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Corrosion Inhibition of Mild Steel in 1M HCL by Ethanolic Stem Extract of *Caralluma DalzielII* N.E. BR.: Potentiodynamic Polarization and Adsorption Analysis

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ABSTRACT
The corrosion inhibition performance of the ethanolic stem extract of *Caralluma dalzielii* N.E. Br. (commonly known as Mosque reed) in 1 M HCl solution was investigated using potentiodynamic polarization. The inhibition efficiency of the extract was evaluated at 303 K and 333 K. Gas Chromatography–Mass Spectrometry (GC–MS) analysis revealed the presence of twenty (20) compounds in the extract, several of which contain heteroatoms (S, O) that are responsible for the corrosion inhibition effect. The functional groups present in the plant extract were further examined and identified by Fourier Transform Infrared (FTIR) spectroscopy. SEM/EDX shows the surface morphology and the elemental composition before and after the inhibition which directly support the electrochemical results. The results of the study showed that *Caralluma Dalzielii* extract effectively inhibited the acid corrosion of mild steel at different concentrations. The inhibition efficiency values at 303 K were: 0% (blank), 67.2% (200 ppm), 76.7% (400 ppm), 80.0% (600 ppm), and 81.0% (800 ppm). At 333 K, the efficiencies were: 0% (blank), 76.2% (200 ppm), 78.2% (400 ppm), 79.3% (600 ppm), and 84.4% (800 ppm). The inhibition efficiency increased with increasing inhibitor concentration at both temperatures. The adsorption of the inhibitor on the mild steel surface was found to follow the Langmuir adsorption isotherm, and the mechanism was dominated by physisorption.

Keywords:
Corrosion inhibition,
Caralluma dalzielii,
Electrochemical study,
Mild steel,
Adsorption.

INTRODUCTION

Acidic solutions such as hydrochloric acid (HCl) are routinely employed in industrial operations including pickling, descaling, and acidizing of steel equipment; however, these processes accelerate the corrosion of carbon and mild steels, jeopardizing asset integrity, product quality, and safety (koch *et al*., 2002). The global economic impact of corrosion is well documented, with comprehensive assessments estimating annual costs on the order of several percent of the world's gross domestic product—costs that can be mitigated substantially through effective corrosion management and inhibitor technologies (Revie *et al*., 2011). Conventional organic corrosion inhibitors (e.g., amines, imidazolines, and heterocyclic compounds) can be highly efficient in strong acid (Verma *et al*., 2015) yet many suffer drawbacks such as toxicity, poor biodegradability, and regulatory constraints, motivating sustained search for "green" alternatives derived from renewable feedstocks (Raja *et al*., 2008). Plant extracts have emerged as promising eco-friendly inhibitors in acidic media owing to their rich phytochemical profiles typically containing alkaloids, flavonoids, phenolic acids, tannins, terpenoids, and glycosides that possess heteroatoms (O, N, S), π-electron systems, and polar functional groups capable of interacting with metallic surfaces (Singh *et al*., 2016). These constituents can adsorb on steel, forming protective, quasi-passivating films that suppress both anodic iron dissolution and cathodic hydrogen evolution (Oguzie *et al*., 2008). Numerous studies have demonstrated that properly selected botanical extracts can attain high inhibition efficiencies for mild steel in 1 M HCl at ambient to moderately elevated temperatures, often rivaling commercial inhibitors while offering advantages in availability and environmental compatibility (El-etre *et al*., 2003). Within this context, members of the genus '*Caralluma'* (family Apocynaceae, formerly Asclepiadaceae) are noteworthy for their secondary metabolites, including pregnane glycosides, flavonoids, and triterpenoids (Abdallah *et al*., 2004), which are frequently implicated in surface adsorption and metal–inhibitor interactions (Al-said *et al*., 1995). *Caralluma Dalzielii* N.E. Br., (Mosque Stalk), which is also known as

Karan Masallaci in Hausa its distributed in parts of West Africa (Bouklah *et at*., 2006) has been studied for its phytochemistry and ethnobotanical relevance; however, its potential as a green corrosion inhibitor for mild steel in hydrochloric acid has received limited systematic attention (Fouda *et al.,* 2013). Ethanolic extraction of the plant's stem tissue is particularly attractive because ethanol efficiently solubilizes a broad spectrum of mid-polarity phytochemicals while remaining consistent with green chemistry principles (Bader et al., 1995). Establishing the corrosion-inhibiting capability of ethanolic stem extract of C. Dalzielii N.E Br. in 1 M HCl would therefore extend the portfolio of bio-derived inhibitors suitable for acidic pickling and cleaning environments (Patil *et al*., 2012). Potentiodynamic polarization (PDP) is a cornerstone electrochemical technique for mechanistic evaluation of acid-media inhibitors (Sedaghi *et al*., 2014) because it yields quantitative kinetic parameters most notably the corrosion potential (*Ecorr*) and corrosion current density (*icorr*), (Chemat *et al*., 2012) that permit calculation of inhibition efficiency and classification of inhibitor type (anodic, cathodic, or mixed-type) (Mansfeld *et al*., 1976) . Changes in Tafel slopes further elucidate whether the inhibitor alters charge-transfer kinetics at anodic and or cathodic sites (ASTM, 2014) while shifts in Ecorr can indicate dominant control of one half-reaction (Popova *et al*., 2007). When combined with comparative blank measurements in 1M HCl, PDP enables a rigorous, model-agnostic assessment of performance across inhibitor concentration and temperature ranges. The protection afforded by plant extracts is commonly interpreted through adsorption isotherms that relate surface coverage to inhibitor concentration at the metal/solution interface. Among these, the Langmuir model is frequently applied to organic inhibitors on steel in acid due to its simplicity and reasonable fit when monolayer adsorption with limited lateral interactions is a good approximation (Quraishi *et al*., 2010). Alternative models (Temkin, Frumkin, Freundlich) may provide better descriptions when adsorbate–adsorbate interactions or surface heterogeneity are significant (Arthur *et al*., 2019). Thermodynamic parameters derived from adsorption analyses such as the equilibrium adsorption constant and standard free energy of adsorption—offer insight into the nature and strength of the metal inhibitor interaction and complement kinetic interpretations derived from polarization data (Abdel-settar *et al*., 2007). In this work, we investigate the corrosion inhibition of mild steel in 1 M HCl by the ethanolic stem extract of *Caralluma Dalzielii N.E. Br.* using potentiodynamic polarization and adsorption analysis. Specifically, we (i) evaluate the inhibition efficiency across a range of extract concentrations; (ii) discern the inhibitor's control mode via Tafel behavior and Ecorr shifts; and (iii) model the adsorption behavior to extract thermodynamic descriptors of the interfacial interaction. By pairing kinetic electrochemical measurements with equilibrium adsorption modeling, this study establishes a coherent structure function rationale for *Caralluma*-derived phytochemicals as sustainable corrosion inhibitors in strongly acidic environments and benchmarks CD against the growing literature on plant-based inhibitors for mild steel in HCl. We also identified the phytochemical constituents in the extracts of *Caralluma Dalzielii*which were characterized via Fourier transform infra-red spectroscopy (FT-IR) and Gas Chromatography and mass spectrum (GC-MS) in the process.

