

Investigative studies on the inhibitive effects of *Newbouldialaervis* extracts and magnetic fields on copper corrosion in aqueous acidic media

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Abstract:- The inhibitive effects of *Newbouldialaervis* (NL) leaf extract and magnetic field on copper corrosion in 0.5M H₂SO₄ aqueous solution were investigated experimentally by gravimetric technique and theoretically using Quantum Chemical calculations. The results show that both NL and the magnetic field caused reduction in corrosion rate. The inhibition efficiency increased with concentration. The magnetic field caused greater increase in the inhibition efficiency. Temperature increase caused a decrease in inhibition efficiency. The activation energy is low and oscillates, possibly due to error factor from non-linearity of the Arrhenius plot. Among the tested isotherms, Langmuir has the highest correlation coefficient of 0.9963 and 0.7935 with and without magnet field respectively. The magnetic field increased the change in free energy, caused the reaction to become spontaneous, one mole of the inhibitor to replace 4 moles of water mole while reducing the number of monolayer of the inhibitor on the metal. The quantum chemical calculations performed on *newbouldiaquinone* and *lapachol* constituents of NL showed that *lapachol* contributed more to the inhibition efficiency due its low binding energy, high dipole moment, chemical softness and fractional electron transfer. The magnetic field and temperature played opposite roles.

Keywords: Copper, *Newbouldialaervis*, Magnetic field, Inhibition Efficiency, Quantum Chemical Calculation

I. Introduction

Copper is extensively used in various industrial and domestic applications due to its favourable high electrical and heat conductivities. The usage includes in electronics for metallization, wire production, heat sink; heat exchanger systems and other electrical appliances [1]. In all these applications the metal is found to be exposed to myriad environmental conditions which adversely affect its physical and chemical properties despite its corrosion resistance under atmospheric conditions. The need to mitigate or control the degradation of copper metals exposed to aggressive conditions has been a subject of study and has attracted many researcher and various inhibitors have been under investigation. These include inorganic inhibitors [2], organic inhibitors of azole derivatives [3-10], amines [11-14]; amino acid [15-16] and green organic inhibitors [17-19]. The inhibitive actions of the various organic molecules and compounds are favoured by the various organic heteroatoms of nitrogen, sulphur, phosphorous and oxygen in the molecules and multiple of bonds or aromatic rings in their structures [1, 19- 20]. Other contributing factors are the molecular chain length, size, and the strength [19]. The underling effects of the inhibition of copper corrosion by organic compounds is attributed to the presence of the vacant d orbital in copper atom that forms coordinative bonds with atoms which are capable of donating electrons and the interaction between the metal and the compounds containing conjugated bonds and π - electrons. Many a times, the consideration in the application of an inhibitor apart from the efficacy is its suitability in terms of low level of toxicity, cheapness and availability, eco-friendliness, and renewable. For these reasons, the studies of bio-gradable substances have become viable options. [21-25]. *Newbouldialaervis* from which *lapachol* and *newbouldiaquinone* are derived is under current investigation. *Lapachol* has been investigated to possess moderate herbicidal, anti-fungal, and antibacterial properties while *newbouldiaquinone* possesses antibacterial properties [26]. The current study involves (i) the gravimetric investigation of the 0.5MH₂SO₄ acid corrosion of copper in both blank and with the extract *newbouldialaervis* in the presence of magnetic fields and (ii) a Quantum Chemical calculations on *lapachol* and *newbouldiaquinone* to determine their contributions to the efficacy of the *newbouldialaervis* extract in the corrosion inhibition.

II. Methodology.

2.1 Materials

A polycrystalline copper (99.9%) coupons of dimensions 0.5x2x5 cm in which a hole of diameter 0.5cm was drilled was used. Before all measurements, the coupons were polished successively with metallographic emery paper between (600 and 1200) grits, then washed with doubly distilled water, degreased with acetone and again washed using distilled water and finally allowed to dry in air at room temperature.

2.2. Corrodent Preparation

0.5M sulphuric acid was prepared from 98% purity concentrated sulphuric acid obtained from Fin Lab. Nigeria Ltd. From which 300ml was introduced in the beaker for the experiments.

