Evaluation of Anticorrosion Potential of African Black Olive (*Canarium schweinfurthi*) Oil as Green Corrosion Inhibtor on Aluminium Sheet in Acidic Medium

*MOHAMMED, J; MOHAMMED, MS; ISAH, J

Department of Chemistry, Faculty of Natural & Applied Sciences, Nasarawa State University, Keffi, Nigeria

Corresponding Author Email: jibrinmohammed@nsuk.edu.ng
Co-Authors Email: jibrinisah@nsuk.edu.ng; ogoshibasata4@gmail.com

ABSTRACT: This study evaluated the anticorrosion potential of African black olive oil obtained from its fruit (pulp) on Aluminium sheet in 2M H_2SO_4 using gravimetric method. The extraction was carried out using soxhlet extractor and the oil was characterised using Fourier Transform Infrared Spectrophotometer (FTIR). The results showed that the oil exhibits maximum inhibitive efficiency of 88.57%. The FTIR analysis showed the presence of C=C-H, Ar-H bending out of plane, C-H bending in plane, C-O, N-O asymmetric stretch, C=C stretch, C=N stretch, and O-H functional groups at various peaks (wave numbers).The adsorption of the African black olive oil onto the Aluminium surface during the inhibition process obeyed Langmuir adsorption isotherm. Hence, based on the outcome of this study, the African black olive oil possessed excellent anticorrosion property for the corrosion of aluminium in the acidic medium and can also be used as green corrosion inhibitor for other metals.

Over the years, the effects of corrosion in the industrial sector had caused loss of billions of dollars (Hussin and Kassim, 2010). Studies revealed that Indian government spends around 3.5% of their nation's gross domestic product (GPD) per annum for losses due to corrosion (Geethamani, *et al.,* 2014). However, corrosion is the manifestation of deterioration of materials or equipment due to failure of maintenance or repairs and replacement of damaged parts (Obo *et al.,* 2009). Thus, corrosion has effects on infrastructures such as chemical processing units, waste water treatment, exposed structures/buildings and other metallic objects in our daily use (Bereket and Yurt, 2001). Furthermore, corrosion is an undesirable phenomenon which destroys the quality and beauty of materials or equipment and also lessens their life-span (Obo *et al.,* 2009). Moreover, the effect of corrosion is not only limited to destruction of equipment but also affects the environment, human safety and industrial operations (Abiola *et al.,* 2017). Aluminium and its

alloys are widely used in various fields because of their physicochemical properties compared to other metals (Safak *et al*., 2012). The corrosive medium of hydrochloric acid is commonly used for chemical or electrochemical cleaning and acid stripping of aluminium. Thus, in aqueous solution, a passive oxide film will be formed which compacts and adheres to the aluminium surface (Abiola *et al.,* 2017). The film (amphoteric) formed is substantially dissolved in an acidic or basic medium and undergoes corrosion process (Li *et al.,* 2014). However, to address this problem, several techniques such as alloy selection, anodic protection and addition of inhibitors have been applied (Ahamad, *et al.,* 2010; Singh*, et al*., 2010).Furthermore, on the application of inhibitors to address this menace, several scientific studies had reported their effectiveness on the protection of metals and alloys against the ravaging effects of corrosion (Solmaz *et al.,* 2008; Eddy *et al.,* 2009). However, current researches on corrosion are focused on green

inhibitors on the basis of their effectiveness, economic, eco- friendly to the environment and toxic free to humans (Nnanna *et al.,* 2010; Adejo *et al.,* 2013).

African black olive *(Canarium schweinfurthi)* is a large, evergreen forest tall tree with many benefits. In Nigeria, it's most common in the Northern and Eastern regions of the country. Thus, it's called ube in Ibo language and Atile in Hausa language. The fruit (pulp) contains about 40-50% oil (Agu *et al.,* 2008) .Thus, the nutritional and medicinal applications of this oil has been reported (Agu *et al.,* 2008; Nyam *et al.,* 2012).In order to extent its applications, there is need to explore its inhibitive potential against corrosion. Therefore, this study aimed at evaluating the inhibitive potential of African black olive *(Canarium schweinfurthi)* oil as green corrosion inhibitor for the corrosion of aluminium in acidic medium.

