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RESEARCH ARTICLE

EXPERIMENTAL AND THEORETICAL STUDIES ON THE CORROSION INHIBITIVE PROPERTIES OF MILD STEEL IN 2M H_2SO_4 ACID SOLUTION BY ETHANOLIC EXTRACT OF BRACHYSTEGIA EURYCOMA SEED

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ABSTRACT

The experimental aspect of the corrosion inhibition potentials of *Brachystegia eurycoma* seed extract was carried out using Phytochemical Screening and gravimetric techniques as well as scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR), whereas the theoretical aspect was studied using the density functional theory calculations to be performed and modeling the electronic structures of some extract constituents, including physiosorptive interactions with the mild steel surface. The analysis of the weight loss results showed that the Inhibition efficiency of the *Brachystegia eurycoma* seed extract is directly proportional to its concentration and inversely proportional to solution temperature and mild steel contact time in the test solution. The inhibition efficiency increases gradually reaching a maximum value of 96% within the first 24 hours at a concentration of 0.5g/l. The kinetic study shows that the inhibitory action is a first order kinetics with the concentration of the seed extract of *Brachystegia eurycoma* which is best fitted with the Langmuir adsorption isotherm. This was further supported by the thermodynamic parameters which indicate that the adsorption of *Brachystegia eurycoma* seed extract onto the metal surface was spontaneous, exothermic and has contributed to physical adsorption process. FTIR results showed that the inhibition mechanism was an absorption process through the functional groups present in the seed extract. Surface morphology also revealed that corrosion product confirmed the protection offered by the extract on the surface of the metal immersed in the acid media. Quantum chemical studies indicated that inhibition was due to adsorption of active molecules leading to formation of a protective layer on surface of mild steel. Quantum chemical parameters such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels, HOMO–LUMO energy gap and electronic density were virtually identified. Quantum analysis demonstrated reactive centres of electrophilic and nucleophilic attack and strong inhibition properties of bioactive molecules of *BE*S extract.

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INTRODUCTION

The use of mild steel and any other metals in chemical industries cannot be overstressed due to its mechanical properties and wide range of application as structural material for vessels reactor, pipelines, tank, construction works and other industrial equipment which are known to corrode invariably in contact with various solvents (S. Junaedi *et al.,* 2012). Acid solutions especially sulfuric acid used for industrial processes such as acid pickling, industrial cleaning, acid descaling, etching of metal and acidic operations may cause damage to metal surface (Akalezi *et al.,* 2012; Okorokwo *et al.,* 2015; Peter *et al.,* 2016; Akalezi and Oguzie, 2015).

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However, contact between the metal and acidic media exposed most industrial equipment to corrosion. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases thereby affecting the tensile strength and utility efficiency of the material (Samuel *et al.,* 2015). In view of the nation's economy and financial implications of corrosion menace, researchers are compelled to do copious scientific studies in an attempt to improve the resistance of metals. Corrosion inhibitors have proven to be the most convenient means of protecting metals due to their unique properties which enhances their capability to resist the corrosion process as compared to other methods (i.e. electroplating, coatings, alloying elements, and plastic deformation) (U. Leon-Silva *et al.,* 2010; Gutierrez *et al.,* 2016; EL-Basiony *et al.,* 2019).

A corrosion inhibitor is a chemical compound which when added to liquid or gas decreases corrosion rate of a material, typically metal or alloys (Yiguang *et al.,* 2006). The effectiveness of a corrosion inhibitor depends on the fluid composition, quantity of water and flow regime (Umoren *et al.,* 2008; Ulaeto *et al.,* 2012). Corrosion inhibitors could be additives to the fluids that surround the metal (Schmit, 2000). In recent time, great achievement has been made in developing the efficiency of organic compounds containing hetero-atoms as corrosion inhibitors for mild steel in acidic media (Banu *et al.,* 2016; EL-Basiony *et al.,* 2019). The interaction between the mild steel and hetero-atoms such as O, N, P, S and double/triple bonds or aromatic rings in the form of a wall, shows a vital role in corrosion prevention processes caused by the free electron pairs (Shubham *et al.,* 2018). However, due to the known hazardous effects of most synthetic corrosion inhibitors coupled with increasing ecological awareness and strict environmental regulations, as well as the inevitable drive toward sustainable and environmentally friendly processes, attention has now focused toward the development of nontoxic alternatives. The exploration of natural products of plant origin as inexpensive eco-friendly corrosion inhibitors are becoming more important. In addition to being environmentally friendly and ecologically acceptable, plant products are low-cost, readily available, biodegradable, non toxic and renewable sources of materials, and they are widely used as corrosion inhibitors for the protection of metals in acid and alkaline environment (Akalezi and Oguzie, 2015; Okorokwo *et al.,* 2015).

The use of plant extracts as corrosion inhibitors is not a new phenomenon and the following plants have been investigated and found to possess inhibitory efficacy. *Gliricidia Sepium* (Okoronkwo *et al.,* 2015), *Azadirachta indica* (A. Peter *et al.,* 2017), *Pterocarpus soyauxii Taul* (Onukwube *et al.,* 2016), *Momordica charantia* (Kavitha *et al.,* 2017), *Boscia senegalensis* (Awe *et al.,* 2015) and lots more. *Brachystegia eurycoma* (achi as its popular called in eastern part of Nigeria) is an economically valuable tree crop mostly grown in the tropical rain forest of West Africa. In Eastern Nigeria, the edible seed is used in soup making as a thickener and is common among the rural dwellers (figure 1.0). It helps in maintaining heat within the body when consumed in other words; it is a good source of nutrient and helps to control body temperature (Ndukwe *et at.,* 2009, A. Uzoma *et al.,* 2011). Due to their absorption capacity, they are useful as functional agents in fabricated foods such as bakery products and meat formulations (Ndukwe *et al.,* 2009; Uzoma *et al.,* 2011). In Nigeria, the seed is used for its anti-Inflammation, anti-malaria, anti- diabetics and anti- corrosion properties (Michael *et al.,* 2000, Okafor *et al.,* 2008,). *Brachystegia eurycoma* seed has been reported to contain 10.47% protein, and 71.94% total carbohydrate content, the timber products are used as building material in carpentry and related applications (Nwosu *et al.,* 2012).

The use of computational methods have been extended to various fields via the developments in software one of which is the application of quantum chemical calculations (QCCS) in the corrosion studies. One can easily ascertain the electronic and geometrical structure of the inhibitor by performing the quantum chemical calculations (Stewart, 1989; Kavitha *et al.,* 2017). The present report investigate the corrosion inhibition potentials and adsorption characteristics of ethanolic extracts of *Brachystegia Eurycoma* seed (*BE*S) on mild steel in solution of 2M H_2SO_4 acid using weight loss and quantum studies.

MATERIALS AND METHODS

Collection of plant material and preparation of seed extracts: The study was carried out on *Brachystegia Eurycoma* seeds (*BE*S). The *Brachystegia Eurycoma* seeds were purchase from Eke-Okigwe market in Okigwe local government area of Imo state, Nigeria. The sample was dried and grounded into powder. Four hundred and fifty gram (450g) of the dehydrated and grounded seeds was soaked in a 500ml solution of ethanol for 48hrs. Sequentially, sufficient grams of the grounded seeds were measured into the ethanol and were extracted until the 450g of the grounded seeds were exhausted. After 48hrs, the samples were filtered using Whatman filter paper No.1 (QUALIGEN- Germany). The filtrates were further subjected to evaporation by rotatory evaporator at 358K in order to leave the sample free of the ethanol. The stock solutions of the extract obtained were used in preparing different concentrations of the extract by dissolving 0.1, 0.2, 0.3, 0.4 and 0.5g of the extract in 1L of 2M H_2SO_4 acid respectively.

