

Theoretical Investigation of Two Antiabetics Drugs as Corrosion Inhibitors of Aluminium in 1.0 M HCl: Combining DFT and QSPR Calculations

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Received May 14, 2020; Revised June 16, 2020; Accepted June 22, 2020

Abstract The behavior of two antidiabetic drugs namely N-[(butylamino) carbonyl]-4-methylbenzenesulfonamide or tolbutamide and N-(hexahydrocyclopentapyrrol-2(1H)-ylcarbonyl)-4-methylbenzenesulfonamide or gliclazide was theoretically evaluated by the Density Functional Theory (DFT) and the Quantitative Structure Property Relationship (QSPR) methods. Theoretical calculations showed a clear correlation between the descriptor parameters and the inhibition efficiencies. It also permitted to identify the reactivity sites. The results reveal that the molecules studied are good inhibitors of aluminium corrosion in 1M hydrochloric acid. Finally, the Quantitative Structure Property Relationship allowed to find the appropriate set of parameters establishing the relationship between the inhibition efficiency and the molecular descriptors.

Keywords: *tolbutamide, gliclazide, density functional theory, quantitative structure property relationship*

Cite This Article: Mougo André Tigori, Amadou Kouyaté, Assouma Dagri Cyrille, Victorien Kouakou, and Paulin Marius Niamien, "Theoretical Investigation of Two Antiabetics Drugs as Corrosion Inhibitors of Aluminium in 1.0 M HCl: Combining DFT and QSPR Calculations." *American Journal of Materials Science and Engineering*, vol. 8, no. 1 (2020): 6-16. doi: 10.12691/ajmse-8-1-2.

1. Introduction

In recent years, corrosion inhibitors have become an effective means of reducing metal corrosion in several sectors [1,2]. Among these metals, we have the aluminum whose lightness is a major asset for the transport equipment and leisure industries. Aluminium is a very active metal [3] which is used in many fields because of its remarkable properties such as its aesthetic qualities and its good corrosion resistance. In particular, it is used in the aviation, automotive, packaging, construction, mechanical engineering and other industries.

This massive use make that aluminium is not escape to corrosion. Indeed, the use of acid solutions [4] in industry during operations such as cleaning, degreasing and pickling of metal structures leads to a corrosive attack on aluminium. Corrosion of aluminium is a fundamental concern in academic and industrial circles and has received considerable attention. This attention has focused on the search for biodegradable, eco-compatible and non-toxic molecules capable of reducing aluminium corrosion in acidic environments [5,6]. These organic or inorganic molecules will be added to acid solutions during the various operations to reduce the dissolution of

aluminium. Inorganic molecules are mostly carcinogenic and pollute the environment. The current trend is to use organic therapeutic compounds [7,8,9,10] because they are generally less toxic and efficient at low concentrations. The literature [11,12,13] shows that organic compounds, which inhibit aluminium corrosion, contain heteroatoms (N, S, O, P, Se) and/or π bonds in their molecular structure and that these molecules inhibit corrosion by adsorption on the metal surface. Experimental practice is a useful means of finding corrosion inhibitors because it helps to explain the mechanism of inhibition. However, these experiments are often expensive and time consuming and some are based on trial and error.

This observation has encouraged the use of new techniques based on numerical simulation and molecular modelling methods. It is within this context that several researchers [14,15,16,17] have used quantum chemical calculations based on Density Functional Theory (DFT) to explain the molecules physicochemical properties and the corrosion inhibition mechanism. DFT is based on Hohenberg and Kohn's theorem [18] which shows that the energy of the fundamental state of the molecule is the only functional electron density. This theory will be elucidated later thanks to Kohn and Sham [19] from a system without interactions between the constituents, it gives access to the global and local parameters of the molecules, which

allows to explain the metal/molecule interactions. This theoretical approach will be supported by the use of the QSPR method (Quantitative Structure Property Relationship) which is a method for experimentation [20] because it permits to find a relationship between inhibition efficiency and quantum chemical parameters.

The objective of this work is on the one hand to study the inhibition properties of two antidiabetic drugs; tolbutamide and gliclazide as an aluminium inhibitor corrosion in 1M acid hydrochloric solution and on the other hand to find the best set of parameters that could correlate the experimental and calculated inhibition efficiencies of the molecules studied using the QSPR approach.

2. Materials and methods

2.1. Gravimetric Method

Gravimetric method is an experimental method which consists of measuring the loss of mass (Δm) suffered by an aluminium sample of surface S , which has been immersed for a time $t = 1h$ in a solution of hydrochloric acid of concentration 1M, maintained at a constant temperature of 298K. During this experiment we used an analytical balance (precision: ± 0.1 mg), a proofer and a thermostat water bath.

The corrosion rate of aluminium (W) and the inhibition efficiency (IE) were evaluated from the following relationships:

$$w = \frac{\Delta m}{S_e \cdot t} = \frac{m_1 - m_2}{S_e \cdot t} \quad (1)$$

$$IE(\%) = \frac{W_0 - W}{W_0} * 100 \quad (2)$$

Δm : is the mass loss (g) ; m_1 and m_2 are respectively, the weight (g) before and after immersion in the solution test; t : the immersion time (h) ; S_e : the total surface of sample (cm^2) ; w_0 and w ; are respectively the corrosion rates of aluminium in the absence and presence of each molecule.

2.2. Density Functional Theory (DFT) Calculations

Quantum chemical calculation methods are based primarily on solving the Schrödinger equation for a given system with the determination of the system clean energy and wave functions. There are several methods of resolution among these methods we have the Density Functional Theory (DFT). According to this theory, electronic properties can be described in terms of electron density functions. These calculations, which have been carried out with the Gaussian 09 W [21] software, using the B3LYP [22] functional with two basis sets including 6-31G (d) and LanL2DZ consist of two steps:

- A graphic presentation of the geometry using a computer graphics software: Gaussview.

- The application of a theoretical method (DFT); this method is implemented in the commercial software (Gaussian).

This method makes it possible to determine the quantum chemical parameters such as E_{HOMO} (Highest Occupied Molecular Orbital Energy), E_{LUMO} (Lowest Unoccupied Molecular Orbital Energy), energy gap (ΔE), dipole moment (μ), electronegativity (χ), hardness (η), softness (S), electrophilicity index (ω), electron affinity (A), ionization energy (I) and the fraction of electron transferred (ΔN) and reactivity parameters.

2.3. Quantitative Structure Property Relationship (QSPR) Method

The QSPR method has been used to develop mathematical models linking physicochemical properties and biological activities to molecular structure [23]. It allows the prediction of inhibition properties of organic compounds. We will apply the non-linear multivariate model proposed by Lukovits et al. [24] to study the interactions between corrosion inhibitors and metal surfaces in 1M HCl, which is based on the Langmuir adsorption isotherm. This model is represented by the relation:

$$IE_{calc}(\%) = \frac{[Ax_j + B]C_i}{1 + [Ax_j + B]C_i} * 100 \quad (3)$$

Where C_i represents the different inhibitors concentrations. A and B are real constants which will be determined when solving the system of equations.