MATERIALS AND METHODS
Extraction of the African Black Olive Oil: The extraction was carried using soxhlet extractor. A total of 80.0 g of the sample was weighed and loaded into the soxhlet extractor containing 250 ml of hexane as solvent for the oil extraction. The mixture was heated at reflux for 5hrs. The solvent was recovered from the oil extract using a rotary evaporator. The oil extract was further concentrated in a fume hood by allowing the residual solvent to be evaporated (Olusegun *et al.,* 2013).

FTIR Analysis of the Oil: After the extraction, the oil was subjected to Fourier Transform Infrared Spectrophotometer for identification of the functional groups presence in the oil.

Metal Preparation: The aluminium sheet was cut into coupons of dimension 3cm x 2cm x 1 cm. The coupons were cleaned followed by polishing with sand paper to expose shining polished surface. The coupons were further degreased with acetone to remove any oil or organic impurities followed by washing with distilled water, sun dried and then stored in desiccators. The weight of each coupon was taken using electronic weighing balance and the initial weight was recorded (Znini *et al.,* 2011).

Corrosion Inhibition Study: Gravimetric method was adopted to examine the inhibitive efficiency of the oil extract at various concentrations. In this method, the coupons were separately immersed completely into 250 ml beaker containing 40 ml solution of 2M H_2SO_4 in the absence and presence of the inhibitor with different concentrations at 25°C ± 2°C for 48 hrs. The coupons were withdrawn from the solution, immersed

in acetone, scrubbed with a brush, washed thoroughly with distilled water and properly dried. Variations in the weight loss of the coupons in the absence of the inhibitor were monitored periodically at the interval of 24, 48, 72, 96 and 120hrs respectively (Umoren *et al.,* 2008). The weight loss by the coupons were calculated as the difference between the initial weight before immersion and the final weight after the removal of the coupons from the solution. However, the corrosion rate(CR), inhibition efficiency (IE)% and surface coverage (θ) were calculated using equation 1, 2 and 3 respectively (Bouklah *et al.,* 2005; Inemesit and Nnanake, 2013).

$$CR\ (g/cm^{-2}h^{-1}) = \frac{w - w_1}{AT} - - -\ (1)$$

Where CR = Corrosion rate (g/cm^{-2}h^{-1}); w and w_1 are the initial and final weight, A = surface area of the coupon (cm^2) and T = time of exposure or immersion.

$$IE(\%) = \frac{CR_B - CR_W}{CR_B}\ \text{x}\ 100\ \ --(2)$$

$$\theta = \frac{CR_B - CR_W}{CR_B}\ \ ---(3)$$

Where IE Inhibition Efficiency; θ = surface coverage; CR_B and CR_W are the corrosion rates in the absence and presence of the inhibitor.

Adsorption Isotherm: Langmuir adsorption isotherm was applied to examine the mechanism of the adsorption process of the inhibitor (oil) onto the Aluminium surface in 2M H_2SO_4. The Langmuir isotherm equation is given in equation 4.

$$\log\frac{C}{\theta} = \log C - loK\ \ ---(4)$$

Where C is the concentration of the inhibitor, K is the adsorption equilibrium constant and θ is the degree of surface coverage.