Phytochemical Screening on BES: Screening of phytochemicals is significant for identification of bioactive principles present in plants. Phytochemical screening was carried out on BES extracts by standard procedures (Khadom *et al.,* 2017). Plant extracts were screened for reducing sugar, alkaloids, protein, phenols, flavonoids, amino acids, tannin, steroids, glycosides and carbohydrates. These compounds are potential corrosion inhibitors for many metals in an acidic medium (Verma and Mehta, 1997)

***Preparation of Specimen*:** The specimens were cut using a saw into the required dimension of 4 x 3 x 0.017cm then descaled by brushing with a emery paper. They were cleaned and dried with acetone, then stored properly in desiccators for further use. The elemental composition of mild steel specimen analyzed and used for this study with iron (Fe) having the highest elemental composition of 93.65%.

Gravimetric Techniques: One hundred millilitres (100ml) each of the 2M H_2SO_4 solution was measured into six different beakers with one as the blank (uninhibited solution) and the remaining five labeled A to E containing different concentrations of the inhibitors ranging from 0.1g to 0.5g/100ml respectively. The test coupons were weighed before immersion in the acid solutions and the measurements were taken down. After weighing, the coupons were immersed in the acids solution. The coupon in each beaker was noted to avoid mix ups during the practical work. The immersion period was 24 hour interval, after 24 hour the coupons were retrieved from the acids, washed with tab water, degreased with ethanol and dried with acetone before the corresponding weights after immersion were recorded. The procedures were repeated for 96 hours i.e. for 4 days. The corresponding weights after immersion were recorded as well after each day. The differences in weight of the coupons were again taken as the weight loss (Kavitha *et al.,* 2017).The rate of corrosion (CR), inhibition efficiency (IE), and degree of surface coverage (Θ) were obtained from the weight loss results. Rate constant and half life ($t_{1/2}$) were also determined using the expressions below. The corrosion rates (C.R) were computed using the formular:

$$C.R = \frac{\Delta W}{A \times T} \quad 1.1$$

Where: ΔW = weight loss (g), A = total surface area of the test coupon (cm^2), T = immersion time (min) The inhibitor efficiency (IE) was computed using the relationship in equation 1.2.

$$\%IE = \frac{(C.R)o-(C.R)inh}{(C.R)o} \times 100 \quad 1.2$$

Where: $(C.R)_o$ and $(C.R)_{inh}$ are the corrosion rates in the absence and presence of different concentrations of the inhibitor, respectively. The surface coverage *(θ)* of the inhibitor was obtained from the experimental data using the equation 1.3 as follows:

$$\theta = \frac{(C.R)o-(C.R)inh}{(C.R)o} \quad 1.3$$

The rate of the reaction as well as the values of the rate constant *k* of the reaction were evaluated using the Equation 1.4 and 1.5 as follows:

$$\log W_f = \log W_o - kt \quad 1.4$$

$$k = \frac{1}{t}\log\left(\frac{Wo}{Wf}\right) \quad 1.5$$

Where W_f = the final weight of metal after time, t, W_i = the initial weight of metal, *t* = the immersion time.

The half-life of the reaction was evaluated using Equation 1.6 as follows:

$$t_{1/2} = \frac{0.693}{k} \quad 1.6$$

Where *k* = the rate constant of the reaction.

Temperature Effect: To study the temperature effect, the mild steel coupons were completely immersed in 100ml of 2M H_2SO_4 solution with and without the various *BE* seed extract concentration using glass hooks and corrosion rate were determined at 313K, 323K and 333K for 2hrs to calculate inhibition efficiency, activation energy (E_a), Standard Gibbs free energy change of Adsorption, $\Delta G°_{ads}$ and heat of adsorption (Q_{ads}).

Fourier Transform Infrared Spectroscopy (FTIR) Analysis: FTIR analysis was used to ascertain the fact that the corrosion inhibition process takes place through the adsorption of the phytochemical constituents on the mild steel surface. The spectra of *BE* seed extract were recorded in a Perkin-Elmer-1600 spectrophotometer using KBr pellet.

Scanning Electron Microscopy (SEM) Analysis: The surface morphology of the mild steel before and after immersion were examined with scanning electron microscopy to analyse the elements on the surface, using a phenom pro X Scanning Electron Microscope (SEM). The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the samples surface topography and composition.

Quantum Chemical Analysis: Quantum chemical calculations were used as a theoretical tool to support the experimental results and to explain the interaction between the inhibitor molecules and the steel surface. Density functional theory (DFT) was use to analyze the characteristics of the plant extracts and to describe the structural nature of the inhibitor on the corrosion process (E.E. Ebenso *et al.,* 2010, N.O. Obi-Egbedi *et al.,* 2011). Structures of arginine and alkaloid in *BE* seed extracts were obtained from literature for computational analysis. 3-Dimensional (3D) structures were retrieved from structural database and was optimized (Fig.1.0) and taken as input file for quantum chemical studies. Mulliken population analysis determines nucleophilic and electrophilic reaction centers in compounds. According to PM3 (Parameterized Model number 3) theorem (Gece, 2008, Kavitha and Gunavathy, 2016), the HOMO energy is related to the ionization potential (IE) whereas the LUMO energy is linked to the electron affinity (EA), as follows:

$$IE = -E_{HOMO} \quad 1.7$$

$$EA = -E_{LUMO} \quad 1.8$$

Other related parameters like electronegativity (χ), electronic chemical potential (μ), hardness (η), and softness (σ) can be expressed as:

$$\text{Electronegativity } (\chi): -\mu = \frac{IE+EA}{2} \quad 1.9$$

$$\text{Electronic chemical potential } (\mu): -\chi \quad 2.0$$

$$\text{Hardness } (\eta): = \frac{IE-EA}{2} \quad 2.1$$

Electronegativity, hardness, and softness have proved to be very useful quantities in chemical reactivity theory.

The global electrophilicity (ω) index was introduced by Parr (1999) as a measure of energy lowering due to maximal electron flow between donor and acceptor and is given by

$$\text{Electrophilicity } (\omega): = \frac{\mu^2}{2}\sigma \quad 2.2$$

Nucleophilicity (ε): nucleophilicity is the reciprocal of electrophilicity expressed as:

$$\varepsilon = \frac{1}{\omega} \quad 2.3$$

RESULTS AND DISCUSSION

Phytochemical screening: The phytochemical constituents of *BE* seed extract, as presented in Table 1.0, indicate the presence of tannins, saponins, et cetera. The presence of these compounds promotes the inhibition of mild steel in sulfuric acid solution. Plant extracts are organic in nature and some of the constituents are tannins, alkaloids, proteins, polysaccharides, polycarboxylic acids, alkaloids, and so forth. These compounds are potential corrosion inhibitors for many metals in an acidic medium (Verma and Mehta, 1997).

Weight Loss Measurements: The weight loss of mild steel coupons due to their immersion in solutions of 2M H_2SO_4 containing different concentrations of *BE* seed extract was

measured as shown in Table 2.0. The results clearly shows a general reduction in the original weight of the metal coupons in the presence of the inhibitor compared to the uninhibited solution (blank), indicating that ethanol extract of *BE* seed inhibited the corrosion of mild steel in 2M H_2SO_4 at the end of the corrosion monitoring process. This is further supported by the decrease in Corrosion rate and Rate constant as the concentration of the extract increases, this also is in tandem with what was observed in the inhibitory action of *Momordica charantia* seed extracts on the corrosion of mild steel (V. Kavitha *et al.,* 2017). This may be attributed to the adsorption of inhibitor on the mild steel surface, producing a barrier, which isolates the surface from the corrosion environment.

