

Computational and Experimental studies on the inhibitive effects of *Newbouldia laevis* extract and Magnetic fields on copper corrosion in aqueous acidic media

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ABSTRACT. A polycrystalline copper (99.99%) coupons of dimension 1x2x5 cm in which a hole of diameter 0.5cm 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.

Explanation of the effects of magnetic fields on inhibition process using the chemical quantum calculations. The dipole moment is the product of a charge and distance of separation of the charges in an atom or molecule. Any process which can cause change in the alignment of the dipoles on the surface of the corroding metal systems can facilitate an increase in inhibition process. The magnetic field acts on the dipoles such that it aligns the charges on the metal thereby providing the needed charge types at the required point. This explains the graph on figure 1 which shows an increase in inhibition efficiency in the presence of magnetic fields.

1. INTRODUCTION

Copper is extensively used in various industrial and domestic applications due to its favorable high electrical and heat conductivities. The usage includes in electronics for metallization, wire production, heat sink; in heat exchanger system and in 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 researchers and various inhibitors have been under investigation. These include inorganic inhibitors [2], organic inhibitors of azole derivatives [3-10], amine [11-14], amino acid [15 -16] and green organic inhibitors [17- 18]. The inhibitive actions of the various organic molecules and compounds are favoured by the various organic heteroatoms of nitrogen, sulphur, phosphorous, and oxygen in molecules and multiple of bonds or aromatic rings in their structures [1, 19, 20]. Other contributing factors are the molecules 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 interaction between the metal and 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 readily available, eco-friendliness, and renewable. For these reasons, the studies of biodegradable substances have become viable options. [21-25]. *Newbouldia laevis* from which lapachol and newbouldia quinone are derived is being investigated. Lapachol has been investigated to possess moderate herbicidal, antifungal, and antibacterial properties while newbouldia quinone possess antibacterial properties [26]. This study involves (i) the gravimetric investigation of the 0.5M H_2SO_4 acid corrosion of copper in both blank and with the extract of *newbouldia laevis* in the presence of magnetic fields and (ii) a Quantum chemical calculations on

lapachol and newbouldia quinone to determine their contributions to the efficacy of the newbouldia laevis extract in the corrosion inhibition.

2. METHODOLOGY

2.1: Materials

A polycrystalline copper (99.99%) coupons of dimension 1x2x5 cm in which a hole of diameter 0.5cm 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 all the experiments.

2.3: Inhibition Preparation

A stock solution of the inhibitor was prepared by refluxing 20g of the dried Newbouldia laevis power with 300ml of 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 (7.0×10^{-3} to $6.0 \times 10^{-2}M$) 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 concentration of the inhibitors were introduced. This process was repeated for the case of the presence of the magnetic fields provided by the laboratory constructed electromagnet that produced flux density of about 0.2T. The effect of temperature was investigated by dipping both the blank and inhibited solutions in water bath for two hours. After the two hours, the coupons were removed from the tests, the weight loss was determined from the difference between the initial weight, w_1 and the final weight, w_2 after the exposed time t and the corrosion rate ρ calculated using equation 1.

$$\rho = \frac{kw}{At} \quad (1)$$

Where A is the area of the exposed coupons and k is a constant given as

3. RESULTS AND DISCUSSIONS

3.1 Corrosion rate

3.1.1 Comparism 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 blank and inhibited samples at $30^\circ C$ and between $40^\circ C$ and $60^\circ C$ at different concentrations are presented in figure 1. The corrosion rate for all the blank coupons increased progressively with increase in temperature, between the temperatures $30^\circ C$ and $60^\circ C$. For all the inhibited samples, the corrosion rate decreased with increase in concentration, but it increased with the increase in temperature.

There was a jump in corrosion rate after the $50^\circ C$. This points to the fact that the inhibitor was able to sustain the corrosion processes within the temperatures of $30^\circ C$ and $50^\circ C$, but above these temperatures, there may have been weaken of the interaction forces between the metal surface and the inhibitor molecules and the inhibitors themselves.

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

The application of heat goes to destroy the electrostatic interaction forces between the positively charged metal surface and the negatively charged centers of the inhibitor molecules Maayta et al, 2010.

