

**INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH
TECHNOLOGY****EXPERIMENTAL AND COMPUTATIONAL STUDY OF SOME IMIDAZOLE
DERIVATIVES AS CORROSION INHIBITORS FOR COPPER IN SULFURIC ACID
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ABSTRACT

Corrosion behavior of copper in 1.0 M Sulfuric acid containing either Imidazole (IM), 2-Methylimidazole (MIM) or Benzimidazole (BIM) was investigated experimentally via weight loss measurements and UV-Spectroscopy. The density functional theory (DFT) at the B3LYP/6-31G+ (2d, p) basis set level in gas phase is also applied here for theoretical study. Some quantum chemical parameters and the Mulliken charge densities on the optimized structures for imidazole compounds were determined. All theoretical results and experimental inhibition efficiencies of inhibitors were subjected to correlation analyses. Results obtained reveal that BIM is the best inhibitor and the inhibition efficiency ($E_w\%$) follows the sequence: BIM > MIM > IM. The adsorption behavior of BIM followed Langmuir's isotherm. Cu(I)-BIM complex formation was confirmed by UV spectroscopy.

KEYWORDS: Copper. imidazole derivatives. Corrosion. Inhibition. Sulfuric acid. Quantum Chemicals calculations. DFT studies.

INTRODUCTION

Copper has an excellent thermal conductivity, good corrosion resistance and mechanical workability for these reasons copper and its alloys are widely used in heating and cooling systems. Unless, during industrial equipment are cleaned by acid pickling, mainly chloride and sulfuric acids, the acid comes into contact with copper metal causing its dissolution. Corrosions inhibitors are usually added to prevent or mitigate the corrosion rate of metallic substrate in acidic environments [1-4]. The remarkable inhibitory effect is reinforced by the presence in organic compound of heteroatom such as sulphur, nitrogen, oxygen and double or triple bonds and also aromatic rings which facilitates its adsorption on the metal surface [4-7].

In the literature, the organic inhibitors such as triazoliderivatives[8,9], 1-Phenyl-5-Mercapto-tetrazole[10], 4-amino-4H-1,2,4-triazole-3thiol, 4-amino-5-methyl-4H-1,2,4-triazole-3thiol, 4-amino-5-ethyl-4H-1,2,4-triazole-3thiol[3], ortho-substituted anilines [11], bis-(1,10-benzotriazolyl)- α,ω -diamide and Schiff bases have been reported as corrosion inhibitors for copper in pickling acids. Likewise[12, 13], Imidazole derivatives have been pointed out as effective inhibitors for copper corrosion in various media by several investigators [14-19].

The effect of the molecular structure on the chemical reactivity has been object of great interest in several disciplines of chemistry. In this respect, quantum chemical calculations have been widely used to investigate the molecule in its electronic structure level and to interpret the experimental results. The inhibition property of a compound has been often correlated with molecular properties like its functional groups, steric effects, and electronic density of donor atoms and orbital character of donating electrons [6,20]. Different quantum molecular properties may be described better by different computational methods, depending on the sophistication of the computational approaches. In view of this, three different computational methods, viz., Density Functional Theory (DFT), Hartree Fock (HF) and second order Møller-Plesset perturbation theory method (MP2) were selected for the study of the compounds used as corrosion inhibitors. We will use only the method DFT B3LYP/6-31G+ (2d,p)

method because this method takes into account a part of correlation and it has been reported to provide fairly good results for the description of various molecular properties such as the energy of the Highest Occupied Molecular Orbital (HOMO), the energy of the Lowest Unoccupied Molecular orbital (LUMO) [21, 22].

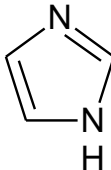
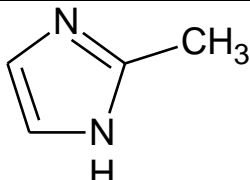
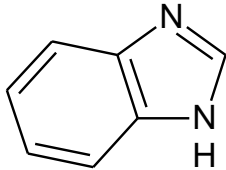
The present work reports the inhibition of copper corrosion in aerated 1.0 M H₂SO₄ solution by imidazole (IM), 2-methyl imidazole (MIM) and benzimidazole (BIM) (Table 1). Weight loss measurements, quantum chemical calculations and UV spectroscopy were used.

