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Polyalthia longifolia as a Corrosion Inhibitor of Brass in Alkaline (KOH) Medium

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Abstract

This study evaluates the inhibition efficiency of *Polyalthia longifolia* leaves extract on brass in an alkaline medium (KOH) using weight loss technique. The weight loss, corrosion rate and inhibition efficiency were determined using standard procedure. FT-IR analysis revealed the presence of some functional groups (-C=O, -C=N, O-H and C-H stretching) indicative of the inherent inhibition potential of the extract. The result showed that the weight loss was higher at 313 K than 303 K and decreased with increasing concentration of the inhibitor. The corrosion rate also increased with increasing concentration of KOH solution and was minimal at 700 mg/dm^3. With the addition of inhibitor (*Polyalthia longifolia*) the inhibition efficiency (% I_E) was found to increase in the order: 100mg/dm^3 ≤ 1000mg/dm^3 at 303K (81.2585% efficiency), and at 313 K (78.3473% efficiency). It also revealed that highest inhibition efficiency was recorded at 303K. The result of SEM analysis showed that the metal surface was protected from corrosion in the presence of plant extract which is acting as an inhibitor. On correlation of the inhibition dynamics to adsorption isotherms, the values of R^2; Langmuir (0.5494, 0.2715), Freundlich (0.7950, 0.7948), BET (0.6893, 0.6363) and Temkin (0.8262, 0.8255), showed that of Temkin to be the highest. This indicates that the system under investigation assumes monolayer adsorption on a homogeneous surface and no interaction between adsorbed molecules, making it suitable for chemical adsorption processes.

Keywords: Inhibition efficiency, *Polyalthia longifolia*, FT-IR analysis, SEM analysis, Adsorption models..

Introduction

The development of modern society and industry has led to a stronger demand for engineers with specialized knowledge in corrosion. There are a number of reasons for this: The application of new material requires new corrosion knowledge. Industrial production has led to pollution, acidification and increased corrosivity of water and the atmosphere [1]. Stronger materials, thinner cross-sections and more accurate calculation of dimensions make it relatively more expensive to add a corrosion allowance to the thickness. The development of industrial sectors like nuclear power production and offshore oil and gas extraction has required stricter rules and corrosion control [2]. Considering the future, it should be noticed that most methods for alternative energy production will involve corrosion problems.

Brass, an alloy of copper (Cu) and zinc (Zn) [3], contains small proportions of a range of other elements including arsenic (As), lead (Pb), phosphorus (P), aluminium (Al), manganese (Mn), and silicon (Si) and is used in applications where corrosion resistance and low friction are required, such as locks, hinges, gears, bearings, ammunition casings, zippers, plumbing, hose couplings, valves, and electrical plugs and sockets [4]. Corrosion is an increasingly serious and costly problem that can lead to plant and equipment failures, leakages in oil and gas pipelines as well as failure of steel bridges, ships, and buildings. These failures range from being an annoyance to being catastrophic. Failures caused by corrosion could lead to a direct failure of a component which could then affect the entire system; and can not only be very expensive in terms of down-time to repair, or replace plant and equipment, but can also be costly in terms of productivity, health or even loss of human life, as well as damage to the environment [5].

Corrosion phenomena, control and prevention are unavoidable major scientific issues that must be addressed daily as long as there is increasing needs of metallic materials in all facets of technological development [6]. The consequences of corrosion are many and varied, and the effects of corrosion on the safe, reliable and efficient operation of equipment or structures are often more serious than simple loss of a mass of a metal. Equipment failure of various kinds leading to the necessary expensive replacements may occur even though the amount of metal destroyed is quite small [7]. It is an ever present and increasing problem, often hard to eradicate totally. Metallic deterioration progresses rather fast after the destruction or penetration of the passive barrier, which is followed by a number of reactions that alter the constituents and behaviour of both the superficial metal surface and the immediate environment [8]. This is observed in, for example, oxides formation, gradual metal cation diffusion into the coating matrix, local pH changes and electrochemical potential.

The use of inhibitors is one of the most practical methods for protection against corrosion in corrosive environments. Inhibitors are substances that directly or indirectly coat a film on a metal surface to protect it from its environment. Most inhibitors are adsorbed by the metal surface from a solution or dispersed, but some are applied directly as coatings. Generally, the dissolution of metal can be suppressed by the action of adsorptive inhibitors which may prevent the adsorption of the aggressive ions, through the development of a more resistant film on the metallic surface [9].

Green approaches to corrosion mitigation entail the use of substances, techniques, and methodologies that reduce or eliminate the use of products, by-products, solvents, reagents, and so forth that are hazardous to human health or the environment in combating corrosion [10]. Among the alternative corrosion inhibitors, organic substances containing polar functions with nitrogen, oxygen and/or sulphur atoms in a conjugated system have been reported to exhibit good inhibiting properties [11]. Plants have been recognized as sources of naturally occurring compounds [12]. Most of the compounds extracted from plants are used in traditional applications such as pharmaceuticals and biofuels. Furthermore, naturally occurring compounds are of interest, because they are cost effective, abundant availability and more importantly their environmental acceptability. Due to these advantages, extracts of some common plants and plant products have been tried as corrosion inhibitors for metals and alloys under different environments [13]. The qualities mentioned above have made plants become an important source of a wide range of eco-friendly (green) corrosion inhibitors. *Polyathia iongifolia* has not been found in literature to have been used as a corrosion inhibitor It is a commonly available plant that does not compete with other food items. It will therefore add to the bank of corrosion inhibitors of plant origin.

Despite the broad spectrum of organic compounds available as corrosion inhibitors, the successful utilization of plant extracts that provide a rich source of naturally synthesized chemical compounds and that can be extracted by simple procedures with low cost as well as biodegradable in nature is a promising alternative [14]. The use of phytochemicals as corrosion inhibitors can be traced back to 1960s when tannins and their derivatives were used to protect corrosion of steel, iron and other tools [15].

In this study, leave extract of *Polyalthia longifolia* was prepared and utilized as an inhibitor against the corrosion of brass in alkaline medium (KOH). The effects of inhibitor's initial concentration on weight loss, corrosion rate and corrosion efficiency were evaluated. FT-IR and SEM analyses revealed chemical functionalities and inhibitory potential of the leave extract respectively. Hence, PL extract could serve as an alternative eco-friendly treatment against metal corrosion.

Materials and Methods

Collection of *Polyalthia longifolia* Leaves

Fresh leaves of *Polyalthia longifolia* were collected and washed with water. The leaves were then chopped into smaller pieces and allowed to dry for four days before grinding into powder for easy extraction [8]. This plant (*Polyalthia iongifolia)* is locally available all year round. It is environmentally friendly and far less costly compared to synthetic corrosion inhibitors.

