophilicity (N) and electronic feedback effect (back donation), followed by electronic energy ( $\Delta$ Eb-d), calculated using the following equations [25-27]:

$$\chi = \frac{VIP + VEA}{2}, \eta = \frac{VIP - VEA}{2}, S = \frac{1}{\eta}, \omega = \frac{\chi^2}{2\eta}, \Delta E_{b-d} = -\frac{\eta}{4},$$
$$\Delta N_{110} = \frac{\Phi_{\rm Fe} - \chi_{\rm inh}}{2(\eta_{\rm Fe} + \eta_{\rm inh})} \text{ and } \Delta N_{max} = \frac{\chi}{\eta}$$

To propose a plausible adsorption mechanism and to identify The centres with the greatest reactivity to electrophilic and nucleophilic attack, Fukui indices (FIs) [28,29] were calculated by applying NBO [30] Performing calculations at a single point for neutral entities. (N), anionic (N+1), and cation (N-1) electronic systems at the optimized geometries of the investigated inhibitor at the same level of theory. The condensed Fukui indices for nucleophilic ( $f_k^+$ ), and electrophilic attacks ( $f_k^-$ ) and their dual Fukui descriptor ( $f_k^2$ ) were determined using the following equations [31,32]:

Nucleophilic attack:  $f_k^+ = q(N) - q(N + 1)$ Electrophilic attacks:  $f_k^- = q(N - 1) - q(N)$ , and Dual condensed Fukui function:  $f_k^2 = q(N + 1) - q(N - 1)$ ,

where q(N), q(N + 1) and q(N - 1) are the Hirshfeld charges or natural charges of the N, N+1 and N-1 systems, respectively. The Fukui functions and their summarized values [33,34] were visualized and computed using the Multiwfn program [35].

# 2.6.1.2. Monte Carlo (MC) and Molecular Dynamic (MD) simulations

Using the Adsorption Locator tool in Material Studio, we investigated potential interactions among the inhibitor molecules and Fe (110) surface [36,37]. The Monte Carlo (MC) method was employed to study surface interactions. The simulated cell had dimensions of 24.82×24.82  $\times 18.24$  Å<sup>3</sup>, incorporating a vacuum slab extending 35 a Å beyond the Fe (110) surface. MC simulations involved introducing inhibitor molecules and an aqueous solution containing corrosive species (H<sub>2</sub>O, chloride ions, and hydronium ions) into the cell [38,39]. Material Studio's Adsorption Locator module simulated the impacts of these corrosive species. The MC simulations focused on the outermost layer of the Fe (110) slab, which was expected to contain potential inhibitor molecule adsorption sites [40-42]. By systematically loading inhibitor molecules and corrosive species into the cell, various adsorption configurations were investigated [25-27]. Upon completion of the simulations, We identified the adsorption configuration at equilibrium with the minimum energy [40,43]. This analysis was crucial for identifying favorable adsorption sites and understanding the energy aspects of the adsorption process [36,41]. The combined use of the Adsorption Locator tool and the MC method in Material Studio facilitated a comprehensive exploration of the potential linkages between inhibitor molecules and Fe (110) surface atoms. Systematic examination of different adsorption configurations allowed us to Identify the adsorption configuration at equilibrium characterized by the lowest energy [40,44,45]. This information is vital for understanding preferred adsorption sites of the inhibitor molecules and optimizing their inhibitory performance. Accurate representation of the adsorption process was achieved by incorporating the precise dimensions of the simulated cell and various corrosive species. Plausible adsorption sites were targeted by focusing on the outermost layer of the Fe (110) slab, which is most relevant for inhibitor adsorption [1,5,46]. This approach provided valuable insights into the interaction

among the inhibitor and the metal surface, facilitating the development of effective corrosion inhibition strategies[41,47–49].

Next, we utilized the widely-known COMPASSII forcefield [50,51] and performed molecular dynamics (MD) simulations in Material Studio's Forcite module at 295 K. During the MD simulations, all Fe (110) atoms, except for the top two layers, were frozen. The simulation duration was 800 ps [2-4,6-8,51–53], and a time step of 1.0 fs was used. To gain insights into the adsorption behavior of the inhibitor molecule on the metal surface, we calculated the radial distribution function (RDF) based on the MD simulation trajectory [40,42,49].

#### **3. RESULTS AND DISCUSSION**

## **3.1. Electrochemical Study**

#### 3.1.1. Stability of Potential Curves

According to Figure 2, the corrosion potential rises as inhibitor concentrations rise and stabilizes at -430 mV after 300 seconds of immersion with  $10^{-2}$  M CBDZ. This finding demonstrates that CBDZ adsorbs readily to the surface of mild steel.



**Figure 2.** Stability of potential curves of the steel in 1 M HCl solution at various concentrations of CBDZ

This increase corresponds to the onset of the corrosion process and, consequently, the substrate degradation [54].

