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A STUDY ON RETARDATION OF RUST BY *CARISSA CARANDAS*

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ABSTRACT

The ethanolic extract of *Carissa carandas* was used on carbon steel in acidic medium for retardation of rust. The phyto constituents, antimicrobial activity were examined and GC-MS analysis was carried out for the plant extract. The retardation property of *Carissa carandas* was determined by weight loss method, for various concentrations of the extract with Zn^{2+} ion and lactic acid as additive in 0.5M HCl medium. The retarding film that protects the surface of the metal was confirmed by the spectral studies such as FT-IR, UV and fluorescence spectra. The film formation is confirmed by the surface morphology SEM analysis. It also shows the formation of complex between the metal cation, additive and the compounds present in the extract of *Carissa carandas*.

KEYWORDS: Retardation, *Carissa carandas*, Carbon Steel, FT-IR, UV, SEM, GC-MS.

INTRODUCTION

Now-a-days metal are used almost in all fields of technology, industries and home appliances. Metallic corrosion is the process of destructive attack on the metal surface through the interaction with the environment. Corrosion is a natural deterioration process which can be controlled but cannot be completely prevented. In past years, chemical inhibitors were used to control corrosion. Later it was found that the chemical inhibitors were hazardous and toxic. So eco-friendly, non–toxic chemical inhibitors were used. In recent days, green inhibitors from natural products have been used as inhibitors which are eco-friendly and completely non-toxic.[1-3] *Carissa carandas* is a plant which belongs to the family *Apocynaceae*. It produces berry-sized fruits that are commonly used as a condiment in Indian pickles and spices. It is a hardy, drought-tolerant plant that thrives well wide in a wide range of soils. It grows naturally in the Himalayas at elevations of 30 to 1,800 metres, in the

Siwalik Hills, the western ghats and in Nepal and Afghanistan. It flourishes well in regions with high temperatures. The present determination is done,

- To examine the phyto-constituents that are present in the ethanolic extract of *Carissa carandas* (CC).
- To evaluate the antimicrobial efficiency of *Carissa carandas* (CC).
- To evaluate the retarding of rust property by *Carissa carandas* (CC) by the inhibition efficiencies of CC-Zn^{2+},CC-Zn^{2+}-lactic systems in retardation of rust on carbon steel in acidic medium.
- To analyse the protective film formed on the metal surface by FT-IR, UV and fluorescence spectra.
- To study the surface morphology by SEM analysis.

Plant Profile

Table 1: Plant Profile.

HEADING	DETAILS
Name	*Carissa carandas*
Botanical name	*Carissa carandas*
Family	*Apocynaceae*
Name in Tamil	Kilaakkaai
Name in Hindi	Karonda
Name in English	*Bengal currant*
Distribution	It grows naturally in the Himalayas at elevations of 30 to 1,800 meter in the Siwalik hills, the Western Ghats and in Nepal and Afghanistan.

Fig.1: *Carissa carandas.*

MATERIALS AND METHODS

Extraction

The leaves of *Carissa carandas* were collected from Pachaimalai hills. The leaves were washed thoroughly for about 7 times in the running tap water and it was taken and dried

under shade. About 100g of the powder was soaked in 500ml of ethanol under cold percolation method. At regular intervals of time the extract was filtered and distillation was carried out to collect the crude extract. The extract was stored in an amper bottle and refrigerated.[4]

Antimicrobial Activity

An antimicrobial is a substance that kills or inhibits the growth of micro-orangisms such as bacteria, fungi or protozoans. Five bacterial and three fungal species are used to screen the possible antimicrobial activity for the ethanolic extracts of the medicinal plant *Carissa carandas*. Both gram positive and gram negative bacteria are chosen namely Escherichia coli (E. coli), Staphylococcus aureus (S, aureus), Pseudomonas aeruginosa (P. aeruginosa), Bacillus subtilis (B. subtilis), Proteus vulgaris (P. vulgaris). Similarly the fungal species that have been taken are Aspergillus niger (A. niger), Cochliobolus lunata (C. lunata), Alternaria solani (A. solani). The anti-microbial screening of the ethanolic extract of *Carissa carandas* was investigated through disc diffusion method. The assay consisted of both anti-bacterial and anti-fungal evaluations.[5]

GC-MS Analysis

Gas Chromatography - Mass Spectrometry is one of the hyphenated analytical techniques. Gas chromatography separates the components of a mixture and mass spectrometry characterizes each of the components individually. By combining the two techniques one can evaluate a solution (both qualitatively and quantitatively) containing a number of chemicals which are used extensively in the medical, pharmacological and law enforcement fields.