Extraction of the Plant Extracts

The plant extract was obtained by soaking 100g of the ground plant leaves (*P. longifolia)* in 500 mL of ethanol (99.7% v/v) for 24 hours. At the end of the 24 hours, the plant mixture was filtered. The filtrate obtained is a mixture of the plant extract and the ethanol. The plant extract obtained in ethanol solvent was concentrated by evaporating the ethanol using rotary evaporator. The plant extract was weighed and stored for the corrosion inhibition study [8].

Preparation of Alkaline Solution

Alkaline solution of 0.5M KOH was prepared by dissolving 28g of KOH in 1 dm^3 of distilled water. KOH was measured with the aid of electronic weighing balance and dissolved in a beaker. It was then transferred into a volumetric flask and made up to mark with distilled water [9].

Preparation of Brass specimen

The brass rod used was obtained from Wukari town. The brass rod was cut into several coupons of uniform dimension of 5cm x 0.3cm and the coupon specimens was descaled by wire brushing. The specimens were mechanically polished with emery papers abrasive for a smoother surface, washed with propanone, air dried and kept in a desiccator to avoid contact with impurities for subsequent corrosion experiments.

FT-IR Analysis of the Plant Extracts (Characterization)

The isolated inhibitor, as well as the protective film that form over the brass surface by the inhibitor molecule, was analyzed separately using FTIR spectroscopy using the KBr pellet method. The brass specimens were immersed respectively in the corrosive medium consisting of 100 mL of the inhibitor for 24 hours, which resulted in formation of a fine protective film over the brass surface. Further, the film was carefully scratched from the brass surface and analyzed by FTIR spectroscopy. The analysis was carried out by using Perkin Elmer System FTIR instrument [10].

Determination of Corrosion Parameters and Adsorption Model Studies

These include the determination of weight loss (Δw), corrosion rate (CR), inhibition efficiency (I_E) and degree of surface coverage (Θ) using the following expressions respectively:

$\Delta w = w_i - w_f$ (1)

Where Δw is weight loss; w_i and w_f are the initial and final weight (mg) of brass metal samples respectively. $CR = \frac{w_i - w_f}{DAT}$ (2)

Where CR is corrosion rate ($mg/cm^2.h$); w_i and w_f are the initial and final weight (mg) of brass metal samples respectively; D is the density of brass; A is surface area of the coupon (cm^2); T is immersion time (h).

$I_E = \frac{\omega_0 - \omega_1}{\omega_0} X\ 100$ (3)

Where I_E = Inhibition Efficiency (%); ω_0 and ω_1 are the weight loss values in absence and presence of inhibitor (Negm *et al*., 2012).

$$\Theta = \frac{\omega_0 - \omega_1}{\omega_0} \quad (4)$$

The Isotherm models that were studied include Langmuir, Freundlich, BET and Temkin.

Results and Discussion

Effect of Inhibitor (*Polyalthia longifolia*) Concentration on Weight Loss of Brass

The weight loss of brass immersed in 0.5M KOH with various concentration of *Polyalthia longifolia* extract at 303 K and 313 K respectively are shown in Table 1 and Figure 1 The weight loss was observed to be slightly higher at 313 K than 303 K. The graph reveals that weight loss was lowest at 1000mg/dm^3 (highest concentration of inhibitor studied). This indicates that *Polyalthia longifolia* inhibits corrosion of brass to some extent, with inhibition increase with increasing inhibitor at lower temperature. Lowest weight loss was observed when the brass sample was immersed in 100 mg/dm^3 *Polyalthia longifolia* at 303 K (0.3539 mg) and 303 K (0.4199 mg). Similar observations were reported on the effect of weight loss of mild steel by aqueous extract of *Polyalthia longifolia* leaves in various concentration of HCl solution [8].

Table 1: Corrosion Parameters for Brass Metal in KOH containing *Polyalthia longifolia* Leaves Extract

Conc. (mg/dm^3)	**Weight Loss (Δw) (g)**		**Corrosion Rate (CR) (10^{-5}) (mg/cm^2.h)**		**Inhibition Efficiency (%)**		**Surface Coverage (θ)**	
	303K	**313K**	**303K**	**313K**	**303K**	**313K**	**303K**	**313K**
100	0.3539	0.4199	2.5530	2.9930	26.2861	23.3749	0.2628	0.2337
200	0.3369	0.4033	2.4300	2.9090	34.6839	31.7727	0.3468	0.3177
300	0.3151	0.3833	2.4273	2.7650	78.4964	75.5852	0.7849	0.7538
500	0.3012	0.3536	2.1730	2.5510	79.4498	26.5386	0.7944	0.7653
700	0.2712	0.3210	1.9560	2.3160	81.2585	78.3473	0.8125	0.7834

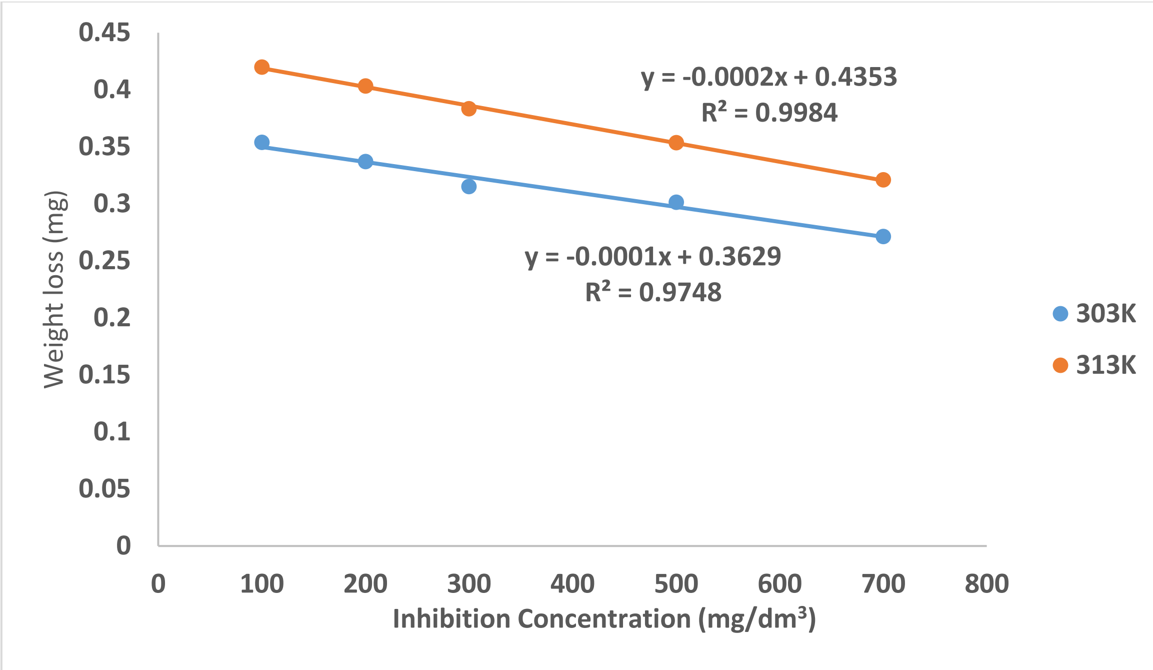

Figure 1: Weight Loss against Inhibition Concentration of *Polyalthia longifolia* Leaves Extract at 303 and 313 K