## 3.1.2. Electrochemical polaraization curves

With an increase in inhibitor concentration in the cathodic range, cathodic current density falls. In the anodic range, the current density decreases only in the range between -0.4 and -0.3

V (Ag/AgCl) in the neighborhood of  $E_{corr}$  (Figure 3). This demonstrates that carbendazim is primarily a cathodic mixed inhibitor [55] because the corrosion potential does not change significantly with inhibitor concentration.



**Figure 3.** Polarization curves for carbon steel in 1 M HCl in the absence and presence of different concentrations of CARBENDAZIME

The electrochemical parameters extracted from these curves, corrosion potential ( $E_{corr}$ ), cathodic ( $\beta c$ ) and anodic ( $\beta a$ ) Tafel slopes, corrosion current density ( $i_{corr}$ ) and inhibition efficiencies IE% are shown in Table 2.

**Table 2.** Electrochemical parameters derived from polarization curves of the E24/1 M HCl interface at different CBDZ concentrations

Concentration	E <sub>corr</sub>	I <sub>corr</sub>	$\beta_a$	β <sub>c</sub>	Е	
(M)	(mV/Ag/AgCl)	$(\mu A/cm^2)$	(mv/dec)	(mV/dec)	(%)	θ
HCl 1 M	-421.08	227.716	98.7	99.7	-	-
10 <sup>-4</sup>	-422.09	121.960	84.3	84.3	46.44	0.46
			0.0.1			
10 <sup>-3</sup>	-412.70	83.204	89.1	89.1	63.46	0.63
5×10 <sup>-3</sup>	-428.96	76.179	73.8	73.8	66.54	0.66
10-2	-430.79	40.29	85.9	87.3	82.30	0.82

The obtained results show that increasing of the inhibitor concentration causes a sharp decrease in the corrosion current density value, from 227.72 A/cm<sup>2</sup> without inhibitor to 49.29 A/cm<sup>2</sup> with  $10^{-2}$  M of CBDZ. The inhibition efficiency reaches 82.30% at  $10^{-2}$  M. These results

confirm the mixed behavior of inhibitor and clearly show that they slow both the rate of  $H^+$  reduction and the rate of steel degradation [56].

## 3.1.3. Electrochemical Impedance Spectroscopy

Figure 4 show the Nyquist diagrams of carbon steel in 1 M HCl in the absence and presence of CBDZ at various concentrations.



**Figure 4.** EIS diagrams of carbon steel in 1 M HCl in the absence and in the presence of different concentrations of CBDZ at 298 K

The impedance diagrams show a capacitive loop for all concentration of CBDZ, which is correlated with charge transfer phenomenon [57]. This loop grows with increasing concentration of CBDZ. This result can be attributed to the adsorption of the inhibitor molecules on the metal surface.

The modeling of these loops in Ec-Lab software reveals that a RC-type equivalent circuit controls the metal/solution interface. The depressed shape of the capacitive loops is characterized in terms of CPE in the equivalent electrical circuit (Figure 5) [57].



Figure 5. Electric equivalent circuit

Analysis of the Figure 4 leads to the following remarks;  $R_t$  values rise significantly when the inhibitor concentration increase, but the capacitance of the film decrease to a value of 533.9 F.cm<sup>-2</sup>. This reduction could be brought about by a rise in the double layer's thickness. This

suggests the formation of an inhibitor layer on metal surface. The inhibition efficiency of the inhibitor improves, and reach 84% at  $10^{-2}$  M of CBDZ (Table 3).

**Table 3.** Electrochemical parameters derived from electrochemical impedance diagrams of the

 E24/HCl 1 M interface at different CBDZ concentrations

Concentration	Re	Rt	Cd	E%	θ
	$(\Omega.cm^{-2})$	$(\Omega.cm^{-2})$	$(\mu F.cm^{-2})$		
HCl 1 M	1.573	49.87	698.4	-	-
10 <sup>-4</sup> M	1.571	111.2	687.5	55.35	0.55
10 <sup>-3</sup> M	1.667	123.5	662.5	59.61	0.59
5×10 <sup>-3</sup> M	1.596	245	542.3	79.64	0.79
10 <sup>-2</sup> M	1.673	316.2	533.9	84.22	0.84

## 3.2. Adsorption isotherm

In the current investigation, the Langmuir adsorption isotherm offers a better explanation of the adsorption behavior of the inhibitor in 1 M HCl medium. Its application presupposes that the solid surface has a specific number of adsorption sites and that each site has just one species of adsorbate. Since all adsorption sites have the same thermodynamic properties, molecules do not interact with one another. Adsorption energy is independent of surface covering rate since they are thermodynamically equal; as a result, it is constant across all locations. According to the following relationship [58], the value of the coverage rate, as function of inhibitor concentration follows the following formula.

$$\frac{C_{\rm inh}}{\theta} = C_{\rm inh} + \frac{1}{k}$$

where,

C<sub>inh</sub>: is the inhibitor concentration
K: is the adsorption constant
θ: is the surface coverage

Figure 6 shows the development of  $C_{inh}/\theta$  as a function of  $C_{inh}$ . This graph demonstrates a linear behavior with a slope almost equal to one and a y-intercept not equal to zero. This suggests that the CBDZ adsorption follows the Langmuir isotherm.