MATERIALS AND METHODS

2.1. Materials

For the investigation, the commercial pure copper (Cu 99.9%) was used. The aggressive solution of 1.0 M sulfuric acid was prepared by dilution of concentrated pure acid of analytical grade 98% H₂SO₄ (Aldrich) with bidistilled water. Imidazolic compounds tested as inhibitors are Aldrich commercial products. The molecular structures of imidazolic derivatives studied are shown in **Table 1**.

Table 1. Chemical and molecular structures of tested Imidazole compounds.

Inhibitor	Name	Structure	Mol. Wt (g mol ⁻¹)
IM	Imidazole		68.08
MIM	2-Methyle imidazole		82.11
BIM	Benzimidazole		118.14

2.2. Weight loss measurements

Gravimetric methods were conducted on copper test samples of a total surface of 12 cm². All experiments were carried out under total immersion in 75 ml of test solutions. Mass loss was recorded by an analytical balance. Prior to all measurements, copper samples were polished with different emery paper to 1200 grade and washed thoroughly with bidistilled water and dried with acetone.

2.3. Quantum chemical calculations

In this study, all theoretical computations were performed using the Gaussian 09 software [23]. The geometry optimizations were conducted by DFT using Becke's three parameter exchange functional [24], the Lee–Yang–Parr correlation functional (B3LYP) with the basis set 6-31G+ (2d,p) were selected for the study of the compounds used as corrosion inhibitors [25].

Some quantum chemical parameters, which influence the electronic interaction between surface atoms and inhibitor, are the energy of highest occupied molecular orbital (EHOMO), the energy of lowest unoccupied molecular orbital (ELUMO) and the energy gap (EHOMO- ELUMO) (ΔE). The energies of the HOMO and the LUMO orbitals of the

inhibitor molecule are related to the ionization potential, I, and the electron affinity, A, respectively, by the following two equations [26]:

$$I = -E_{\text{HOMO}} \quad (1)$$

$$A = -E_{\text{LUMO}} \quad (2)$$

Chemical hardness (η) measure the resistance of an inhibitor molecule to a charge transfer [27], is given in the following equation:

$$\eta = \frac{I - A}{2} \quad (3)$$

The softness (σ), is the inverse of the hardness ,describes the capacity of a molecule or group of molecules to receive electrons and is estimated by using the equation [27]:

$$\sigma = \frac{1}{\eta} \quad (4)$$

TNC is the summation of the total negative charges on the heteroatoms for each inhibitor molecule [28].

The number of electrons transferred ΔN in a chemical reaction is given by the equation [29];

$$\Delta N = \frac{\chi_{\text{Cu}} - \chi_{\text{inh}}}{2(\eta_{\text{Cu}} - \eta_{\text{inh}})} \quad (5)$$

Where χ_{Cu} and χ_{inh} are the absolute electronegativity of copper and inhibitor molecule, respectively; η_{Cu} and η_{inh} are the absolute hardness of copper and the inhibitor molecule, respectively. The theoretical values of $\chi_{\text{Cu}} = 4.48$ eV/mol and $\eta_{\text{Cu}} = 0$ eV/mol were used for the computation of the number of transferred electrons [29].

2.4. UV-spectroscopy

UV spectra were performed with a UV-visible spectrophotometer type JENWAY using chemstation software programme for aqueous solutions.

RESULTS AND DISCUSSION

The results and discussion may be combined into a common section or obtainable separately. They may also be broken into subsets with short, revealing captions.

3.1 Weight loss studies

Weight Loss Measurement, corrosion rates and inhibition efficiency of copper are determined in 1.0 M sulfuric acid solution with and without imidazole compounds at 10^{-3} M in various immersion times (4h, 24h, 48h, 72h and 168h) at 298K.

The inhibition efficiency IE(%) of three tested imidazole derivatives were determined by using equation (6):

$$E_{\text{W}}(\%) = \frac{W_{\text{corr}} - W'_{\text{corr}}}{W_{\text{corr}}} \times 100 \quad (6)$$

Where W_{corr} and W'_{corr} are the uninhibited and inhibited corrosion rate, respectively, determined by weight loss measurement.