Effect of Inhibitor (*Polyalthia longifolia*) Concentration on Corrosion Rate of Brass

Figure 2 shows the variation in corrosion rate of brass by *Polyalthia longifolia* at different concentrations. The corrosion rate was observed to be slightly higher at 313 K than 303 K. It was observed that corrosion rate of brass increased with concentration of KOH solution. This could be attributed to the fact that the rate of chemical reaction increases with increase in acid concentration and temperature. The corrosion rate was minimal at 700 mg/dm^3.

Similar behaviour of aqueous extract of *Polyalthia longifolia* leaves on the corrosion rate of mild steel in dilute H_2SO_4 solution was observed in previous works [20]. Generally, it could be observed that the corrosion rate is decreased gradually with the level of extract concentration used. The reduction in the corrosion rates could be attributed to possibility of adsorption of bioactive inhibitor molecules on the metal surface forming a thin coating film that grows with time on the metal surface which hinders corrosive attack on the metal thereby reducing weight loss of the specimen.

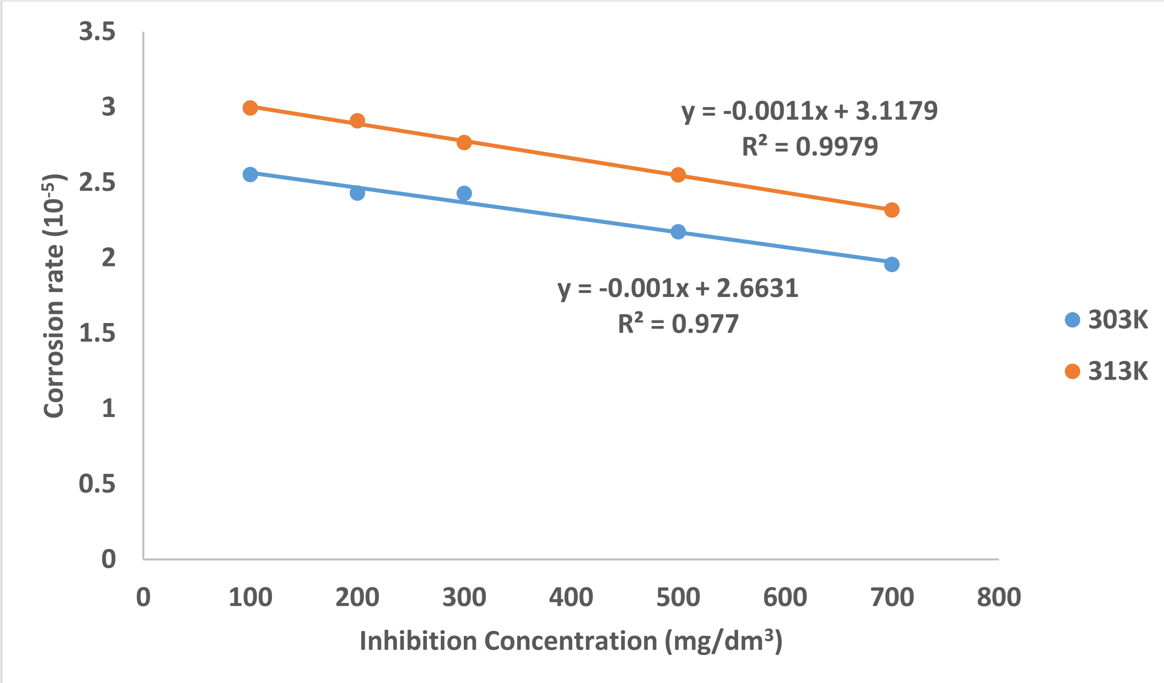

Figure 2: Corrosion Rate against Inhibition Concentration of *Polyalthia longifolia* Leaves Extract at 303 and 313 K

Effect of Inhibitor (*Polyalthia longifolia*) Concentration on Inhibition Efficiency of Brass

Figure 2 illustrates the evaluation of inhibition efficiency of *Polyalthia longifolia* against inhibitor concentration of aluminum corrosion in 0.5M KOH solution after 24 hours immersion respectively for different temperatures. With the addition of inhibitor (*Polyalthia longifolia*) the inhibition efficiency (% I_E) was found to increase in the order: 100mg/dm$^3 \leq$ 1000mg/dm^3 at 303 K (81.2585% efficiency), and at 313 K (78.3473% efficiency). It also revealed that highest inhibition efficiency was recorded at 303 K. The increase in the inhibition efficiency with concentration may be due to adsorption of *Polyalthia longifolia* onto the brass surface through the non-bonding electron pairs of N and O atoms as well as the л-electrons of the aromatic ring [25].