Using four inhibitors concentrations, which are $50\mu M$, $100\mu M$, $500\mu M$ and $1000\mu M$. We tested sets of three parameters (x_1, x_2, x_3). In this case, the equation becoming:

$$IE_{calc}(\%) = \frac{[Ax_1 + Bx_2 + Dx_3 + E]C_i}{1 + [Ax_1 + Bx_2 + Dx_3 + E]C_i} * 100 \quad (4)$$

This equation allows us to have a system of four equations with four unknowns A , B , D and E . It is thus a question of finding for the molecule the set of coefficients A , B , D and E that permits to obtain the value of the inhibition efficiency closest to the experimental value. The calculations were carried out using the EXCEL software.

3. Results and Discussion

3.1 Molecular and Reactivity Parameters

The Chemical structure and the optimized structure of the studied molecules are given by Figure 1.

The values of the inhibition efficiencies determined using the gravimetric method for five different concentrations of each compound are listed in Table 1.

Table 1. Inhibition efficiencies (IE%) of TB and GC at 298K

Concentration(mM)	TB IE%	GC IE%
0.05	65.44	68.64
0.1	70.75	72.22
0.5	78.16	79.72
1	82.66	84.56
2	85.31	87.13

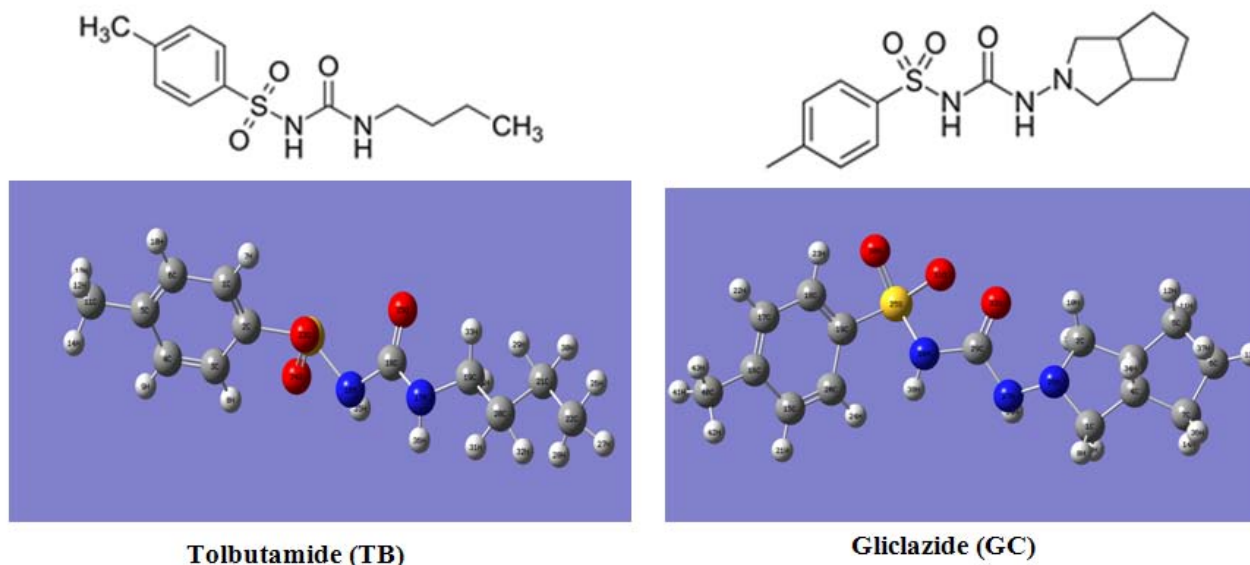


Figure 1. Chemical and Optimized structure of tobutamide and glioclazide by B3LYP/6-31G (d)

Table 2. Quantum chemical parameters of TB and GC calculated by B3LYP

Parameters	Tolbutamide (TB)		Glioclazide(GC)	
	6-31G(d)	LanL2DZ	6-31G(d)	LanL2DZ
E_{HOMO} (eV)	-5.9777	-7.1522	-5.5675	-5.9573
E_{LUMO} (eV)	-2.0308	-2.1488	-2.1942	-2.5862
Energy gap ΔE (eV)	3.9469	5.0034	3.3733	3.3711
Dipole moment μ (D)	5.0515	5.7377	7.4851	9.8876
Ionization energy I (eV)	5.9777	7.1522	5.5675	5.9573
Electron affinity A (eV)	2.0308	2.1488	2.1942	2.5862
Electronegativity χ (eV)	4.0043	4.6655	3.881	4.2718
Hardness η (eV)	1.9735	2.5017	1.6867	1.6856
Softness S (eV) ⁻¹	0.5067	0.400	0.5929	0.5932
Fraction of electron transferred ΔN	0.06985	-0.0770	0.1182	0.0024
Electrophilicity index ω	4.0625	4.350	4.4651	5.4131
Total energy E_{T} (Ha)	-1200.4088	-811.8512	-1371.7479	-983.8490

The main quantum chemical parameters were calculated using the B3LYP/6-31G(d) and B3LYP/LanL2DZ are listed in Table 2.

The ability of a molecule to inhibit corrosion depends on the value of E_{HOMO} , as the inhibiting effect of a molecule is generally usually ascribed to adsorption of the molecule on the metal surface. A molecule with a high E_{HOMO} value has the ability to give electrons to a suitable low energy [25], empty molecular orbital and this facilitates its adsorption on the metal surface. The high E_{HOMO} values of the molecules studied justify their good inhibition efficiencies, therefore these molecules can adsorb to the aluminium surface thus creating a protective layer that will isolate it from the aggressive environment. GC has the highest E_{HOMO} value -5.5675eV and -5.9573 eV respectively for B3LYP/6-31G (d) and B3LYP/LanL2DZ) which justifies its greater inhibition efficiency, and this is in agreement with the experimental results.

According to the literature, a molecule with a low value of E_{LUMO} can easily accept electron from an occupied orbital of a metal [26]. In our case, the low E_{LUMO} values

of the studied molecule show that they have a tendency to accept electrons from the aluminium. In the Table 2 E_{LUMO} values follow the trend: GC < TB. Accordingly, GC accepts more electrons than TB, confirming its greater inhibition efficiency.

Energy gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) is a suitable indicator for interpreting the reactivity of an inhibitor. Indeed, a molecule with a low value of ΔE is more polarizable and generally has a high chemical reactivity [27]. The results obtained in the two different basis (Table 2) show that the molecules studied have a low value of ΔE , which therefore favours the exchange of electrons between these molecules and aluminium, as it is easier to remove an electron from the HOMO to the LUMO orbital. This confirms the high inhibition efficiency values obtained experimentally. GC has the best inhibition efficiency as it has the lowest value of ΔE .

According to some authors [28,29] high value of dipole moment (μ) lead to a good inhibition efficiency of an organic molecule. However, many other authors [30,31] state that low dipole moment values favour the adsorption process.

Considering these contradictory views on this indicator, no interpretation related to the behavior of the studied molecules can be made in our work.