The percentage inhibition efficiency of the imidazole derivatives at 10^{-3} M after different immersion times are summarized in **Table 2**. Graphically, the evolutions of corrosion rates with the immersion time are showed in **Figure 1**.

Table 2. Effect of addition of imidazole organic compounds at 10^{-3} M on the corrosion of copper in 1.0 M H_2SO_4 after different immersion times at 298K.

Solutions	t (h)	W_{corr} ($\mu g\ cm^{-2}h^{-1}$)	E_w (%)
Blank	4	40.2	-
	24	28.4	-
	48	26.4	-
	72	27.2	-
	168	29.0	-
IM	4	27.8	31
	24	17.7	38
	48	16.0	37
	72	19.0	30
	168	16.7	31
MIM	4	24.5	46
	24	13.8	51
	48	16.4	38
	72	15.2	44
	168	10.1	42
BIM	4	19.0	53
	24	10.1	64
	48	12.4	53
	72	12.6	54
	168	09.3	55

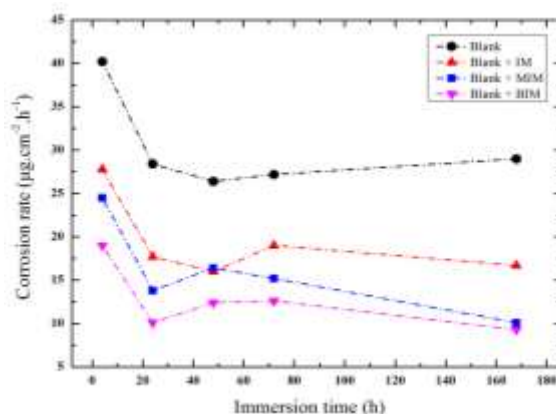


Figure 1. Evolution of corrosion rate for copper in 1.0 M H_2SO_4 with and without 10^{-3} M of IM, MIM and BIM with the immersion time at 298K

It can be seen from the **Table 2** that the addition of IM, MIM and BIM conducted to a decrease in the corrosion rate, and the corresponding increase in efficiency, which was particularly important with BIM compound (64%). Equally, the corrosion rate curves (**Figure 1**) illustrate that the copper dissolution decreased with time and become generally stable after 48h indicating a formation of the protective film on the copper surface [30].

It is obvious from **Figure 1** and the presented data in **Table 2** that the inhibition efficiency E_w (%) of the compounds tested follows the sequence:

$$IM < MIM < BIM$$

The significant efficacy of BIM is explained by the presence in the molecule at the same time of the imidazole ring and the aromatic ring which may be favorable adsorption sites of the molecule on the surface of copper.

3.2. UV spectroscopic analyzes

Figure 2 and 3 showed the UV spectra of sulfuric acid (1.0M) solutions after immersion of copper for 4h at 298K in the absence and presence of imidazole derivatives at 10⁻³ M. Table 3 presents the values of absorbance peaks associated with UV spectra.

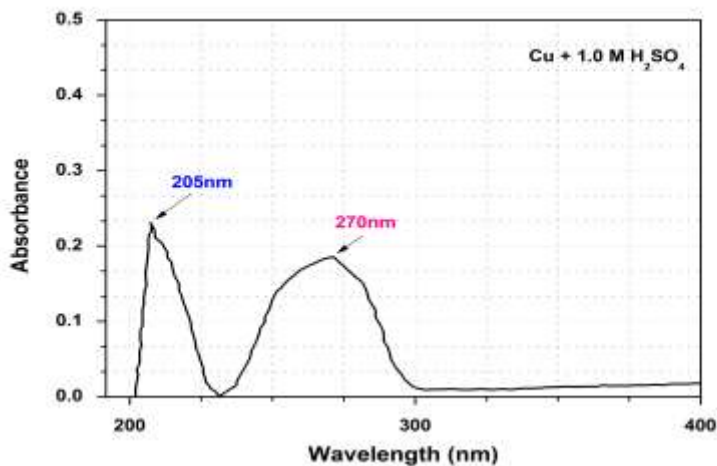


Figure2. UV spectra of solution after copper corrosion for 4h of immersion in 1.0 M H₂SO₄ at 298K.

