

Research Article**A study on anticorrosion property of *Drypetes sepiaria* on carbon steel in acidic medium**JK. Alphonsa Juliet Helina¹, A. Peter Pascal Regis^{2*}¹Research Scholar, PG and Research, Department of Chemistry, St. Joseph's College, Trichy-620002, Tamil Nadu, India²Associate Professor, PG and Research, Department of Chemistry, St. Joseph's College, Trichy-620002, Tamil Nadu, India

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Abstract

Objective: The ethanolic extract of *Drypetes sepiaria* was used as corrosion inhibitor on carbon steel in acidic medium. The phytochemical screening, antimicrobial activity and GC-MS analysis of the plant extract were carried out. **Material and Methods:** The anticorrosion property of *Drypetes sepiaria* was determined by weight loss method, for various concentrations of the extract with Zn²⁺ ion and tartaric acid, citric acid and lactic acid as additives in 0.5M HCl medium. **Results and Conclusion:** The protective film that formed on the surface of the metal which resists the corrosion was confirmed by the spectral studies such as FT-IR, UV and fluorescence spectra. The film formation is also confirmed by the surface morphology SEM analysis. This shows the complex formation between the metal cation, additive and the phytoconstituents present in the extract of *Drypetes sepiaria*.

Keywords: *Drypetes sepiaria*, Carbon Steel, Corrosion, FT-IR, SEM, GC-MS

Introduction

In day today life metals are used almost in all fields of technology and industries. Metallic corrosion is the progression of vicious attack on the metal surface through the contact with the environment. Corrosion is a natural deterioration progression which can be restricted but cannot be completely prevented. In past years, chemical inhibitors were used to control corrosion. Later it was found that the chemical inhibitors were dangerous and venomous. So eco-friendly, non-venomous chemical inhibitors were used. In recent days, green inhibitors from natural products have been used as inhibitors which are eco-friendly and completely non-hazardous were reported by (Kilbourn, 1985; Bethencour et al., 1998; Arenas et al., 2002). *Drypetes sepiaria* is a plant which belongs to the family 'Putranjivaceae (Euphorbiaceae)'. It is an evergreen tree commonly grown in foothills and shrub jungles which is widely distributed in Srilanka and some places of Tamil Nadu as reported in (Nganga et al., 2008).

The objective of present determination was to evaluate the anticorrosion property of *Drypetes sepiaria* (DS) by the inhibition efficiencies of DS-Zn²⁺, DS-Zn²⁺ - Additives (Tartaric acid, Citric acid, Lactic acid) systems in resisting the corrosion on carbon steel in acidic medium. Additionally the phytoconstituents, antimicrobial activity and GC-MS for the ethanolic extract of *Drypetes sepiaria* were also studied. The protective film formed on the metal surface was observed by FT-IR, UV, fluorescence spectra and SEM analysis.



Figure 1. Digital image of *Drypetes sepiaria*

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Materials and methods

Metal Specimens

The metal specimens is carbon steel with the composition (wt%) of S-0.026 , P -0.06, Mn- 0.4, C- 0.1 and balance iron. The dimensions of the metal active surface are 1.2 X 4.1 X 0.2 cm which is used for weight loss measurements. The carbon steel specimens were polished, washed in double distilled water and degreased with acetone and used for the weight loss method.

Extraction of Plant Material

The leaves of *Drypetes sepiaria* were collected from Pachaimalai hills near Trichy (Dt) of Tamil Nadu, India. 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 and then stored in an amber bottle and refrigerated as followed by (Kumar et al., 2011). The crude extract is used for phytochemical screening and for other studies as reported by (Helina et al., 2015)

Determination of Corrosion Rate

The specimens were immersed in beaker containing 100ml acid solutions without and with different concentration of *Drypetes sepiaria* leaves extract using hooks. Before it was immersed, the specimens were cleaned and the weight is recorded. After 72 hours, 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. From the change in weight of specimens the corrosion rate was calculated using the following relationship,

where, W is loss in weight (mg), A is surface area of the specimen (cm²), T is time in hr and D is density (7.2g/cm³). In addition, Corrosion Inhibition Efficiency (IE) was then calculated using the equation as follows,

$$\text{Corrosion Rate (CR)} = \frac{87.6 \times W}{A \times T \times D} \text{ (mpy)} \quad \dots\dots\dots(1)$$

$$\text{Corrosion Inhibition Efficiency (IE)} = 100[1-(W_2/W_1)] \% \quad \dots\dots\dots(2)$$

where, W₁ is corrosion rate in the absence of inhibitor and W₂ is corrosion rate in the presence of inhibitor respectively.