RESULTS AND DISCUSSION
Variation of Corrosion Rate with Immersion Time in the Absence of the Inhibitor: Table 1 shows the result of the variations in corrosion rate with immersion time of the coupons in 2M H_2SO_4 in the absence of the inhibitor. It was observed that the coupons immersed in the acidic medium without inhibitor showed the highest corrosion rates compared to those immersed in the acidic medium containing various concentrations of the inhibitor (Table 2). It was also observed that there was increase in the corrosion rate as the time of immersion increased from 24hrs to 48 hrs and a decreased in the corrosion rate as the immersion time

increased from 72hrs to 96hrs and also, a slight increase was observed at 120hrs compared to the immersion time of 72hrs to 96hrs.These observations are in closed agreement with most previous studies on corrosion (Wiskic *et al*., 2000; Omotioma & onukwulia, 2016; Abiola *et al.,* 2007; Nadia *et al.,* 2019).However, the variations observed in the corrosion rate from 72hrs to 96hrs immersion time could be attributed to the fact that the oxide film formed on the metals surface which was relatively stabled at 96hrs and subsequently destroyed when the immersion time increased to 120hrs was growing under tension, hence the formation of discontinued porous film possessing low protective properties(Nadia *et al.,* 2019).

Table 1: Variation of Corrosion Rate with Time of Immersion in 2M H_2SO_4

Coupons	Immersion Time (hrs)	Weight loss(g)	CR (g/cm^2h^{-1})
A1	24	0.06000	0.00042
A2	48	0.10000	0.00350
A3	72	0.32000	0.00074
A4	96	0.63000	0.00110
A5	120	1.21000	0.00168

Variation of Corrosion Rate and Inhibition Efficiency in Presence of the Inhibitor: Table 2 shows the result of the corrosion rates and inhibition efficiencies of Aluminium in 2 M H_2SO_4 in the presence of the inhibitor at different concentrations. From the result, it was noticed that increase in concentrations of the inhibitor increased the inhibition efficiencies (IE) while the corrosion rate (CR) decreased. Similar scenario was observed in the relationship between the degree of surface coverage (θ) and the concentrations of the inhibitor in the system (Table 2). These observations are also in closed agreement with many related literatures (El-Etre, 2003;Radojcic *et al.,* 2008; Lashgari and Malek, 2010).Furthermore, the

continues decrease in the corrosion rate of the test coupons with increase in the concentrations of the inhibitor in the solution is due to the fact that, the more the concentration of the extract in the solution, the more readily the extract molecules get adsorbed on the metal's surface and the smaller the anodic area becomes, thus, favouring anodic polarization (Omotioma and onukwulia, 2016).

Table 2: Corrosion Rates and Inhibition Efficiencies of Aluminium in 2 M H_2SO_4 in the Presence of African Black Olive Oil at various Concentrations

Inhibitor Conc. (ml)	CR (g/cm^2h^{-1})	(θ)	IE (%)
2.00	0.0018	0.4857	48.57
4.00	0.0013	0.6286	62.86
6.00	0.0007	0.8000	80.00
8.00	0.0006	0.8286	82.86
10.00	0.0004	0.8857	88.57

FTIR Analysis the African Black Olive Oil: Figure 1 and Table 3 present the peaks of spectrum of the Atili oil extract and the peak values, intensity and assigned functional groups corresponding to the peak values respectively. The peaks in indicate the presence of C=C-H, Ar-H bending out of plane, C-H bending in plane, N-O asymmetric stretch, C=C stretch, C=N stretch, and O-H stretch functional groups in the oil extract as clearly indicated in Table 1. However, according literature, heteroatoms (N-O), polar functional groups –(OH), electron donating –(CH_3) group, π -electrons and aromatic rings are good adsorption centres (Nadia *et al.,* 2019).Therefore, the presence of these functional groups in the oil extract is suggested to be responsible for the corrosion inhibition since most of the adsorption centres mentioned above are identified in the African black olive oil . In addition, the inhibition process could be regarded as intermolecular synergistic effect of the various components of the African black olive oil.
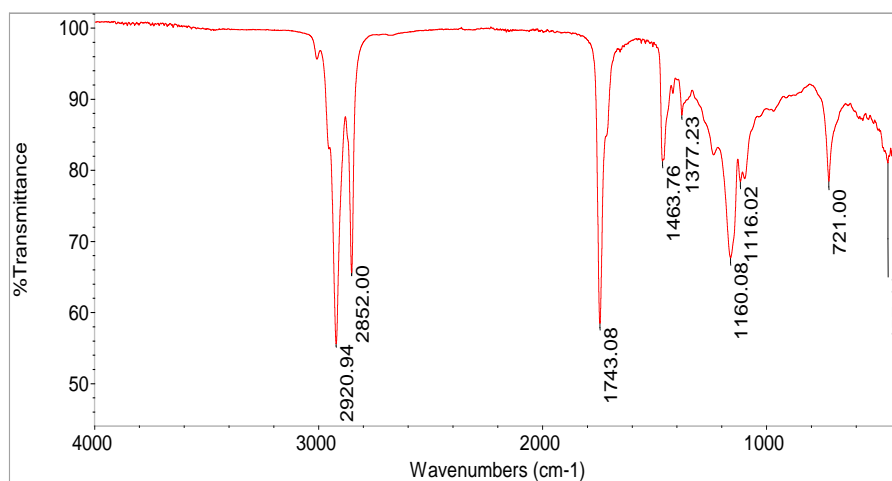