2.3 Inhibition Preparation

A stock solution of the inhibitor was prepared by refluxing 20g of the dried *Newbouldialaevis* leaf powder with 300ml of the dilute 0.5M H_2SO_4 for three hours. Then the refluxed solution was allowed to cool and filtered using weighed handkerchief. From the solution different concentrations of (7.0×10^{-3} to 6.0×10^{-2} M) were obtained.

2.4 Gravimetric Technique

The pre-weighed copper specimens (in triplicate) were suspended for two hours in the 0.5M H_2SO_4 in both blank and after different concentrations of the inhibitors were introduced. This process was repeated for the presence of magnetic fields provided by the laboratory constructed electromagnet which produced magnetic field of flux density of about 0.2T. The effect of temperature was investigated by dipping both the blank and the inhibited solution in water bath for two hours. After the two hours, the coupons were removed, washed with the distilled water, dried in air, and re-weighed. The weight loss was determined from the difference between the initial weight w_1 and the final weight w_2 . The corrosion rate was obtained using equation (1)

$$\rho = \frac{kW}{A t} \quad (1)$$

Where w is the weight loss, A is the exposed area, t is the time of exposure, and k is constant given as 3.16×10^6 to give ρ in mm/y.

And a number of authors have used the inhibition efficiency expressed [7, 27] as (2):

$$IE = \left(\frac{\rho_0 - \rho_1}{\rho_0} \right) \times 100 \quad (2)$$

The surface coverage as:

$$\theta = \left(\frac{\rho_0 - \rho_1}{\rho_0} \right) \quad (3)$$

Where ρ_0, ρ_1 are the corrosion rates of the blank and the inhibited samples.

III. Results and Discussions

3.1 Corrosion rate

3.1.1 Comparison of the effects of heat on the blank and inhibited samples of copper in 0.5M H_2SO_4 acid solution.

The corrosion rates for the blank and inhibited samples between 30 $^{\circ}C$ and 60 $^{\circ}C$ at different concentrations are presented in Fig. 1. The corrosion rate for all the blank coupons increased progressively with temperature, between the temperatures 30 $^{\circ}C$ and 60 $^{\circ}C$. In all the inhibited samples, the corrosion rate decreased with increase in concentration but increased with temperature.

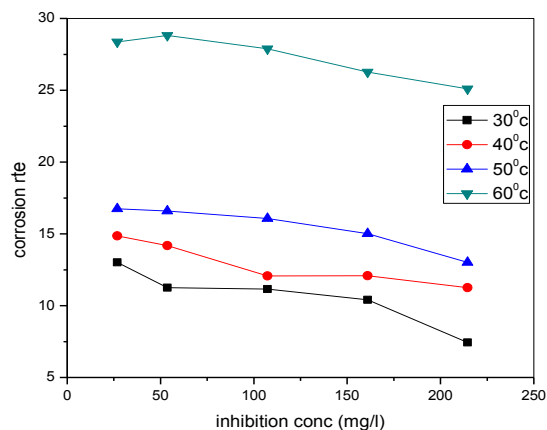


Fig1: Shows the variation of corrosion rate with inhibitor concentration at different temperatures.

The graphs plotted in figure 1 shows a jump in corrosion rate after the 50°C. This points to the fact that the inhibitor was able to reduce corrosion processes within the temperature range of 30°C and 50°C, but above these temperatures, there may have been weakened of the interaction forces between the metal surface and the inhibitor molecules and the inhibitor molecules themselves. Therefore the application of heat energy goes to destroy the electrostatic interaction forces between the positively charged metal surface and the negatively charged inhibitor molecules [28].

3.1.2: The corrosion processes in the presence and in the absence of magnetic for the inhibited samples.

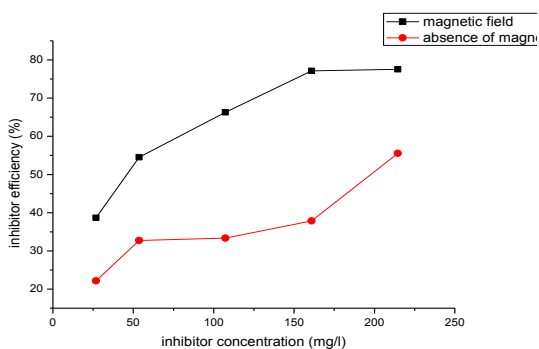


Fig.2: Shows the graph of inhibition efficiency against concentrations in presence and in the absence of Magnetic fields for 2hours exposure in copper corrosion in 0.5MH₂SO₄ sulphuric acid solution.