Fig 1. *Caralumma Dalzeilii N.E Br. Stem*

MATERIALS AND METHODS

EXPERIMENTAL

Sample Preparation

The stems of *Caralluma Deilzelii* N.E Br. used for this research work were found around the bushes area of Shinkafi local government of Katsina (Rural) Katsina State, Nigeria. Latitude: 13.03 North, Longitude: 7.64 East, Altitude: 492.00m/1614.17 ft. The plant was authenticated at the herbarium Biological Science Department, Federal University Gusau, Zamfara state with Voucher ID : FUG/BOI/HEB/2023/103, the stems were washed, and dried in the shade away from sun light for up to three (3) months, purposely to prevent the loss of active components in the plant, some of the stems were preserved in the refrigerator while others were grounded well into a fine powder using local motor and pestle, transferred into an air tight container with proper labeling for immediate used (Hojatollah *et al*., 2013).

Preparation of Metal Specimen

The metal coupons used for this research work were Mild Steel sheets. The composition of the Mild Steel is 0.35% C, 0.032% Mn, 0.028% P, 0.03% S and the remaining Fe. The mild steel sheet was cut into coupons of dimensions 4 cm x 1.5 cm, length of 17.18 mm, thickness of 41.42 mm (which is a common unit for measuring thickness in metric system) and width 0.85 mm and were used for electrochemical measurement. The coupons were polished with a series of abrasive 200, 400 to 1200 grits of silicon carbide (SiC) waterproof paper, to a mirror-like surface. Then they were subjected to chemical treatments, degreased with absolute ethanol and dried with acetone and preserved in a desiccator prior to corrosion study. The chemicals used in this research were purchased and are of analytical grade quality, also the corrosive media used was 1M HCl solution prepared by using 35% HCl with double-distilled water as the corrodent. Using the prepared plant stem inhibitors/extracts, the stock solution of the inhibitor (*Caralluma Dalzeilii N.E Br.*) was made by weighing amount of previously prepared stem inhibitor in this prepared 1M HCl solution and kept for 48 hours to allow proper dissolution of the inhibitor (Chigondo *et al*., 2016). From the stock solution, the concentration range of the inhibitor was 0.2g/L/200 ppm, 0.4g/L/400 ppm, 0.6g/L/600 ppm,0.8g/L/800 ppm with the Blank

Maceration Procedure

300 g of powdered stem of *Caralluma Dallzeilii* N.E Br.were soaked in 1.25 L of ethanol, which serves as an extraction solvent for 48 hours. The extracts collected were concentrated using a rotary evaporator (RE-52A) to obtain the crude extracts (Patil *et al*., 2012). The percentage yield is 15%. The ethanol was also recovered completely and the crude extracts were further air dried and packed in a glass bottle with proper labeling and kept under a refrigerator between 0 ^{o}C to 4 ^{o}C away from sunlight by wrapping it with aluminum foil until required for use.

$$\boldsymbol{percentage\ yeild}\ (\%) = \frac{\boldsymbol{final\ weight\ of\ extract}}{\boldsymbol{initial\ weight\ of\ extract}} \times 100 \quad (1)$$

Electrochemical Method

The electrochemical measurement used is Tafel polarization to evaluate the corrosion inhibition performance of the inhibitor on mild steel by using direct current (DC). The electrochemical analyzer model used was AVM Bio-logic, Model S.P 300. The three-electrode setup used were; Silver Chloride (Ag/AgCl) as reference electrode (RE) with 3.5 M KCL electrolyte contained in it. Then 6.15 mm diameter/50mm length graphite rod was used as the counter electrode (CE). These were dipped and arranged in a hollow glass container and connected to the instrument by alligator clips. The hollow glass container with its contents were placed in a hot water bath and allowed to attain the desired temperature of 303 K and 333 K for the plant inhibitor, using a scan rate of 0.1667 mv/s and the instrument used in this chemical analysis was carried out in an atmospheric condition. The Mild steel of a measured dimension 4 cm x 1.5 cm, length of 17.18 mm, thickness of 41.42 mm and width 0.85 mm with measured surface area, was used as working electrode (WE) and was placed in depth of the hollow glass container, containing the two electrodes (Bader *et al*.,2003). The coupons were polished with a series of 200 to 1200 grits of emery paper to mirror-like surface. The parameters used for the mild steel were, Average surface area = 14.77 cm^2, Equivalent weight of the mild steel = 28.25 g, Density of the Mild Steel = 7.85 g/cm^2**,** Average Mass of coupons = 4.4 g**.** The electrochemical system was maintained at 30 minutes over open circuit potential (OCP); this is the time given for the electrodes to attain equilibrium states with the electrolytes in the system. The Polarization parameters were evaluated by performing Tafel fits from the analysis bottom of the lab software at a potential range of -250 mV to +250 mV relative to the corrosion potential (Eddy *et al*., 2010). The percentage of inhibition efficiency from Tafel polarization study was calculated by the following formula;

$$\textbf{Inhibition efficiency}\ (\eta\%) = \frac{(\textbf{Icorr})\textbf{o} - (\textbf{Icorr})}{(\textbf{Icorr})\textbf{o}} \times 100 \quad (2)$$

Where$(\text{Icorr})\text{o} - (\text{Icorr})$are the current densities with and without the inhibitor, respectively.

Surface Characterization using SEM/EDX

In order to observe any changes in the surface morphologies of the mild steel samples after testing,

the specimens were first immersed in the test media with and without inhibitor for 24h, then washed with distilled water and acetone and dried in cool air. The morphology of the tested samples was observed with energy-dispersive X-ray spectroscopy analysis (EDX), conducted with a scanning electron microscope (SEM). JEOL, Model 5300.

Adsorption study

The adsorption studies support the inhibition behavior of an inhibitor molecule on the mild steel surface, and the adsorption isotherm also provides valuable information on the interaction of the inhibitor and the surface of the metal. The mechanism of adsorption needs was discussed and understood thoroughly in the present literature (Hajotollah *et al*., 2013). The degree of surface coverage (θ) for the inhibitor was obtained from the Tafel polarization method data by dividing the inhibition efficiency by 100%. Different isotherms were plotted in order to find out the suitable adsorption isotherms for the adsorption of *Caralluma Dallzeilii N.E Br*. (Mosque Reed) molecules on mild steel surface in 1M HCl solution such as Temkin, Freundlich and Langmuir, but in the present study Langmuir adsorption isotherm was identified as the suitable for the process.

Surface coverage $(\theta) = \frac{\eta\%}{100}$ (3)

$\frac{C}{\theta} = \frac{1}{K} + C$ (4)

$\Delta G_{ads} = -RTln(55.5Kads)$ (5)

The above equations were used in the calculation of surface coverage, Langmuir adsorption isotherm and ΔG_{ads}

RESULTS AND DISCUSSION

Characterization

FTIR Analysis

The vibrational frequencies, functional groups and the frequency of the stem extract of the *Caralluma Dalzeilii* N.E Br. are presented in Table 1, while the FT-IR spectrum is presented as Fig. 2.