3.1.2 In the presence of magnetic fields

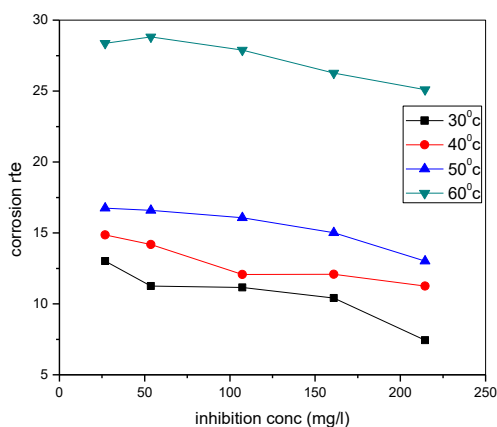


Fig.1

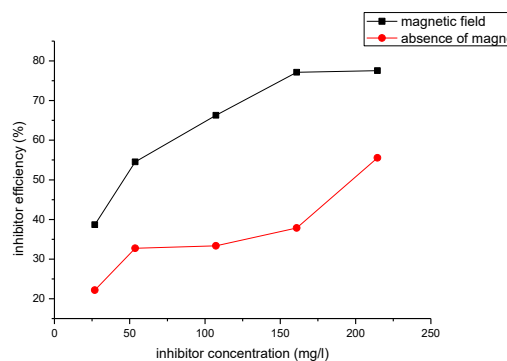


Fig. 2

Table 1 and figure2 show the effects of the application of magnetic fields on both the blank and inhibited corroding samples of 0.5M sulphuric acid environment for two hour duration at room temperature of 30°C.

Table 1: Shows the inhibition efficiency for blank and different inhibitors concentrations of copper coupons in presence and absence of magnetic fields.

Inhibition efficiency %	Inhibitor concentration (mg/l)	
	Without magn. Fields	with magn. fields
Blank	-	1.1
In the inhibitor		
Conc. (mg/l)		
26.82	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, column 2 gives the inhibition efficiency in the absence of magnetic field for 2hours in 0.5MH₂SO₄ corrosion of copper in different inhibitor concentrations. It can be seen that the efficiency increases with increase in the 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 caused an efficiency of 1.1% for the blank, this is negligible. For the inhibited coupons that were subjected to magnetic fields shows increase in the efficiency more than without magnetic fields. It is particularly interesting to note that the efficiency in the presence of magnetic fields for the inhibited system is higher than in the absence of magnetic fields. This means that the magnetic fields increase the corrosion rate resistance for the inhibited coupons, hence increase in efficiency. This increase could be attributed to the role of magnetic fields in the formation of well-oriented, and well-ordered chains of the aligned molecules on the metal surface. The interaction prevented corrodent penetration, hence increase in the corrosion inhibition.

3.2: The kinetic and thermodynamic corrosion parameters

The thermal corrosion data is presented in figure by the plot of the Arrhenius equation to determine the pre-exponential factor A and the apparent activation energy E_{ac} , using the following relationship[]

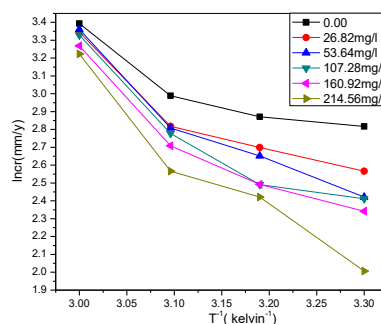


Fig. 3

$$\ln R_c = \ln A - \frac{E_{ac}}{RT} \quad (2)$$

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. The plot of $\ln R$ against T^{-1} gives the result presented in table

Table: 2 The values intercept, slope, B_1 and correction factor, B_2 and R^2 values of the Arrhenius plot for the blank and inhibited samples for 0.5M sulphuric acid solution.

	Intercept	slope, B_1	correction error, B_2	R^2
Blank	92.46917	-58.9967	9.12153	0.9460
Inhibitor (mg/l)				
26.82	106.40695	-67.34317	10.34861	0.9028
53.64	84.54445	-52.91143	7.96932	0.9505
107.28	123.54983	-77.69776	11.89617	0.9994
160.92	113.98552	-71.71849	10.95732	0.9726
214.56	75.93777	-46.80837	6.87367	0.8722

The table shows that the obtained values of intercept, the slope, B_1 , correction error, B_2 , regression coefficient R^2 , when the experimental data for the blank and the inhibited at various concentration

were fitted in the Arrhenius equation, the linear fitting gave a very low regression co-efficient R^2 , to obtain a higher value of R^2 , polynomial fitting was applied and the result is show on the last column of the table.