Table1: presents the variation of inhibition efficiency and inhibitor concentration, (Conc.) for the blank and inhibited samples in presence, (PMF) and in the absence, (AMF) of magnetic fields.

	Inhibition efficiency	
	AMF	PMF
Blank	-	1.1
	Inhibited samples	
Conc. (mg/l)		
26.86	22.18	38.69
53.64	32.72	54.51
107.28	33.33	66.29
160.92	37.84	77.15
214.56	55.56	77.53

From the table 1, column 2 gives the inhibition efficiency in the absence of magnetic fields for 2 hour exposure in 0.5M sulphuric acid corrosion of copper in different inhibitor concentrations. It can be seen that the inhibition efficiency increased with concentration of the inhibitor. The third column shows the blank and the inhibited samples in the presence of magnetic fields. It can be observed that the magnetic fields have very little effects

causing of 1.1% efficiency. For the inhibiting coupons that were exposed to magnetic fields, it is particularly interesting to note that efficiency increased with concentration and the efficiency is higher than in the inhibited and in the absence of magnetic fields. This means that the magnetic fields increase the corrosion resistance for the inhibited samples, hence increase in efficiency. This increase may be attributed to the role of magnetic fields in enhancing the attractive forces between the inhibitor molecules and the surface of the corroding metal. These result to the formation of well-oriented and well-ordered chains of aligned molecules on the surface of the metal. This interaction prevented corrodent penetration, hence increase in corrosion inhibition. Comparing the results of the last section and the present, it can be inferred that the magnetic energy is playing an opposing roles with the thermal energy.

3.2 Kinetic and Thermodynamic corrosion parameters.

The data obtained when the corroding systems were subjected to temperatures between 30⁰C and 60⁰C are fitted into Arrhenius equation so as to determine the pre-exponential factor, A and the apparent activation energy, E_{ac} , using the following relationship:

$$\ln R_c = \ln A - \frac{E_{ac}}{kT} \tag{4}$$

Where R_c is the corrosion rate, A, is the pre-exponential factor, E_{ac} , is the apparent activation energy for the corrosion process and T is the absolute temperature, k is the Boltzmann constant. The plot of $\ln R_c$ against T^{-1} is shown in the figure3 below.

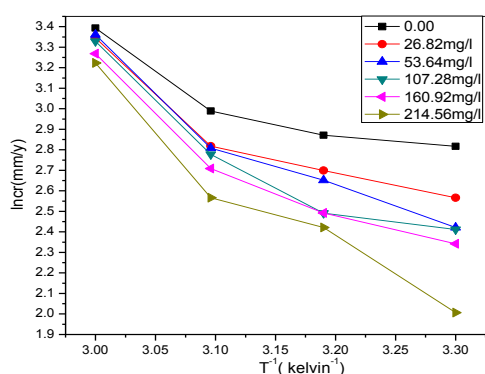


Fig. 3: The graph of $\ln R_c$ against T^{-1} for copper corrosion for blank and inhibited in 0.5M H_2SO_4 solution between 30⁰C and 60⁰C.

These graphs were analyzed for linear relationship between the $\ln R_c$ and T^{-1} , the regression coefficient, R^2 was very low, then when polynomial fitting was applied the regression coefficient, R^2 close 1 was realized and the results are shown on the table 2.

Table 2: shows the intercept value, (IV), slope, B_1 , the apparent activation energy, correction factor, B_2 on the activation energy and R^2 values of the Arrhenius plot for the blank and inhibited samples for copper corrosion in 0.5M H_2SO_4 within 30⁰C and 60⁰C.