The value of  $K_{ads}$  the free energy  $\Delta^{\circ}G_{ads}$  were calculated by the following equation [59]:

$$\Delta G_{abc}^{0} = -2.303 RT \log(55, 5K_{abc})$$

with; **R:** 8,31.10<sup>-3</sup> kj k<sup>-1</sup>mol<sup>-1</sup> **T:** 298 k<sup>-1</sup> 0,000

0,002



The value 55.5 is the concentration of water in solution (mol/l).



0,004

0,006

 $C_{inh}(M)$ 

0,008

0,010

Table 4.	Thermodynamic	parameters	derived f	rom Lan	gmuir isot	therm p	olot

Milieu	Coefficient de corrélation linéaire	K (mol <sup>-1</sup> )	$\Delta G^{\circ}_{ads}$ (kJ/ mol)
CBDZ + HCl	0.99922	4252.29	-30.64

The negative value of  $\Delta G^{\circ}_{ads}$  in Table 4 indicates the spontaneity of the adsorption process. The value of  $\Delta G^{\circ}_{ads}$  obtained (-30.64KJ/mol) is confined between -40 and -20, which indicates that the free energy of adsorption  $\Delta G^{\circ}_{ads}$  is in favor of physicochemical adsorption [50].

## 3.3. The synergy effect with KI

The evaluation of the synergistic effect of the inhibitor with KI was carried out on the basis of impedance spectroscopy.

The sort of adsorption involved can be seen in the synergy parameter S calculation. The formula below was used to determine this parameter [60,61]:

$$S = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}}$$
$$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$$

where  $\Theta_1$ ,  $\Theta_2$  and  $\Theta_{1+2}$  are the surface coverage rates of KI, CBDZ and (CABDZ and KI) respectively.

The S parameter is used to determine the type of adsorption involved: if S < 1 is competitive adsorption and if S > 1 is cooperative adsorption.

The Figure 7 show the Nyquist diagrams of mild steel in 1M HCl, in the absence and presence of CBDZ alone and in combination with KI, at a concentration of  $10^{-2}$  M.



**Figure 7.** Nyquist diagrams of carbon steel in 1 M HCl in the absence and in the presence of different inhibitors alone and combined

Figure 7 shows that the electrochemical impedance diagrams present a capacitive loop, whose size increases when the CBDZ inhibitor is combined with KI.

Concentration	Re $(\Omega)$	$\operatorname{Rt}(\Omega)$	Cd(µF.cm <sup>-2</sup> )	E%	θ	S
HCl 1 M	1.573	49.87	698.4	-	-	-
10 <sup>-2</sup> CADZ	1.67	321.9	494.9	84.50	0.8450	-
10 <sup>-2</sup> KI	1.323	330.8	464	84.92	0.8492	-
$10^{-2}$ CAB + $10^{-2}$ KI	1.812	420.8	453	88.15	0.8815	0.19

 Table 5. Electrochemical parameters derived from Figure 7

According to the findings in Table 5, when CBDZ and KI are combined, inhibitory efficacy rises from 84 to 88%. The synergy is competitive because the parameter's value is less than 1.

## **3.4.** Computational results

# 3.4.1. DFT detail

The DFT study was carried out to confirm the experimental results and to study the possible effect of tautomerisation on the inhibition efficiency of the inhibitor under investigation. To this end, three tautomers and their protonated forms were considered see Figure 8.



**Figure 8.** Schematic representation of the possible neutral and protonated tautomeric forms of the inhibitor under examination

Protonation calculation (pKa), pH=0-14, using Marvin sketch [62] shows that the protonation interaction takes place at imine nitrogen atom of the imidazole ring (nitrogen in blue color in Figure 8) with a percentage of 80-100 % in the pH range of 0.0 - 3.70. Therefore, the protonated form that is shown in Figure 8 will be discussed. For the neutral species, it is found that the **CBDZ** form is found to be 5.2 and 1.9 kcal/mol more stable than **CBDZ-A and CBDZ-B** forms. Similarly, the protonated form **CBDZH**<sup>+</sup> is found to be 6.1 and 1.9 kcal/mol more stable than the **CBDZ-AH**<sup>+</sup> and **CBDZ-BH**<sup>+</sup> forms. Based on these preliminary calculations, our study will focus on the analysis of the results obtained for the **CBDZ** form.

# 3.4.2. Frontier molecular orbitals and electrostatic potential maps

Molecular orbitals (HOMO) and (LUMO) are called frontier molecular orbitals (FMO). Qualitative information can be extracted from these FMOs, as they allow us to determine how the molecule interacts with the metal surface (electron donation or acceptance). In particular, the HOMO is the molecular orbital that can donate electrons, since it is the outermost (most energetic) orbital containing electrons, while the LUMO is the orbital that can accept electrons, since it is the innermost (least energetic) orbital that has a virtual MO to accept electrons [29,30,63,64].