Weight-Loss Method

Determination of Corrosion Rate

The specimens were immersed in beaker containing 100ml acid solutions without and with different concentration of *Carissa carandas* leaves extract using hooks. Before it was immersed, the specimens were cleaned and the weight is recorded. After 3 days, the test specimens were removed and then washed with double distilled water, dried and reweighed. The average mass loss of two parallel carbon steel specimens was obtained. Weight loss measurements were carried out using an ACCULAB Electronic top loading balance, with readability/sensitivity of 0.1 mg in 210g range.[6]

From the change in weight of specimens the corrosion rate was calculated using the following relationship,

$$\text{Corrosion Rate} = [87.6 \times W] / [A \times T \times D] \text{ (mpy)}$$

W= Loss in weight in mg

A = Surface area of the specimen (cm^2)

T = Time in hours

D = Density ($7.2 g/cm^3$)

Corrosion Inhibition Efficiency (IE) was then calculated using the equation

$IE = 100[1-(W_2/W_1)]$ %

Where,

W_1 = Corrosion rate in the absence of inhibitor and

W_2 = Corrosion rate in the presence of inhibitor

Infra Red (IR) Spectroscopy

Infrared spectroscopy is a well developed technique to identify the functional groups of the chemical compounds that are present. The specimens were suspended by means of hooks in solution having with and without inhibitor for 3 days. Later the specimen was taken out. Then the film formed on the metal surface was scratched off and taken for FT-IR spectral study.

UV-Visible Spectroscopy

The possibility of the formation of film on the metal surface was examined by mixing the respective solution and recording their UV-Visible absorption spectra using Lambda 35 UV-Visible spectrophotometer which is a PC controlled single beam scanning spectrophotometer. It covers wavelength range from 200 nm to 1000 nm with a setting accuracy of ±1 nm.

Fluorescence

Fluorescence spectroscopy is a type of electromagnetic spectroscopy which analyzes fluorescence from a sample. Fluorescence spectra of solution and the film formed on the metal surface were also recorded using ElicoSL174 Spectro fluorometer.

SEM Analysis

The carbon steel specimen immersed in blank solution and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology. The surface morphology

measurements of the carbon steel were examined using SUPRA 55 Field Emission Scanning Electron Microscope (FESEM).

RESULT AND DISCUSSION

Qualitative Preliminary Phytochemical Screening

The results of the screening of the ethanolic extract of the leaves of *Carissa carandas* (CC) are shown in Table (2). It illustrates that the active compounds such as alkaloids, carbohydrates, proteins, amino acids, glycosides, saponins, terpinoids, phenolic compounds and flavonoids are present. These active phyto-constituents are responsible for the retardation ability of *Carissa carandas* (CC) against rust formation.

Table 2: Qualitaive preliminary screening of Carissa carandas.

Phyto-constituents	Inferrence	Phyto-constituents	Inferrence
Carbohydrates	+	Anthraquinone Glycosides	+
Reducing Sugar	-	Saponin Glycosides	+
Non-Reducing Sugar	-	Cyanogenic Glycosides	-
Proteins	+	Alkaloids	+
Amino Acids	+	Tannins	-
Tyrosine	-	Phenolic Compounds	+
Steroids	+	Flavonoids	+
Glycosides	+	Terpenoids	+
Cardiac Glycosides	+	Saponins	+

Antimicrobial Activity

Antibacterial Activity

The results given below are the anti-bacterial activity for the various concentrations 50, 100, 200 µg/mL of the ethanolic extract of *Carissa carandas*. It is observed that the ethanolic extract of the plant at 200 µg/mL of concentration has a high inhibition activity against the bacteria. On comparing with the standard tetramycin, the inhibitive property of the plant *Carissa carandas* has been analyzed. The order of inhibition efficiency is predicted by the zone length. Thus the order of inhibition is,

B.subtitis > P. vulgaris > S.aureus > E.coli > P. aeroginosa

Table 3: Variation in Zone of Inhibition of *Carissa carandas* against the bacterial species.