	IV	B_1	E_{ac}	B_2	R^2
Blank	92.47	-59.00	-409.59	9.12	0.9460
Inhibited					
Conc.					
26.82	106.41	-67.34	-559.93	10.34	0.9460
53.64	84.54	-52.91	-439.95	7.97	0.9505
107.28	123.55	-77.70	-646.08	11.90	0.9994
160.92	113.99	-71.72	-596.35	10.96	0.9726
214.56	75.97	-46.81	-389.23	6.87	0.8722

The table shows that B_1 which represents the apparent activation energy, E_{ac} , is low and oscillates. This indicates that the reaction process of the corroding system is not only concentration dependent rather it depends also on the temperature. The fourth column B_2 is an additional parameter which may be regarded as a correction factor or deviation factor and is a function of the temperature. The last column is the regression coefficient R^2 , which gives a high correlation between the experimental data with the Arrhenius equation. With this result shows that a modify Arrhenius equation may be proposed as:

$$R_C = Ae^{[-\frac{E_{ac}}{RT} + \frac{B}{RT^2}]} \quad (5)$$

B is the correction factor on the activation energy.

In this corroding system, the trend of activation energy does not correspond to the trend of the changes in corrosion rate, large values of activation energy does not correspond to low values of corrosion rate. This substantiates the fact that the corrosion activities in this system may not only be concentration dependents. More so, the presence of the correct factor indicates that other physical properties can be explored.

3.3 The Isotherms

To further analyze the obtained data the following isotherms Langmuir, Temkin, Frumkin, Damaskin-Parson and Flory-Huggin are carefully fitted to determine the isotherm with highest regression coefficient, R^2 that can be used to represent the corrosion processes in both absence and in the presence of magnetic fields. The general formula used to describe these isotherms is given [14]:

$$f(\theta, x) \exp(-2a\theta) = KC \quad (6)$$

Where $(f(\theta, x))$ is configuration factor, θ , the surface coverage, C , the inhibitor concentration, K is the adsorption constant and a is the molecular interaction parameter. The adsorption of the inhibitor molecule, (NBL) and the number of moles of water displaced can be represented [8]:



And the Gib's free energy can be determined from

$$-\Delta G = RT \ln(55.5K) \quad (8)$$

Where χ is the number of water molecules displace by the inhibitor. R , is the gas constant. 55.5 is water concentration in the solution in mol/L.

The data in table 1 were used to determine which isotherm that has the best fit. The results of the following isotherms:

Langmuir, Temkin, Frumkin, Flory-Huggin, and Damaskin-Parson [7] were obtained and are presented in table 3.

Table 3: Comparison of the Langmuir, Temkin, Frumkin, Flory-Huggin, and Damaskin- Parson isotherms for inhibited copper corrosion 0.5MH₂SO₄ solution (a) in the absence (b) in the presence of magnetic fields.

(a) Absence of magnetic fields

	Slope	Intercept	R ²
Langmuir	1.6153	101.681	0.7935
Temkin	0.1269	-0.202	0.6886
Frumkin	1.6959	4.452	-0.0346
Flory-Huggin	-1.8834	4.656	0.3274
Damaskin-Parson	--	--	---

(b) Presence of magnetic fields

	Slope	Intercept	R ²
Langmuir	1.0864	40.563	0.9963
Temkin	0.1935	-0.238	0.9800
Frumkin	0.7022	3.4669	0.4212

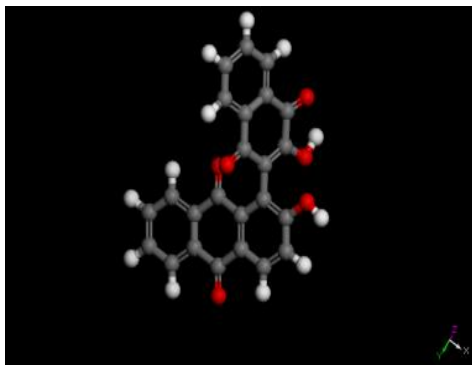
Flory-Huggin	-1.2607	3.630	0.9546
Damaskin-Parson	-7.1608	5.206	0.9581
($\chi = 4$)			

From the data presented in table 3, the effects of magnetic field (b) have distinguishing features in the coefficient of regression, the slope, and the intercepts. The regression coefficients are very low in the absence of magnetic fields, implying high randomness and deviation of the experimental data from the theory; however, data obtained for the case of the presence of magnetic field have very high regression coefficients. This means that the presence of magnetic fields reduce the degree of randomness and the experimental data fitted very well to the theory, these bring out the effects of magnetic fields on the corrosion process. The magnetic field might have caused reduction in the randomness of the corrosion activities by increasing the amount of cohesive forces between the molecules.