The corrosion rate for the mild steel and the inhibition efficiency of the plant extract in $2MH_2SO_4$ containing different concentrations of the plant extracts as a function of time (in days) are also presented in figure 1.1-1.2. The inhibition efficiency increased with increase in concentration of inhibitor from 0.1 to 0.5g/l at room temperature (Fig.1.2). Maximum inhibition efficiency was 96% in case of *BES* /$2MH_2SO_4$ for immersion period of 24h at a concentration of 0.5g/l (Fig.1.2). These results suggest that adsorption model arrangement and orientation of constituents present in *Brachystegia eurycoma* seed extract on the surface of mild steel may change with time (N. Rekha *et al.,* 2010). Decrease in inhibition efficiency thereafter with increasing time may be due to shift in adsorption and desorption equilibria which takes place simultaneously on prolonged exposure to corrosive media (V. Kavitha *et al.,* 2016). Adsorbed organic molecules prevent further interaction of metal with acid (O. Lahodny-Sarc and F. Kapor, 2002). Figure 1.3 shows the plot of log W_f against Time (hrs), for *BE* seed extracts indicating a linear variation at all concentrations. The linearity of the plots confirmed a first order reaction kinetics with respect to the corrosion of mild steel in the acidic medium (2M H_2SO_4). This implies that the rate of the reaction was directly proportional to the concentration of the extracts (I.L. Rozenfeld, 1981). From Table 2.0, the values of rate constant of the reaction decreases as the concentration of *BE* seed extracts increased and were in agreement with the assertion that the rate of the reaction was directly proportional to the concentration of the of *BE* seed extracts (A.O. James and O. Akaranta, 2009).

Since the rate of the reaction was first order, the half-life of the reaction which were determined using the expression for the half-life for a first order reaction, showed the time required for the concentration of *BE* seed extracts to be reduced to half its initial value. Table 2.0, also shows that the half-life of the reaction increased as the concentration increased. The increase in half-life as the concentration of the extracts increased indicated a decrease in the dissolution rate of the mild steel and hence more protection of the metals by the *BE* seed extracts (C.O. Akalezi and E.E. Oguzie, 2015, A.O. James and O. Akaranta, 2009).

Temperature Effects: The weight loss experiment were also carried out at different temperature range of 313 – 333K in 1M H_2SO_4 to investigate the influence of temperature on the rate of corrosion and inhibition efficiency for immersion time of 2hrs. The variation of inhibition efficiency with temperatures at different concentration of *BE* seed extract is shown in Figure 1.4. From the plot, the inhibition efficiency increases with an increase in *BE* seed extract concentration but decreases with an increase in temperature.

According to I.J. Alinor and P.M. Ejimeke (2012), at higher temperatures, the average kinetic energy of components of extracts increases, thus making adsorption between components of extracts and a metal surface insufficient to retain the species at the binding site and this could lead to desorption or cause the species to bounce off the surface of the metal instead of colliding and combining with it. Moreover, the solubility of the protective films on the metal surface would have occurred at a higher temperature, hereby exposing the metal surface to the aggressive medium, leading to more dissolution at this temperature. The values of the corrosion rate at different temperatures are summarised in Table 3.0. It is clear from the table that the corrosion rate increases with a rise in temperature. This happened to be the case because, as the temperature increases, the average kinetic energy of the reactant molecules increases, thereby increasing the rate of the reaction. A decrease in inhibition efficiency with a rise in temperature and a corresponding increase in activation energy (E_a) in the presence of an inhibitor is termed physical adsorption mechanism (Ebenso *et al*, 2008).

The values of activation energy (E_a) for the corrosion process were calculated using Arrhenius equation represented by Equation 2.4.

$$\log(\frac{C2}{C1}) = \frac{Ea}{2.303R}(\frac{1}{T1} - \frac{1}{T2}) \qquad 2.4$$

Where C_1 is the corrosion rate at temperature, T_1, C_2 is the corrosion rates at temperature, T_2, E_a is the Activation Energy, R is the universal gas constant. Protective films formed on the surface of the mild steel, increases the activation energy of the metal dissolution. In a chemical reaction, when the activation energy increases, the rate of the reaction decreases (A.E. Okorokwo *et al.,* 2015). This is also seen in the results shown in Table 3; the addition of the inhibitor increases Ea, thereby reducing the rate of the metal dissolution into the electrolyte.

Thermodynamics and Adsorption Mechanism: The heat of adsorption (Q_{ads}) of *BE* seed extract on the surface of mild steel has been calculated using equation 2.5 (Ebenso, 2003a, b, 2010; Umoren *et al*., 2006a, 2006b, 2007).

$$Q_{ads} = 2.303R(\log[\frac{\theta 2}{1-\theta 2}] - \log[\frac{\theta 1}{1-\theta 1}]) \times [\frac{T1T2}{T2-T1}] \qquad 2.5$$

Values of Q_{ads} calculated through equation 2.5 are recorded in Table 3. These values are negative and ranged from -16.32 to -56.19 KJ/mol indicating that the adsorption of the extract is exothermic (E.E. Ebenso, 2003a, b, 2010; H.M. Bhajiwala and R.T. Vashi, 2001). Values of free energy of adsorption of *BE* seed extract were calculated using equation 2.6.

$$\Delta G°_{ads} = - RTIn(55.5K_{ads}) \qquad 2.6$$

Where $K_{ads} = \frac{\theta}{C(\theta-1)}$ is the adsorption equilibrium constant, C is the concentration of the inhibitor, R is the universal gas constant. The calculated values of $\Delta G°_{ads}$ for the plant extract are also recorded in table 3. From the result obtained, The values are found to be negatively less than the threshold value of -40 kJ mol^{-1} required for the mechanism of chemical adsorption to take place. This indicates that the adsorption of the studied plant extract on the mild steel surface is spontaneous and is consistent with the mechanism physical adsorption (Ebenso, 2003a, 2004; Bhajiwala and Vashi, 2001; Loto, 2011).

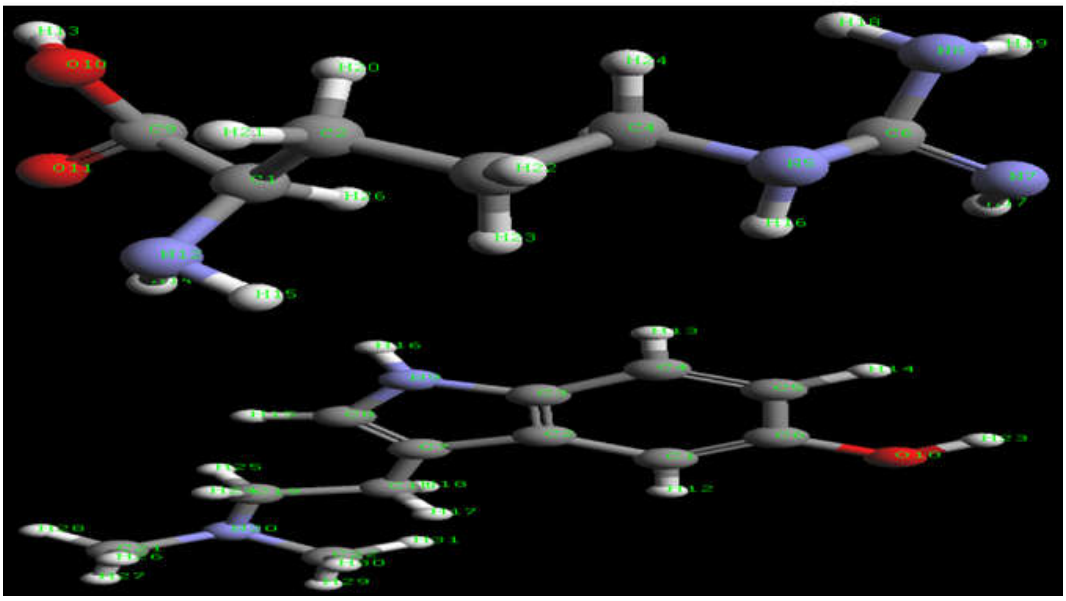

Figure 1.0. Molecular structure of arginine and alkaloid

Table 1.0. phytochemical constituents of *BE* seed extract

Phytochemiacal constituents	Tannins	Flavonol	Amino acids	Alkaloid	Carbohydrates
Ethanolic extract of AAS	+++	++	++	+	+++