Bacterial Species	Zone of Inhibition (mm)		
	50 µg/mL	100 µg/mL	200 µg/mL
E.coli	6	7	12
S.aureus	7	8	13
P. aeroginosa	6	7	11
B.subtitis	6	9	15
P. vulgaris	8	11	14

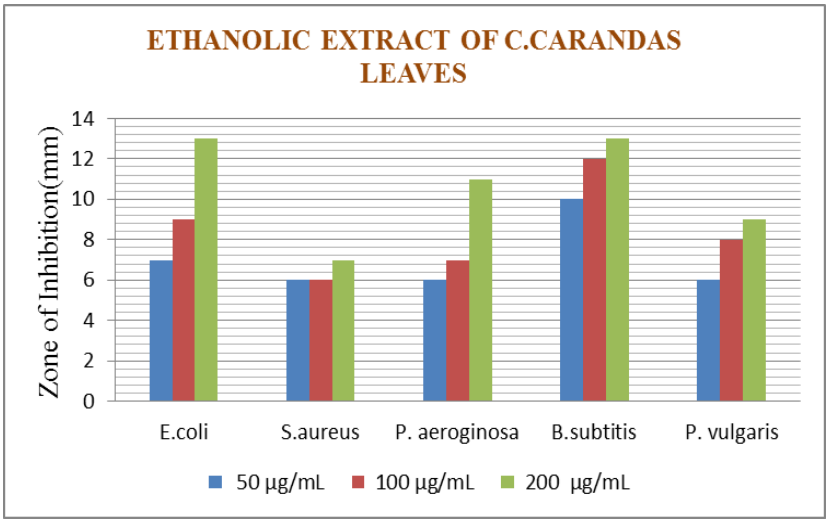
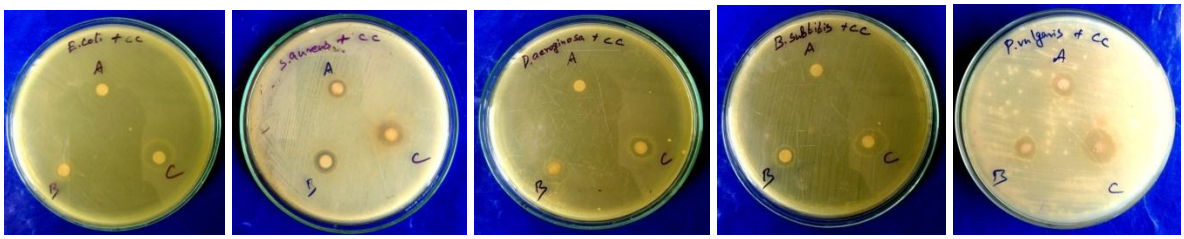


Fig.2: Variation in Zone of Inhibition of *Carissa carandas* against the bacterial species.



E.coli **S.aureus** **P.aeroginosa** **B.Subtitis** **P.vulgaris**

Fig.3: Antibacterial activity by Disc Diffusion Method.

Antifungal Activity

The results given below are the anti-fungal activity for the various concentrations 50, 100, 200 µg/mL of the ethanolic extract of *Carissa carandas*. It is observed that the ethanolic extract of the plant at 200 µg/mL of concentration has a inhibition activity against the fungal species such as A. niger and C. lunata. On comparing with the standard ketoconazole, the inhibitive property of the plant *Carissa carandas* has been analyzed.

Table 4: Variation in Zone of Inhibition of *Carissa carandas* against the fungal species.

Fungal Species	Zone of Inhibition (mm)		
	50 µg/mL	100 µg/mL	200 µg/mL
A. niger	11	18	20
C. lunata	18	20	20
A. solani	-	-	-

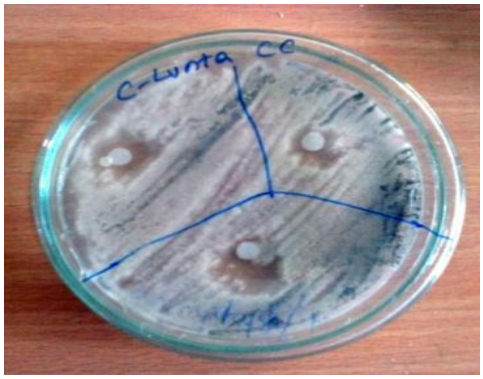


Fig.4: Antifungal activity by Disc Diffusion Method.

GC-MS Analysis

GC-MS chromatogram of the ethanolic extract of *Carissa carandas* shows 20 peaks which indicates the presence of 20 active phyto-constituents in Fig.5. The 20 active constituents with their retention time (RT), molecular formula, molecular weight (MW) and peak area (%)which are present in the ethanolic extract of *Carissa carandas* are presented in Table - 5. On comparison of the mass spectra of the constituents with the NIST library the 3 predominant constituents were characterized and identified. The structure and nature of the compound are presented in Table - 6.