The results show that 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 depends also on the temperature. The fourth column shows an additional parameter $B(T)$ which is a function of temperature. This additional parameter may modify the Arrhenius equation as

$$R_c = Ae^{[-\frac{E_{ac}}{RT} + \frac{B}{RT^2}]} \quad (3)$$

In this corroding system, the trend of activation energy E_{ac} does not correspond to the trend of changes in corrosion rate, large values of activation energy does not correspond to low values of corrosion. This substantiates the fact the corrosion activities in the system may not only be said to be solely inhibitor concentration dependent.

3.3 Isotherms

The obtained data were fitted into Langmuir, Temkin, Frumkin, Damaskin-Parson and Flory-Huggin in order to determine the isotherm that best describes the corrosion process in both absence and presence of magnetic fields. The obtained results are presented in the table 3

Table:3 The various tested isotherms, their intercepts, slope and coefficient R^2 .

	Absence of magnetic field			presence of magnetic fields		
	R^2	slope	intercept	R^2	slope	intercept
Langmuir	0.7935	1.6153	101.681	0.9963	1.0864	40.5635
Temkin	0.6886	0.1269	-0.2024	0.9800	0.1935	-0.2387
Frumkin	-0.0346	1.6959	4.4517	0.4212	0.7022	3.4669
Flory- Huggins	0.3274	-1.8834	4.6556	0.9546	-1.2607	3.6300
Damaskin-Parson -----				0.9581	-7.1608	5.2061

[for (x=4)]

From the data presented in table 3, the effects of magnetic fields have distinguishing features in the coefficient of correlations, the slopes and the intercepts. These values are very low in the absence of magnetic fields than in the presence of magnetic fields. These points bring out the effects of magnetic fields on the interactions of the inhibitor molecules on the surface of the metal. Remarkably, the slopes of the Langmuir isotherm shows that for the case in presence of magnetic fields one monolayer of the inhibitor molecules is adsorbed compare with about two monolayers in the case of absence of magnetic fields, the implication is that the application magnetic fields reduces the amount of energy used and hence causes increase in the inhibition efficiency. Considering the Damaskin- Parson isotherm, the systems in the absence of magnetic fields have no data, but when they are subjected to magnetic fields it is noticed that the number of water molecules displaced by a molecule of the inhibitor is 4 indicating that the presence of magnetic fields facilitates the inhibition process. Also comparing the regression coefficient for the absence and presence of inhibitors, it can be observed that in the presence of magnetic fields the values are higher. It can be seen that for Frumkin isotherm which showed negative coefficient changed to

positive in the presence of magnetic field, showing improvement in quality. The results from the isotherms indicate enhancement in an attractive interaction between the inhibitor molecules and the corroding system in the presence of magnetic fields. These may have been as a result of well aligned molecules of the inhibitors, which results to higher regression coefficient observed for when the corroding systems were exposed in the presence of magnetic fields.

3.4 Quantum chemical calculations on *Lapachol* and *newbouldia quinone*

Quantum chemical calculations were performed on lapachol and newbouldia quinone constituents of *Newbouldia laevis* in order to compare their contributions to the efficiency of the inhibitor materials on the corroding system.