The ionization potential (I) and electron affinity (A) of the molecules are calculated according to Koopmans's theorem [32] using the following equations

$$I = -E_{HOMO} \quad (5)$$

$$A = -E_{LUMO}. \quad (6)$$

The two quantum chemical parameters I and A are related respectively to the HOMO and LUMO energies. According to the literature [33] a molecule with a low ionization energy value is high reactive. The values obtained in the different basis of TB and GC are low compared to values obtained in the literature [34,35], which justifies their high inhibition efficiency. The lower value of GC confirms its greater inhibition efficiency.

Referring to Koopmans theorem [32], the electronegativity (χ) and the global hardness (η) can be written in terms of ionization potential (I) and the chemical affinity (A).

$$\chi = \frac{I + A}{2} \quad (7)$$

$$\eta = \frac{I - A}{2}. \quad (8)$$

Chemical softness S [36] is estimated by the above equation :

$$S = \frac{2}{I - A}. \quad (9)$$

The electronegativity (χ) of a molecule reflects its ability to attract electrons when forming a chemical bond with another element. In general, TB and GC have lower electronegativity values than aluminium (4.28eV), which shows that aluminium attracts more electrons than TB and GC. This implies that the electrons move easily from each molecule to aluminium.

Global softness (S) and global hardness η (eV) are also used to measure the molecular stability and reactivity. A hard molecule has a large energy gap and a soft molecule has a small energy gap [37]. It is shown from the calculations that GC has the least value of global hardness (1.6867 eV, 1.6856eV) and the highest value of global softness ($0.5929(\text{eV})^{-1}$, $0.5932(\text{eV})^{-1}$) is expected to have the highest inhibition efficiency. These results are consistent with experimental inhibition efficiencies.

According to Pearson theory [38] the fraction of transferred electrons (ΔN) from the inhibitor molecule to the metallic atom can be expressed by:

$$\Delta N = \frac{\chi_{Al} - \chi_{inh}}{2(\eta_{Al} + \eta_{inh})} \quad (10)$$

Where χ_{Al} and η_{Al} , χ_{inh} and η_{inh} denote electronegativity and hardness of aluminium and the inhibitor molecule respectively.

We use the theoretical value of $\chi_{Al} = 4.28 \text{ eV/mol}$ [39] and $\eta_{Al} = 0$ [40], for the calculation of the number of transferred electrons.

In our case, the values of ΔN are positive in the 6-31G(d) basis set for the inhibitors and only positive for

GC in LanL2DZ basis set, which could explain that the molecules provide electrons to the aluminium [41], these electrons transfers justify the existence of the chemical adsorption. Whereas in LanL2DZ basis ΔN value of TB is negative, this means that TB does not provide electrons to the aluminium, which would rather militate in favour of a physical adsorption process.

The global electrophilicity index (ω), introduced by Parr [42], and calculated using the electronic chemical potential and chemical hardness is given by:

$$\omega = \frac{\mu_P^2}{2\eta} \quad (11)$$

According to the definition, this index measures the ability of a chemical species to accept electrons [42]. The low value of ω defines the nucleophilic character and the high value defines the electrophilic character. In our study, the compounds studied have low values of ω which reflects their electrophilic character, so the molecules have the possibility to receive electrons from the aluminium orbitals.

The best way to analyze the local selectivity of a corrosion inhibitor is to use the Fukui function and the dual descriptor. The Fukui function [43] is defined as the derivative of the electronic density $\rho(r)$ with respect to the number N of electrons:

Nucleophilic attack:

$$f^+(r) = \rho_{N+1}(r) - \rho_N(r) \approx \rho_{BV} \quad (12)$$

Electrophilic attack:

$$f^-(r) = \rho_N(r) - \rho_{N-1}(r) \approx \rho_{HO} \quad (13)$$

Where $\rho_N(r)$ is the electron density at a point r in space around the molecule, N corresponds to the number of electrons in the neutral molecule, $N + 1$ corresponds to an anion with an electron added to LUMO of the neutral molecule and $N - 1$ corresponds to a cation with an electron removed from HOMO of the neutral molecule

In practice, Mulliken charges lead to the condensed Fukui functions [44]:

Nucleophilic attack:

$$f_k^+ = q_k(N + 1) - q_k(N) \quad (14)$$

Electrophilic attack:

$$f_k^- = q_k(N) - q_k(N - 1) \quad (15)$$

In order to determine precisely the individual sites of attack having a particular behavior within the molecule the dual descriptor [45,46] is used, expressed by the following relationship:

$$\Delta f_k(r) = \left(\frac{\partial f_k(r)}{\partial N} \right)_{v(r)}. \quad (16)$$

The condensed form of the dual descriptor is given by the following relation:

$$\Delta f_k(r) = f_k^+ - f_k^- \quad (17)$$

For $\Delta f_k(r) > 0$, the process is driven by a nucleophilic attack, when $\Delta f_k(r) < 0$ the process is driven by an electrophilic attack.

All the Fukui functions and dual descriptors are tabulated in Table 3 and Table 4.

Table 3. Mulliken atomic charges, Fukui functions and dual descriptor by B3LYP/6-31G(d) of TB

atom	$q_k(N + 1)$	$q_k(N)$	$q_k(N - 1)$	f_k^+	f_k^-	$\Delta f_k(r)$
1 C	-0.146795	-0.155773	-0.174256	0.008978	0.018483	-0.009505
2 C	-0.085356	-0.067053	-0.043367	-0.018303	-0.023686	0.005383
3 C	-0.103746	-0.106285	-0.122178	0.002539	0.015893	-0.013354
4 C	-0.157772	-0.17104	-0.186346	0.013268	0.015306	-0.002038
5 C	0.144023	0.141134	0.138521	0.002889	0.002613	0.000276
6 C	-0.176803	-0.18549	-0.200985	0.008687	0.015495	-0.006808
7 H	0.17775	0.163369	0.125295	0.014381	0.038074	-0.023693
8 H	0.190651	0.177052	0.148162	0.013599	0.02889	-0.015291
9 H	0.158992	0.131526	0.076413	0.027466	0.055113	-0.027647
10 H	0.156586	0.131049	0.077965	0.025537	0.053084	-0.027547
11 C	-0.51973	-0.518544	-0.516746	-0.001186	-0.001798	0.000612
12 H	0.177186	0.162666	0.137655	0.01452	0.025011	-0.010491
13 H	0.19046	0.171757	0.141844	0.018703	0.029913	-0.01121
14 H	0.17542	0.160818	0.135944	0.014602	0.024874	-0.010272
15 S	1.033419	0.928891	1.071576	0.104528	-0.142685	0.247213
16 N	-0.666702	-0.65821	-0.676871	-0.008492	0.018661	-0.027153
17 N	-0.589849	-0.58239	-0.599049	-0.007459	0.016659	-0.024118
18 C	0.653385	0.650789	0.638988	0.002596	0.011801	-0.009205
19 C	-0.314743	-0.270298	-0.265271	-0.044445	-0.005027	-0.039418
20 C	-0.169273	-0.252536	-0.242122	0.083263	-0.010414	0.093677
21 C	-0.422636	-0.374262	-0.425067	-0.048374	0.050805	-0.229179
22 C	-0.57991	-0.556648	-0.520963	-0.023262	-0.035685	0.012423
23 O	-0.434257	-0.471769	-0.596179	0.037512	0.12441	-0.086898
24 O	-0.478106	-0.510671	-0.625893	0.032565	0.115222	-0.082657
25 O	-0.452823	-0.478599	-0.507625	0.025776	0.029026	-0.00325
26 H	0.270463	0.18198	0.127875	0.088483	0.054105	0.034378
27 H	0.322564	0.221177	0.165068	0.101387	0.056109	0.045278
28 H	0.303015	0.218069	0.197014	0.084946	0.021055	0.063891
29 H	0.321623	0.277188	0.233202	0.044435	0.043986	0.000449
30 H	0.255731	0.151708	0.142927	0.104023	0.008781	0.095242
31 H	0.24778	0.164359	0.158277	0.083421	0.006082	0.077339
32 H	0.185363	0.137277	0.129665	0.048086	0.007612	0.040474
33 H	0.295707	0.249712	0.237092	0.045995	0.01262	0.033375
34 H	0.257635	0.183959	0.179831	0.073676	0.004128	0.069548
35 H	0.343092	0.322209	0.274952	0.020883	0.047257	-0.026374
36 H	0.349502	0.328355	0.307338	0.021147	0.021017	0.00013