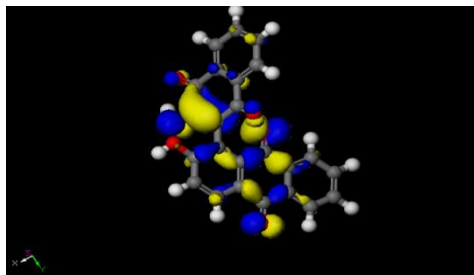
Remarkably, the slope of the Langmuir isotherm shows that in the presence of magnetic fields, one monolayer of the inhibitor molecule is adsorbed compare with approximately two monolayers for the case of absence of magnetic fields. The implication is that the application of magnetic fields reduces the amount of energy (inhibitor) used, hence causing increase in the inhibition efficiency. Considering the Damaskin- Parson isotherm, there are no results in the case of absence of magnetic fields, but in the presence of magnetic fields, it is noticed that the number of water molecules displaced by a molecule of the inhibitor is 4. This is an indication of the effect of the magnetic field on the inhibition by newbouldialaavis extract on corroding copper in 0.5M H₂SO₄ aqueous solution. This implies that the magnetic fields facilitated the inhibition process. Furthermore, comparing the values of the regression coefficient for the absence and presence of magnetic fields, it can be observed that in the presence of magnetic fields, the coefficients of regression have higher values. It can be noticed that for the Frumkin isotherm, the coefficient of regression changed from negative value in the absence of magnetic field to positive value in the presence of magnetic fields. This implies improvement in the quality due to the application of magnetic field. Another effect of magnetic field on the inhibited corrosion of copper in 0.5M H₂SO₄ solution can be deduced from the value of free energy of the corrosion, this is calculated as [8] using equation (8). The change in free energy can be used to assess the spontaneity and direction of the corrosion reaction taking place in the copper corrosion. For the case without magnetic field, $\Delta G = 1.51 \text{ kJ/Mol}$, while in the presence of magnetic field it is -0.783 kJ , these values show that the magnetic field caused the reaction to change from nonspontaneous to spontaneous, but did not change the nature of the reaction, both are physically adsorbed, since $\Delta G \leq -20 \text{ kJ/mol}$. The results from the isotherms indicate enhancement in the attractive interaction between the inhibitor molecules and the corroding system due to the presence of magnetic fields. These may have been as a result of well aligned molecules of the inhibitors, which resulted in the improvement of the quality of the inhibition and hence in higher regression coefficient due to application of magnetic fields. The results discussed are in accordance with the observations made by Maayta, *et al* [28] as they discussed the effects of magnetic field on corrosion of iron using linear Alkyl benzene sulphonate in the presence of magnetic field.

3.4 Quantum Chemical Calculations on *Lapachol* and *Newbouldiaquinone*.

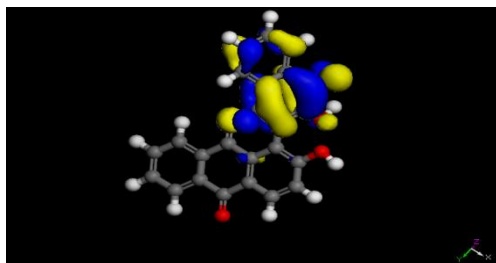
Quantum chemical calculations were performed on *lapachol* and *newbouldiaquinone* constituents of *newbouldialaavis* in order to compare their roles and contributions to the efficiency of the inhibitor materials on the corroding system. The structures and optimized structures are shown in figures 4 and 5.