The optimized molecular structures (MS) and electron distribution of the HOMO and LUMO surfaces of the CBDZ and CBDZH<sup>+</sup> forms are shown in Figure 8. The blue and yellow colours correspond to the positive and negative phases respectively. The chemical activity of the molecule can be determined by the HOMO (donor) and LUMO (acceptor) energies and the energy gap ( $\Delta E$ ). The results obtained for the overall quantum chemical reactivity of the species studied are summarised in Table 6.

The distribution of electrons on the HOMO and LUMO surfaces depends on the structure. Figure 9 shows that the electron density of the HOMO surface of the CBDZ molecule is mainly located on the heteroatoms and certain carbon atoms, which have a delocalised behaviour showing that these atoms are the most favourable adsorption sites. LUMO is predominantly concentrated on the carbonyl carbon atom and some carbon atoms of the benzoimidazol unit, which exhibit more  $\pi$  characteristics than HOMO, although the surface reflects predominantly  $\pi$  orbitals, showing that these atoms are the preferred electron acceptance sites. Similar observations were also made for the CBDZH<sup>+</sup> form.

In general, molecules with a higher EHOMO have a greater capacity to donate an electron, while those with a higher LUMO must have a greater capacity to gain an electron. The lowest energy gap favours a strong interaction between the HOMO and the LUMO and, consequently, the most reactive species [65-68]. Table 6 and Figure 9 show that the EHOMO of the neutral forms of the tautomers CBDZ, CBDZ-A and CBDZ-B is -6.239, -6.306 and -6.230 eV respectively. The ELUMO values for the same species are -0.951, -1.008 and -0.958 eV respectively. The low ELUMO values indicate that the electron affinities of these forms are low, reflecting their high capacity to receive electrons from the occupied 3d orbitals of the metal surface.

The  $E_{HOMO}$  values as well as the  $E_{LUMO}$  values of the different tautomers are very close to each other, signifying that their chemical reactivities are almost similar. Therefore, the global and local chemical reactivity of the most stable tautomer (**CBDZ**) will be only considered only during this study.



**Figure 9.** Optimized molecular structure (MS) and the frontier molecular orbitals of the most stable CBDZ isomer in (*Left*) neutral state and (*Right*) protonated state in aqueous solution using PCM model of solvation at B3LYP/6-311+G(d,p) level of theory

## 3.4.3. Molecular electrostatic potential analysis and total densities of HOMO and LUMO

Figure 10 shows the molecular electrostatic potential maps and the total densities of the HOMO and LUMO surfaces of the neutral state of the CBDZ molecule and its protonated form.



**Figure 10.** Molecular electrostatic potential (MEP) map and total densities maps of TD-HOMO and TD-LUMO of the most stable isomer of the CBDZ molecule in its forms (left: neutral and right: protonated) using PCM model of solvation at B3LYP/6-311+G(d,p) level of theory

The colours of the maps correspond to the highest positive regions (blue), the neutral regions (green) and the highest negative regions (red). These positive and negative regions are, respectively, the preferred sites for nucleophilic and electrophilic attacks [17,37,53,69-76]. This type of map can provide very useful qualitative information for studying molecular structure and physicochemical characteristics. The minimum ESP of the CBDZ molecule can be visualised at the imine nitrogen (N4) and carbonyl oxygen (O2) atoms, which are the most reactive regions for electrophilic attack and can interact with the Fe surface by electron donation. In contrast, the maximum ESP of the CBDZ molecule is located on the carbonyl carbon atom (C14) and the carbon atom (C8) of the imidazole ring, which is surrounded by N3 and N4, which are the most reactive sites for nucleophilic attack and can accept electrons from the metal surface. On the other hand, the ESP map of the proton attached to the N4 atom.

In the protonated form, almost all the atoms favour nucleophilic attack. The visualisation of the total density on the HOMO and LUMO surfaces (TD-HOMO and TD-LUMO) also confirms these results. The blue shaded regions are responsible for the acceptance of electrons from the occupied orbitals of the metal surface. On the other hand, the imino nitrogen atom and the carbobonyl oxygen atoms, as well as the delocalised electrons  $\pi$  from the phenyl group, are responsible for donating electrons to the 3d orbitals of the metal surface.

The chemical reactivity of atoms, molecules or compounds has been studied using an important global descriptor, the energy gap. Reactive compounds are those with a small HOMO-LUMO energy gap and vice versa. In addition, the charge transfer interaction taking place within chemical compounds can be justified by the decrease in HOMO-LUMO energy.