Table 4. Mulliken atomic charges, Fukui functions and dual descriptor by B3LYP/6-31G(d) of GC

atom	$q_k(N + 1)$	$q_k(N)$	$q_k(N - 1)$	f_k^+	f_k^-	$\Delta f_k(r)$
1 C	-0.135659	-0.116755	-0.10218	-0.018904	-0.014575	-0.004329
2 C	-0.168649	-0.141965	-0.11171	-0.026684	-0.030255	0.003571
3 C	-0.118985	-0.11439	-0.112165	-0.004595	-0.002225	-0.00237
4 C	-0.139787	-0.131853	-0.12531	-0.007934	-0.006543	-0.001391
5 C	-0.298245	-0.295552	-0.292087	-0.002693	-0.003465	0.000772
6 C	-0.312126	-0.314089	-0.315703	0.001963	0.001614	0.000349
7 C	-0.285575	-0.281456	-0.276804	-0.004119	-0.004652	0.000533
8 H	0.18756	0.161285	0.135426	0.026275	0.025859	0.000416

atom	$q_k(N+1)$	$q_k(N)$	$q_k(N-1)$	f_k^+	f_k^-	$\Delta f_k(r)$
9 H	0.148999	0.122451	0.099679	0.026548	0.022772	0.003776
10 H	0.201795	0.187136	0.183896	0.014659	0.00324	0.011419
11 H	0.158542	0.141658	0.125454	0.016884	0.016204	0.00068
12 H	0.159689	0.151051	0.144172	0.008638	0.006879	0.001759
13 H	0.175574	0.15078	0.125192	0.024794	0.025588	-0.000794
14 H	0.146975	0.133776	0.120754	0.013199	0.013022	0.000177
15 C	-0.138307	-0.160793	-0.17756	0.022486	0.016767	0.005719
16 C	0.147726	0.136884	0.137034	0.010842	-0.00015	0.010992
17 C	-0.163261	-0.186955	-0.203089	0.023694	0.016134	0.00756
18 C	-0.137702	-0.165025	-0.163415	0.027323	-0.00161	0.028933
19 C	-0.123679	-0.125629	-0.083098	0.00195	-0.042531	0.044481
20 C	-0.161634	-0.172703	-0.171903	0.011069	-0.0008	0.011869
21 H	0.179568	0.124319	0.075666	0.055249	0.048653	0.006596
22 H	0.184655	0.126178	0.079821	0.058477	0.046357	0.01212
23 H	0.230685	0.187558	0.168074	0.043127	0.019484	0.023643
24 H	0.151268	0.113625	0.090311	0.037643	0.023314	0.014329
25 S	1.036376	0.867568	0.75926	0.168808	0.108308	0.0605
26 N	-0.327981	-0.343045	-0.32468	0.015064	-0.018365	0.033429
27 N	-0.437417	-0.460475	-0.486881	0.023058	0.026406	-0.003348
28 N	-0.681	-0.685198	-0.69791	0.004198	0.012712	-0.008514
29 C	0.751746	0.731956	0.67444	0.01979	0.057516	-0.037726
30 O	-0.3718	-0.44837	-0.616422	0.07657	0.168052	-0.091482
31 O	-0.244581	-0.281706	-0.427996	0.037125	0.14629	-0.109165
32 O	-0.231251	-0.290958	-0.377611	0.059707	0.086653	-0.026946
33 H	0.154561	0.135624	0.121932	0.018937	0.013692	0.005245
34 H	0.171004	0.159141	0.148045	0.011863	0.011096	0.000767
35 H	0.155949	0.138826	0.120746	0.017123	0.01808	-0.000957
36 H	0.167812	0.147969	0.127326	0.019843	0.020643	-0.0008
37 H	0.176264	0.16963	0.164355	0.006634	0.005275	0.001359
38 H	0.366811	0.339527	0.286225	0.027284	0.053302	-0.026018
39 H	0.353191	0.319374	0.280421	0.033817	0.038953	-0.005136
40 C	-0.522404	-0.517917	-0.516945	-0.004487	-0.000972	-0.003515
41 H	0.209818	0.169945	0.141969	0.039873	0.027976	0.011897
42 H	0.188971	0.15635	0.134067	0.032621	0.022283	0.010338
43 H	0.1945	0.162222	0.139202	0.032278	0.02302	0.009258

The dual descriptor is able to unambiguously specify true sites for nucleophilic and electrophilic attacks; furthermore, the dual descriptor is less affected by the lack of relaxation terms than the Fukui function [45].

The atom that has the high value of f_k^+ and $\Delta f_k(r)$ represents the most probable site for nucleophilic attacks. While the atom that has the highest value of f_k^- and the lowest value of $\Delta f_k(r)$ represents the most probable site for electrophilic attacks.

Thus, the analysis of the Table 3 indicates that S(15) atom is the most probable site for nucleophilic attacks and O(23) atom is the most probable site for electrophilic attacks for TB.

For GC, S(25) atom is the most likely site for

nucleophilic attacks because it has the highest values of f_k^+ and $\Delta f_k(r)$. Although O(30) atom has the highest value of f_k^- , it is not the most likely site for electrophilic attacks because it has not the lowest value of $\Delta f_k(r)$. In this case, O(31) atom which has the lowest value of $\Delta f_k(r)$ is the most likely site for electrophilic attacks.

The most likely center for nucleophilic attacks where the system receives electrons is located in the LUMO electron density region, while the most likely center for electrophilic attacks where the system provides electrons is located in the HOMO electron density region.

The HOMO and LUMO density diagrams are given in Figure 2.