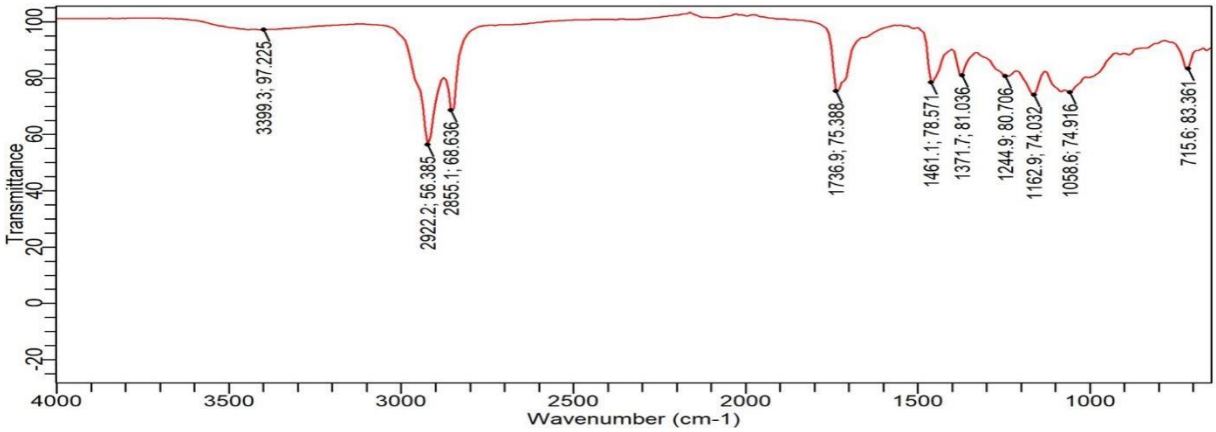


Figure 2. FT-IR spectrum characteristics for *Caralluma Dalzeilii N.E Brown* stem extracts.

Table 1. FT-IR peaks and assignment for *Caralluma Dalzeilii N.E Brown* stem extract

Peak No	Frequency of leaves (cm^{-1})	Intensity	Functional groups	Assignment (mode)
1	745.47	80.91	Aromatic C–H (lignin/phenolics)	Out-of-plane C–H bending of substituted aromatic ring
2	1021.29	66.86	C–O (polysaccharides: cellulose/hemicellulose)	C–O stretch / C–O–C skeletal vibration
3	1095.84	72.23	C–O–C, secondary alcohols (carbohydrates)	Asymmetric C–O–C stretch / C–O stretch
4	1222.57	70.57	Aryl–O / C–O (lignin, phenolics; also, amide III region)	C–O stretch (phenolic/ether) / amide III contribution
5	1341.84	70.57	CH_2/CH_3 (carbohydrates) ± phenolic O–H	CH bending (CH_2 sciss /CH_3 deform.) / O–H in-

6	1528.21	81.32	Aromatic C=C (lignin) ± amide II / NO_2 (asym)	plane bend Ring C=C stretching (lignin); possible amide II component
7	1684.76	79.70	C=O (conjugated ketone/aldehyde/acid) or amide I	C=O stretching (conjugated) / amide I (proteins)
8	2899.87	93.13	Aliphatic C–H (lipids/waxes/cutin)	C–H stretching (CH_2/CH_3)
9	3324.79	87.18	O–H (H-bonded water, phenolics) ± N–H	Broad O–H stretching; possible N–H stretching
10				

Discussion on the FT-IR spectrum of *Caralluma Dalzeilii* N.E Br. stem extract

The peak (1) 745.47 cm^{-1} (Aromatic C–H out-of-plane bending) ranges between 680–900 cm^{-1}.This region corresponds to aromatic C–H out-of-plane bending vibrations. It is highly characteristic of substituted benzene rings, which are abundant in lignin (a structural polymer in plant cell walls). Peak (2) 1021.29 cm^{-1} (C–O stretching, polysaccharides) between 1000–1100 cm^{-1} which is C–O stretching vibrations, often coupled with C–O–C skeletal modes. These are particularly strong in cellulose and hemicellulose. Peak (3) 1095.84 cm^{-1} (C–O–C stretching, carbohydrates) ranges between 1060–1120 cm^{-1} Asymmetric stretching of the glycosidic C–O–C linkage and C–O stretching of secondary alcohol groups. The Peak (4) 1222.57 cm^{-1} (C–O and amide III region) range in between 1210–1270 cm^{-1}.This band often arises from C–O stretching in phenolic compounds (lignin derivatives) or aryl–O vibrations. It also overlaps with the amide III band from proteins (N–H bending and C–N stretching).Peak (5) 1341.84 cm^{-1} (CH_2/CH_3) bending, phenolic ranges between 1320–1375 cm^{-1}.This peak corresponds to C–H bending vibrations in aliphatic groups (CH_2 scissoring or CH_3 deformation). In leaves, it can also indicate O–H in-plane bending in phenolics. Peak (6) 1528.21 cm^{-1} (Aromatic C=C, Amide II) ranges 1500–1560 cm^{-1}, the vibrations in this region usually arise from aromatic C=C stretching (again pointing to lignin) It also overlaps with the amide II band (mainly N–H bending with some C–N stretching) of proteins. Indicates contributions from lignin (aromatic character) and proteins (enzymes, structural proteins in leaves). Peak (7) 1684.76 cm^{-1} (C=O stretching / Amide I) ranges in between 1650–1690 cm^{-1}, and this strong band arises from C=O stretching. In biological samples, it can be assigned either to conjugated carbonyls (ketones, aldehydes, carboxylic acids, esters) or to the amide I band of proteins and it Indicates protein content in the leaves (amide I), and possibly carbonyl-containing compounds such as chlorophyll breakdown products or cell wall esters. Peak (8) 2899.87 cm^{-1} (C–H stretching, lipids/cutin) ranges in 2850–2960 cm^{-1} which is C–H stretching vibrations of aliphatic CH_2 and CH_3 groups. These come from lipids, waxes, and cuticular compounds, Points to the presence of leaf cuticle waxes, lipids, and fatty acid chains, which help regulate water loss and protect the plant from environmental stress. Peak (9) 3324.79 cm^{-1} (O–H / N–H stretching) between 3200–3500 cm^{-1}, this broad band corresponds to hydrogen-bonded O–H stretching (from water, cellulose, lignin phenolics) and/or N–H stretching from proteins, indicates the presence of bound water, hydroxyl groups in polysaccharides and phenolics, and leaf proteins. This is often one of the most intense and broad bands in plant FTIR spectra.

The GC-MS Study for *Caralluma Dalzeilii* (N.E Brown) Stem Extracts

The GC-MS chromatogram of *Caralluma Dalzeilii* N.E Br. extract is presented in Figure 3 and the major phytochemical compounds contained in the alcoholic extract of the extracts (with higher concentration percentage) are presented in Table 2 which is the representative structures of this major components.