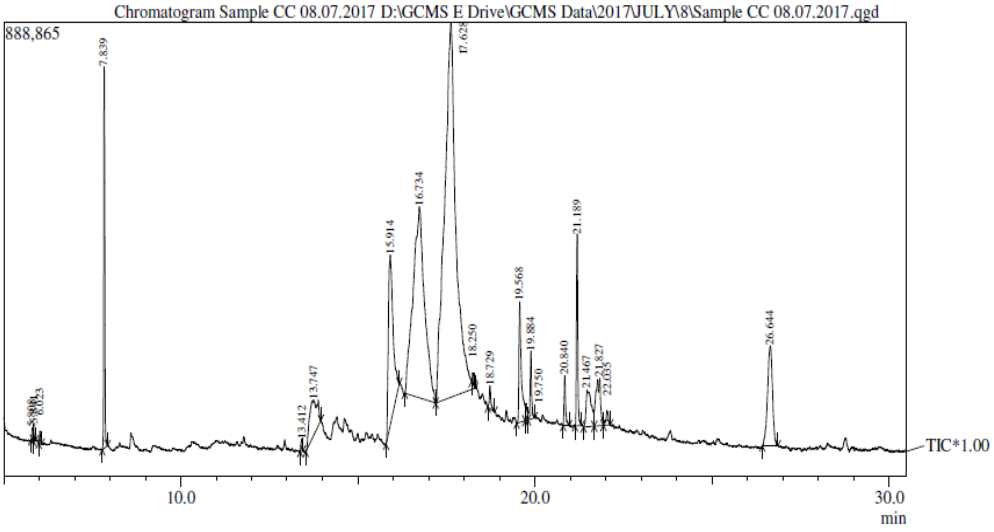
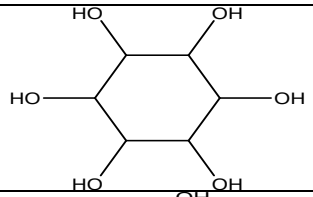
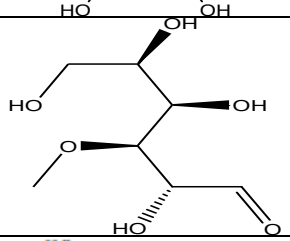
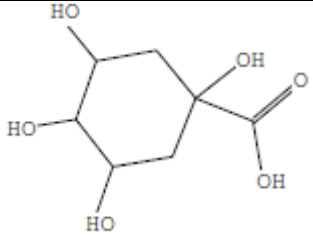


Fig. 5: GC-MS chromatogram of *Carissa carandas*.

Table 5: Phytocomponents identified in the ethanolic extract of the leaves of *Carissa carandas* by GC-MS.

Sl.No.	RT	Name Of The Compound	Molecular Formula	Molecular weight	Peak Area %
1	5.808	Butane, 1,1-diethoxy-3-methyl-	$C_9H_{20}O_2$	160	0.12
2	5.841	1,1-diethoxy pentane	$C_9H_{20}O_2$	160	0.15
3	6.023	3,3-diethoxy-2-butanone	$C_8H_{16}O_3$	160	0.12
4	7.839	Propane, 1,1,3-triethoxy-	$C_9H_{20}O_3$	176	3.99
5	13.412	1,11-dodecadiyne	$C_{12}H_{18}$	162	0.14
6	13.747	Xanthosine	$C_{10}H_{12}N_4O_6$	284	2.95
7	15.914	1,3,4,5-tetrahydroxy-cyclohexanecarboxylic	$C_7H_{12}O_6$	192	8.33
8	16.743	3-o-methyl-d-glucose	$C_7H_{14}O_6$	194	22.53
9	17.628	Mome Inositol	$C_7H_{14}O_6$	194	43.81
10	18.250	Pentadecanal-	$C_{15}H_{30}O$	226	0.11
11	18.729	1-Hexadecanol	$C_{16}H_{34}O$	242	0.36
12	19.568	Octadecanoic Acid	$C_{18}H_{36}O_2$	284	2.98
13	19.750	1,2-benzenedicarboxylic acid, butyl octyl ester	$C_{20}H_{30}O_4$	334	0.28
14	19.884	Hexadecanoic Acid, Ethyl Ester	$C_{18}H_{36}O_2$	284	1.03
15	20.840	Phosphonic Acid, Dioctadecyl Ester	$C_{36}H_{75}O_3P$	586	0.76
16	21.189	2-hexadecen-1-ol, 3,7,11,15-tetramethyl-, [R-[R*,R(E)]]	$C_{20}H_{40}O$	296	2.66
17	21.467	9-octadecenoic acid (Z)-	$C_{18}H_{34}O_2$	282	2.03
18	21.827	9,12,15-octadecatrienoic acid, ethyl ester, (Z,Z,Z)-	$C_{20}H_{34}O_2$	306	2.21
19	22.035	Octadecanoic Acid, Ethyl Ester	$C_{20}H_{40}O_2$	312	0.37
20	26.644	Squalene	$C_{30}H_{50}$	410	5.05