Infrared (IR) Spectroscopy

Infrared spectroscopy is a well-developed technique to identify chemical compounds. The specimens were suspended by means of hooks in solution having with and without inhibitor for 72 hours. After 72 hours the specimen were 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.

Fluorescence Spectroscopy

Fluorescence spectra of solutions and also the films formed on the metal surface were recorded using Jasco F-6300 spectrofluorometer.

SEM Analysis

A Scanning Electron Microscope (SEM) is a type of electron microscope that images a sample by scanning it with a beam of electrons in a raster scan pattern. It contains the information about the sample's surface topography. The specimens were suspended by means of hooks in solution in the presence and in the absence of inhibitor for 72 hours. Then the specimens were taken out and the metal specimen was analyzed.

Results and discussion

Qualitative Preliminary Phytochemical Screening

The results of qualitative analysis was showed in table 1. It illustrates that phytoconstituents such as alkaloids,

Table 1. Qualitative preliminary phytochemical screening of ethanolic extract of *Drypetes sepiaria* (DS)

Phyto-constituents	Inference	Phyto-constituents	Inference
Carbohydrates	+	Anthraquinone Glycosides	+
Reducing Sugar	+	Saponin Glycosides	+
Hexose Sugar	+	Cyanogenic Glycosides	-
Non-Reducing Sugar (Starch)	+	Alkaloids	+
Proteins	-	Tannins	+
Amino Acids	-	Phenolic Compounds	-
Tyrosine	-	Flavonoids	-
Steroids	+	Terpenoids	+
Glycosides	+	Saponins	+

+ means present; - means absent

terpenoids, saponins are present except cyanogenic glycosides, and proteins. The presence of these active compounds is responsible for the inhibitive nature of the plant extract.

Antibacterial Activity

The evaluation of the antibacterial activity of an ethanolic leaf extract of *Drypetes sepiaria* at various concentration (50,100 and 200 µg/mL) for both gram positive (*S.aureus* and *B.Subtilis*) and gram negative (*E. coli*, *P. aeruginosa*, *P. vulgaris*) bacterial species by using disc diffusion method is given in table 2.

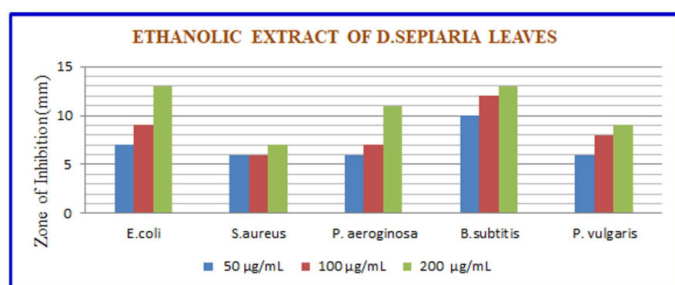


Figure 2. Antibacterial activity-Zone of inhibition of ethanolic extract of *Drypetes sepiaria* (DS)

It was found that the inhibitive power of the plant against the bacterial species was good at a higher concentration (200µg/mL). The plant extract is a good inhibitor against *E. coli* (9), *S. aureus* (12) and *P. aeruginosa* (11). It moderately inhibits *B. subtilis* (11) and *P. vulgaris* (8). On comparing with the standard chloramphenicol, the inhibitive property of the plant *Drypetes sepiaria* (DS) has been analyzed. The graphical representations of the inhibition zone length at various concentrations of DS against the bacterial species were depicted in figure 2.

Table 2. Antibacterial activity- Zone of inhibition of ethanolic extract of *Drypetes sepiaria* (DS)

Bacterial Species	Zone of Inhibition (mm)		
	50 µg/mL	100 µg/mL	200 µg/mL
<i>E. coli</i>	6	7	9
<i>S. aureus</i>	8	9	12
<i>P. aeruginosa</i>	8	10	11
<i>B. subtilis</i>	8	9	11
<i>P. vulgaris</i>	6	7	8

Antifungal Activity

The evaluation of antifungal activity of the ethanolic leaves extract of DS at various concentration (50,100 and 200 µg/mL) against the fungal species. It was found that the inhibitive power of the plant against the fungal species was at a higher concentration (200µg/mL). It moderately inhibits against *A.*

niger (10), *C. lunata* (9) and very negligible against *A. solani* by using disc diffusion method. On comparing with the standard Ketoconazole, the antifungal activity of the plant extract of DS shows moderate inhibition zone against the fungal species.