Legend: + = Sparingly Present; ++ = Moderately Present; +++ = Highly Present

Table 2.0. Deduced data for inhibition efficiency, corrosion rate, rate constant and half life obtained from gravimetric method for mild steel in $2MH_2SO_4$ after 24hrs

Concentration of inhibitor (g/l)	ΔW (g)	Corrosion Rate $(gcm^{-3}hrs^{-1}) \times 10^{-3}$	% IE	Rate Constant (day-1) 10^{-3}	Half Life (days)
Blank	0.336	57.76	--------	1.90	3.65
0.1	0.144	24.75	57.15	0.79	8.77
0.2	0.096	16.50	71.43	0.52	13.33
0.3	0.047	8.08	86.01	0.25	27.72
0.4	0.027	4.64	92.00	0.15	46.20
0.5	0.015	2.58	96.00	0.08	86.63

Table 3.0. Temperature effect on corrosion rate (CR), activation energy (E_a), standard free energy (ΔG^o_{ads}) and heart of adsorption for mild steel in 2M H_2SO_4 in absence and presence of *BE* seed extract for an immersion time of 2hrs

Concentration of inhibitor (g/l)	Temperature						E_a KJmol^{-1}	K_{ads}	ΔG^o_{ads} KJmol^{-1}	Q_{ads} KJmol^{-1}
	313K		323K		333K					
	CR $(gcm^{-3}hrs^{-1}) \times 10^{-3}$	IE %	CR $(gcm^{-3}hrs^{-1}) \times 10^{-3}$	IE %	CR $(gcm^{-3}hrs^{-1}) \times 10^{-3}$	IE %				
Blank	115.51	-----	156.77	-----	222.77	-----	28.45	-----	------	-----
0.1	57.76	50.00	86.63	44.74	132.01	40.74	35.81	1.00	-10.45	-16.32
0.2	49.51	57.10	78.38	50.00	123.76	44.44	39.70	0.67	-9.41	-17.19
0.3	37.13	67.86	66.01	58.90	107.26	51.85	46.00	0.71	-9.56	-12.26
0.4	24.75	78.57	49.51	68.42	92.82	58.33	57.26	2.88	-13.21	-41.82
0.5	14.44	87.50	37.13	76.32	76.32	65.74	72.12	4.24	-14.21	-56.19

Table 4.0. Quantum Chemical Parameters of *BES* Phytoconstituents

Component Parameters	Alkaloid	Arginine
E_{HOMO} (eV)	-0.3052	-0.3302
E_{LUMO} (eV)	-0.0020	-0.0505
$\Delta E_{(LUMO-HOMO)}$ (eV)	0.3032	0.2797
EA (eV)	0.0020	0.0505
IE (eV)	0.3052	0.3302
χ (eV)	0.1536	0.1904
η (eV)	0.1516	0.1399
σ (eV^{-1})	6.5963	7.1480
ω (eV)	0.0778	0.1296
ε (eV)	12.8535	7.7161
μ (debye)	3.0395	4.1139

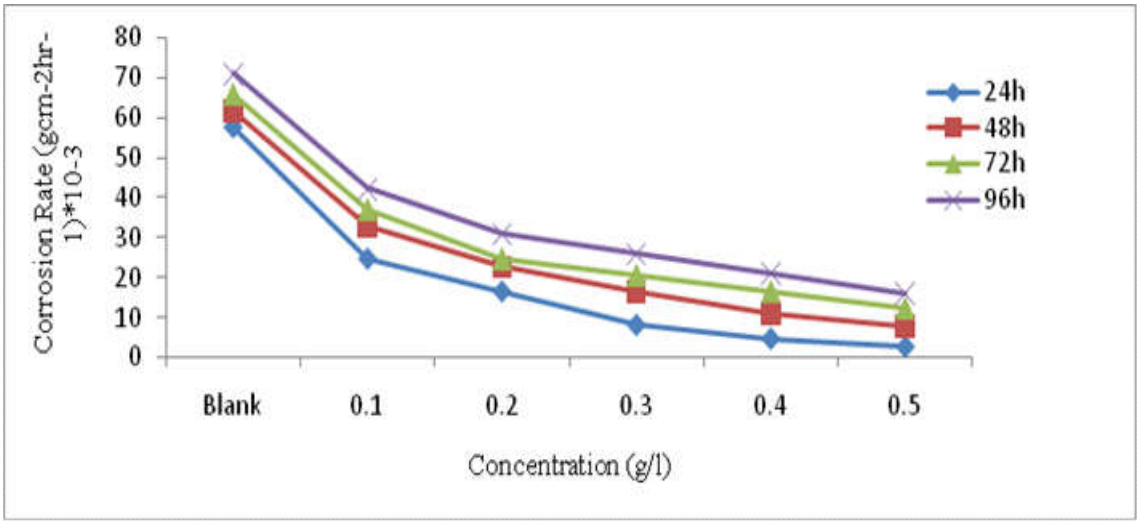

Figure 1.1. Variation of corrosion rate of mild steel corrosion in 2M H_2SO_4 with different concentration of *BE* seed extract showing the effect of time

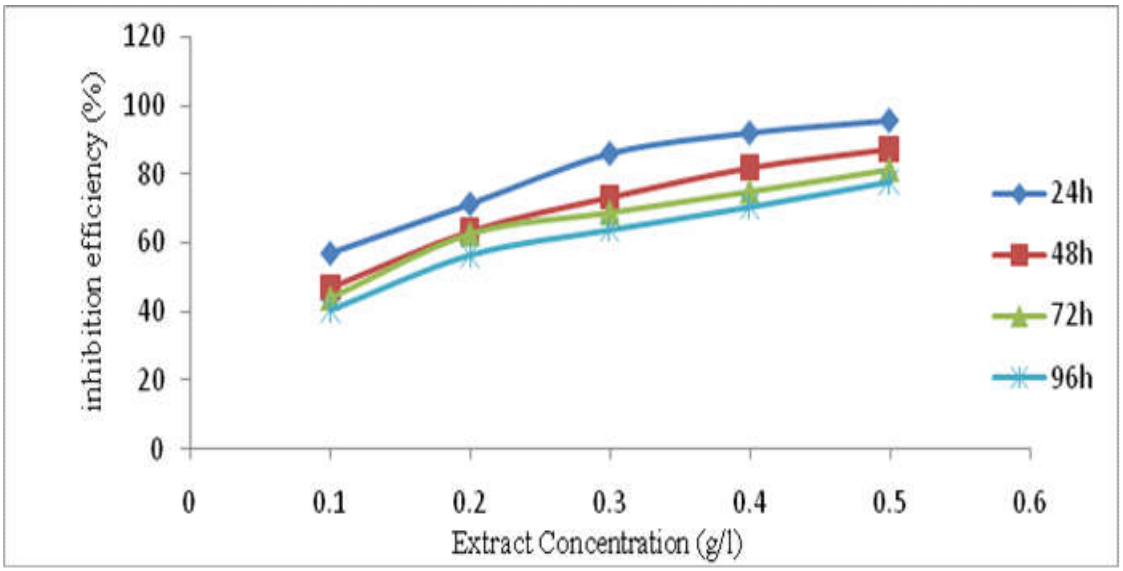

Figure 1.2. Variation of inhibition efficiency of *BE* seed with concentration and time