Table 6: The structure and nature of the predominant phytocomponents identified in the ethanolic extract of the leaves of *Carissa carandas* by GC-MS.

Sl. No.	Name of the Compound	Structure	Nature
1.	Mome inositol		Inositol
2.	3-O-Methyl-d-glucose		Carbohydrate
3.	1,3,4,5-tetrahydroxy-cyclohexanecarboxylic acid		Carboxylic acid

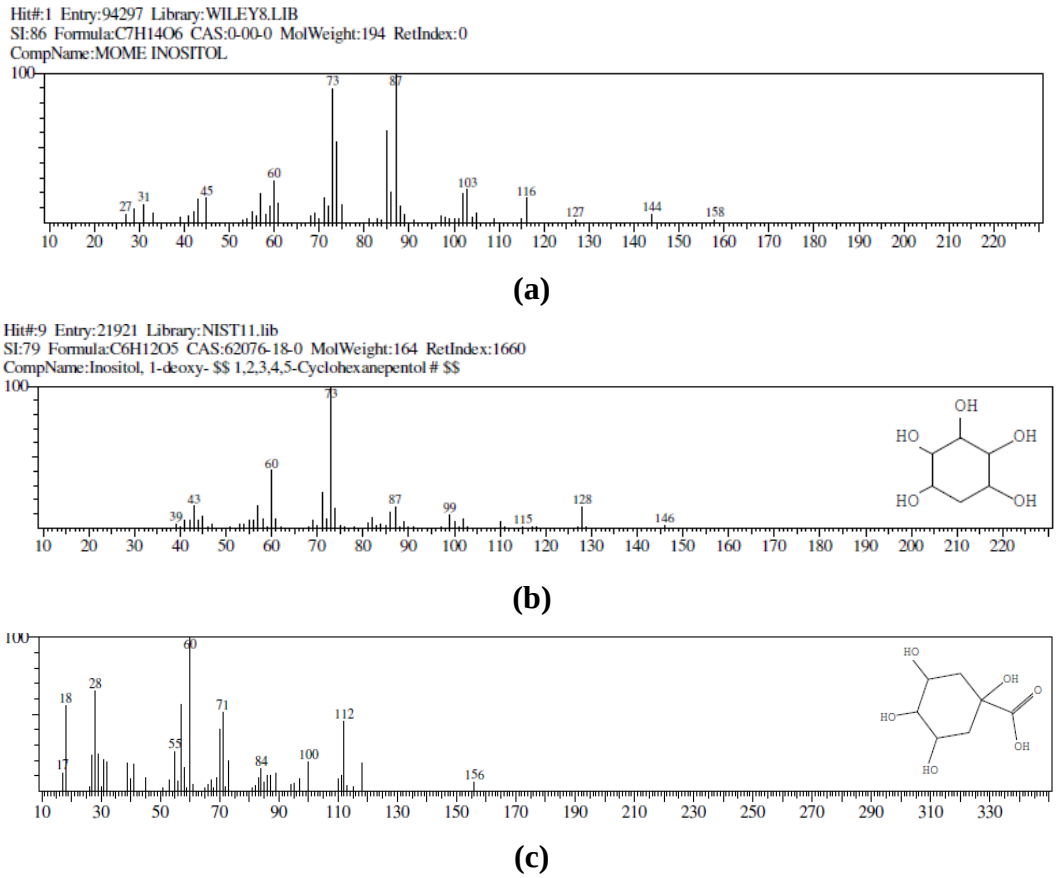


Fig.6 (a,b,c): Mass Spectrum of predominant phytoconstituents present in *Carissa carandas*.