The low values of the energy gaps between the two forms of the CBDZ inhibitor (neutral: 5.289 eV; protonated: 5.395 eV) indicate high chemical reactivity and significant interaction between the inhibitor's frontier orbitals. In addition, the small difference between the gap energies of the two forms (0.107 eV) in favour of the neutral form shows that it is slightly more reactive than the protonated form the HOMO - LUMO metal-inhibitor energy gaps predict the electron flow from the inhibitor to metal or vice versa, which can be determined by estimating the values of  $\Delta E_1$  and  $\Delta E_2$  energy gaps. The  $\Delta E_1$  corresponds to electron flow from the HOMO of the metal (Lewis's base) to the LUMO of the inhibitor (Lewis acid), while  $\Delta E_2$  represents the electron flow from the HOMO of the inhibitor (Lewis base) to the LUMO of the metal (Lewis base) to the LUMO of the inhibitor (Lewis base) to the metal (Lewis acid), and are given by:

$$\Delta E_{1} = E_{LUMO}(inhibitr) - E_{HOMO}(metal)$$
$$\Delta E_{2} = E_{LUMO}(metal) - E_{HOMO}(inhibitor)$$

In the above equations,  $E_{HOMO} = -7.902$  eV and  $E_{LUMO} = -0.151$  eV for Fe metal were taken [76] and the results obtained are also listed in Table 6.

	Neutral			Protonated			
	CBDZ	CBDZ-A	CBDZ-B	CBDZH <sup>+</sup>	CBDZ-AH <sup>+</sup>	CBDZ-BH <sup>+</sup>	
E(N) (eV)	-18050.088	8-18049.864	-18050.005	-18062.158	-18061.892	-18062.075	
E(N+1) (eV)	-18051.209	9-18051.040	-18051.131	-18064.092	-18063.906	-18064.017	
E(N-1) (eV)	-18043.942	2-18043.651	-18043.868	-18055.018	-18054.693	-18054.943	
E <sub>HOMO</sub> (eV)	-6.239	-6.306	-6.230	-7.205	-7.264	-7.197	
E <sub>LUMO</sub> (eV)	-0.951	-1.008	-0.958	-1.810	-1.888	-1.817	
ΔE (eV)	5.289	5.298	5.272	5.395	5.376	5.379	
$\Delta E_1(eV)$	6.952	6.894	6.944	6.093	6.014	6.085	
$\Delta E_2(eV)$	6.088	6.155	6.079	7.054	7.113	7.046	
IPV (eV)	6.146	6.214	6.137	7.140	7.199	7.132	
EAV (eV)	1.120	1.176	1.126	1.934	2.014	1.942	
χ (eV)	3.633	3.695	3.632	4.537	4.606	4.537	
η (eV)	2.513	2.519	2.506	2.603	2.593	2.595	
s (eV <sup>-1</sup> )	0.398	0.397	0.399	0.384	0.386	0.385	
ω (eV)	2.627	2.710	2.632	3.954	4.092	3.966	
$\Delta N_{max}$	1.446	1.467	1.773	1.743	1.820	1.748	
$\Delta N_{110}$	0.236	0.223	0.237	0.054	0.041	0.055	
$\Delta E_{b-d}(eV)$	-0.628	-0.630	-0.626	-0.651	-0.648	-0.649	
μ (Debye)	4.5	3.6	5.8	4.9	7.9	1.5	

 Table 6. Global quantum chemical reactivity descriptors

Table 6 shows that the flow of electrons from the inhibitor to the metal or from the metal to the inhibitor differs according to the state of the inhibitor. As a result, the value  $\Delta E2$  (6.088 eV) <  $\Delta E1$  (6.952 eV) means that electron flow is from the HOMO of the inhibitor to the LUMO of the Fe metal and is energetically favoured. In this case, the inhibitor molecule acts as a Lewis base, while the Fe metal acts as a Lewis acid. The situation is reversed in the case of the protonated for, which shows that  $\Delta E2$  (7.054 eV) >  $\Delta E1$  (6.093 eV), indicating that electron flow takes place from the HOMO of Fe to the LUMO of the inhibitor molecule and that it is energetically more favoured. In this case, the inhibitor acts as a Lewis acid and the Fe as a Lewis base. This finding is acceptable in spite the interaction between the inhibitor molecule and the acid proton in the aqueous solution.

From the values of vertical ionisation potential and vertical electron affinity, several global descriptors such as global electronegativity ( $\chi$ ), global hardness ( $\eta$ ), global softness (S), global electrophilicity ( $\omega$ ), electron transfer fraction ( $\Delta$ N110), maximum electron transfer ( $\Delta$ Nmax) and donation-backdonation exchange energy ( $\Delta$ Eb-d) were calculated and compared. The results are presented in Table 6. The electron transfer fraction ( $\Delta$ N110) values for both forms are less than 3.6, indicating that CBDZ is a good corrosion inhibitor [78,79]. The negative value of  $\Delta$ Eb-d means that charge transfer to a molecule followed by retro-donation of the molecule is energetically favourable [80]. Finally, the compound studied in its two forms has a higher dipole moment (neutral: 4.5; protonated 4.9 Debye) than that of water (1.8 Debye), which reflects its ability to expel water from the surface and may act as a good corrosion inhibitor.

## 3.4.4. Local reactivity descriptors

#### 3.4.4.1. Natural Atomic charges

In order to calculate the natural atomic charges of the two forms of the inhibitor studied (neutral and protonated), the calculation of the natural population analysis was carried out within the framework of the natural bond orbital (NBO) analysis as implemented in Gaussian 09 [51]. The column plot of the natural atomic charges of CBDZ and CBDZH<sup>+</sup>, obtained using natural population analysis [62], is shown in Figure 11. The numerical results are listed in Table 7.