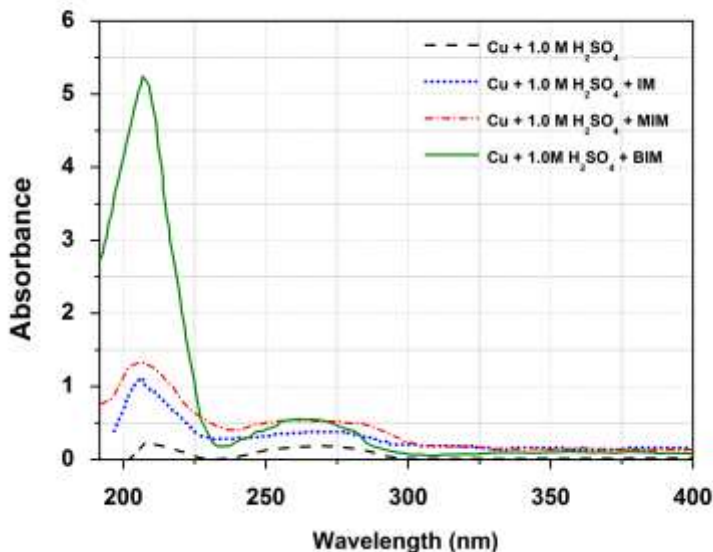


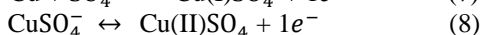
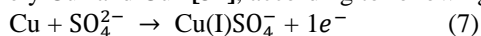
Figure 3. UV spectra of solution after copper corrosion for 4h of immersion in 1.0 M H₂SO₄ with and without IM, MIM and BIM compounds 10⁻³ M at 298K.

Table 3. The absorbance of the two observed peaks in the obtained UV spectra.

Solutions	Absorbance	
	1 st peak (at 205 nm)	2 nd peak (at 270 nm)
Cu + 1.0 M H ₂ SO ₄	0.23	0.18
Cu + 1.0 M H ₂ SO ₄ + IM	1.15	0.37
Cu + 1.0 M H ₂ SO ₄ + MIM	1.35	0.52

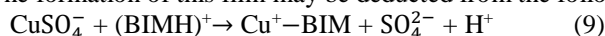
Cu + 1.0 M H₂SO₄ + BIM	5.26	0.50
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The **Figure 2** shows two peaks one at 205 nm and other at 270 nm, which could due to complex formation between sulfates ion and copper species, namely Cu⁺ and Cu²⁺[31], according to following reactions:



As can be seen in Figure 3 and Table 3, the intensity of the absorbance peak was increased in the presence of the molecule inhibitors, particularly for the first peak (at 205 nm) in medium containing BIM or MIM. This could be explained by the formation of complex between Cu (I) and the inhibitor molecule. The change in the absorbance value indicates the formation of complexes with the species Cu (II) [31, 32]. In the case of BIM the high intensity of first peak is probably due to the strong complexation between Cu (I) and BIM through the adsorption sites of the molecule namely the imidazole ring and the aromatic ring.

The formation of the protective film with the inhibitors IM, MIM and BIM would be initiated by the adsorption of the protonated form of inhibitor to the surface of copper in sulfuric acid, which is observed for the BIM molecule. Indeed, complexed ions Cu⁺ by the ions SO₄²⁻ react with the protonated species to form the protective film Cu⁺-Inhibitor [31,32]. The formation of this film may be deducted from the following step:



3.3. Adsorption isotherm of BIM

The results obtained by the gravimetric and UV-spectroscopy methods show that BIM compound is the most effective inhibitor among all tested imidazole derivatives. For this reason, the effect of concentration inhibitor has been study for BIM to know the additional information about the kind of adsorption isotherm, and then, the nature of adsorption of BIM to the surface of copper.

A direct relationship between inhibition efficiency E_w(%) and the degree of surface coverage (θ) [E_w(%) = 100 × θ] can be assumed for the different concentrations of the inhibitor (**Table 4**). The degree of surface coverage (θ) for the different concentrations of BIM has been evaluated from the weight loss measurements in 1.0 M H₂SO₄ at 298K. The data were tested graphically by fitting to various adsorption isotherms. The correlation coefficient (R²) was used to determine the best fit isotherm which was obtained for Langmuir (**Figure 5**). According to this isotherm, θ is related to the inhibitor concentration by the following equation [33]:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (10)$$

Where θ is the surface coverage, C is the concentration, K_{ads} is the equilibrium constant of adsorption process. K_{ads} is related to the standard Gibbs free energy of adsorption ΔG^o_{ads} by the equation (11) [34].