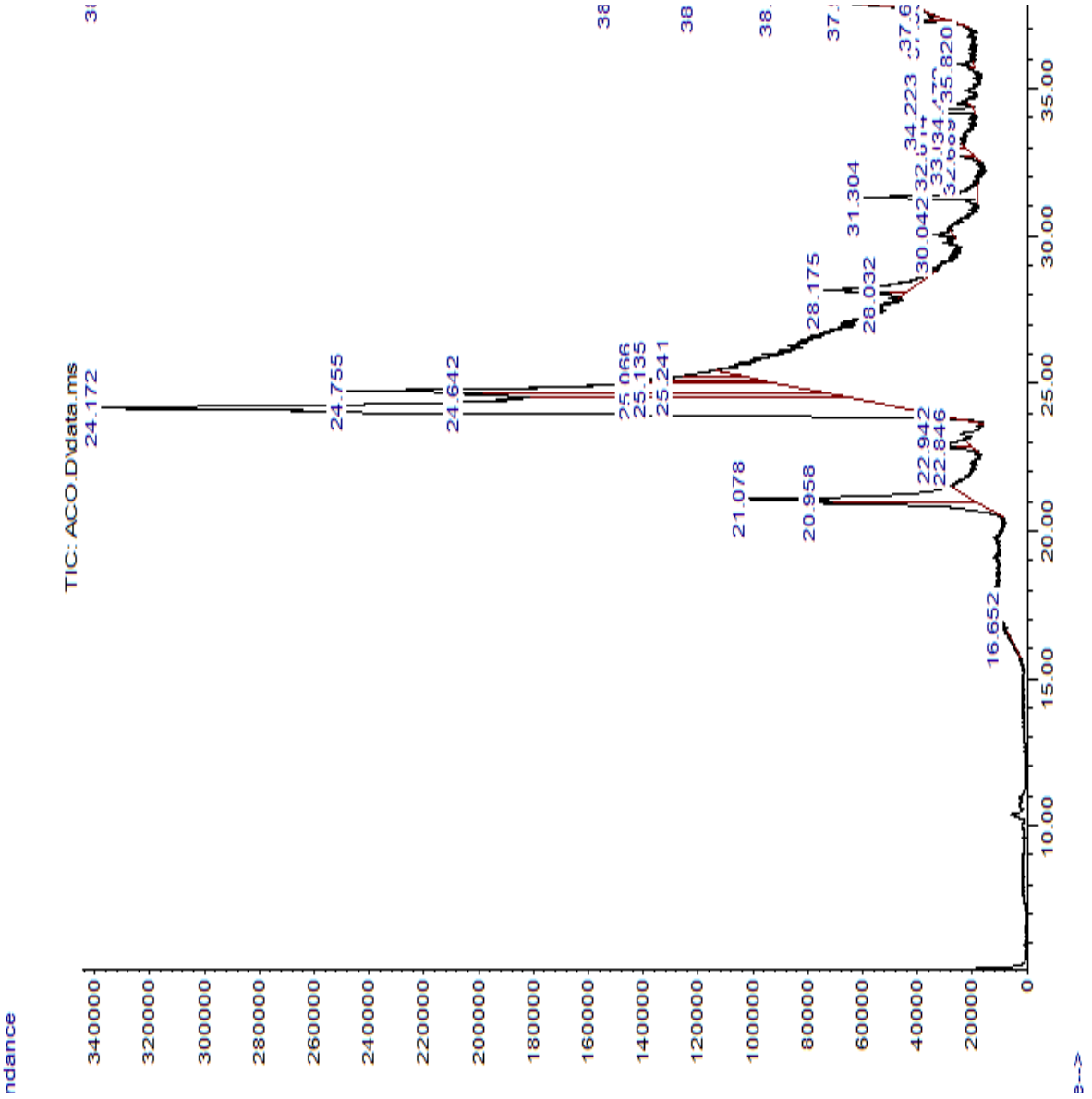


Figure 3. GC-MS chromatogram of ethanolic extract of *Caralluma Dalzeilii N.E Brown's stem*

The retention time, molecular formula, mass peaks, and the concentrations of major fractions from reliable spectral library, are presented in Table 2. From the result obtained, it's evident that the separated compounds can be classified into hydrocarbons (2(1H)-Napthaleneone, octahydro-4a-methyl-7-(1 methylethyl), (4a.alpha.,7.beta.,8a.beta.), Cyclopropaneoctanal 2-octyl- etc. Sulphur compounds such as 1-Octadecanesulphonyl chloride. The spectra pointed out the attendance of carboxylic acid such as Octadecanoic acid, Octadecanoic acid, 9-Oxabicyclo[6.1.0]nonane, Octadecanoic acid ethyl ester,5-Ecosene (E)-,9-Octadecanoic acid (Z)-,2,3,-dihydroxypropyl ester, Eicosanoic acid ethyl ester and Docosanoic acid, ethyl ester alkanoate and alkanol (Arthur & Abechi, 2019). etc. and these compounds possess π-electrons and heteroatoms like N, S and O which acted as adsorption center's (Eddy & Ebenso, 2010).

Table 2. Presents the main phytochemical compounds in the crude extract of *Caralluma Dalzeilii N.E Br. stem*

Line	Concentrations(%)	Chemical Formula	Rentation Time	Molecular Weight(g/mol)	Name of the copoumnd	Mass Peak
1	0.1233002	$C_6H_{12}O5$	16.6516	164.16	Beta.-l-	21

2	6.3228126	$C1_8H_{36}O_2$	21.0785	284.478	Arabinopyranoside, methyl Octadecanoic acid	117
3	47.702695	$C_8H_{14}O$	24.1719	126.2	9-Oxabicyclo[6.1.0]nonane, cis-	
4	7.2823146	$C_{19}H_{36}O$	24.6418	280.5	Cyclopropaneoctanal, 2-octyl-	72
5	15.378031	$C_{20}H_{40}O_2$	24.7551	312.5	Octadecanoic acid, ethyl ester	88
6	1.2205024	$C_{20}H_{40}$	25.0655	280.5	5-Eicosene, (E)-	122
7	1.3467027	$C_{21}H_{40}O_4$	25.1354	356.54	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	
8	1.0511021	C_20H40	25.2413	280.5	3-Eicosene, (E)-	121
9	0.3085006	$C_{18}H_{37}ClO_2S$	30.0415	353	1-Octadecanesulphonyl chloride	62
10	0.1708003	$C_{17}H_{32}O$	32.6885	252.4	8-Hexadecenal, 14-methyl-, (Z)-	121
11	0.8278017	$C_{17}H3_{4O}$	32.8144	254.5	Heptadecanal	106
12	0.1760004	$C_{37}H_{70}$	33.025	490.9	17-Pentatriacontene	366
13	0.8437017	$C_{19}H_{38}O_2$	34.2225	298.5	Ethyl 14-methyl-hexadecanoate	NILL
14	0.2428005	$C_{25}H_{42}$	34.4723	342.6	2,6,10,14,18-Pentamethyl-2,6,10,14,18-eicosapentaene	220
15	0.2402005	$C_{20}H_{41}Br$	35.8199	361.4	1-Bromoeicosane	176
16	0.5286011	$C_{28}H_{48}O_2$	37.2913	416.7	.gamma.-Tocopherol	223.01
17	0.3102006	$C_{15}H_{24}$	37.942	204.35	(E)-.beta.-Famesene	41
18	0.518201	$C_{11}H_{20}O$	38.1088	168.28	(2E)-1-Methoxy-3,7-dimethylocta-2,6-diene	99
19	0.7473015	$C_{18}H_{34}O2$	38.2427	282.5	11,13-Dimethyl-12-tetradecen-1-ol acetate	174
20	0.6763014	$C_{14}H_{24}O$	38.3806	208.34	2(1H)-Naphthalenone, octahydro-4a-methyl-7-(1-methylethyl)-, (4a.alpha.,7.beta.,8a.beta.) -	70

The GC-MS analysis of *Caralluma Dalzeilli N.E Br.* stem extracts revealed the presence of many compounds containing sulphur and oxygen in their hydrocarbon chain (phytochemical constituents) in fractions. The peaks in the chromatogram were integrated and compared with the database of spectra of known components stored in the GC-MS library (Eddy *et al*., 2008). In the stems of *Caralluma Deilzeilii N.E Br*, the GC-MS analysis identifies the presence of many chemical constituents in fractions with their concentrations, the compound with the highest concentration in *Caralluma Dalzeilli N.E Br.* stem inhibitor is 9-Oxabicyclo [6.1.0] nonane (47.704%). (1)3.5768% Octadecanoic acid (2) 6.3228% Octadecanoic acid (3) 0.308%) 1-Octadecanesulphonyl chloride(4) 7.282% Cyclopropaneoctanal 2-octyl- (5)15.378% Octadecanoic acid ethyl ester, the second most highest (6) 1.220% 5-Ecosene (E)- (7) 1.346% 9-Octadecanoic acid (Z)-,2,3,-dihydroxypropyl ester (8) 1.051% 3-Ecosene (E)- (9) 2.691% Eicosanoic acid ethyl ester (10) 2.566% Docosanoic acid, ethyl ester (12) 3.6250% Campesterol, etc.