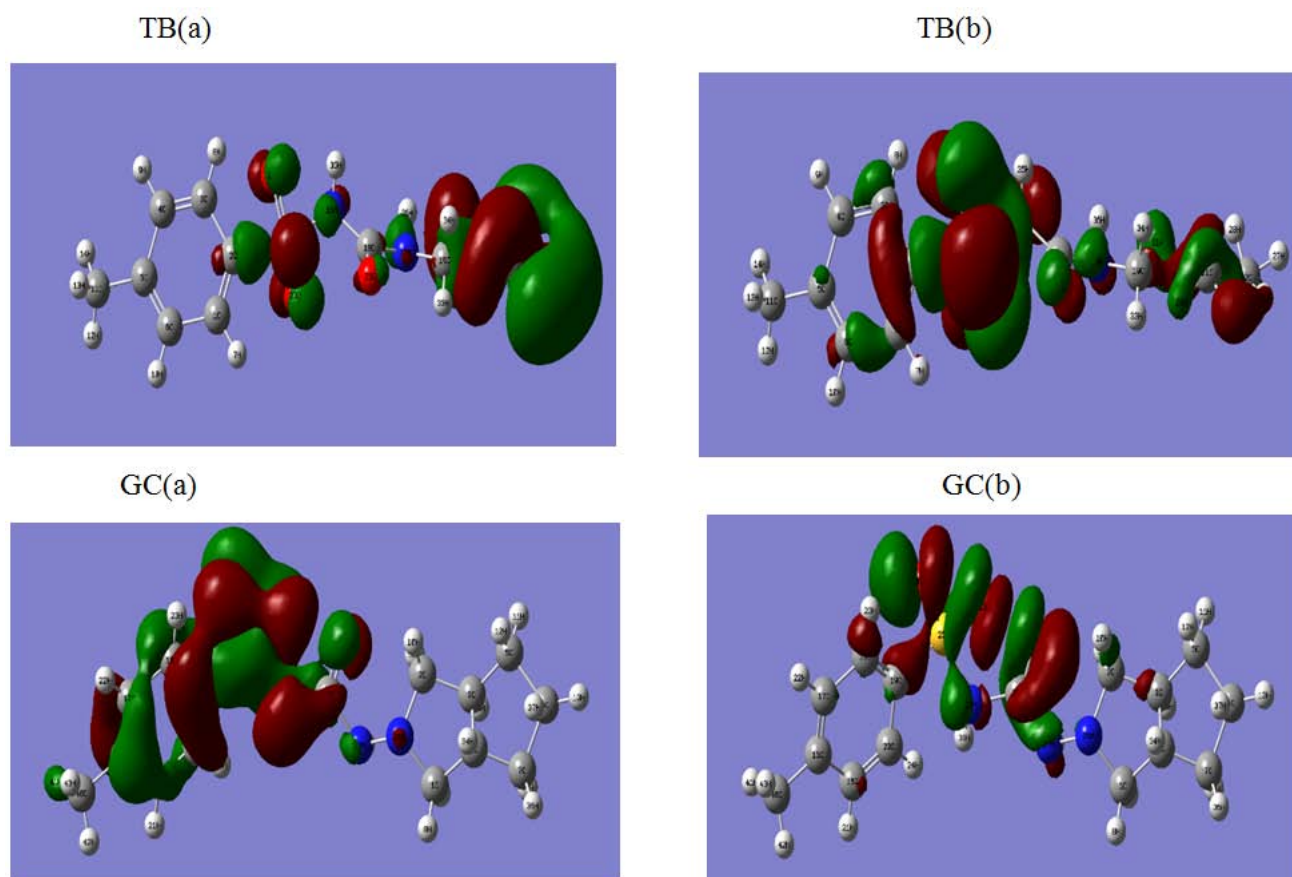


Figure 2. Density Diagrams (a) LUMO, (b) HOMO of TB and GC

3.2. QSPR Interpretation

The method consists to correlate some sets of composite indexes (quantum chemical and reactivity parameters) with the experimental corrosion inhibition efficiency of the molecules studied. The chemical

structure is represented at the molecular level by some sets of descriptors that can be mathematically related to experimental properties with the QSPR model.

The values of the different coefficients calculated with the EXCEL software for the different sets of parameters are recorded in the Table 5 and Table 6.

Table 5. Values of coefficients A, B,D and E for different sets of three quantum chemical parameters of TB

Set of Parameters	A	B	D	E
$(\Delta N, S, \eta)$	-50634.6711	825.173994	15064.3687	-17630.7459
(E_{HOMO}, ω, χ)	-8444.21824	-8962.81184	-25147.0664	86630.8341
$(\chi, \Delta E, \eta)$	-38032.6296	-40823.3925	8387.08155	296868.016
$(\Delta E, \mu, \omega)$	-91946.6172	-10275.6085	61640.8762	164395.306
(E_{LUMO}, E_{HOMO}, S)	$-3,2183 \times 10^{13}$	20020.8243	-2.7586×10^{13}	$-5,2735 \times 10^{13}$
$(E_{HOMO}, \mu, E_{LUMO})$	4.78365×10^{12}	-113612.976	-7.17547×10^{12}	1.40233×10^{13}

Table 6. Values of coefficients A, B,D and E for different sets of three quantum chemical parameters of GC

Set of Parameters	A	B	D	E
$(\Delta N, S, \eta)$	37228.31324	75086.89209	2.00745×10^{13}	-3.38596×10^{13}
(E_{HOMO}, ω, χ)	-13244.437	-4112.75771	4023.46079	-70989.16
$(\chi, \Delta E, \eta)$	2642.9473	0.02028987	-1538.32398	-7662.6434
$(\Delta E, \mu, \omega)$	675.280658	1246.48419	-425.049281	-9710.04462
(E_{LUMO}, E_{HOMO}, S)	1091.92515	3703.45848	-716.837928	23439.9296
$(E_{HOMO}, \mu, E_{LUMO})$	-8773.70619	-1214.94513	1908.99351	-35564.9014

The calculated inhibition efficiencies versus the experimental are shown in Figure 3 for TB and Figure 4 for GC.