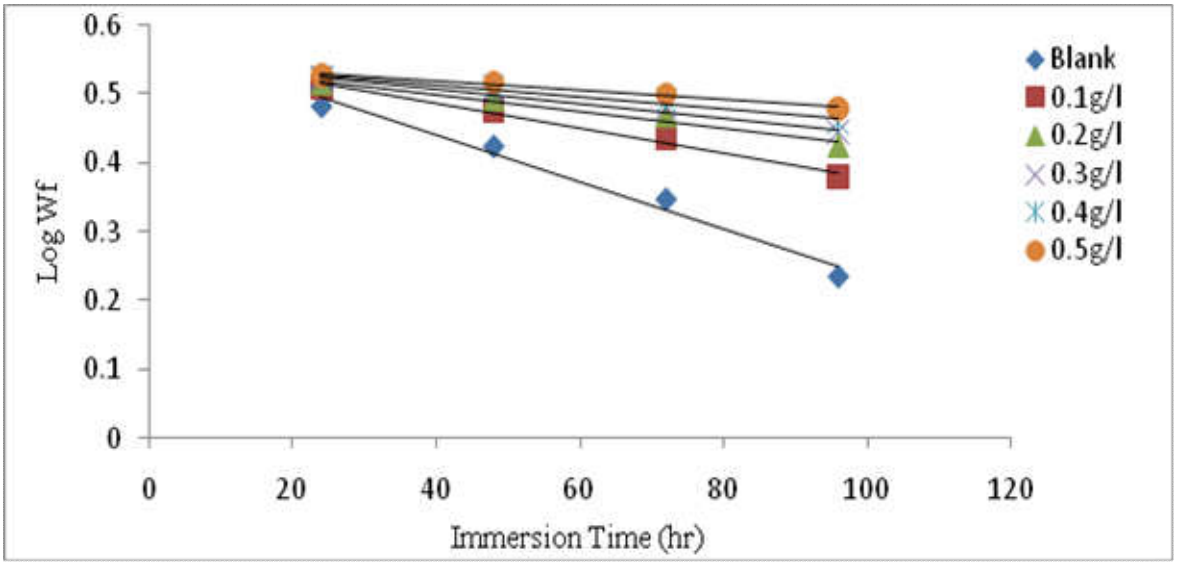

Figure 1.3. Variation of $\log W_f$ with time for mild steel of in 2M H_2SO_4 solutions containing *BE* seed extract

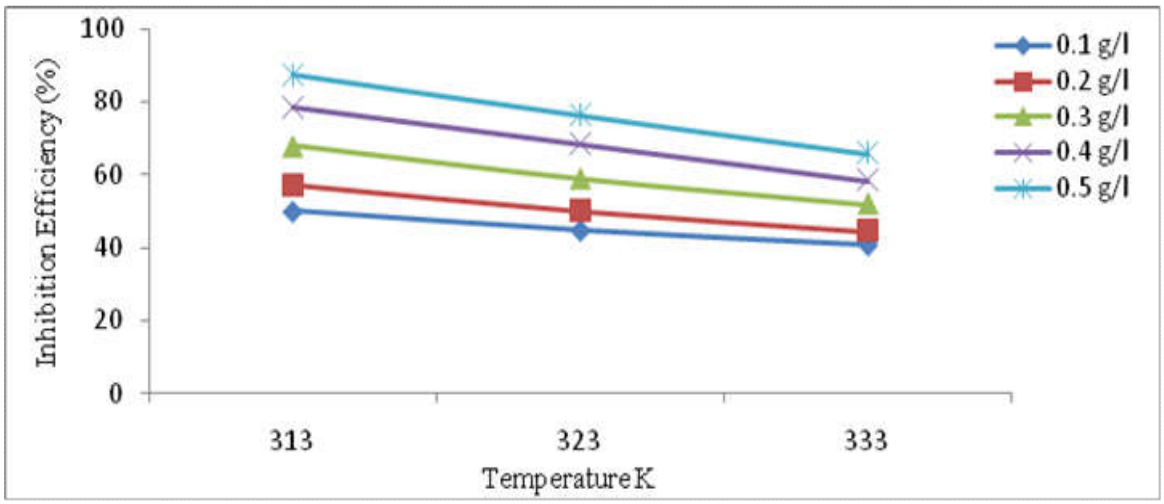

Figure 1.4. Effect of Temperature on inhibition efficiency for mild steel corrosion in 2M H_2SO_4 at different concentration of *Brachystegia eurycoma* seed extract for immersion period of 2h

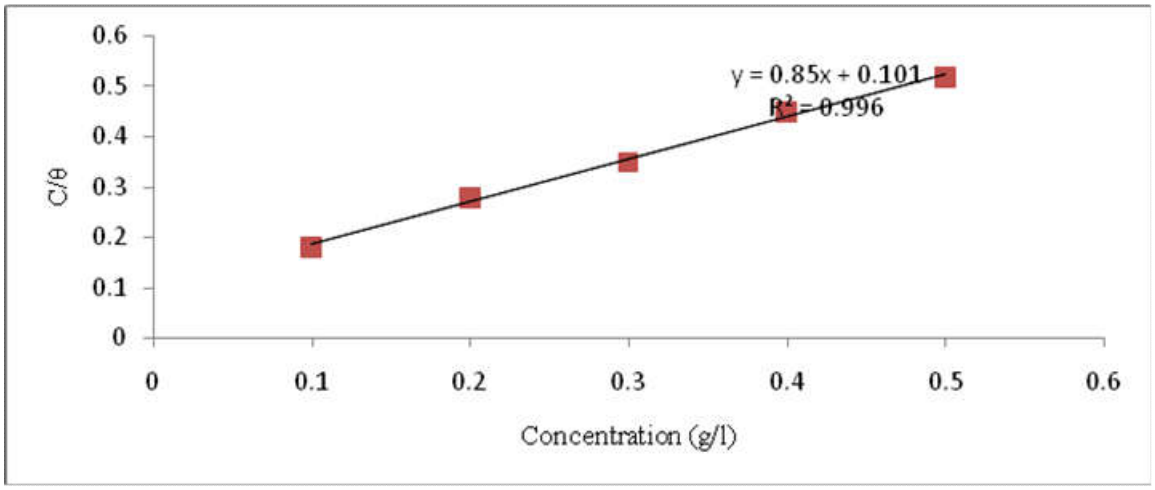

Figure 1.5. Langmuir adsorption isotherm plot for the adsorption of *BES* on the surface of mild in 2M H_2SO_4 acid