(i)

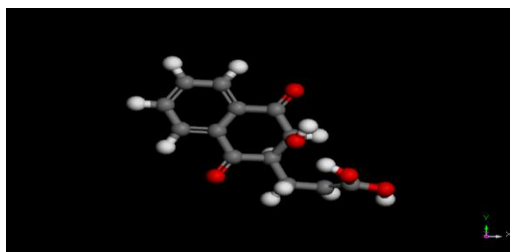


(ii)

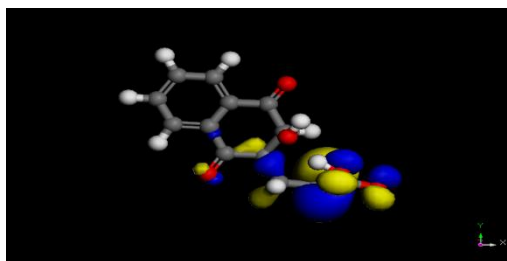


(iii)

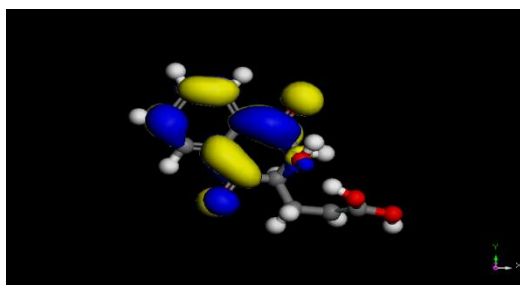
Fig4 shows the (i) structure, (ii) HOMO and (iii) LUMO of *newbouldiaquinone*.



(i)



(ii)



(iii)

Fig. 5 shows the (i) structure (ii) HOMO (iii) LUMO of *lapachol*

In figure 4 is presented (i) structure, and the optimized structures (ii) HOMO and (iii) LUMO of *Newbouldiaquinone* and Figure 5 is presented (i) the structure and optimized structures (ii) HOMO and (ii) LUMO of *lapachol*.

Table 4: shows the results of the quantum chemical calculations performed on *newbouldiaquinone* and *lapachol*.

Properties	<i>Lapachol</i>	<i>Newbouldialaevis</i>
E _{HOMO} (eV)	-4.766	-5.635
E _{LUMO} (eV)	-3.655	-3.914
Dipole moment (D)	4.575	1.686
Energy gap (eV)	-1.111	-1.721
Chemical softness	0.901	0.578
Fractional Electron Transfer	0.286	0.171

The quantum chemical calculations were performed on *newbouldiaquinone* and *lapachol* using DMol 3, version 7 of Materials Studio. The quantum chemical data: dipole moment, binding energy, chemical softness, fractional electron transfer, energy of highest occupied molecular orbit (E_{HOMO}), energy of the lowest unoccupied molecular orbit, (E_{LUMO}) are some of the properties that can be used to describe or predict direction of corrosion inhibition processes. According to the frontier orbital theory, E_{HOMO} is often associated with the electron donating ability of a molecule. High values of E_{HOMO} indicate a tendency of a molecule to donate electrons to appropriate acceptor molecules with low energy and empty electron orbital. Also, E_{LUMO}, represents the ability of a molecule to accept electrons. The lower the E_{LUMO} value, the more likely it is for the molecule to accept electrons [29]. In addition, the energy gap, (ΔE), the difference between E_{LUMO} and E_{HOMO} is another important parameter to be taken into consideration, it has been reported that low values of energy gap provides good inhibition efficiency since electrons will take least energy to react, [29]. From the data in table, *Newbouldiaquinone* has higher E_{HOMO}, *Lapachol* has lower E_{LUMO}, it then means that *Newbouldiaquinone* has more donating capability, while *lapachol* is more capable of accepting electrons. Energy gap is an important stability index; a large energy gap implies high stability for a molecule in a chemical reaction. This means that molecules with low energy gap will react faster in the chemical reaction. Applying this to the two molecules under consideration, it means that *lapachol* with energy gap of -1.111eV would readily react than *newbouldiaquinone* with energy gap of -1.721eV since in the reaction; electrons will take less energy to surmount the energy gap.

Dipole moment is defined by the product of a charge and distance of its separation from an opposite charge, and it measures the polarizability in a bond and it relates to the distribution of electron in a molecule [30]. Ebenso, *et al* (2010) [30] observed that increase in inhibition efficiency is related to high dipole moment; this may be used as an indication that *lapachol* which has higher dipole moment 4.575D may have contributed more to the inhibition efficiency than *newbouldiaquinone*.