Table 4. Different concentration of BIM according to this surface coverage and the efficiency

C (M)	$\frac{C}{\theta}$ (M)	E _w (%)
10 ⁻²	0.01553	63
5 x10 ⁻³	0.00780	63
10 ⁻³	0.00163	64
5 x10 ⁻⁴	0.00083	63
10 ⁻⁴	0.00017	62

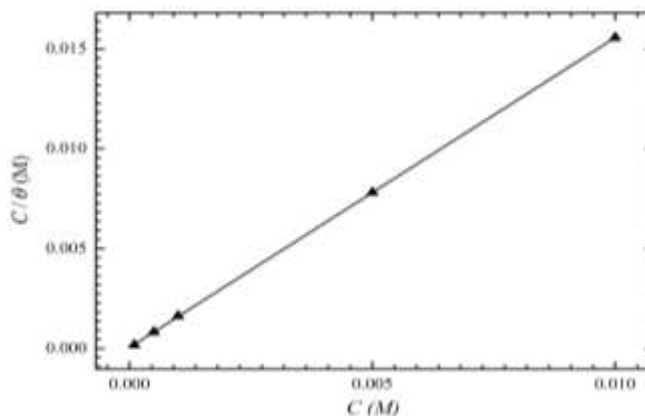


Figure 4. Plots of Langmuir adsorption isotherm (C/θ vs C) of BIM on the copper surface after 4h of immersion in 1.0 M H_2SO_4 at 298K.

The data was obtained from **Figure 4**. The intercept of the lines in this figure yielded K_{ads} (in $dm^3 \cdot mol^{-1}$) and the corresponding standard Gibbs free energy of adsorption (in $Kj \cdot mol^{-1}$) was then calculated from equation (11) [34]:

$$K_{ads} = \frac{1}{C_{solvent}} \exp\left(\frac{-\Delta G_{ads}^{\circ}}{RT}\right) \quad (11)$$

where R (in $J \cdot mol^{-1} \cdot K^{-1}$) is the gas constant, T (in K) is the temperature, and $C_{solvent}$ is the molar concentration of the solvent, which in this case, is water ($C_{H_2O} = 55.5 \text{ mol} \cdot dm^{-3}$). Using this equation, the various adsorption parameters are obtained from the studied isotherm including the standard Gibbs free energy of adsorption of BIM on the copper surface at 298 K was calculated and listed in **Table 5**.

Table 5. Some parameters from Langmuir isotherm model for the adsorption of BIM in 1.0 M H_2SO_4 on the copper at 298K.

Inhibitor	Langmuir			
	ΔG_{ads}° (kJ/mol)	Slop	K_{ads} ($dm^3 \cdot mol^{-1}$)	R^2
BIM	-34.8	1.5528	22772.3	0.9999

The relatively high value of the adsorption equilibrium constant (K_{ads} , Table 5) reflects the strong adsorption of BIM on the metal surface [35], which explains the inhibitory efficacy of this compounds [36].

Generally, the values of ΔG_{ads}° up to -20 kJ/mol are consistent with physisorption, while those around -40 kJ mol^{-1} or higher are associated with chemisorptions as a result of the sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate bond [36]. In our study, the calculated ΔG_{ads}° value (-34.8 kJ/mol ; Table 5) indicates that, the adsorption of BIM molecule is typically a chemisorptions mechanism.

3.4. Computational Study

Recently, the density functional theory (DFT) has been used to analyze the characteristics of the inhibitor/surface mechanism and to describe the structural nature of the inhibitor on the corrosion process [37, 38]. Furthermore, DFT is considered a very useful technique to probe the inhibitor/surface interaction as well as to analyze the experimental data.

We start by considering the local properties of inhibitor molecules, such as, frontier molecular orbitals. These properties are presented graphically only for molecules in gas phase [39]. To establish correlation between experimental data and structural and electronic characteristics of the studied compounds, the geometry of the molecules (**Figure 5**) was optimized by (DFT) method level with B3LYP exchange correlation functional, using 6–

31 +G (2d, p) basis set. This basis set provided accurate geometry and electronic properties for a wide range of organic compounds.