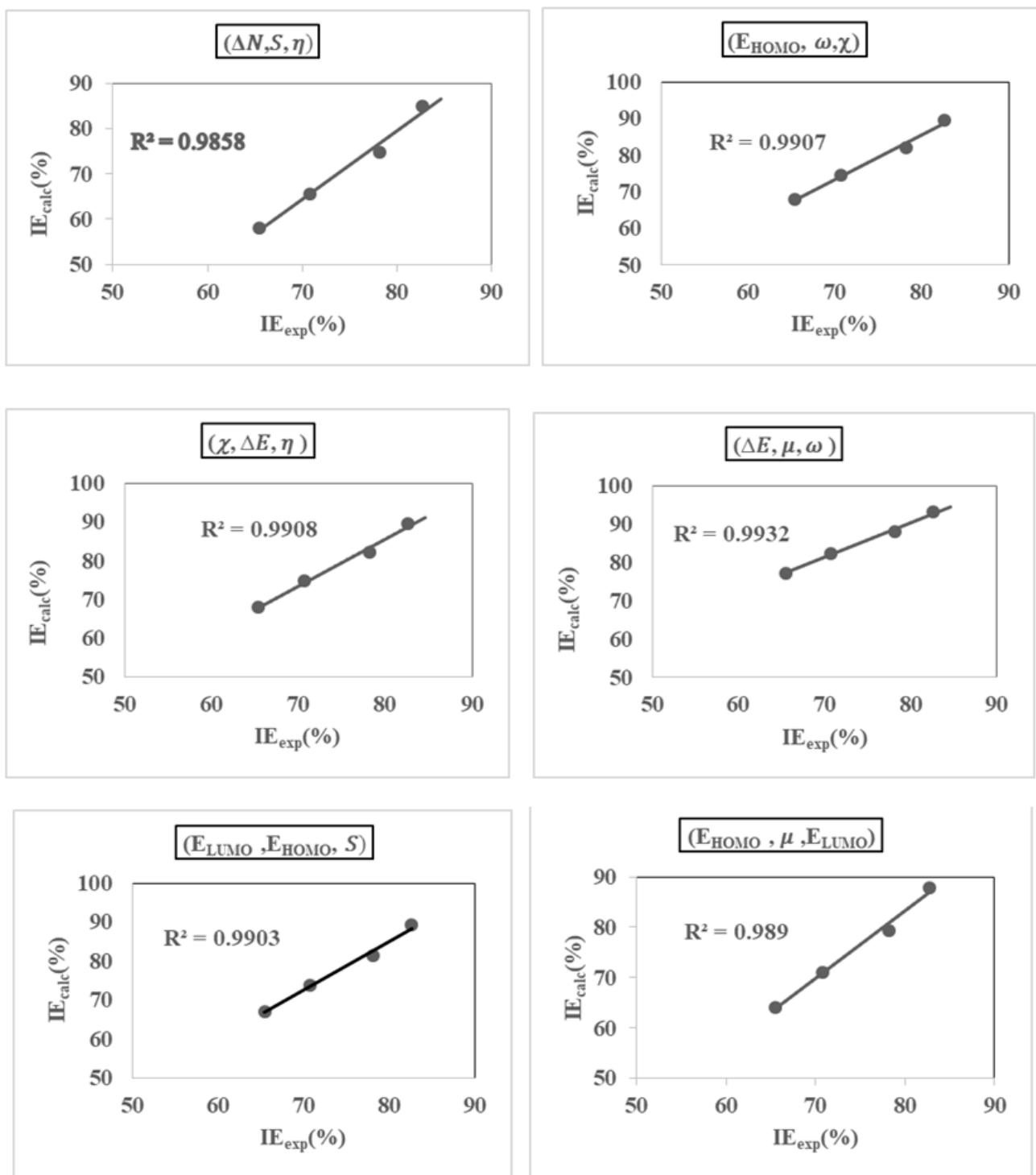


Figure 3. Correlation between calculated and experimental efficiencies of TB for different set of parameters

An examination of Figure 3 and 4 reveals that the correlation coefficients are nearly equal to unity. We are going to analyze some statistical parameters in order to find the set of parameters which best describes the behavior of the molecules.

Three statistical parameters were determined to unambiguously find the best set of parameters. They are expressed as:

The Sum of Square Errors (SSE) :

$$SSE = \sum_{i=1}^N (IE_{exp} - IE_{calc})^2 \quad (18)$$

The Root Mean Square Error (RMSE) :

$$RMSE = \sqrt{\frac{\sum_{i=1}^N (IE_{exp} - IE_{calc})^2}{N}} \quad (19)$$

The Mean Percent Deviation (MPD):

$$MPD = \frac{1}{N} \sum_{i=1}^N \left| \frac{(IE_{exp} - IE_{calc})}{IE_{exp}} \right| \quad (20)$$

The different values of these statistical indicators of TB and GC are recorded in [Table 7](#).

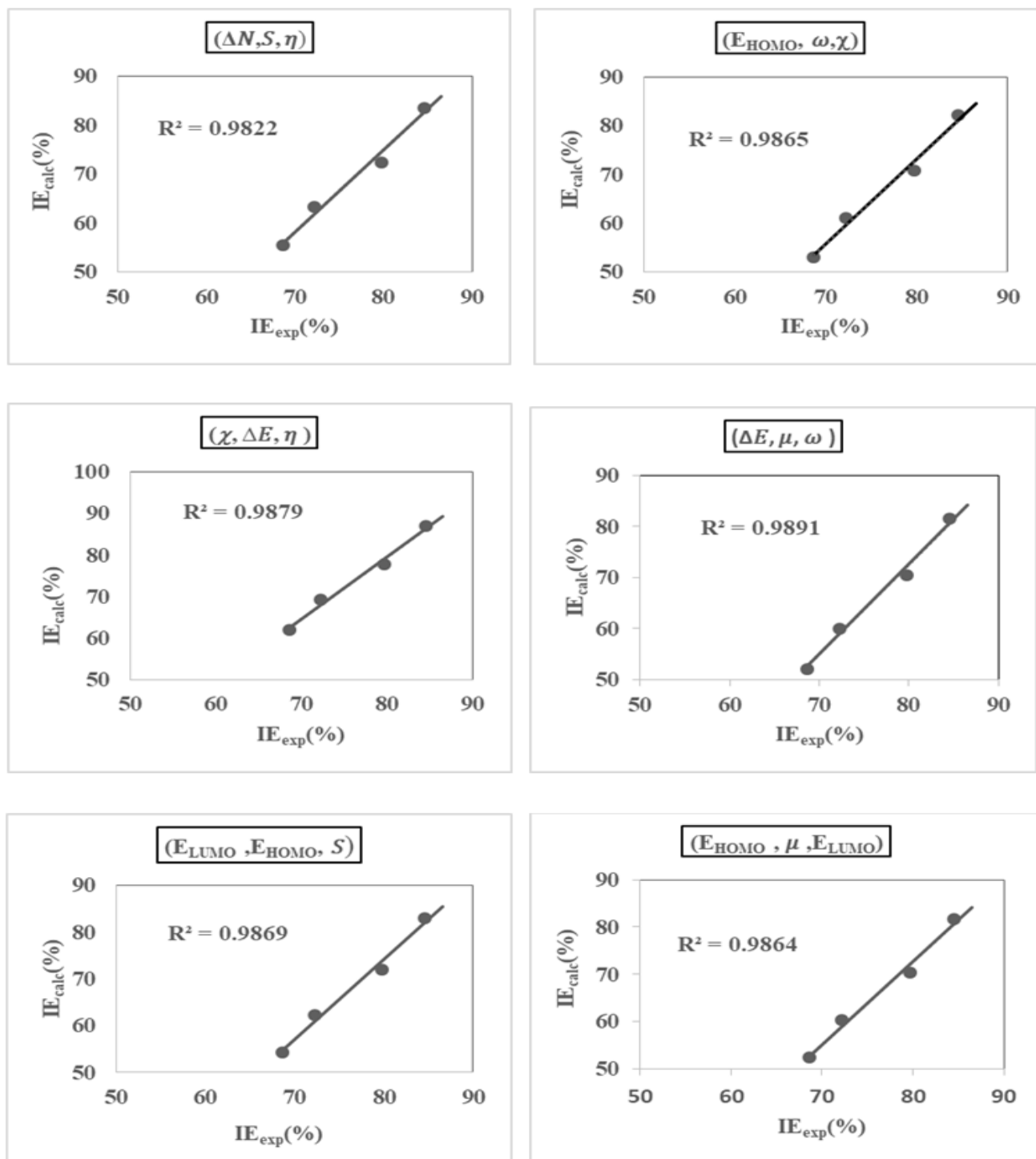


Figure 4. Correlation between calculated and experimental efficiencies of GC for different set of parameters