First inspection of the results shows that very similar net charges are obtained for both forms. The natural charges of the protonated form CBDZH<sup>+</sup> show more positive (less negative) values than those of the neutral form CBDZ.

The charges of al of hydrogen atoms are almost similar and ranges from 0.194 - 0.226 e (CBDZ) and 0.200 - 0.241 e (CBDZH<sup>+</sup>), with the exception of the hydrogen atoms attached to N3 and N5, respectively, which are 0.456 and 0.443 e in CBDZ, and 0.476 and 0.458 e in CBDZH<sup>+</sup>.

	Mulliken		NBO	
	CBDZ	CBDZH <sup>+</sup>	CBDZ	CBDZH <sup>+</sup>
01	-0.1043	-0.0923	-0.5377	-0.5171
O2	-0.3796	-0.3284	-0.6667	-0.6347
N3	-0.2923	-0.2758	-0.5509	-0.5005
N4	-0.2862	-0.2467	-0.5585	-0.4962
N5	-0.5662	-0.5464	-0.6088	-0.5966
C6	0.7993	0.6597	0.1149	0.1312
C7	0.6985	0.8462	0.1001	0.1327
C8	0.4773	0.7396	0.5661	0.6506
C9	-0.9712	-0.8798	-0.2356	-0.2085
C10	-0.7263	-0.8617	-0.2211	-0.2105
C11	-0.1363	-0.1004	-0.2237	-0.1958
C12	-0.3088	-0.2448	-0.2301	-0.1948
C13	0.1487	0.1471	0.9040	0.9178
C14	-0.1199	-0.1233	-0.2189	-0.2184
H15	0.3639	0.3931	0.4550	0.4760
H16	0.1291	0.1468	0.2263	0.2408
H17	0.1259	0.1486	0.2213	0.2409
H18	0.1401	0.1566	0.2159	0.2274
H19	0.1388	0.1577	0.2150	0.2274
H20	0.3492	0.3691	0.4425	0.4583
H21	0.1717	0.1803	0.1943	0.2001
H22	0.1769	0.1846	0.2022	0.2079
H23	0.1717	0.1803	0.1943	0.2001
H24		0.3898		0.4620

 Table 7. Natural atomic charges (NBO charges) and Mulliken charges in (e.) elementary charge

The high positive charges of these hydrogens are attributed to the possible formation of the hydrogen bonds with oxygen atoms (O2 and O1). All heteroatoms N, and O atoms are negatively charged and they are ranged from highest negative to lowest negative values as: O2 > N5 > N4 > N3 > O. Furthermore, some of carbon atoms are negatively charged, which are C9, C12, C11, C10 and C14, while other are positively charged, which are C13 > C8 > C6 > C7.

These results indicate that heteroatomic O and N atoms and some C atoms have the ability to donate electrons to vacant 3d orbitals during the adsorption process, while carbon atoms

C13, C8, C6 and C7 tend to receive electrons from occupied 3d orbitals (retro-donation). These results confirm the qualitative results shown by the visualisation of the HOMO and LUMO boundary orbital surfaces, as well as the ESP maps.



**Figure 11.** Graphical representation of the Natural charge of the CBDZ molecule and its protonated form CBDZH<sup>+</sup>

#### 3.4.5. Fukui Functions

Figure 12 plots the condensed Fukui indices for the nucleophilic  $(f_r^+)$  and electrophilic  $(f_r^-)$  attacks and their dual descriptors  $(f_r^2)$ . Natural charges for N, N+1 and N-1 electron systems are summarized in Table 8.

It is worthy to mention that the results are for the C, O and N atoms only. Graphical representation of the condensed Fukui functions and condensed dual descriptors of the CBDZ molecule and its protonated form CBDZH<sup>+</sup>. In addition, the 3D-isosurfaces of the Fukui functions of the nucleophilic and electrophilic attacks and the dual Fukui functions are shown in Figure 12.

As can be shown in Table 9 and Figure 12, the preferred sites of the CBDZ molecule for nucleophilic attacks  $(f_r^+)$  are C11> N4 > C6 > C7, while those favourable for electrophilic attacks  $(f_r^-)$  are C10 > C9 > C8 > C11. For more accurate results, the values of the double condensed descriptor  $(f_r^2)$  indicate that the active sites that are favored by nucleophilic attacks  $(f_r^2 > 0)$  are, respectively, C6 > C11 > N5 > N4. Whereas, the sites that are the active sites that are favored by electrophilic attacks  $(f_r^2 < 0)$  are C9 > C10 > C13 > N3. For the protonated **CBDZH**<sup>+</sup> form, the results obtained show that the active sites that are favorable for a nucleophilic attack  $(f_r^+)$  are C11> C12 > C7 > C6.



**Figure 12.** Left The condensed Fukui functions and the condensed dual functions for the CBDZ (blue columns) and CBDZH<sup>+</sup> (red columns). Right: the 3D-isosurfaces of the Fukui functions and the Fukui dual functions For 3D- isosurfaces (sovalues = 0.005 au.)