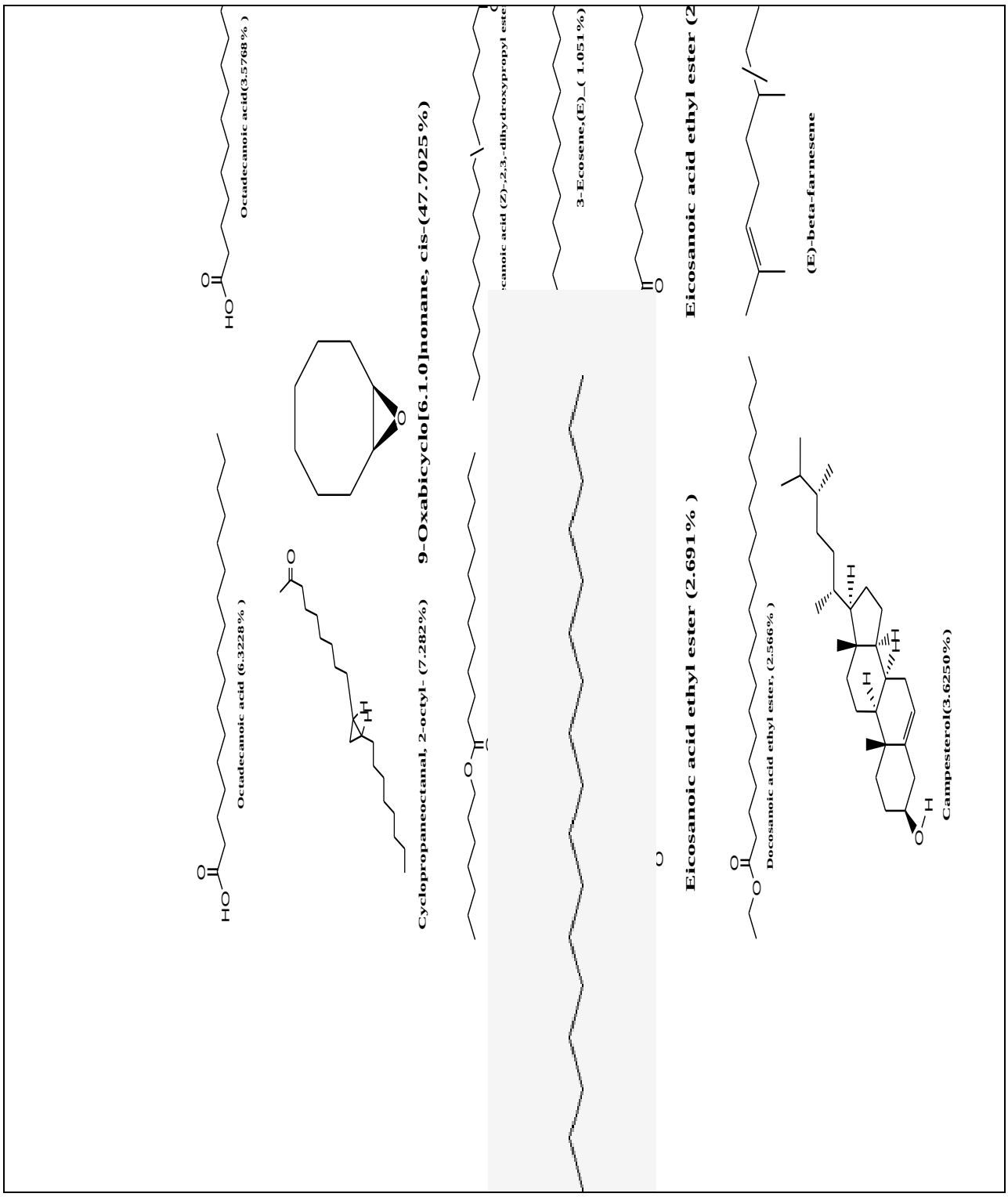


Figure 4. Phytochemicals with many O-containing and one S-containing compounds (1-Octadecanesulphonyl) in the crude extract of *Caralluma Dalzeilii* N.E Br.

Electrochemical Studies

The experimental result for Potentiodynamic Polarization behavior of Mild Steel In 1 M HCl done at different concentrations of (a) blank (b) 200ppm (c) 400ppm (d) 600 (e) 800ppm for *Caralluma Dallzeilii* N.E Br. inhibitor at 303 K and 333 K, respectively.