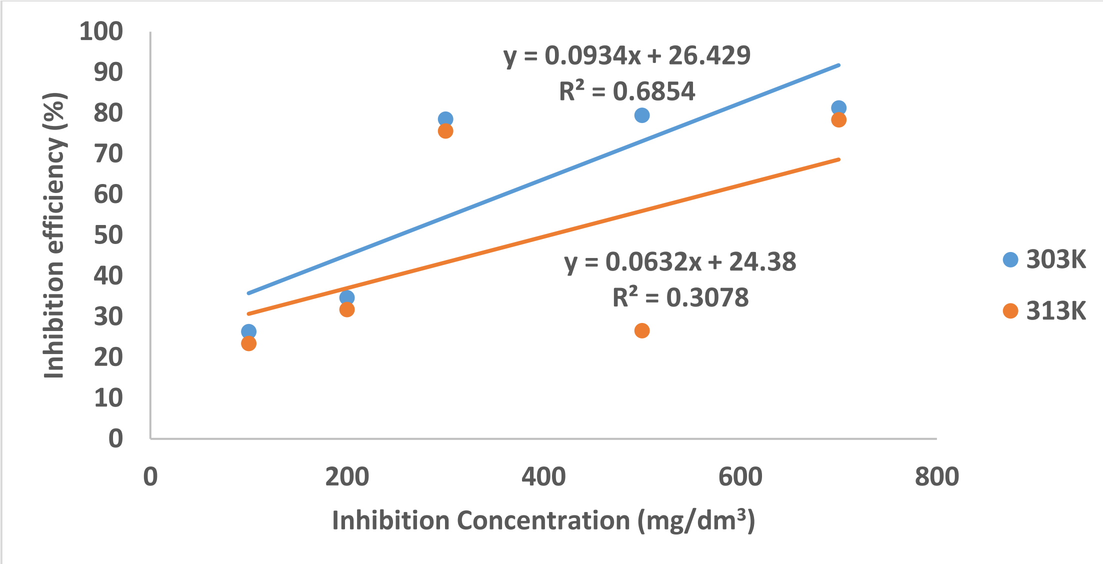

Figure 3: Graph of Inhibition Efficiency (%) against Inhibition Concentration of *Polyalthia longifolia* Leaves Extract at 303 and 313 K

Isotherm Studies

This section presents data on adsorption model studies. These include the plots and correlation coefficients, R^2 of the Langmuir, Freundlich, BET and Temkin's isotherms. A comparative analysis on these models follows afterward.