Weight Loss Measurements

Effect of Inhibitor Concentration

The corrosion rate is monitored by weight loss method.[7] Inhibition efficiency of carbon steel with different concentration of *Carissa carandas* (CC) extract and Zn^{2+} in 0.5M HCl at room temperature are presented in Table (7). From the table, it is clear that the corrosion rate decreases with an increase in inhibitor concentration, i.e. the corrosion inhibition enhances with the inhibitor concentration. This behavior is due to the fact that the adsorption and coverage of the inhibitor on the carbon steel surface increase with the inhibitor concentration. The maximum inhibition efficiency of 85%was obtained at 50ppm of CC and 50 ppm of Zn^{2+} in 0.5M HCl at 3 days immersion period in Table-8. The table also illustrates the inhibition efficiency and corrosion rate of the inhibitor CC- Zn^{2+}- additives (lactic acid). The high retarding performance of *Carissa carandas* suggests a higher bonding ability of inhibitor on carbon steel surface. It is observed that the inhibition efficiency increases further due to the addition of additive, it is found that the concentration of additive at 40 ppm of lactic acid shows IE of 87%.

Table 7: Inhibition efficiency and corrosion rate of carbon steel in CC and Zn^{2+} in 0.5M HCl.

Sl.no.	Concentration (ppm)		IE (%)	CR (mpy)	Concentration (ppm)		IE (%)	CR (mpy)
	CC	Zn^{2+}			CC	Zn^{2+}		
1	0	25	46	4.6	10	0	52	2.6
2	0	50	72	2.3	20	0	59	2.2
3	0	75	67	2.8	30	0	65	1.8
4	0	100	78	1.9	40	0	70	1.5
5	0	125	76	2.0	50	0	67	1.7
6	0	150	36	5.4	60	0	72	1.3
7	Blank			8.5		Blank		8.5

Immersion Period = 3 days

Table 8: Inhibition efficiency and corrosion rate of carbon steel in CC-Zn^{2+} ion and CC-Zn^{2+} - Additive (Lactic Acid) in 0.5M HCl

Con. of CC (ppm)	Con. of Zn^{2+} ion (ppm)				Con. of CC-Zn^{2+} ion (ppm)	Con. of additive (ppm)	Lactic Acid	
	25		50					
	IE%	CR (mpy)	IE%	CR (mpy)			IE%	CR (mpy)
10	68	2.9	75	2.1	**50:50**	10	78	1.7
20	72	2.5	78	1.5		20	71	2.7
30	70	2.8	80	1.2		30	80	1.5
40	75	2.0	82	0.9		**40**	**87**	1.3
50	76	1.8	**85**	0.7		50	75	1.9
Blank		8.5		8.5	Blank			8.5

Immersion Period = 3 days

Analysis of FTIR

FTIR is a technique used for identifying the functional groups associated with the adsorption of an inhibitor. The FTIR spectrum of the extract and the film formed on the surface of the metal immersed in 0.5M HCl in the presence of the inhibitor were taken. FTIR spectroscopy has been used to analyze the protective film formed on the metal surface.[8-10] The FTIR spectrum of the pure extract CC, CC-Zn $^{2+}$, CC-Zn $^{2+}$-Additive(lactic acid) are shown in Fig.(7). The OH stretching for the pure extract the band observed at 3345.24cm^{-1}. There is a decrease in the frequency from 3600.00 cm $^{-1}$ to 3345.24 cm^{-1} and the broadening of the band indicates the presence of intermolecular hydrogen bonding. Similar decrease pattern is observed for CC-Zn $^{2+}$and CC-Zn $^{2+}$-Additive (Lactic acid), the bands were observed at 3384.62 and 3354.68 cm^{-1} respectively. This decrease trend indicates the presence of intermolecular hydrogen bonding. The bands at 1632.51 cm^{-1} and 1451.19cm^{-1} which are due

to the coupling of -C-O stretching and -C-O-H in-plane bending of the carboxylate anion are shifted to 1627.20cm^{-1} and 1401.74cm^{-1} in CC-Zn^{2+}. Similar shift in bands were observed in CC-Zn^{2+}-lactic acid (1627.98& 1238.26cm^{-1}). The bands at 1117.13cm^{-1} and 681.31cm^{-1} (due to the ring oxygen) are shifted to 1114.55cm^{-1} and 677.17, 824.82cm^{-1}. Similar shift in bands were observed in CC-Zn^{2+}-lactic acid (1116.86 & 848.34, 685.91cm^{-1}). This reveals that due to interaction between the metal and the active constituents there is a change in the chemical nature of the active constituents.[11]

Table 9: FTIR spectrum data interpretation.