Fig 2: FTIR Spectrum of African black olive Oil

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Table 3: Peak, Intensity and Assignment of FTIR Analysis

Peak(cm^{-1})	Intensity	Assigned Functional Groups
721.00	78.40	C=C-H, Ar-H bend out of plane
1116.02	78.377	C-H bend in plane
1160.08	67.659	C-O- symmetric stretch
1377.23	87.748	N-O asymmetric stretch
1463.76	81.279	N=O symmetric stretch
1743.08	58.415	C=C stretch, C=N stretch
2852.00	55.558	C-H, O-H, N-H stretch
2920.94	55.558	C-H, O-H, N-H stretch

Adsorption Isotherm Analysis: Generally, adsorption isotherms are very important mathematical models used in understanding the nature and mechanism of surface reactions (Jibrin *et al.,* 2019). Figure 2 shows the Langmuir adsorption plots for the inhibition process of Aluminium in 2M H_2SO_4 in the presence of the inhibitor. The data obtained from the degree of surface coverage (Table 2) were tested graphically into Langmuir adsorption isotherm and were found fit based on the correlation coefficient value of 0.6998. However, this suggests that the adsorption of the inhibitor onto the aluminium surface in 2M H_2SO_4 solution obeys Langmuir adsorption isotherm. Furthermore, this implies that inhibition process is due to the formation of mono layer on the Aluminium surface which inhibits electrolyte access.
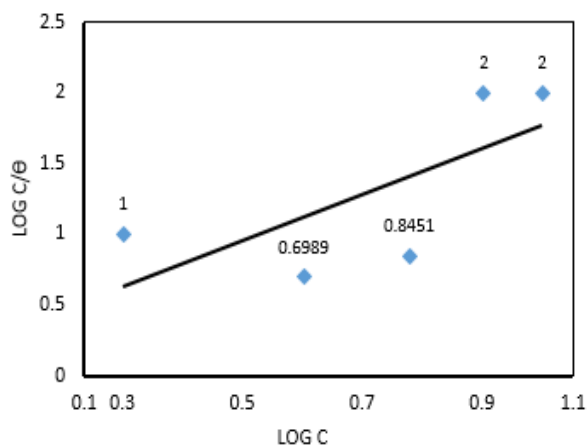

Fig 2: Langmuir adsorption plot for the Corrosion inhibition of Aluminium in 2M H_2SO_4 in the presence of African black olive oil

Conclusion: The study revealed that the inhibition efficiency increased with increase in the concentrations of the oil and it showed the maximum inhibition efficiency of 88.57%. Therefore, based on outcome this study, the African black olive oil possessed excellent anticorrosion potential for the corrosion of aluminium in the acidic medium and can be used as an excellent green corrosion inhibitor for the treatment of metals against corrosion.

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