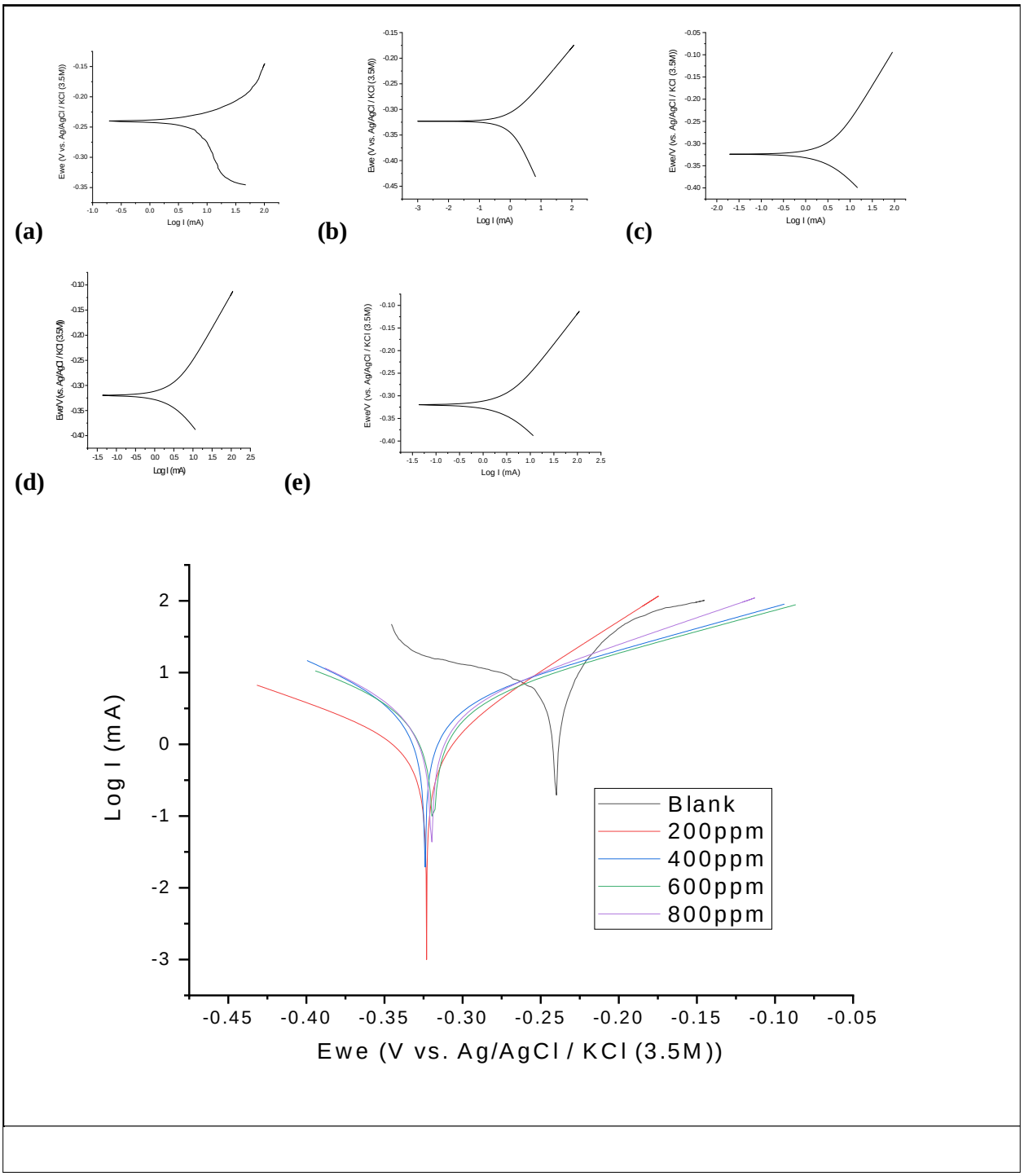


Fig. 6. The general Tafel polarization curve, for mild steel in 1M HCl in the inhibited and uninhibited of different inhibitor concentration of *Caralluma Dalzeilii N.E Br. stem* at 333 K

Table, 3. Tafel fits parameter values for *Caralluma Dalzeilii N.E Brown* stem inhibitor and the inhibition efficiency for Mild steel in 1M HCl performed at different inhibitor concentration at 303 K and 333 K

Temp.	Inhibitor Conc. (mgL^{-1})	Ecorr (mV)	Icorr (uA)	βc (mV)	βa (mV)	C.R (V_{corr})	(I.E%)	Surface Coverage (θ)
303 K	Blank	-323.91 mV	6070.82 uA	164.8 mV	120.6 mV	4.83	0.0%	0.00
	200 ppm	-323.09 mV	2014.94 uA	234.5 mV	72.6 mV	0.83	67.2%	0.67
	400 ppm	-347.75 mV	1398.43 uA	123.9 mV	117.3 mV	1.11	76.9%	0.76
	600 ppm	-344.85 mV	1208.48 uA	108.7 mV	113.4 mV	0.96	80.0%	0.80
	800 ppm	-346.72 mV	1147.43 uA	123.4 mV	116.2 mV	1.00	81.0%	0.81
333 K	Blank	-393.351 mV	17974.04 uA	404.0 mV	127.6 mV	14.60	0.0%	0.00
	200 ppm	-325.692 mV	4275.2 uA	95.0 mV	138.3 mV	4.50	76.2%	0.762
	400 ppm	-324.120 mV	3916.94 uA	118.2 mV	116.2 mV	3.60	78.2%	0.782
	600 ppm	-318.771 mV	3705.884 uA	155.5 mV	171.6 mV	3.30	79.3%	0.793
	800 ppm	-317.332 mV	2719.94 uA	230.1 mV	120.9 mV	3.10	84.8%	0.848

The inhibition efficiency was calculated from the I_{corr} value using the equation (2) above

From the above equation, the parameter $(I_{corr})_o$, represent the corrosion current in the absence of inhibitor and the parameter represents thecorrosion current at any particular inhibitor concentration. The efficiency (η%)of the inhibitor at different temperature was calculated using equation (1) using the corrosion current density values, the result was summarized in the Table 1 at 303 K and 333 K respectively. It's evident that inhibition efficiency (η%)is proportional to the concentration (in ppm by weight), the highest inhibition efficiency values were 80.0% at 600 ppm and 81.0% at 800ppm by weight at 303 K , then 79.3 at 600 ppm and 84.8 at 800 ppm by weight at 333K, the relatively high values of (η%)are attributed to the existence of different fatty alkyl chain in the inhibitor molecules and the increase in the values of (η%)from 67.2% at blank to 81.0% at 800ppm at 303 K **,** and from 76.2% of the blank to 84.8%at 800ppm at 333 K**.** When taken a close examination of the polarization curve in Figure 2 at 303 K and Figure 3 at 333 K above, it's clear that, the addition of inhibitor to acid solutions reduces both the anodic metal dissolution and the cathodic hydrogen evolution reactions (Hegazy*et al*., 2010). This indicates the addition of the plant extract (*Caralluma Dalzeilli N.E Br. stem*) in 1M HCl affect both anodic and cathodic parts of the curve. It can be seen from the Table 1 that, both corrosion current density (I_{corr})valuesat 303 K and 333 K respectively, decreasednoticeably with increase in the inhibitor concentrations from the blank to 800ppm, and also from the Table 1. can be seen that, the corrosion potential (E_{corr})**,**values shows a shift toward the negative potential with increase in the inhibitor the concentrations from the blank to the last concentration, it's evident that, a negative shifts in the E_{corr} value of -323.91 from blank to -346.72 of 800 ppm at 303 K, and the values of -393.351 from blank to -317.332 of 800ppm at 333K, with the addition of inhibitor concentration, is a characteristics of mixed type inhibitor (Bolzoni*et al*., 2007). However, considering the displacement in the E_{corr} exhibited by the extract, an inhibitor can be classified as an anodic or cathodic type or mixed-type inhibitor. Literatures suggest that, if the maximum displacement in the E_{corr} is greater than 85 mV, then the inhibitor is either anodic or cathodic, and if the maximum displacement in the E_{corr} is less than 85mV, the inhibitor is mixed-typed (Solmaz *et al*., 2008). In the present study, the largest displacement in the E_{corr} exhibited by the inhibitorat 303 K was calculated to be 23mV vs. Ag/AgCl / KCl (3.5M) and the largest displacement in the E_{corr} exhibited by the inhibitor at 333 K was calculated to be 76mV vs. Ag/AgCl / KCl (3.5M) which also can be concluded that the *Caralluma Dalzeilii N.E Br. Stem* extract acts as a mixed-typed inhibitor. On the other hand, also the cathodic Tafel slope(β_c) and Tafel anodic slope (β_a), values of the inhibited solution have changed with respect to uninhibited acid solution which also a fact that the plant stem extract is a mixed-typed inhibitor, and there sharp changes may be attributed to the adsorption of the inhibitor molecules on the surface of the mild steel.Thus subsequently slow down the corrosion process by blocking the reaction site of the mild steel.