**Table 8.** Natural charges for N, N+1 and N-1electronic systems, condensed Fukui functions (*elctrophilic atatcks*:  $f_r^-$  and nucleophilic attacks:  $f_r^-$ ) and condensed dual descriptors ( $f_r^2$ ) for the neutral CBDZ (above) and protonated (CBDZH<sup>+</sup>). Units used below are "e" (elementary charge)

	q(N)	q(N+1)	q(N-1)	q(N)	q(N+1)	q(N-1)
	CBDZ			$CBDZH^+$		
01	-0.5376	-0.5617	-0.5146	-0.5171	-0.5497	-0.4947
O2	-0.6667	-0.7273	-0.6208	-0.6347	-0.7108	-0.5985
N3	-0.5509	-0.5807	-0.5409	-0.5005	-0.5497	-0.4831
N4	-0.5585	-0.6103	-0.4429	-0.4962	-0.5459	-0.4753
N5	-0.6088	-0.6050	-0.5378	-0.5966	-0.6020	-0.5178
C6	0.1149	0.1146	0.2126	0.1312	0.1314	0.2662
C7	0.1001	0.0677	0.1946	0.1327	0.1331	0.2688
C8	0.5661	0.4700	0.6444	0.6506	0.4825	0.7049
C9	-0.2356	-0.4129	-0.2254	-0.2085	-0.3359	-0.2116
C10	-0.2211	-0.4069	-0.1584	-0.2105	-0.3355	-0.2127
C11	-0.2237	-0.3127	-0.0421	-0.1958	-0.2466	-0.0374
C12	-0.2301	-0.2618	-0.1843	-0.1948	-0.2495	-0.0417
C13	0.9040	0.8301	0.9070	0.9178	0.8375	0.9153
C14	-0.2189	-0.2165	-0.2199	-0.2184	-0.2160	-0.2191

The active sites that are favorable for electrophilic attacks  $(f_r^-)$  are C8 > C9 > C10 > C13. In an accurate way, the values of the double condensed descriptor  $(f_r^2)$  show that the active sites that are favored by nucleophilic attacks  $(f_r^2 > 0)$  are C7 > C6 > C11 > C12. Whereas, the sites that are the active sites that are favored by electrophilic attacks  $(f_r^2 < 0)$  are, respectively, C9 > C10 > C8 > C13.

	$f_r^-$	$f_r^+$	$f_r^2$	$f_r$	$f_r^+$	$f_r^2$
	CBDZ			<b>CBDZH</b> <sup>+</sup>		
01	0.0230	0.0240	-0.0010	0.0224	0.0326	-0.0102
O2	0.0459	0.0606	-0.0147	0.0362	0.0760	-0.0398
N3	0.0100	0.0298	-0.0199	0.0174	0.0492	-0.0318
N4	0.1156	0.0518	0.0638	0.0209	0.0497	-0.0288
N5	0.0711	-0.0038	0.0748	0.0789	0.0054	0.0735
C6	0.0977	0.0003	0.0975	0.1350	-0.0002	0.1352
C7	0.0945	0.0324	0.0621	0.1361	-0.0005	0.1366
C8	0.0783	0.0961	-0.0178	0.0543	0.1681	-0.1138
C9	0.0102	0.1773	-0.1671	-0.0031	0.1273	-0.1304
C10	0.0627	0.1858	-0.1232	-0.0021	0.1249	-0.1271
C11	0.1816	0.0890	0.0926	0.1584	0.0508	0.1076
C12	0.0458	0.0317	0.0140	0.1532	0.0547	0.0985
C13	0.0029	0.0740	-0.0710	-0.0025	0.0803	-0.0828
C14	-0.0010	-0.0024	0.0014	-0.0006	-0.0024	0.0018

**Table 9.** The condensed Fukui functions and condensed dual descriptors of the CBDZ molecule and its protonated form CBDZH<sup>+</sup>. Units used below are "e" (elementary charge)

These condensed descriptors explain the mechanism by which the studied compound can interact with the metal surface through electron donation and acceptation.

## 3.4.6. Monte Carlo and dynamic molecular simulations

The calculation of the adsorption energy ( $E_{ads}$ ) of a molecule on the Fe(110) surface involves the utilization of the following equation [24,31,32,37]:

$$E_{adsorption} = E_{Fe(110)||inhibitor|} - (Fe_{(110)} + E_{inhibitor})$$

where  $E_{Fe(110)||inhibitor|}$  is the total energy of the simulated system,  $E_{Fe}$ , and  $E_{inhibitor|}$  is the total energy of the Fe(110) surface and the corresponding free inhibitor molecules.

Following successful Monte Carlo (MC) calculations, a detailed study of the adsorption geometry of the CBDZ inhibitor was carried out to validate the experimental results. By comparing the steady-state energy values with the initial energy values, the achievement of equilibrium in the Monte Carlo simulation was assessed. The minimum energy of the system was reached about halfway through the simulation, which means that the configuration is stable. Figure 13 shows the actual arrangement of the adsorbed inhibitor on the simulated Fe(110) plane, which accurately represents the features used to simulate the corrosion environment. To inhibit the Fe(110) surface, molecular dynamics (MD) simulations were performed, with the inhibitor exhibiting an almost parallel orientation as it decorates the surface.