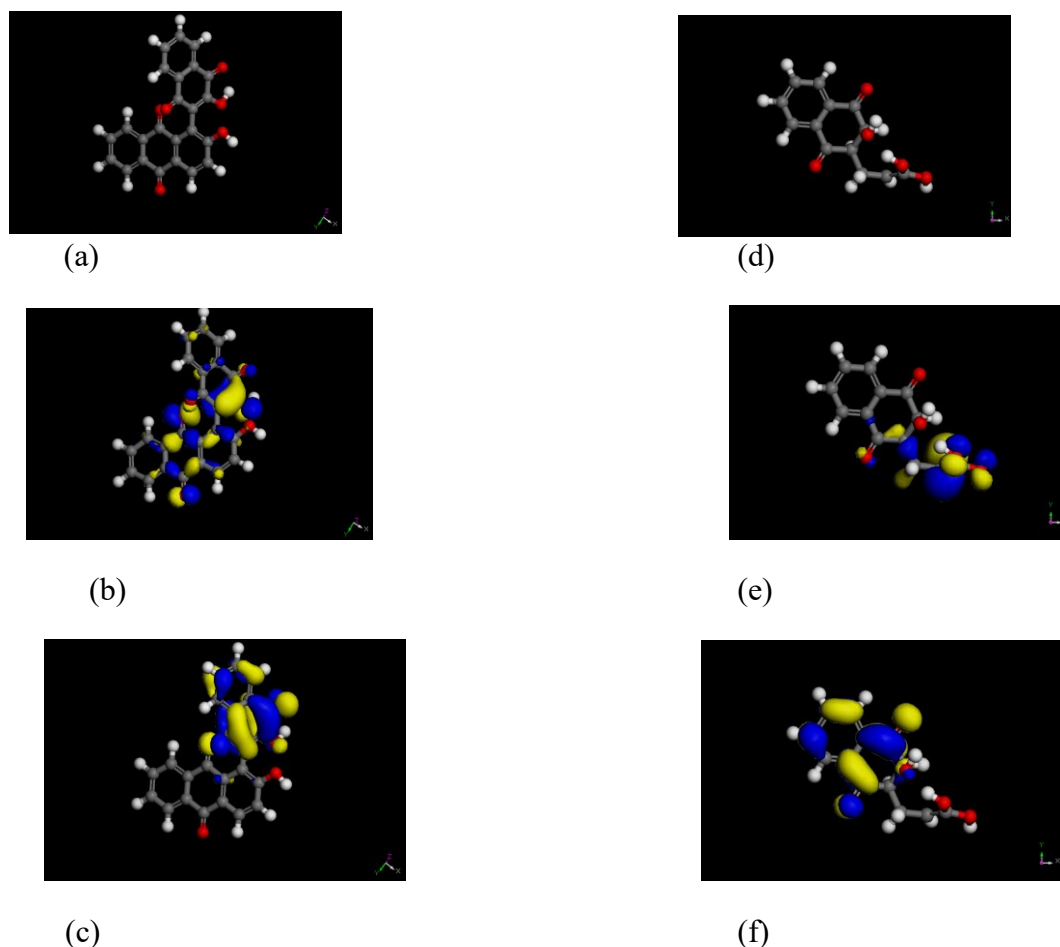


Fig. 4: Shows (a) structures, (b) HOMO (c) LUMO of *Newbouldia quinone*, and (d) the structure, (e) the HOMO and (f) the LUMO of *Lapachol*

Table 4: Shows the results of the Quantum Chemical calculations on *Newbouldia quinone* and *Lapachol*.

<i>Properties</i>	<i>Lapachol</i>	<i>Newbouldia quinone</i>
E_{HOMO} (eV)	-4.766	-5.635
E_{LUMO} (eV)	-3.655	-3.914
Dipole moment (D)	4.575	1.686
Binding energy (eV)	1.111	1.721
Chemical softness	0.901	0.578
Fractional electron transfer	3.047	1.633

In figure 4 is presented (a) structure, and the optimized structures (b) HOMO and (c) LUMO of *Newbouldia quinone*, while (d) the structure and (e) and (f) are the HOMO and LUMO respectively for *Lapachol*. The Quantum chemical calculated values of dipole moment, binding energy, chemical softness and fractional electron transfer may be used to describe or predict the the direction of corrosion inhibition process. Dipole moment measures the polarity in a bond and relates to the distribution of electrons in a molecule. Ebenso et al (2010) observed that increase in inhibition efficiency is related to high dipole moment; this may be used as an indication lapachol which has higher dipole moment may have contributed more to the inhibition efficiency. Binding energy or 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 binding energy will react faster in a chemical reaction, this points to the substantial the fact that lapachol with energy gap 1.111eV would have reacted very easily with the corroding surface so as to prevent further corrosion. Chemical softness for a molecule is measure of the readiness of a molecule to participate in a chemical reaction, high value of chemical softness implies high tendency to take part in any chemical reaction this indicates that lapachol with chemical softness of 0.901 compare with 0.578 for *newbouldia quinone* is more readily reactive and then can react with the surface of the corroding copper in order to inhibit further deterioration. The number of electrons transferred from the inhibitor to the metal surface determines the capability of such inhibitor to donate electrons to the corroding metallic surface; this causes metallic reduction and therefore protects the metal from corroding. Considering these values for the two molecules under investigation, lapachol has higher dipole moment, higher chemical softness; higher electron transfer value but lower binding energy than *newbouldia quinone*. This means that lapachol may have contributed more in the inhibition process than *Newbouldia quinone*.

4. CONCLUSIONS

Explanation of the effects of magnetic fields on inhibition process using the chemical quantum calculations. The dipole moment is the product of a charge and distance of separation of the charges in an atom or molecule. Any process which can cause change in the alignment of the dipoles on the surface of the corroding metal systems can facilitate an increase in inhibition process. The magnetic field acts on the dipoles such that it aligns the charges on the metal thereby providing the needed charge types at the required point. This explains the graph on figure 1 which shows an increase in inhibition efficiency in the presence of magnetic fields.

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