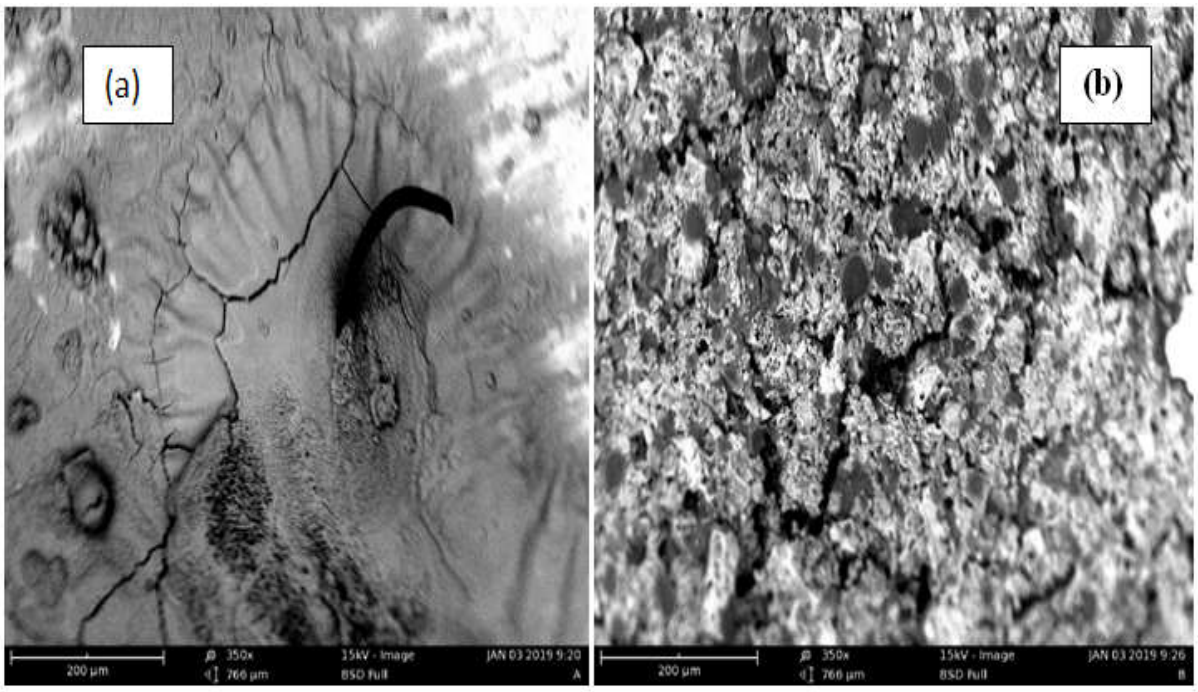

Figure 1.6. (a) SEM of the mild steel immersed in 2M H_2SO_4 solution without inhibitor for 5 hrs at 200 magnification and (b) SEM of the mild steel immersed in 2M H_2SO_4 solution in the presence of *BE* seed extract

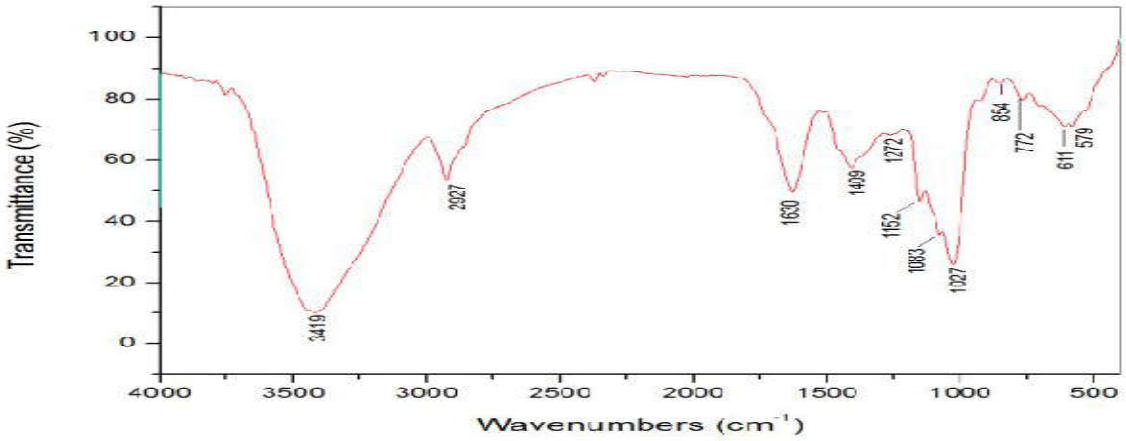

Figure 1.7: FTIR spectra of *Brachystegia eurycoma* seed extract (*BE*SE)