Figure 13. Lowest energy geometries derived the MC and MD calculations



**Figure 14.** The adsorption energies of the two forms of the molecule CBDZ and CBDZH<sup>+</sup> are as follows

Figure 13 shows the adsorption pattern observed on the Fe(110) plane, which can be attributed to the interaction between the backbone of the inhibitor molecule and the atoms of the metal surface, mainly influenced by the presence of heteroatoms. This adsorptive behaviour results from the molecule's ability to expose its heteroatomic atoms and electron-rich rings to the surface, thus contributing to its adsorptive characteristics [46,81,82].

The adsorption energies ( $E_{ads}$ ) derived from Monte Carlo (MC) calculations for the inhibitors used in the simulated corrosion environment are shown in Figure 14. The large  $E_{ads}$  values show strong adsorption of the inhibitor onto the metal surface. This strong interaction leads to the formation of a protective layer on the metal surface, providing a defence against further corrosion [37,80,83-86]. In terms of adsorption dynamics, molecular dynamics is widely recognised as a more accurate representation [50,51,87,88]. In Figure 14, it is evident that after several hundred picoseconds of NVT simulation, the inhibitors adopt a more planar conformation, with the molecular ring firmly adsorbed onto the Fe surface. the radial distribution function (RDF) analysis technique is used to study the adsorption of corrosion inhibitors onto metal surfaces, this technique being based on the MD trajectory obtained during the corrosion simulation technique [48,84,85].



**Figure 15.** The radial distribution function of the heteroatoms (O and N) for the two forms of the inhibitor CBDZ and CBDZH<sup>+</sup> on the Fe (110) surface obtained from the MD trajectory analysis

The RDF plot shown in Figure 15 allows the adsorption process to be predicted by observing peaks at specific distances from the metal surface [38,78]. Peaks appearing between 1 and 3.5 Å from the surface correspond to chemisorption processes, while peaks beyond 3.5 Å indicate physical adsorption processes [46,89]. In the case of the heteroatoms on the Fe surface (O and N), RDF peaks were observed at distances of less than 3.5 Å (Figure 15). This

reflects the strong interaction between the inhibitor and the metal surface, as shown by the relatively high negative energy values and the presence of RDF peaks [34,43,90].

## **4. CONCLUSION**

The study carried out in the context of this work focused on used the Carbendazim as organic inhibitor of carbon steel in 1M HCl 1M. To carry out this study, we used elctrochemical technics to study the concentration effect and the synergy effect with potassium iodide KI. findings of this study can be outlined as follows:

- The potentiodynamic curves schows that the addition of inhibitor studied resulted in reduced current densities in both the cathodic and anodic branches, accompanied by a slight alteration in the corrosion potential. The CBDZ is qualified as mixed type inhibitor. The inhibition efficiency increases with increasing CBDZ concentration, and reach 82,3%.

- The Nyquist impedance diagrams has shown a single capacitive loop. The charge transfer resistance value increase with increasing Carbendazim concentration, while the value of double-layer capacitances decreases. These results justify the action of the inhibitor used, which takes place via the formation of a thick protective layer on the metal surface. This film acts as a barrier, isolating the metal from the corrosive environment.

- Measurements of the synergy effect were studied by electrochemical impedance technics. This study showed that inhibitory efficacy increases when CBDZ is combined with KI. It rises from 84.2% for CBDZ alone to 88% for CBDZ combined with KI at 10-2M for each compound.

- The adsorption of CBDZ on the steel surface follows the Langmuir isotherm. The free energy value indicates that CBDZ acts through physicochemical adsorption.

- DFT study showed that the neutral and protonated forms of the CBDZ molecule may act as a good inhibitor against the corrosion of the Fe-metal. The HOMO-LUMO energy gap within the CBDZ itself or between the CBDZ and Fe metal illustrated the efficacy of the CBDZ to act as inhibitor. The condensed Fukui descriptors and the condensed dual descriptors indicated that the benzoimidazole ring is the responsible moiety to donate and/or accept the electron during the adsorption process at the surface of the metal.

- This study employed density functional theory (DFT) simulations and molecular dynamics (MD) simulations to investigate the adsorptive behavior of inhibitors on the Fe(110) surface. Through Monte Carlo and Molecular Dynamics simulations, the stable adsorption geometry of the inhibitor on the Fe(110) surface was confirmed, validating the experimental findings. The obtained adsorption energies indicated strong adsorption and the formation of a protective layer, which effectively defends against corrosion. This study significantly contributes to our understanding of corrosion inhibition phenomena by exploring the adsorptive behavior of inhibitors. The findings presented in this research provide valuable

insights and serve as a foundation for further exploration in the field of corrosion inhibition studies.

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## **Declarations of interest**

The authors declare no conflict of interest in this reported work.

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