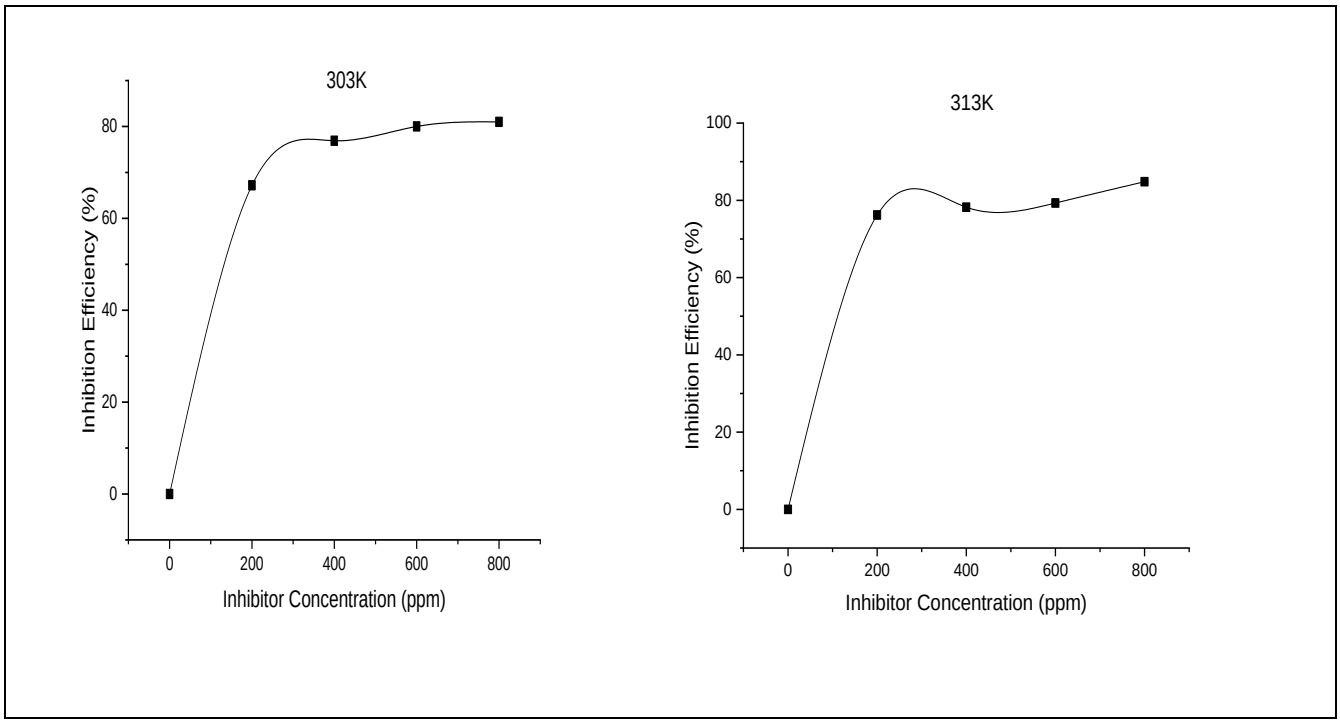
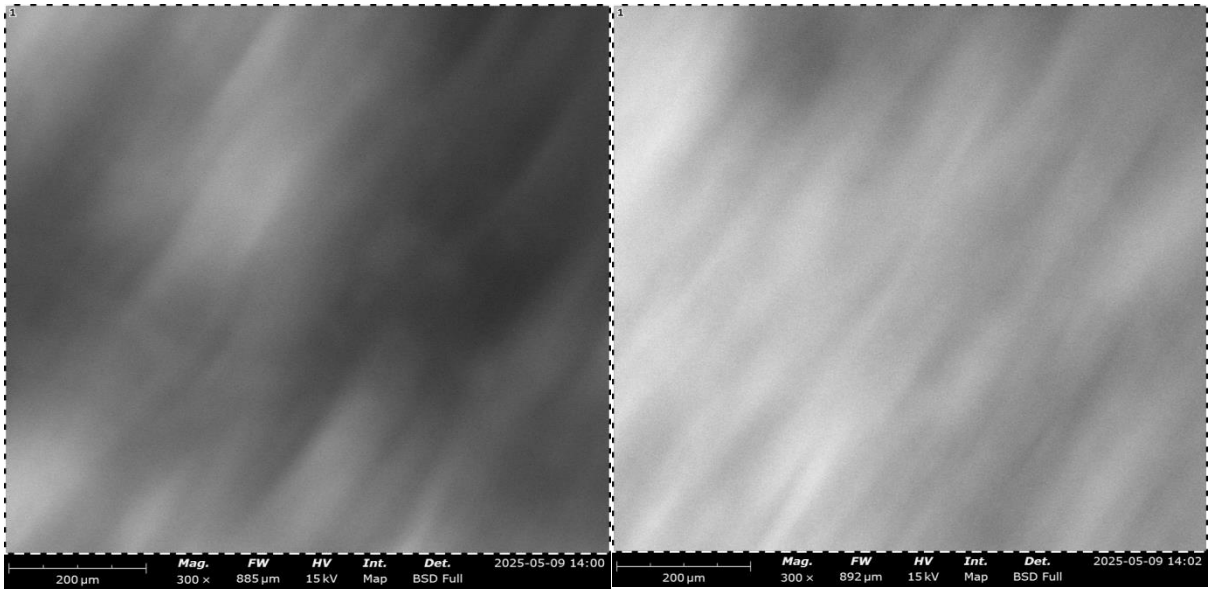


Fig. 7. Effect of inhibitor concentration of *Caralluma Dalzeilii N.E Br.* stem on the inhibition efficiency for mild steel in 1M HCl solution.



(A) **(B)**

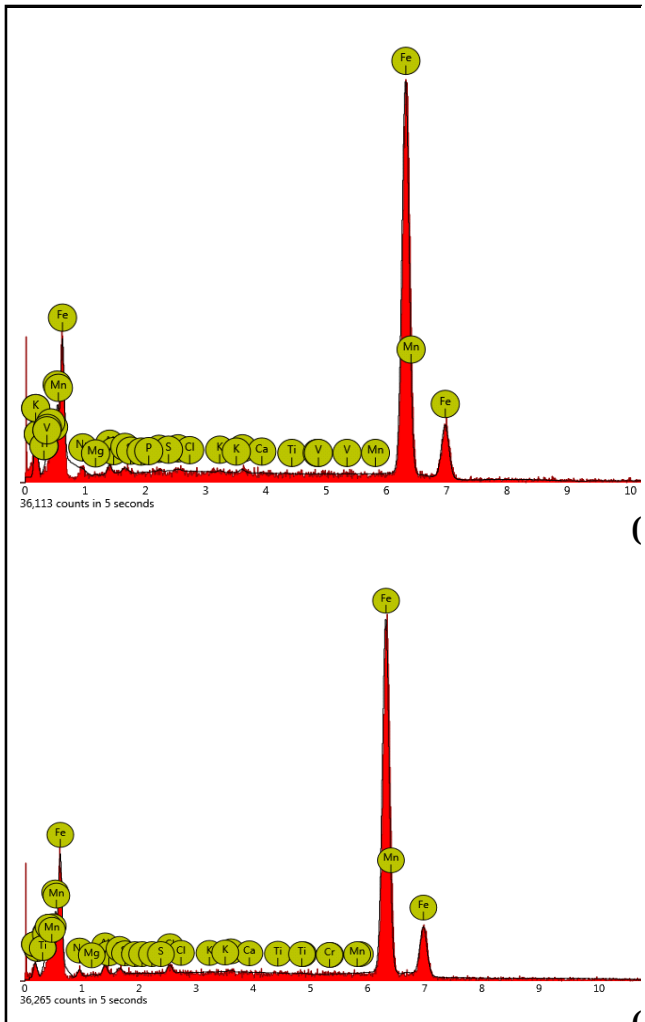
Fig. 8. SEM image of Mild Steel Surface before and after 30 min immersion in 1M HCl solution.