Table 7. Different values of Statistical parameters of TB and GC

Set of Parameters	TB				GC			
	R ²	SSE	RMSE	MPD	R ²	SSE	RMSE	MPD
($\Delta N, S, \eta$)	0.9858	145.91	6.04	0.079	0.9822	310.91	8.81	0.105
(E_{HOMO}, ω, χ)	0.9907	86.36	4.64	0.057	0.9865	456.65	10.68	0.131
($\chi, \Delta E, \eta$)	0.9908	42.98	3.28	0.003	0.9879	62.58	3.96	0.047
($\Delta E, \mu, \omega$)	0.9932	479.17	10.94	0.149	0.9891	519.53	11.40	0.140
(E_{LUMO}, E_{HOMO}, S)	0.9903	65.05	4.03	0.047	0.9869	367.98	9.59	0.116
(E_{HOMO}, μ, E_{LUMO})	0.9890	30.62	2.77	0.032	0.9864	504.69	11.23	0.139

Analyzing the Table 7, the best set for correlating experimental and theoretical inhibition efficiency for TB and GC is the set of parameters (χ , ΔE , η) because the statistical parameters values SSE, RMSE and MPD of QSPR model are low. This set of parameters will allow to theoretically calculate the inhibition efficiency of each molecule tested, which can guide the experimenter in the practical phase.

Therefore, correlation coefficients alone are not recommended to validate the QSPR model when describing the behavior of a molecule. Statistical parameters need to be combined in order to have a rigorous and complete validation. In this work the set of parameters (ΔE , μ , ω) which has the correlation coefficient closest to the unity (0.9932 for TB and 0.9891 for GC) is not the best set for interpreting the behavior of the inhibitors because the statistical parameters are not the lowest.

4. Conclusion

Within the framework of this work, the following conclusions can be drawn:

1. The two compounds (TB and GC) exhibit a very good performance as inhibitors for aluminium corrosion in 1M HCl
2. GC has the highest inhibition efficiency than TB because it has the highest E_{HOMO} and lowest energy gap.
3. Theoretical and experimental results are in agreement.
4. The electrophilic and nucleophilic attack sites corresponding to the active atoms responsible for the local reactivity of each inhibitor were identified using Fukui functions and the dual descriptor.
5. (χ , ΔE , η) is the best set of parameters for modeling the inhibition efficiency of TB and GC molecules in the studied solution.
6. QSPR model can be used to forecast the inhibition efficiency of an inhibitor because it allows to find the set of parameters capable of predicting the capacity of an organic compound to be an inhibitor.

Acknowledgements

The authors gratefully acknowledged the support of Environmental Training and Research Unit of Daloa (Côte d'Ivoire).and the Laboratory of physical chemistry of Felix Houphouët Boigny university of Abidjan (Côte d'Ivoire).

References

- [1] I. Lukovits, J. Bako, A. Shaban, E. Kalman, "Polynomial model of the inhibition mechanism of thiourea derivatives" *Portugaliae Electrochimica Acta*, 43 (1), 131-136. February 1998.
- [2] F.B. Growcock, W.W. Frenier, P. A. Andreozzi, "Inhibition of steel corrosion in HCl by derivatives of cinnamaldehyde: Part II. Structure-Activity correlations" *Corrosion*, 45, 1007-1015. December 1989.
- [3] A. S. Fouda, A. A. Al Sarawy, F. S. Ahmed, H. M. El-Abbasy, "Corrosion inhibition of aluminium 6063 using some pharmaceutical compounds" *Protection of Metals and Physical Chemistry of Surfaces*, 45(5) 635-643. September 2009.
- [4] G. TrabANELLI, "Inhibitors an old remedy for a new challenge", *Corrosion*, 47(6), 410-419. June 1991.
- [5] M. Abdallah, I. Zaafarany, S.O. Al-Karane, A.A. Abd El-Fattah, "Antihypertensive drugs as an inhibitor for corrosion of aluminum and aluminum silicon alloys in aqueous solutions" *Arabian Journal of Chemistry*, 5(2), 225-234. April 2012.
- [6] A.S. Fouda, G.Y. El-Ewady, K. Shalabi, "Effect of b-blocker inhibitors on aluminum corrosion" *Journal of the Korean Chemical Society*, 55, 268-278. 2011
- [7] Bashir, S., Sharma, V., Kumar, S., Ghelichkhan, Z., Obot, I. B. and Kumara, A. "Inhibition Performances of Nicotinamide against Aluminum Corrosion in an Acidic Medium" *Portugaliae Electrochimica Acta*, 2020, 38 (1), 107-123. January 2020.
- [8] N.O. Eddy, E.E. Ebenso, U.J. Ibok, "Adsorption, synergistic inhibitive effect and quantum chemical studies of ampicillin (AMP) and halides for the corrosion of mild steel in H₂SO₄" *Journal of Applied Electrochemistry*. 40(1) 445-456. October 2009.
- [9] Mamadou Yeo, Paulin Marius Niamien, Ehui Bernadette Avo Bilé, Albert Trokourey, "Thiamine Hydrochloride as a Potential Inhibitor for Aluminium Corrosion in 1.0 M HCl: Mass Loss and DFT Studies" *Journal of Computational Methods in Molecular Design*, 8 (1):13-25. Setember 2018.
- [10] I.B. Obot, N.O. Obi-Egbedi, "Fluconazole as an inhibitor for aluminium corrosion in 0.1 M HCl" *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 330(2-3), 207-212. December 2008.
- [11] I. B. Obot, N. O. Obi-Egbedi, "Inhibitory Effect and Adsorption Characteristics of 2, 3-Diaminonaphtalene at Aluminium/Hydrochloric Acid interface: Experimental and Theoretical Study" *Surface Review and Letters*, 15(06), 903-910. April (2008).
- [12] I. A. Adejoro, D. C. Akintayo, C. U. Ibeji, "The efficiency of chloroquine as corrosion inhibitor for Aluminium in 1M HCl: Experimental and DFT study" *Jordan Journal of Chemistry*, 11(1), 38-49. March 2016.
- [13] H Shi, EH Han, F Liu, "Corrosion protection of aluminium alloy 2024-T3 in 0.05 M NaCl by cerium cinnamate" *Corrosion Science*, 53(7), 2374-2384. July 2011.
- [14] N.A. Wazzan, F. M. Mahgoub, "DFT calculations for Corrosion Inhibition of Ferrous Alloys by Pyrazolopyrimidine Derivatives" *Open Journal of Physical Chemistry*, 4(1), 6-14, February 2014.
- [15] F. Kandemirli, S. Sagdinc, "Theoretical study of corrosion inhibition of amides and thiosemicarbazones" *Corrosion Science*. 49(5), 2118-2130. May 2007.
- [16] D. Wang, S. Li, Y. Ying, M. Wang, H. Xiao, Z. Chen, "Theoretical and experimental studies of structure and inhibition efficiency of imidazoline derivatives" *Corrosion Science*, 41 (5) 1911-1999. May 2007.
- [17] N. O. Eddy, H. Momoh-Yahaya, E. E. Oguzie, "Theoretical and experimental studies on the corrosion inhibition potentials of some purines for aluminium in 0.1 M HCl" *Journal of Advanced Research*, 6(2), 203-217. March 2015.
- [18] P. Hohenberg, W. Kohn, "Inhomogeneous Electron Gas", *Physical Review*, 1964, 136, B864B871.
- [19] W. Kohn, L.J. Sham, "Self - Consistent Equations Including Exchange and Correlation Effects" *Physical Review*, 140 (4A), A1133-A1138. November 1965.
- [20] I. Lukovits, A. Shaban, E. Kalman, "Quantitative structure activity relationships" *Russian Journal of Electrochemistry*, 39(2), 177-181. April 2003.
- [21] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador,