Types of Vibration	Peaks (cm^{-1})		
	CC	CC-Zn^{2+}	CCL
O-H Str	3345.24	3384.62	3354.68
NH_2 Str	-	-	3852.84
C-H Str	2924.60, 2854.53, 2198.60	2925.28, 2855.33	2926.20, 2657.21
C-O str	1632.51	1627.20	1627.98
C-OH inplane bending	1451.19, 1385.24	1401.74, 1383.52	1238.26
C-O (ring vib.)	1117.13,	1114.55	1116.86
C-H bending(C-O ring vib.)	681.31	824.82, 677.17	848.34, 685.91
M-O bond	-	-	479.88

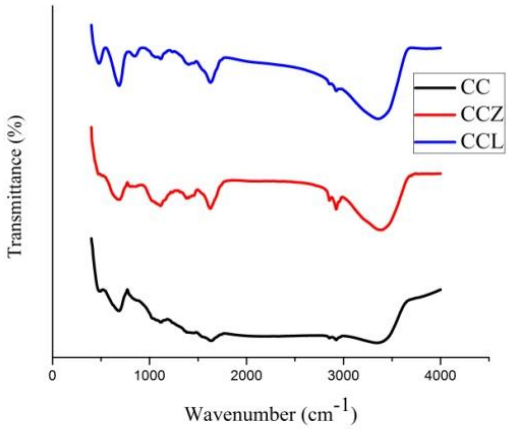


Fig.7: FTIR Spectra Correlation Daigram.

Analysis of UV-Visible absorption spectra

The UV-Visible absorption spectra of the solution containing CC, 50ppm CC – 50ppm Zn^{2+}, (50:50) CC - Zn^{2+} - 40ppm lactic acid are shown in Fig. 11. A peak appears at 256.35nm (0.2984au), when Zn^{2+} ion is added a peak disappears, the intensity decreases. This indicates

that a complex formation occurs between CC and Zn^{2+}ion. It is observed that, when additive are added to CC- Zn^{2+} - additive (lactic acid) systems the peak appears at 205.70nm (3.6837au), the intensity decreases on comparing with the CC and CC-Zn^{2+} systems. This indicates the complexation of CC - Zn^{2+} & Additive (Lactic acid).

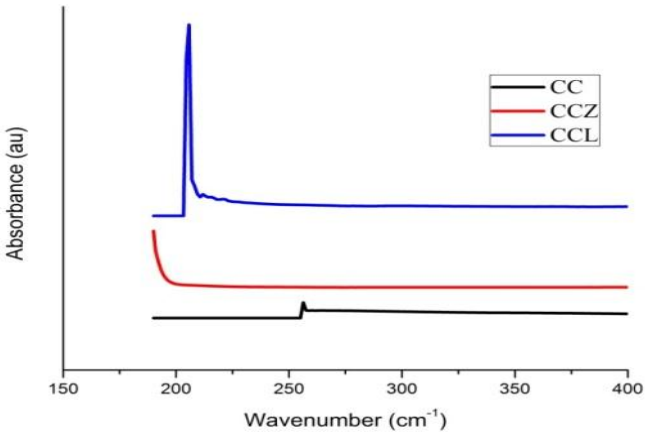


Fig.8: UV-Visible Spectra Correlation.

Analysis of Fluorescence

Fluorescence spectrum is used to detect the presence of the inhibition complex formed on the metal surface. The λ_{ex} for the emission spectrum of the pure CC is found to be 332.74nm and for CC-Zn^{2+} the peak is obtained at 262.99nm. Fig 12 (c),shows the λ_{ex} for the emission spectrum of the 50ppm CC-50ppm Zn^{2+}-40ppm Lactic acid, the peak is obtained at 290.78nm. There is a decrease in the intensity, which indicates the formation of protective film on the surface of the metal. The shift in the intensity on comparing with the pure CC fluorescence value indicates the formation of protective film on the surface of the metal.

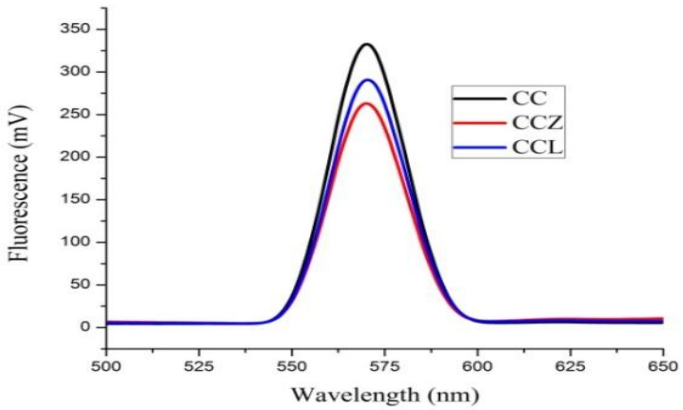


Fig 9: Fluorescence Spectra Correlation.