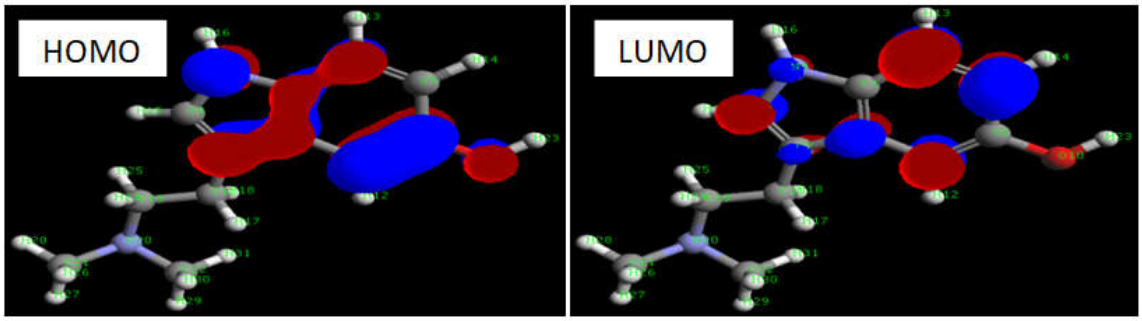

Figure 1.8. HOMO and LUMO orbitals of Alkaloid

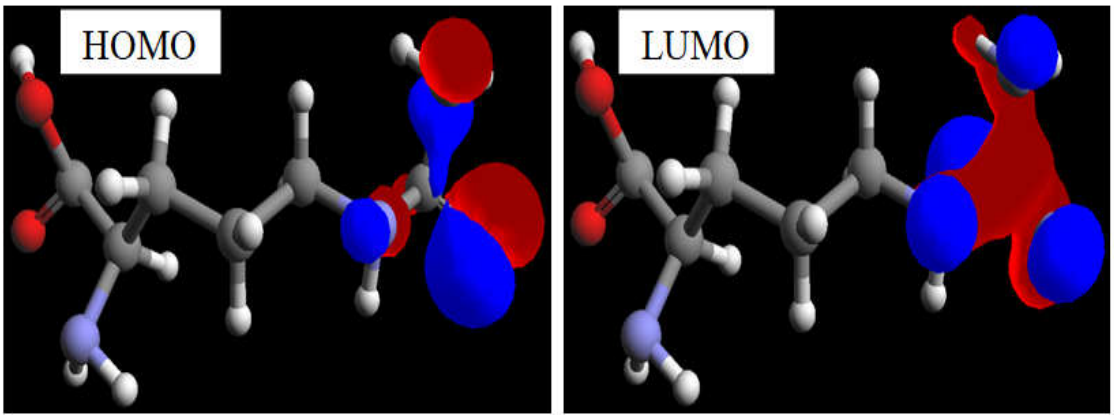

Figure 1.9. HOMO and LUMO orbitals of Arginine

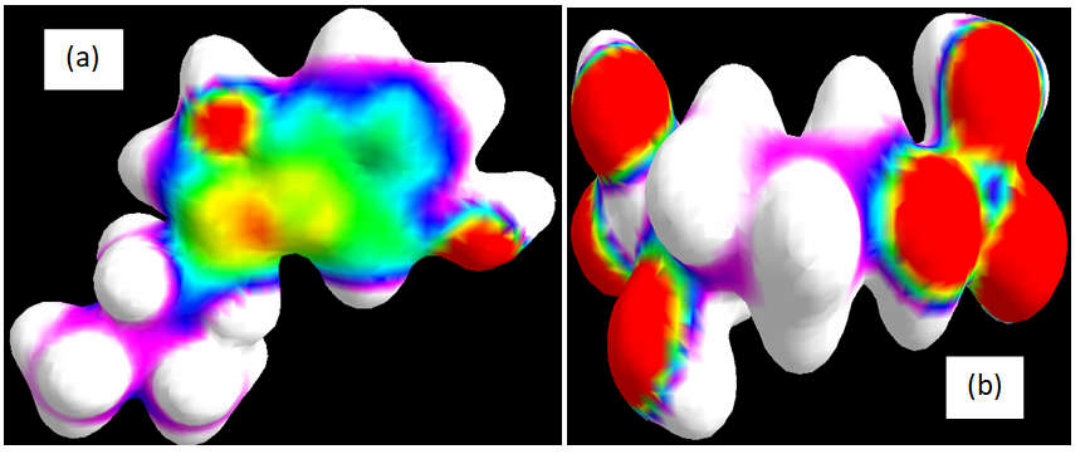

Figure 2.0. ESP Optimized mapped density of (a) Alkaloid and (b) Arginine

Table 5.0. Mulliken Charge Distribution on Alkaloid and Arginine

Atomic Charges on Alkaloid			Atomic Charges on Arginine		
1	C	-0.1902	1	C	-0.1281
2	C	-0.0442	2	C	-0.2523
3	C	-0.2005	3	C	-0.2597
4	C	-0.1394	4	C	-0.2707
5	C	-0.2596	5	N	0.0292
6	C	0.0637	6	C	-0.0416
7	C	-0.1367	7	N	-0.4039
8	C	-0.2989	8	N	-0.0212
9	N	0.1830	9	C	0.2933
10	O	-0.2452	10	O	-0.2877
11	C	-0.1708	11	O	-0.3290
12	H	0.2166	12	N	-0.0691
13	H	0.1947	13	H	0.2359
14	H	0.1928	14	H	0.0785
15	H	0.2328	15	H	0.0601
16	H	0.1181	16	H	0.1041
17	H	0.1299	17	H	0.1851
18	H	0.1430	18	H	0.0544
19	C	-0.1985	19	H	0.0878
20	N	-0.1021	20	H	0.1414
21	C	-0.2714	21	H	0.1638
22	C	-0.2835	22	H	0.1522
23	H	0.2188	23	H	0.1128
24	H	0.1030	24	H	0.1464
25	H	0.1217	25	H	0.1135
26	H	0.0839	26	H	0.1051
27	H	0.1118			
28	H	0.1108			
29	H	0.1092			
30	H	0.0937			
31	H	0.1136			

Adsorption isotherms are very important in determining the mechanism of corrosion reactions. The most frequently used isotherms are Langmuir, Frumkin, Hill de-Boer, Parsons, Temkin, Flory-Huggin, Freundlich, Dhar-Flory-Huggin, Kinetic/Thermodynamic model of El-Awady et al. and Bockris-Swinkels. All these isotherms are of the general form:

$$f(\theta,\chi)\exp(-2\alpha\theta) = KC \qquad 2.7$$

where f (θ,χ) is the configurational factor which depends upon the physical model and the assumptions underlying the derivation of the isotherm, θ, the surface coverage, C, the inhibitor concentration in the electrolyte, χ, the size factor ratio,α the molecular interaction parameter and K the equilibrium constant of the adsorption process. The degree of surface coverage (θ) was evaluated from the weight loss measurements. In this study, Langmuir adsorption isotherm was found to be suitable for the experimental findings and has been used to describe the adsorption characteristic of this inhibitor.

Figure 1.5, shows the linear plots for Langmuir adsorption isotherm. The plots clearly revealed that the surface adsorption process of the *BE* seed extracts on the mild steel surface obeyed the Langmuir adsorption isotherm as their linear regression approaches unity (L. Bammou *et al.,* 2014). The plots support the assertion that the mechanism of corrosion inhibition is due to the formation and maintenance of a monolayer protective film on the metal surface and producing uniform energies of adsorption onto the surface of the metal following Langmuir isotherm. It can therefore be inferred that physisorption occurred (O.A. James and O. Akaranta, 2009, A.E. Okoronkwo *et al.,* 2015). Assumptions of Langmuir adsorption isotherm is expressed in equation 2.8 below (H. Shockry et al., 1998):

Surface Studies by Scanning Electron Microscopy: Morphological analysis using SEM shows differences in the morphologies of the samples in the uninhibited and inhibited medium. Figure 1.6 showed the SEM image of the mild steel surface immersed in the uninhibited medium for 5 hours, big pits and cracks observed in the image are due to the effect of corrosion on the specimen infused by the acid. Similar image of mild steel immersed in the inhibited medium are also shown in Figure 1.6, Smother surfaces with little cracks observed are due to the formation of a thin film layer infused by the complexation between the mild steel and the phyto- chemical constituents in the extract. This implies corrosion rate was lowered by the extract which is in agreement with the results obtained from the weight loss analysis.

Infrared Spectroscopy Analysis: FTIR analysis is used to ascertain the fact that the corrosion inhibition process takes place through the adsorption of the phytochemical constituents on the mild steel surface. The spectra of the extract are presented in figure 1.7. from the result obtained, the strong and broad peak of O-H stretching that obscured the appearance of other peaks basically N-H peak occurs at 3419 cm^{-1} with C-H stretching vibration occuring at 2927 cm^{-1}. The strong band at 1630 cm^{-1} is assigned to C=C and C=O stretching vibration. Owing to the conjugation effect of flavonoids of *BE* seed extract, the C=O peak shifts from about 1700 cm^{-1} to lower wave number (approximately 1630 cm^{-1}), C=C and C=O stretching vibration bands are superposition (Q.Y. Deng *et al.*, 2007). The C-H bending bands in $–CH_2$ and $–CH_3$ are found to be at 1409 cm^{-1}. The absorption bands at 1272 cm^{-1} could be assigned to the framework vibration of aromatic ring. The IR spectra of the extracts showed peaks attributed to the characteristics of the functional groups. The presence of these functional groups indicates the effectiveness of the extract constituents to interact with the mild steel surface and that adsorption between the extract and the mild steel occurs through the identified functional groups (A.E. Okoronkwo *et al.,* 2015). Hence, protection of metallic surface is done via the functional groups presented in the flavonoids, tannin, carbohydrates, alkaloid and amino acids as the main constituents of *Brachystegia eurycoma* seed extracts.

Theoretical and Quantum Chemical Studies: Arginine, and Alkaloid represent the most effective component of the *BE* seed extract. Quantum chemical calculations have proved to be a veritable tool for studying corrosion inhibition mechanism (K. Kalaiselvi *et al.,* 2014, A.A. Khadom *et al.,* 2016). Thus in the present investigation, quantum chemical calculation were performed using density functional theory (DFT) to explain the experimental results obtained in this study and to give an insight into the inhibition action of the *BE* seed extract on the mild steel surface. The structures are sketched with ACD chemsketch and structural geometries were optimized to obtain a stable structure. The calculated values of the quantum chemical parameters obtained using the Hartree-fock/ Density functional theory (HF-DFT) by Becke 3 Lee Yang Parr (B3LYP) method with 6-31G* basis set of SPARTAN 06 V112 program are presented in Table 3.0. The relation between inhibition efficiency of inhibitor and the quantum chemical calculation parameters like E_{HOMO}, E_{LUMO}, ΔE, χ, η, σ, ω, ε, and dipole moment were investigated. Positive and negative regions in HOMO and LUMO orbitals, Mulliken charges, Electrostatic potential map of compounds were computed using ArgusLab 4.0.1 (J.J.P. Stewart, 2013, M.A Thompson, 2004).

Their examination is very important so as to determine the electronic properties of the compounds theoretically using PM3. For a molecule to be effective corrosion inhibitor, it must donate electrons to the vacant d orbital of the metal for bonding and as well receive free electrons from the metal surface. The reactive ability of the inhibitor is considered to be closely related to their frontier molecular orbitals, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (N.O. Obi-Egbedi *et al.,* 2011). The highest occupied molecular orbital (HOMO) is usually the region of high electron density, therefore is often associated with the electron donating ability of the molecule and lowest unoccupied molecular orbital (LUMO) is associated with the electron accepting ability of the inhibitor molecule from the metal. The optimized geometry of the components of *BE* seed extract is shown in Figure 1.0. The positive and negative phases of orbital are represented by two colours, blue regions represent an increase in electron density and red region represents a decrease in electron density (K. Laxmi, 2014). The Positive and negative regions in HOMO and LUMO orbitals of arginine, flavonol and alkaloid components of *BE* seed extract were plotted and are shown in Figure 1.8-1.9 respectively. From the Figure 1.8-1.9, It can be seen that the frontier orbitals, the HOMO and the LUMO were distributed all around each molecule most dominated by bonded heteroatoms (oxygen atoms and Nitrogen atoms of both amino and carboxylic group) and some of the carbon atoms basically those containing unsaturated bonds in their molecule, and on the entire aromatic rings.