Figure 5. The optimized geometries of the studied inhibitors at B3LYP/6-31+G(2d,p) method.

Table 6. The calculated quantum chemical parameters for IM, MIM and BIM obtained using DFT method at B3LYP/6-31+G(2d, p) basis set.

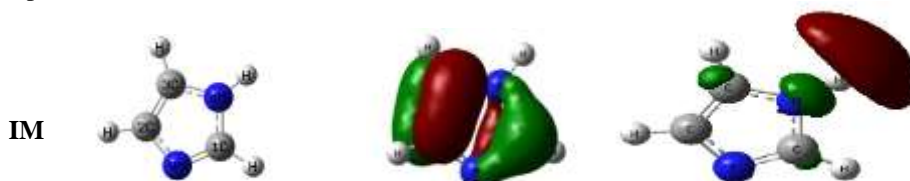
	$E_{LUMO}(eV)$	$E_{HOMO}(eV)$	$\Delta E(eV)$	TNC(e)	$\eta(eV)$	$\sigma(eV^{-1})$	$\Delta N(e)$	$E_w(\%)$
DFT/6-31+G(2d,p)								
IM	-0.0071	-0.2380	0.2309	-0.275	0.1154	8.6617	0.2657	38
MIM	-0.0063	-0.2264	0.2201	-0.375	0.1100	9.0868	0.2529	51
BIM	-0.0298	-0.2343	0.2045	-0.478	0.1022	9.7799	0.2358	64

The separation energy ($E_{LUMO} - E_{HOMO}$) is a parameter that allows us to study the reactivity of the inhibitor molecule towards the metallic surface. As ΔE decreases, the reactivity of the molecule increases leading to increase the inhibitory efficacy of the molecules used [40].

The calculations from **Table 6** show the decreasing values of the energy gap in the following order: BIM < MIM < IM, which does not follow the same order of inhibition efficiency obtained for the inhibitors [41]. The smaller value of ΔE of BIM causes high inhibition efficiency of the molecule. This can be explained by the presence in BIM at time of two nitrogen atoms of imidazolic ring and phenyl group which activates and increases the electron-donating ability of this molecule. Nitrogen atoms and phenyl group have lonely electron pairs that are important for bonding unfilled 3d orbitals of copper ion Cu⁺; they determine the adsorption of the molecules on the metal surface. This confirms the experimental results that interaction between BIM and metal probably is (Chemisorptions). The latter process includes charge sharing or charge transfer from the inhibitor molecule to the metal surface. The presence of the transition metal having vacant orbital of low energy with the inhibitor molecule having relatively loosely bound electrons or hetero atom with lone pair of electrons facilitates this adsorption [40].

The hardness, η , of a species is the amount by which its electronegativity (its ability to accept electrons) decreases when an infinitesimal amount of electronic charge is added to it. It is possible to observe that molecule BIM with the largest IE% (64%), has a lower value of global hardness $\eta = 0.1022 eV$. Additionally, BIM has the largest softness (the inverse of hardness), $\sigma = 9.7799 eV^{-1}$. So η , σ which are parameters required for a molecule to be more reactive as a corrosion inhibitor. The calculated results are in agreement with experimental results [28, 37, 42].

A large TNC value indicates that the inhibitor will be favorably adsorbed on the Cu surface. The calculations showed that the inhibitors with the highest inhibition efficiency have the highest TNC values which agree well with the experimental observations (**Table 6**). The best inhibitor in this series, BIM, has the largest TNC (-0.478) [28].