Scanning Electron Microscope (SEM) Analysis

The texture and pore structure of the inhibited and uninhibited surface in acidic medium are shown in Fig.10 (a-c). It is confirmed that the inhibitor has formed a dense film over the metal surface.

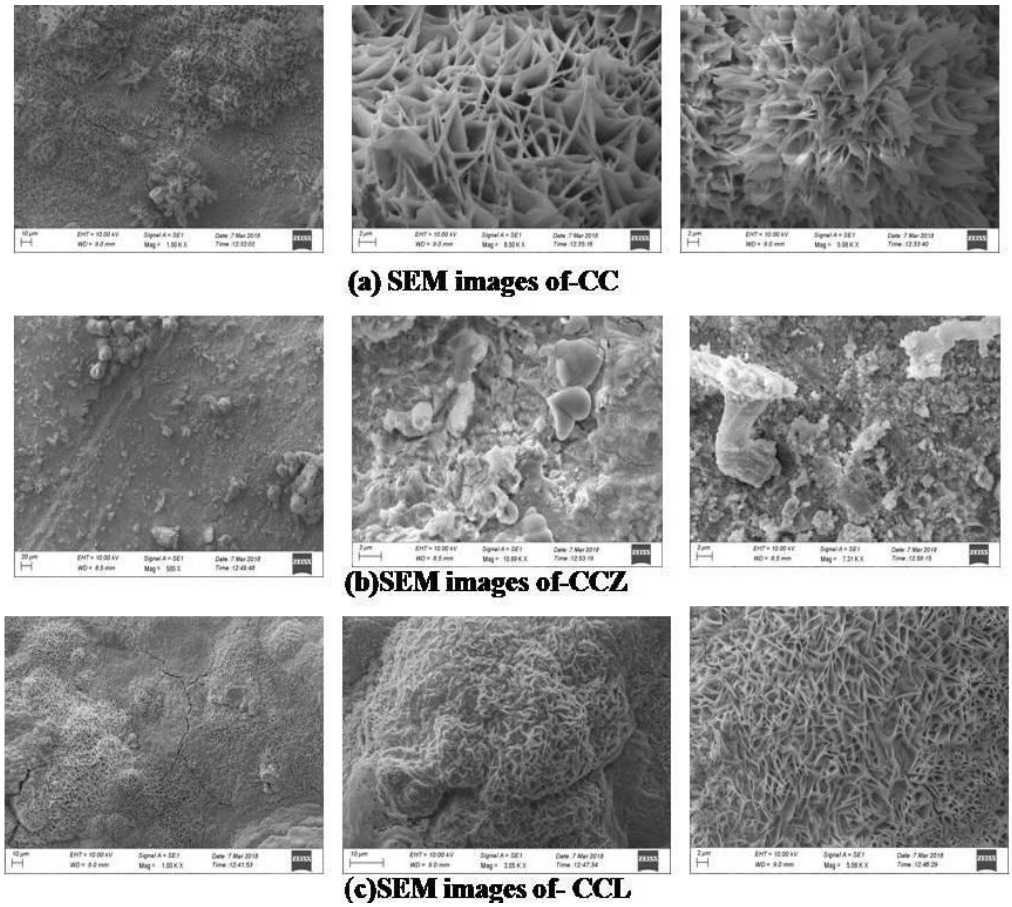


Fig.10: (a-c) SEM images of *Carissa carandas* with Zn^{2+} ion and additive.

CONCLUSION

From the above study it is concluded that:

- The ethanolic extract of *Carissa carandas* possess active phyto constituents.
- It also has a resistivity against the microbes. GC-MS analysis confirms the presence of active phyto constituents.
- *Carissa carandas* has a good retardation ability against rust for carbon steel in 0.5 M HCl solution. The maximum efficiency was found to be 85% at 50ppm CC + 50ppm Zn^{2+}. And the inhibitive efficiency was found to be increased from the maximum efficiency with the additive lactic acid (40ppm) is found to be 87%.
- The FT-IR, UV-Visible and the fluorescence spectra proves the formation of the film on the surface of the metal.

- The SEM image finally confirms the formation of the protective film on the metal surface.

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