Another important parameter to be considered is fractional electron transfer, ΔN. The number of electrons transferred from an inhibitor to a corroding metal surface determines the capacity of such inhibitor molecule to donate or accept electrons to/ from the corroding metallic surface; this causes the metal to participate in chemical reaction and therefore prevents the metal from further corrosion. From table 4, the fractional electron transfer for *lapachol* and *newbouldiaquinone* is 0.286 and 0.171 respectively. This implies that *lapachol* provides more electrons than *newbouldiaquinone*. The fractional electron transfer is given as [31]:

$$\Delta N = \frac{\chi_{Cu} - \chi_{inh}}{2(\eta_{Cu} + \eta_{inh})} \quad (9)$$

Where χ_{Cu} and χ_{inh} denote the absolute electronegativity of copper and inhibitor molecules respectively; η_{Cu} and η_{inh} denote the absolute hardness of copper and the inhibitor molecules respectively. These quantities relate to electron affinity, (A) and ionization potential, (I) which are useful to predict chemical behavior, [31]. The absolute electronegativity (χ) and absolute hardness for the inhibitor are calculated from equations (10) and (11) below.

$$\chi = \frac{I+A}{2} \quad (10)$$

$$\eta = \frac{I-A}{2} \quad (11)$$

I and A are related to E_{HOMO} and E_{LUMO} as:

$$I = -E_{HOMO} \quad (12)$$

$$A = -E_{LUMO} \quad (13)$$

Values of χ and η are calculated by using the values of I and A obtained from quantum chemical calculations for the inhibitor. Using the theoretical values of χ value of 4.48eV/mol. and η of 0eV/mol. for copper and the calculated values for the inhibitors from table 4 on equation 7, then ΔN for *lapachol* and *newbouldiaquinone* are 0.286 and 0.171 respectively.

This again buttresses the fact that *newbouldiaquinone* will transfer less electrons than *lapachol* since the later has higher fractional electron transfer of 0.286 compare with 0.171 for *newbouldiaquinone*. However, ΔN for the two molecules is less than 3.6, which Al-Mobarak, et al [32] observed as the maximum value for inhibition efficiency to increase with increasing electron donating ability at the metal surface.

Chemical softness for a molecule is a measure of the readiness of the molecule to participate in a chemical reaction, this indicates that *lapachol* with chemical softness 0.901 compare with 0.578 for *newbouldiaquinone* is more readily reactive and in competition will participate more readily on the surface of the corroding copper in order to inhibit further deterioration. In conclusion, the quantum chemical data supports the fact that *lapachol* molecule would contribute more than *newbouldiaquinone* to the reduction of copper corrosion in 0.5H₂SO₄ aqueous solution. From the discussion on the quantum chemical calculations, it is evident that *lapachol* might have contributed more to the inhibition efficiency of the *newbouldialaevis*.

The effects of the magnetic fields on the inhibition process can be explained by using the properties determined from quantum chemical calculations. The dipole moment is the product of a charge and the distance of separation of the charges in an atom or molecule. Any process which can cause an adjustment on the alignment of the dipole on the surface of the corroding metal surface would facilitate an increase in the inhibition process. The magnetic field acts on the dipole such that it aligns the charges on the metal thereby providing the needed charge type at the required point and this results to increase in the inhibition efficiency. This explains the graph on figure 2, which shows an increase in the inhibition efficiency in the presence of magnetic fields.

IV. Conclusions

Experimental investigations on the inhibitive effects of *newbouldialaevis* extracts and magnetic fields on copper corrosion in aqueous media of 0.5M sulphuric acid using weight loss shows that the plant extract provided high level of inhibition. The inhibition efficiency increases with inhibitor concentration. The inhibition efficiency decreases with increase in temperature, the rate of change is low within the temperature range of 30°C and 50°C, after which it increase very rapidly. The analysis of the data obtained using the Arrhenius equation revealed the need for correction factor in the value of the activation energy. This is a source for further investigations. Among the isotherms tested, Langmuir has the best fit.

The magnetic fields increased the efficiency of the inhibitor even when there was very negligible efficiency in the blank. This is the evidence that the magnetic fields acted more on the interaction between inhibitor and the corroding metal. The quantum chemical computation revealed that *lapachol* contributed more to inhibition efficiency than *newbouldiaquinone* considering their energy gaps, dipole moments, chemical softness and electron transfer abilities. The computational investigation is ongoing as other constituents of *newbouldialaevis* shall be studied.

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