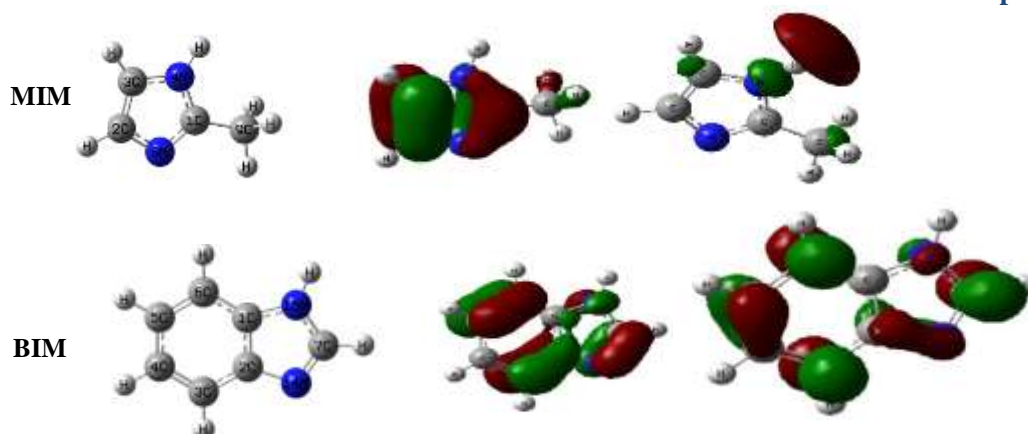


Figure 6. The frontier molecular orb (a) sity of IM, MIM, BI (b) OMO and (b) LUMO

The HOMO and the LUMO for the studied molecules are shown in **figure 6** together with the total electron density. In the BIM molecule, the HOMO and the LUMO are delocalized throughout the system with the HOMO and LUMO orbitals having the maximum amplitude coefficients on C and N atoms. The LUMO on these centers has an anti-bonding character; the total electron density shows that the negative charge (indicated in red color) is strongly localized on the N atom while the rest of the molecule appears to have a neutral distribution of charges (green color). The negative charge on the N atom is likely due to the electron cloud of the lone pair of electrons [38].

There is a general consensus between several authors that the negatively charged heteroatoms are the more adsorbed ones on the metal surface through donor– acceptor type reaction. Which explain that from the values of Mulliken charges in **Table 7**, the larger electronic charge is obtained for the BIM derivative, it could be readily observed that nitrogen (-0.247; -0.231), and negative charges around most carbon atoms of the aromatic rings (-0.772; -0.539; -0.191; -0.154) have high charge densities[43, 44]

Table 7. Mulliken charge density of the IM, MIM and BIM molecules

	DFT/B3LYP/6-31+G(2d,p)
IM	—
C1	-0.131
C2	-0.123
C3	-0.196
N4	-0.102
N9	-0.173
MIM	—
C1	0.579
C2	-0.090
C3	-0.185
C9	-1.041
N4	-0.167
N8	-0.208
BIM	—
C1	0.656
C2	0.493
C3	-0.772
C4	-0.154
C5	-0.191
C6	-0.539
C7	0.039
N14	-0.247
N15	-0.231

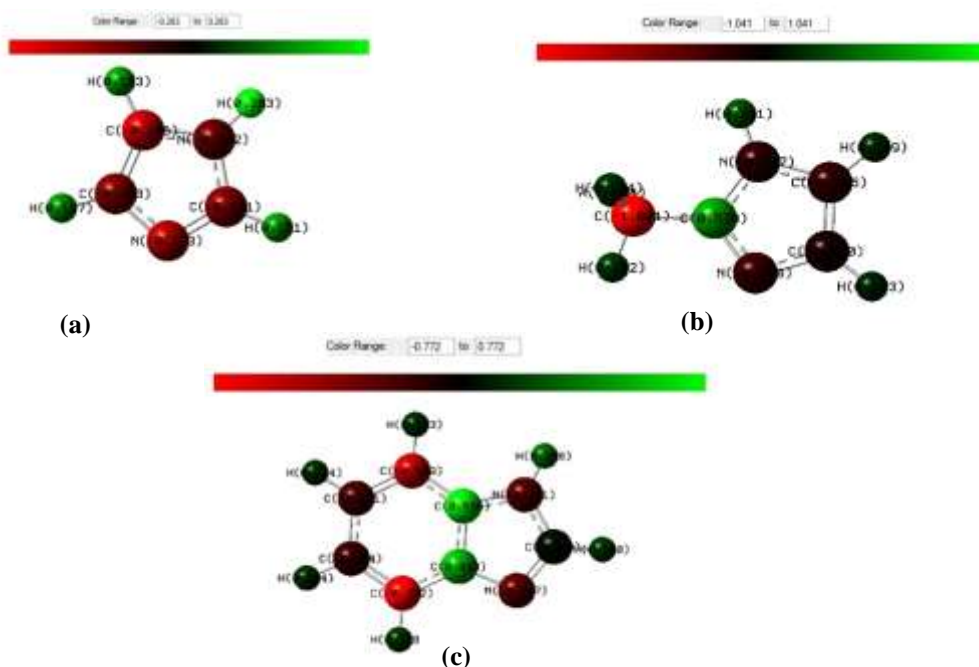


Figure7. Mulliken charges on the optimized structure of (a) IM, (b) MIM and (c) BIM using B3LYP/6-31+G(2d,p). (The load value of each atom is indicated in the Table 7)