These regions are the sites at which electrophiles attack and represent the active centers, with the utmost ability to bond to the metal surface, whereas the LUMO orbital can accept the electrons in the d-orbital of the metal using antibonding orbitals to form feedback bonds (S. Martinez and I. Tagljar, 2003, K.F. Khaled, 2010). It has been reported that excellent corrosion inhibitors are usually those organic compounds that does not only offer electrons to unoccupied orbital of the metal but also accept free electrons from the metal (N. Soltani *et al.,* 2012). It is also well documented in literature that the higher the HOMO energy of the inhibitor, the greater its ability of offering electrons to unoccupied d-orbital of the metal, and the higher the corrosion inhibition efficiency. It is evident from Table 4.0 that flavonol had the highest value of E_{HOMO} -0.3302 (ev) and increased in the order: Arg>Alk which suggest that arginine would be better adsorbed on the metal surface than alkaloid. E_{LUMO} represent the ability of the molecule to accept electrons from a donor reagent and the lower the value of E_{LUMO}, the greater the tendency of the molecule to accept electrons. Results from Table 4.0 also show that alkaloid had the lowest value of E_{LUMO} -0.0020 (ev) and decreases in the order: Alk<Arg which suggest that alkaloid will readily accept electron from the metal than arginine. The above assertion indicate that *BE* seed extract is a good corrosion inhibitor capable of donating electrons to the mild steel surface, by forming an inhibition barrier (I.B. Obot *et al.,* 2015). This also confirms that the presence of this component molecules in the seed extract increases its inhibition efficiency which is in line with the experimental results. Apart from E_{HOMO} and E_{LUMO}, energy gap ($\Delta E=E_{LUMO}-E_{HOMO}$) is another essential quantum chemical parameter for explaining surface adsorptive behaviour of the inhibitor molecules. Generally, Larger value of ΔE implies that the inhibition efficiency of the inhibitor is less due to low reactivity with the metal surface and lower value of ΔE implies that the inhibitor is having higher inhibition efficiency due to high reactivity with metal surface. Low values of the energy gap (ΔE) will provide good inhibition efficiencies, because the excitation energy to remove an electron from the last occupied orbital will be low (G. Gece, 2008). A molecule with a low energy gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is termed soft molecule (A. Dwivedi and N. Misra, 2010). In this study, Table 4.0 shows the lower values of $\Delta E_{(LUMO-HOMO)}$ in the following order Arginine (0.2797) < Alkaloid (0.3032). The adsorption of inhibitor onto a metallic surface occurs at the part of the molecule which has the greatest softness and lowest hardness (Z. Wang, 2012). Chemical hardness (η) and softness (σ) are significantly related to the band gap (HLG). They are important properties to measure the stability and reactivity of a molecule. A soft molecule has a small energy gap and a hard molecule has a large energy gap (N.O. Obi-Egbedi *et al.,* 2011). According to Pearson, hard molecules with large energy gaps cannot act as good corrosion inhibitors. Conversely, soft molecules with small energy gaps are efficient corrosion inhibitors because they can easily donate electrons to metal atoms at the surface. Table 4.0 reveal that constituent of *BE* seed extract have greater values of softness (σ) and lower values of hardness (η).

The *BE* seed (σ) values of the studied extract increases in the order: Arginine (7.1480) > Alkaloid (6.5963) and the corresponding hardness values decreases in the reverse form of the order: Arginine (0.1399) < Alkaloid (0.1516). This confirmed the extract molecule as efficient corrosion inhibitor. Moreover the mapping of molecular electrostatic potential (ESP) can allow an observation of the regions of high and low electron density in an organic corrosion inhibitor molecule. This can help determine the possible sites in the inhibitor molecule which are susceptible to undergo adsorption interaction with a metal surface (P. Dohare *et al.,* 2017, J. Haque *et al.,* 2017a). The ESP mapping of the Component of *BE* seed extract are displayed in Figure 2.0. The different values of ESP are shown in different colours where the most negative ESP regions are shown in red colour i.e. regions rich in electron, blue colour shows the region of the most positive ESP thal is electron deficiency while the green colour shows the regions with zero ESP values (J. Haque *et al.,* 2017b, D.S. Chauhan *et al.,* 2018) . It can be seen that in the Component of *BE* seed extract, the most negative potential (red color) is around the heteroatoms (oxygen and nitrogen). Upon protonation at nitrogen, a deep blue coloured region can be observed around the nitrogen atoms showing a deficiency of electrons and the possible centre's susceptible for undergoing physical adsorption via electrostatic interaction.

Mulliken charge distribution of Arginine, Flavonol and Alkaloid: Mulliken population analysis is mostly used for calculation of charge distribution in a molecule (S. Martinez and I. Tagljar, 2003). Mulliken charge distribution of flavonol and alkaloid are presented in Table 5.0. It shows Mulliken charge distribution of all heteroatoms and some of carbon atoms are negatively charged. Thus, considered as active sites for adsorption process of inhibitor molecule onto the mild steel surface (R. Lgaz *et al.,* 2016). More negative the atomic charges of adsorbed centre, more easily atom donates its electron to unoccupied orbital of the metal (A.Y. Musa *et al.,* 2010). The inhibition efficiency of inhibitors under study depends on presence of electronegative atoms in their molecular structure.

It can be readily observed that oxygen atoms followed by nitrogen and most of the carbon atoms have higher charge densities/negative charges. Arginine has more electronegative N7 and O11 with charges -0.4039 and -0.3290. In Arginine, C4, C3, C2, O10, N7 and O11 are most susceptible sites for electrophilic attacks as they present highest values of negative charge. On other hand, C9 in Arginine is the most susceptible sites for the nucleophilic attacks as its present the highest values of positive charge. The regions of highest electron density are generally sites to which electrophiles can attack (A.Y. Musa *et al.,* 2010). Alkaloid has O10, C8, C22, C5, C21 and C22 as the most susceptible sites for electrophilic attack as they offer the highest values of negative charge. The susceptible sites for nucleophilic attacks possess highest values of positive charge at N9 and C6 atoms were active centers that possess strong ability of bonding to metal surface occur. Therefore, Arginine and Alkaloid can accept electrons from metal through these atoms and hence these compounds could serve as good corrosion inhibitor against metal surface protection.

Conclusion

- From the above results and discussions, the following conclusion was drawn:
- All the studied phytochemical constituent of the seed extracts acts as an effective corrosion inhibitor of mild steel in 1M H_2SO_4 acid solution and their inhibition efficiency increases with increase in the concentration of the seed extracts with maximum efficiency obtained at an optimum concentration of 5.0g/l within the first 24 hours.
- The adsorption data was best fitted into Langmuir adsorption models.
- The results of SEM and Fourier transform infrared spectroscopy (FTIR) all indicate that the corrosion reaction was inhibited by the adsorption of the extract's organic matter onto the corroding mild steel surface.
- The trends of inhibition efficiency with temperature as well as values of kinetic and activation parameters for corrosion and corrosion inhibition processes point toward significant physiosorption of the extract constituents on the mild steel surface.
- DFT-based quantum chemical computation was used to theoretically model the physiosorptive interactions between the plant extract's molecules, which are the active components of the extract and mild steel surface. The magnitude of the obtained adsorption energy confirms strong physiosorption of the molecules.
- Phytochemical screening, weight loss measurements, and quantum analysis confirmed the corrosion preventive property of *Brachystegia eurycoma* seed (*BE*S) in 1M H_2SO_4 medium. The investigation shows *Brachystegia eurycoma* seed *(BE*S) extract as an excellent inhibitor for mild steel corrosion in 1M H_2SO_4.

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