- J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and A. D. J. Fox, Gaussian, Inc., Wallingford, 09.2009.
- [22] W. Yang, R. G. Parr, "Hardness, softness, and the Fukui function in the electronic theory of metals and catalysis" *proceeding of the National Academy of Sciences*, 82(20), 6723-6726. October 1985.
- [23] Jian Fang, Jie li, "Quantum chemistry study on the relationship between molecular structure and corrosion inhibition efficiency of amides" *Journal*, 593(1-3), 179-185. September 2002.
- [24] I. Lukovits, E. Kalman, F., "Corrosion Inhibitors—Correlation between Electronic Structure and Efficiency" *Corrosion (NACE)*, 57(1), 3-8. January 2001.
- [25] Gece, G. and Bilgic, S., "Quantum chemical study of some cyclic nitrogen compounds as corrosion inhibitors of steel in NaCl media" *Corrosion Science*, 51(8), 1876-1878. August 2009.
- [26] Ahamad, I., Prasad, R. and Quraishi, M.A., "Adsorption and inhibitive properties of some new Mannich bases of Isatin derivatives on corrosion of mild steel in acidic media" *Corrosion Science*, 52(4), 1472-1481. April 2010.
- [27] A Singh; KR Ansari; A Kumar; W Liu; C Songsong; Y Liu. "Electrochemical, surface and quantum chemical studies of novel imidazole derivatives as corrosion inhibitors for J55 steel in sweet corrosive environment" *Journal of Alloys and Compounds*. 72, 121-133. July 2017.
- [28] M. Lagren'ee, B. Mernari, N. Chaibi, M. Traisnel, H. Vezin, F. Bentiss, "Investigation of the inhibitive effect of substituted oxadiazoles on the corrosion of mild steel in HCl medium" *Corrosion Science*, 43(5), 951-962. May 2001.
- [29] M. Sahin, G. Gece, F. Karei, S. Bilgic. "Experimental and theoretical study of the effect of some heterocyclic compounds on the corrosion of low carbon steel in 3.5% NaCl medium" *Journal of Applied Electrochemistry*, 38(1), 809-815. February 2008.
- [30] M. K. Pavithra, T. V. Venkatesha, and M. K. Punith Kumar, "Inhibiting Effects of Rabeprazole Sulfide on the Corrosion of Mild Steel in Acidic Chloride Solution" *Hindawi Publishing Corporation International Journal of Electrochemistry*, 2013,1-9. April 2013.
- [31] I. B. Obot, Z. M. Gasem, "Theoretical evaluation of corrosion inhibition performance of some pyrazine derivatives" *Corrosion Science*, 83, 359-366. March 2014.
- [32] Koopmans, T. "Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines Atoms, *Atoms*". *Physica*, 1(1-6), 104-113. 1934.
- [33] Obi-Egbedi N. O., Oboti B., "Inhibitive properties, thermodynamic and quantum chemical studies of alloxazine on mild steel corrosion in H₂SO₄" *Corrosion Science*. 53(1), 263-275. January 2011.
- [34] Saranya J., Sounthari P., Paranswari K., Chitra S. "Adsorption and density functional theory on corrosion of mild steel by a quinoxaline derivative" *Der Pharma Chemica*, 7 (8), 187-196, 2015
- [35] Geerlings P and De Proft F., "Chemical Reactivity as Described by Quantum Chemical Methods" *International Journal of Molecular Sciences*, 3(4), 276-309. April 2002.
- [36] [R. G. Parr, R. G. Pearson, "Absolute hardness: companion parameter to absolute electronegativity" *Journal of the American chemical society*, 105(26), 7512-7516. December 1983.
- [37] Badhin Gómez, N. V. Likhanova, M. A. Domínguez-Aguilar, R. Martínez-Palou, Alberto Vela, José L. Gázquez, "Quantum Chemical Study of the Inhibitive Properties of 2-Pyridyl-Azoles" *Physical Chemistry B*, 110(18), 8928-8934. April 2006.
- [38] R. G. Pearson, "Absolute electronegativity and hardness: application to inorganic chemistry" *Inorganic chemistry*, 27(4), 734-740. February 1988.
- [39] RG Pearson, "Hard and soft acids and bases — the evolution of a chemical concept" *Coordination Chemistry Reviews*. 100, 403-425, 1990.
- [40] A Kokalj; N Kovacevic. "On the consistent use of electrophilicity index and HSAB-based electron transfer and its associated change of energy parameters" *Chemical Physics Letters*, 507(1-3), 181-184, April 2011.
- [41] K.F.Khaled, "The inhibition of benzimidazole derivatives on corrosion of iron in 1 M HCl solutions" *Electrochimica Acta*, 48(17), 2493-2503. July 2003.
- [42] Robert G. Parr, László v. Szentpály, and Shubin Liu, "Electrophilicity Index" *Journal of the American Chemical Society*, 121 (9), 1922-1924. February 1999.
- [43] F. Mendez, J. L., Gázquez, "Reactivity of Enolate Ions: The Local Hard and Soft Acids and Bases Principle Viewpoint". *Journal of the American Chemical Society*, 116(20), 9298-9301. October 1994.
- [44] W. Yang, W. J. Mortier, "The use of global and local molecular parameters for the analysis of the gas-phase basicity of amines. *Journal of the American Chemical Society*, 108(19), 5708-5711. September, 1986.
- [45] Martínez-Araya, J.L., "Why the dual descriptor is a more accurate local reactivity descriptor than Fukui functions?" *Journal of Mathematical Chemistry*, 53, 451-465. February 2015.
- [46] Christophe Morell André Grand Alejandro Toro-Labbé, "New Dual Descriptor for Chemical Reactivity" *Journal of Physical Chemistry. A*, 109(1), 205-212. December 2004.