As shown from **Figure7** the high electron density is represented by a red color, and the low electron density is represented by a green color. The electron density decreases in the following order: red > orange > brown > green, we show that the BIM has more negatives centers due to aromatic group [28].

Therefore, N and some C atoms were the active centers, which had the strongest ability of bonding to the metal surface. Consequently, BIM can accept electrons from Cu through these atoms. It has been reported that excellent corrosion inhibitors can not only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal [44]. For BIM compound, it is important to acknowledge the contribution of the high electron density of the aromatic ring which is very rich in π electrons plays a key role in the inhibition process. These strengthens the chemisorption of BIM on copper surface leading to a stable protective layer and thus, retarding further corrosion of the metal in sulfuric acid solution [28, 40, 43, 44].

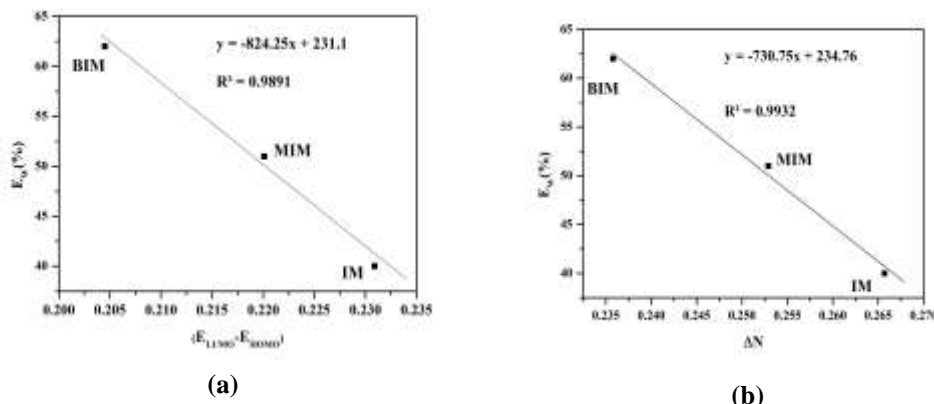


Figure 8. Correlations between experimental $E_w\%$ and (a) $(\Delta E = E_{HOMO} - E_{LUMO})$, (b) ΔN values of IM, MIM and BIM calculated at DFT with 6-31+G (2d,p).

Figure 8 shows the correlation between E_w (%) and $(\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}})$. Examination of this figure shows the linear representations and a good correlation between the energy gap ($E_{\text{HOMO}} - E_{\text{LUMO}}$) ($R^2 = 0.990$), ΔN ($R^2 = 0.993$) and with experimental inhibition efficiency of the tested inhibitors. Thus, the energy gap and ΔN are important parameters that control the adsorption of the inhibitor on the metal surface [28].

CONCLUSION

From the obtained results, we can deduce the following conclusions:

- All investigated imidazole compounds (IM, MIM and BIM) have shown inhibiting properties for copper corrosion in 1.0 M sulfuric acid.
- The examination of the UV spectrum of the corrosive solution after immersion of copper in the absence and presence of IM, MIM and BIM compounds revealed the adsorption of these compounds to the metal surface by forming stable complexes with Cu^+ ions.
- The comparative study of the action of imidazole derivatives showed that the BIM compound is the best inhibitor of the proposed series (BIM > MIM > IM).
- The values of K_{ads} and $\Delta G^{\circ}_{\text{ads}}$ suggest strong interaction of BIM with copper surface and adsorption phenomenon is typical chemisorptions mechanism that follows the Langmuir isotherm.
- The quantum chemical calculations show that the energy band gap (ΔE) and the number of electrons transferred (ΔN) are found to correlate well with experimental inhibition efficiencies of inhibitors.

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