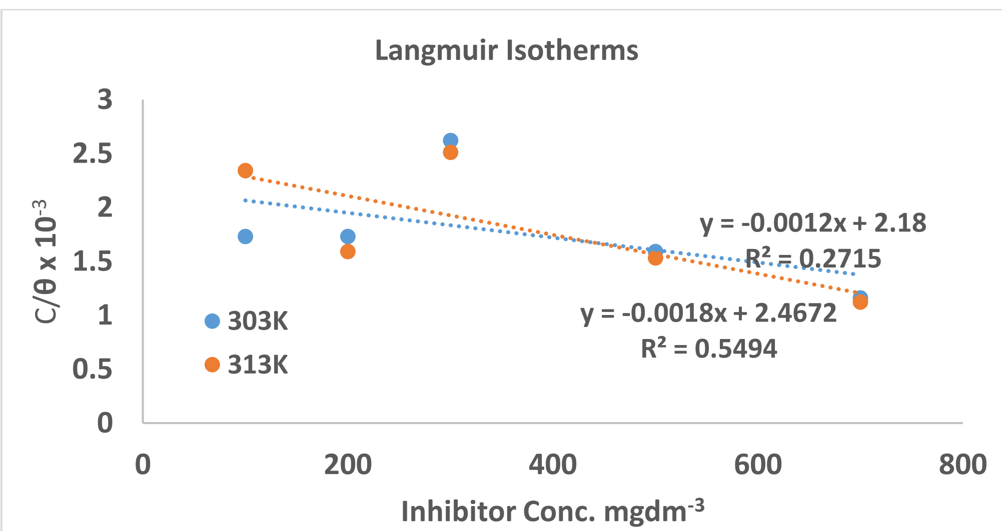

Figure 4: Langmuir Isotherm Plots

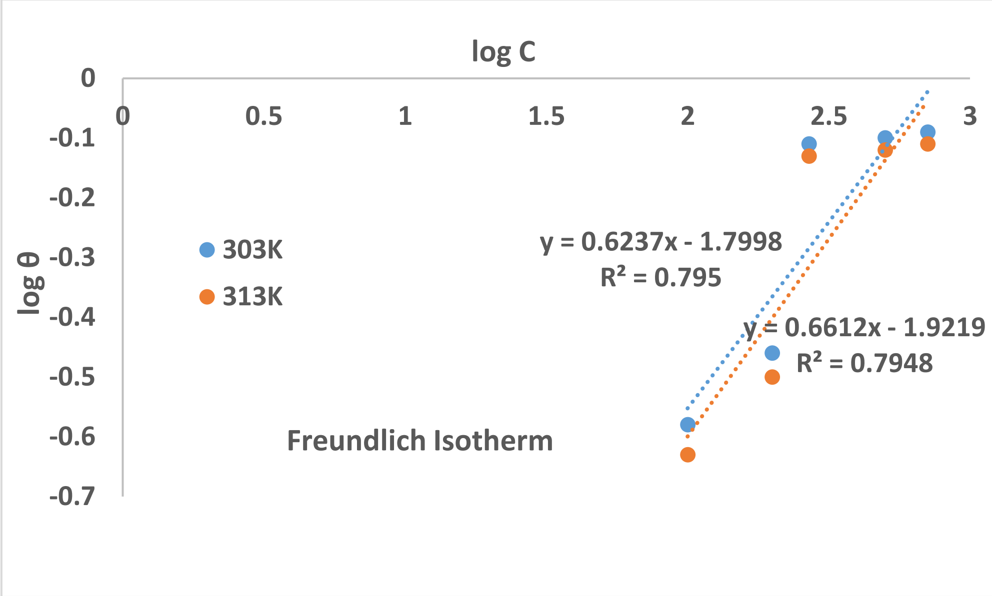

Figure 5: Freundlich Isotherm Plots

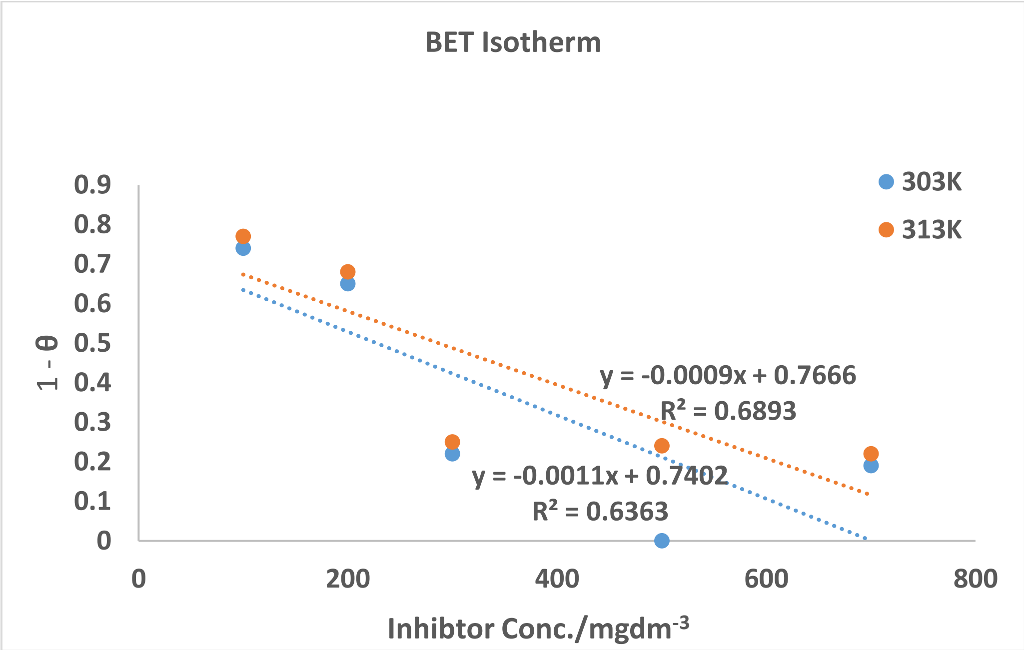

Figure 6: BET Isotherm Plots

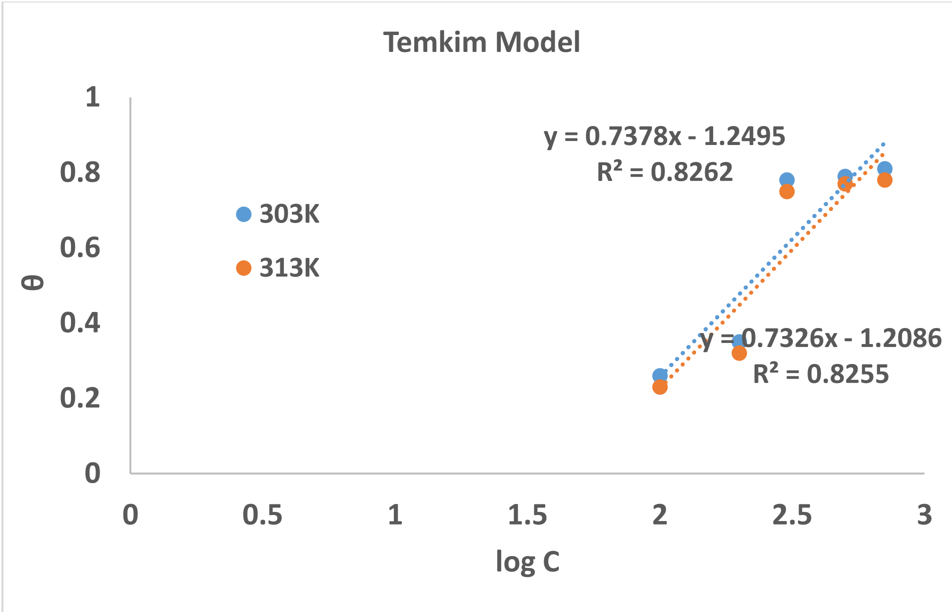

Figure 7: Temkin's Isotherm Plots

Table 2: R^2 Values of Adsorption Isotherms

Isotherm	**R^2 Values**	
	303K	**313K**
Langmuir	0.5494	0.2715
Freundlich	0.7950	0.7948
BET	0.6893	0.6363
Temkin	0.8262	0.8255

Comparative Analysis of Adsorption Isotherms

This analysis compares four adsorption isotherm models-Langmuir, Freundlich, BET, and Temkin-based on their correlation coefficient (R^2) values derived from experimental data.

The Temkin isotherm exhibits the highest R^2 values of 0.8262 and 0.8255 at 303 and 313 K respectively, suggesting the best fit among all models for the adsorption data. This model assumes monolayer adsorption on a homogeneous surface thereby accounting for the interaction between adsorbed molecules [21]. The adsorption is characterized by a uniform distribution of binding energies.

Freundlich model follows closely with R^2 values of 0.7950 and 0.7948 at 303 and 313 K, indicating a very strong fit. This model is particularly suitable for multilayer adsorption on non-uniform surfaces and are widely applied in surface area analysis [22]. It shows a non-linear relationship between the adsorbent and the adsorbate.

BET and Langmuir models, with R^2 values of 0.6893, 0.6363 and 0.5494, 0.2715 respectively, show relatively lower fits. BET isotherm is empirical and describes physical adsorption of gas molecules on solid heterogeneous surfaces [23], while the Langmuir model accounts for adsorbate-adsorbent interactions and assumes a linear decrease in adsorption heat with coverage [24].

Hence, the Temkin and Freundlich models are more appropriate for describing the current system under investigation.

Fourier Transform Infrared Spectrophotometer (FTIR) Analysis

The FTIR spectrum of brass metal in KOH and presence of *Polyalthia longifolia* leaves extract (Tables 3 and 4) shows different peaks and assignments. The shift/disappearance of some functional groups observed were as a result of the active functional groups that actually inhibit the metals during corrosion process.

Table 3 presents the analysis of brass metal in KOH. The FTIR spectra of the brass metal revealed a shift in O–H stretching from 4327.00 to 3492.00 cm^{-1}. The shift from 3207.00 to 2925.00 cm^{-1} corresponds to a C-H stretching C=C stretching and C=N stretching was observed in the shift from 2860.00 to 1650.00 cm^{-1}. The peak at 1455.78 cm^{-1} corresponds to N-O asymmetric stretching. C-O stretching is observed in the peak at 1251.00 cm^{-1}. The peak shift from 1159.00 to 1020.00 cm^{-1} corresponds to C-H bend in plane. The peak shift from 861.00 to 579.00 cm^{-1} corresponds to C=C-H, Ar-H bend out of plane.

Table.4 presents the analysis of brass metal in the presence of inhibitor (*Polyalthia longifolia* leaves extract). The FTIR spectra of adsorbed protective layer formed on the brass surface after immersion in KOH containing *Polyalthia longifolia* leaves extract revealed that the O–H stretching at 4367.00 cm^{-1} shifted to 3977.00 cm^{-1}. The shift from 3391.00 to 2925.87 cm^{-1} corresponds to a C-H stretching on the adsorbed brass film of the *Polyalthia longifolia* spectra. C=C stretch, C=N stretch was observed in the shift from 2859.00 to 1652.21 cm^{-1}. Shift from 1543.00 to 1451.41 cm^{-1} is identified as N-O asymmetric stretching. The peak shift from 1251.00 to 1165.00 cm^{-1}, 1159.00 to 1025.00 cm^{-1} and 871.00 to 456.00 cm^{-1} corresponds to the C-O stretch, C-H bend in plane and C=C-H, Ar-H bend out of plane on the adsorbed brass film of the *Polyalthia longifolia* spectra. The result indicates that the adsorption of the inhibitors took place via –OH stretching, N–H bending, C–O stretching for extracts, and –C, C–H:C–H bending and C–C stretching (in ring) and is in line with the work of [17].