In other to determine the inhibition effect of the investigated inhibitor, scanning electron photographs were taken. The SEM photographs of the mild steel after immersion in 1M HCl in the presence and absence of the 200ppm are presented in Fig. A&B. in the absence of of *carallumaDalzeili* N.E Br. Stem extract a rough metal surface covered with some porous layer oxide layer due to corrosion is observed as seen I the Fig.(A), while in the presence of the 200ppm inhibitor concentration, the surface of the mild steel is comparatively more smoother than in the absence which points the inhibiting effect of *carallumaDalzeili* N.E Br. Stem.

Energy Dispersive X-Ray spectroscopy (EDX)

The protective film formed is on the mild steel surface

was analyzed using an EDX analysis. The strength of the Fe peak in the absence and the presence of the inhibitor provide an idea about the protective film formation. In the absence of the inhibitor, Fig. A, exhibits the characteristic peaks which are related to Fe, Mn, Ca, Ti and oxygen elements. This indicate that the corrosion product on mild steel surface being a metal oxide. The electrode surface after the exposure to 1M HCl containing 200ppm of *carallumaDalzeili* N.E Br. Stem inhibitor shows the presence of Sulphur and nitrogen which are not present in the meta surface exposed to pure acids in Fig B. this confirms the adsorption of the inhibitor molecule on the metal surface. By the addition of the inhibitor, the surface of mild steel is greatly protected due to the formation of ab adherent film of the adsorbed inhibitor, leading to a high degree of inhibition efficiency, the percentage of the atomic content of the elements on mild steel from the EDX analysis is presented inset Fig.9 A&B



Fig,9. EDX analysis of the mild steel surface after exposed of the inhibitor after 24 hours

Adsorption studies for corrosion of the Mild Steel in the presence and absence of *Caralluma Dalzeilii N.E Br.* stem inhibitor in 1M HCl

The negative value of ΔG_{ads} indicates that the adsorption process is spontaneous, and the adsorbed layer on the surface of the mild steel is very stable. The value of ΔG^{o}_{ads} calculated for this study ranges between (-18 kjmol^{-1} to -19 kjmol^{-1}). The numerical value of ΔG^{o}_{ads}., suggest the typed of adsorption process, if ΔG^{o}_{ads} is less than -20 kjmol^{-1} the adsorption occur through physisorption process, If ΔG^{o}_{ads} is more than -40 kjmol^{-1}, the adsorption involves chemisorption, which are considered as a threshold value, between the typed of adsorption processes since the adsorption of the inhibitor molecule usually takes place in two ways(physisorption and chemisorption). The decreased in $-\Delta G^{o}_{ads}$ values from -19.2 kjmol^{-1} at 303 K and -19.08 kjmol^{-1} at 333 K with increased in temperature shows the denomination of adsorption over desorption process. The physisorption involves the electrostatic interaction between the inhibitor molecule and the metal surface, whereas the chemisorption involves the chemical interaction of lone pair of electrons of the inhibitor molecule and the empty d-orbital of the mild steel) as suggested by Popova*et al*., (2007). In this present study, the values obtained suggest that, the process undergoes electrostatic interaction between the inhibitor molecule and the metal surface which is known as physisorption. The Langmuir adsorption isotherm tested and fitted in this study for the plant extract is reported in Fig. 9.

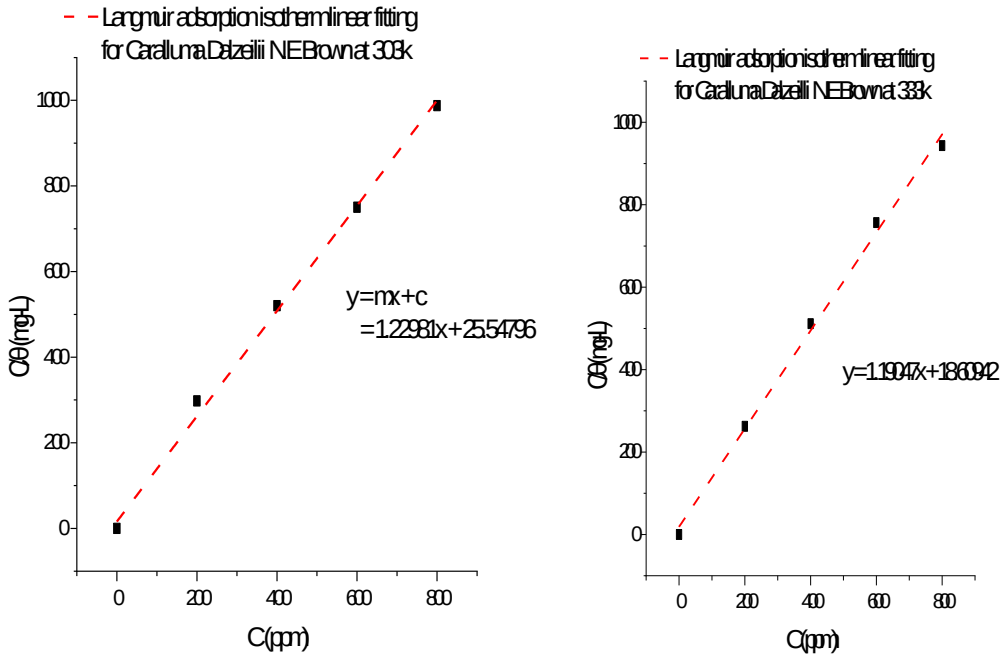


Fig.10. Linear fitting of Langmuir Adsorption isotherm for *Caralluma Dalzeilii N.E Br.* stem at 303 K

Table 4. Shows the Linear fitting of adsorption parameters of Langmuir Adsorption Isotherm for *Caralluma Dalzeilii N.E Br.* Stems Inhibitor behavior in 1M HCl on Mild Steel at 303 K and 333 K respectively.

Plant inhibitors	***Temp.(k)***	***Q max***	***Slope***	***Log Kads.***	**R^2**	***ΔGads (kjmol^{-1})***
Caralluma Dalzeilii N.E Br.	303 K	0.032246481	1.21384	0.039142068	0.99857	−19.62
Caralluma Dalzeilii N.E Br.	333 K	0.840004368	1.19047	0.045138665	0.99651	−19.08

CONCLUSION

Ethanolic stem extract of *Caralluma Dalzielii* N.E Br. inhibited mild-steel corrosion in 1 M HCl with concentration-dependent efficiencies up to ~85% at 800 ppm (333 K). Potentiodynamic polarization showed |ΔE_corr| < 85 mV and concurrent changes in β_a and β_c, indicating mixed-type inhibition. Langmuir adsorption and ΔG°_ads ≈ −19 kJ mol⁻¹ support predominantly physisorption. FT-IR/GC–MS identified O, S-containing, constituents (fatty acids/esters, sterols and sulphides) consistent with surface adsorption..

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