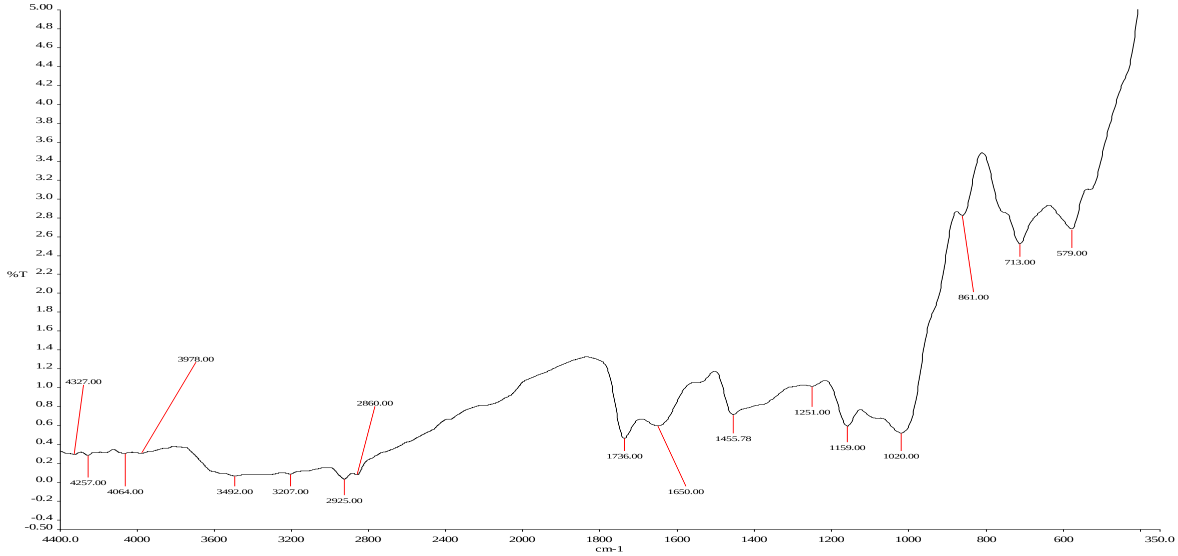

Fig 8: FTIR Spectrum of Brass Metal in KOH

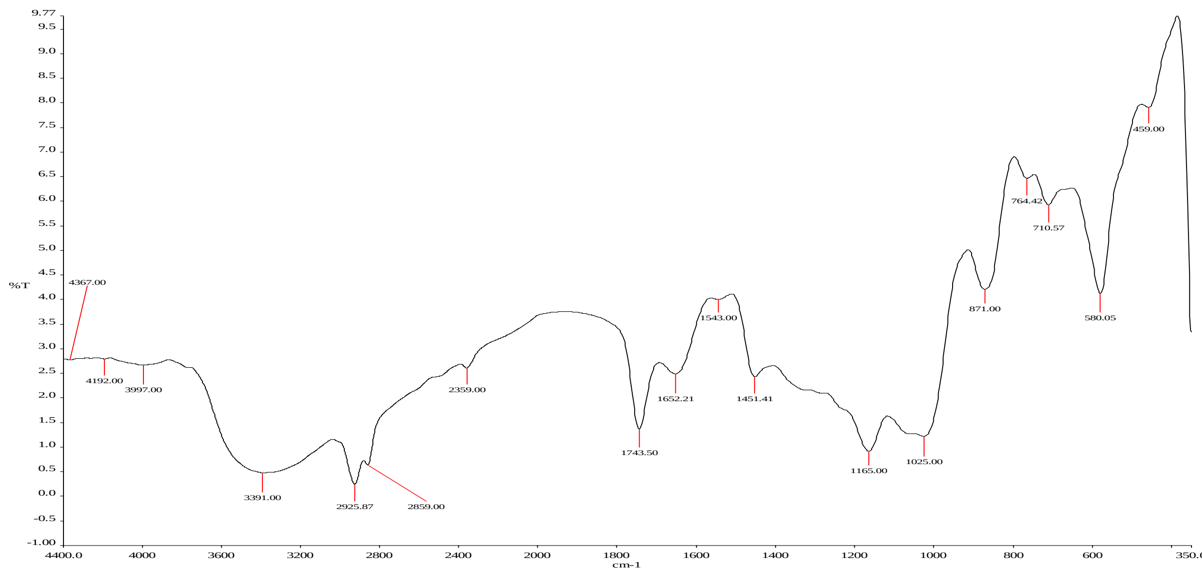

Fig 9: FTIR Spectrum of Brass Metal in the Presence of *Polyalthia longifolia* Leaves Extract

Table 3: FTIR Spectra of Brass Metal in KOH

Peak (cm^{-1})	Assignment
579.00	C=C-H, Ar-H bend out of plane
713.00	C=C-H, Ar-H bend out of plane
861.00	C=C-H, Ar-H bend out of plane
1020.00	C-H bend in plane
1159.00	C-H bend in plane
1251.00	C-O stretch
1455.78	N-O asymmetric stretch

1650.00	C=C stretch, C=N stretch
1736.00	C=C stretch, C=N stretch
2860.00	C=C stretch, C=N stretch
2925.00	C-H stretch
3207.00	C-H stretch
3492.00	O-H stretch
3978.00	O-H stretch
4064.00	O-H stretch
4257.00	O-H stretch
4327.00	O-H stretch

Table 4: FTIR Spectra of Brass Metal in the Presence of Inhibitor (*Polyalthia longifolia* Leaves Extract)

Peak (cm^{-1})	Assignment
456.00	C=C-H, Ar-H bend out of plane
580.05	C=C-H, Ar-H bend out of plane
710.57	C=C-H, Ar-H bend out of plane
764.42	C=C-H, Ar-H bend out of plane
871.00	C=C-H, Ar-H bend out of plane
1025.00	C-H bend in plane
1159.00	C-H bend in plane
1165.00	C-O stretch
1251.00	C-O stretch
1451.41	N-O asymmetric stretch
1543.00	N-O asymmetric stretch
1652.21	C=C stretch, C=N stretch
1743.50	C=C stretch, C=N stretch
2359.00	C=C stretch, C=N stretch
2859.00	C=C stretch, C=N stretch
2925.87	C-H stretch
3391.00	C-H stretch
3977.00	O-H stretch
4192.00	O-H stretch
4367.00	O-H stretch

Metal surface study using Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) provides a pictorial representation of brass metal in KOH and the presence of the inhibitor (*Polyalthia longifolia*). The result is presented in Figure 10a, 10b, 10c, 11a and 11b. From the image, there was significant differences in the morphology of brass metal surface in KOH and the presence of *Polyalthia longifolia* leaves extract. The brass surface was strongly damaged owing to corrosion in the absence of the inhibitor (Figures 10a, 10b, 10c). The surface of the corroded area was protected by the addition of the inhibitor as evident from Figure 11a and 11b.

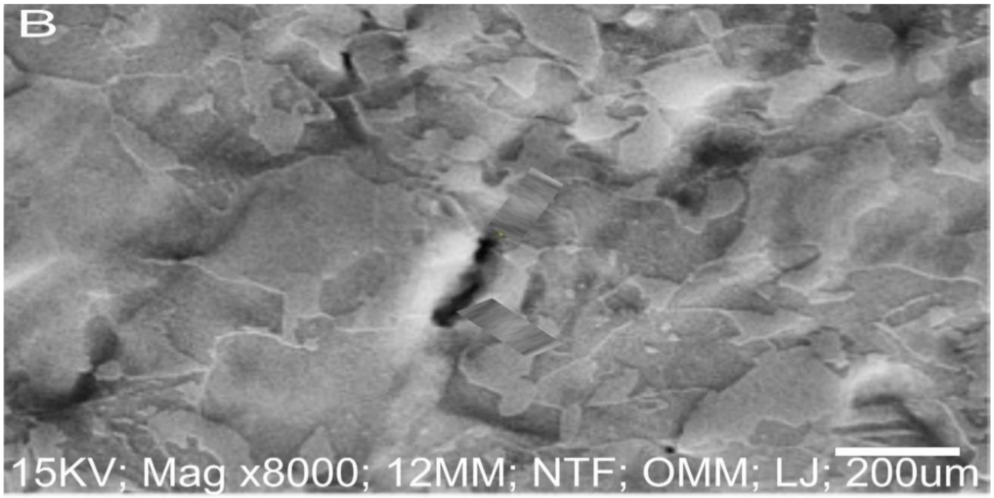

Figure 10a: Micrograph of Corroded Brass Metal in KOH

The SEM image clearly indicates that the metal surface was protected from corrosion in the presence of plant extract which is acting as an inhibitor. This is attributed to the formation of a good protective film on the metal surfaces by the inhibitors [18]. The micrographs have close correlation with the results obtained from the weight loss method. This is in agreement with the previous study by Loto and Popoola, [19]. The surface-nature of the corroded metals in the presence and absence of the plant extracts shows that the inhibitors suppressed the corrosion process.

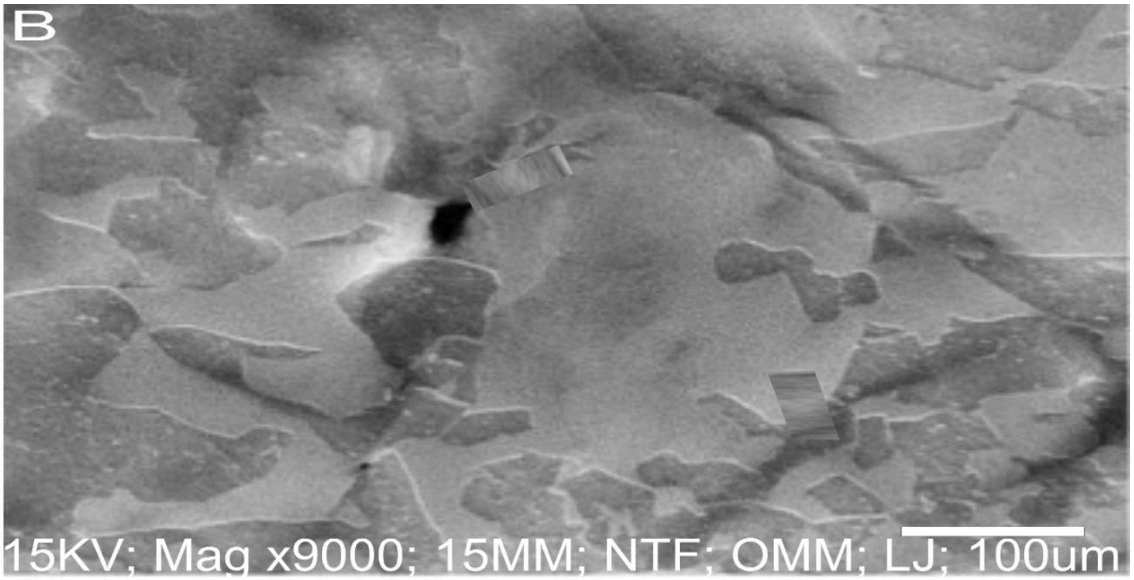

Figure 10b: Micrograph of Corroded Brass Metal in KOH

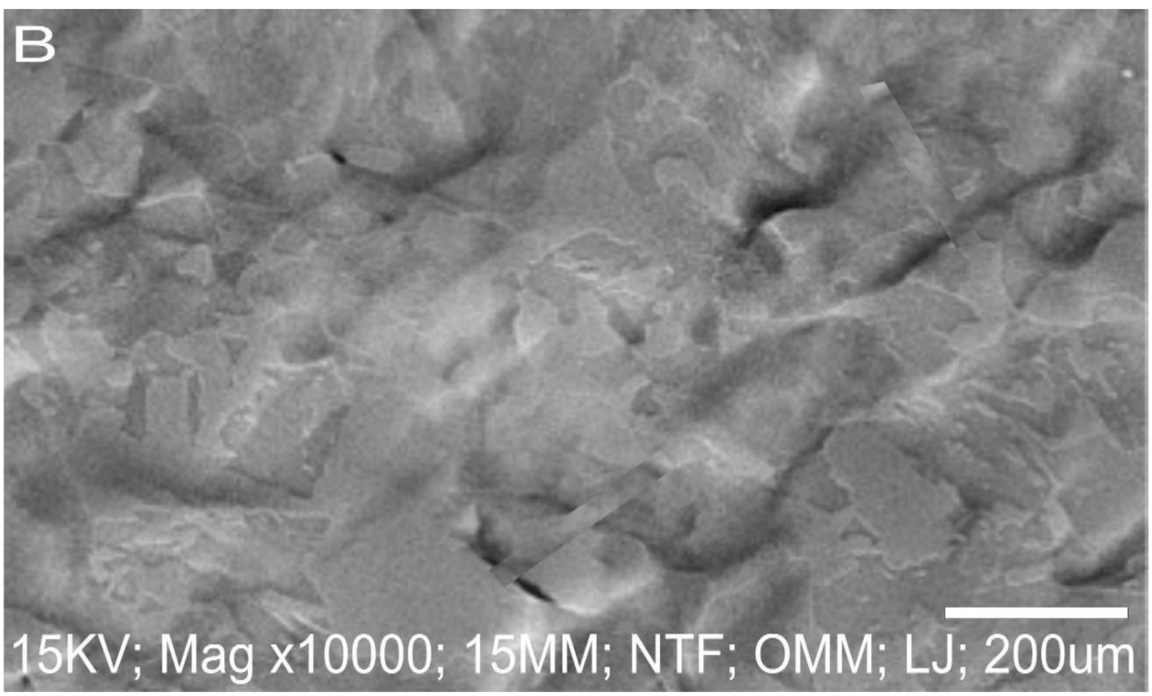

Figure 10c: Micrograph of Corroded Brass Metal in KOH

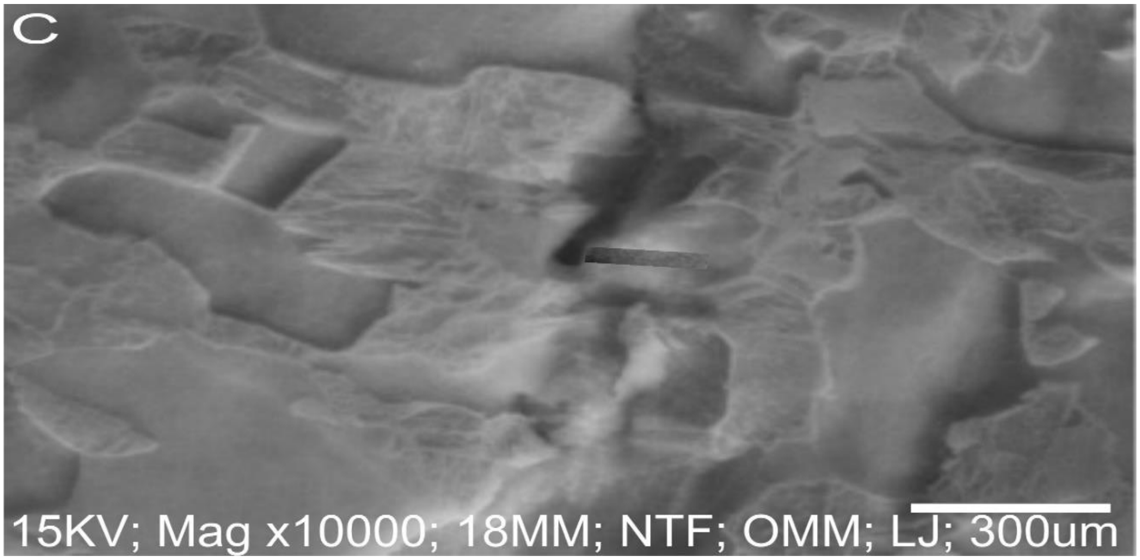

Figure 11a: Micrograph of Corroded Brass Metal in the Presence of Inhibitor (*Polyalthia longifolia* Leaves Extract)

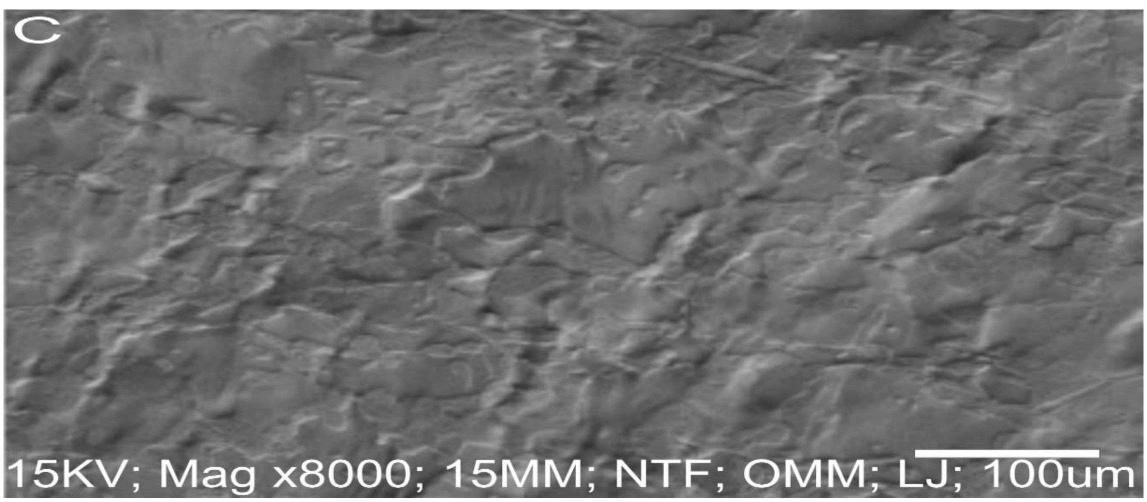

Figure 11b: Micrograph of Corroded Brass Metal in the Presence of Inhibitor (*Polyalthia longifolia* Leaves Extract)

Conclusion

The solvent extract from *Polyalthia longifolia* leaves was found to be effective green corrosion inhibitor that inhibits the corrosion of brass in different concentrations of KOH solution at slightly above room conditions. The use of *Polyalthia longifolia* leaves extract as corrosion inhibitor decrease the alkaline corrosion of brass to appreciable extent being physically adsorbed on the metal surface.

The 700 mg/cm^3 *Polyalthia longifolia* inhibitor reduced the weight loss and corrosion rate of brass. The efficiency (%I_E) of inhibitor increased with increase in the inhibitor concentration and decreased with increase in temperature. Furthermore, the inhibition efficiency significantly increases with concentration.

Among the values of the Correlation Coefficients, R^2; Langmuir (0.5494, 0.2715), Freundlich (0.7950, 0.7948), BET (0.6893, 0.6363) and Temkin (0.8262, 0.8255), that of Temkin is found to be the highest. This indicates that the system under investigation assumes monolayer adsorption on a homogeneous surface and no interaction between adsorbed molecules, making it suitable for chemical adsorption processes [21].

To advance this study, it is recommended that the utilization of *Polyalthia Longifolia* leaf extracts should be examined as potential green inhibitor for other metals and alloys under lower temperature condition and in different environments such as neutral and acidic media.

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