Table 3. Antifungal activity- Zone of inhibition of ethanolic extract of *Drypetes sepiaria*

Fungal Species	Zone of Inhibition (mm)		
	50 µg/mL	100 µg/mL	200 µg/mL
<i>A. niger</i>	6	9	10
<i>C. lunata</i>	-	7	9
<i>A. solani</i>	-	-	-

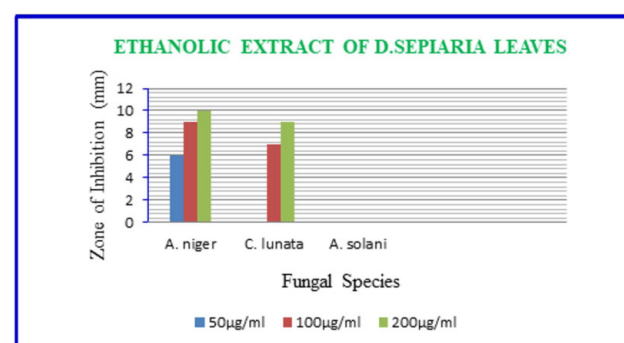


Figure 3. Anti-fungal activity: Inhibition zone length of the ethanolic extract of *Drypetes sepiaria* (DS)

Gas Chromatography-Mass Spectrum Study (GC-MS)

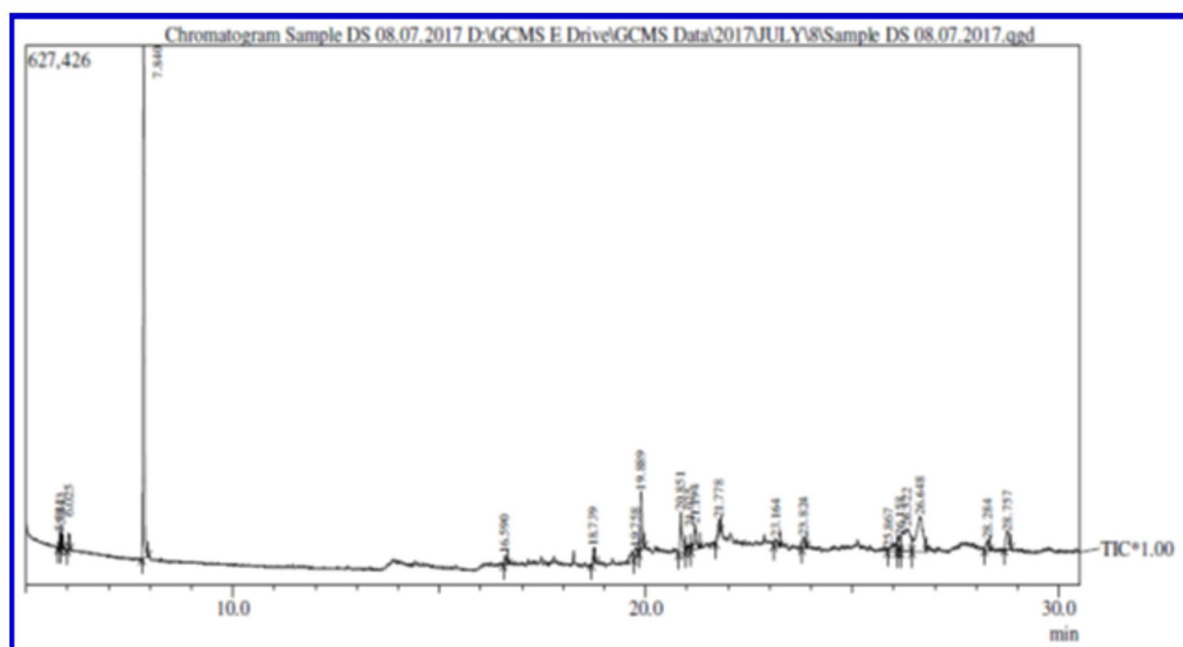
On comparing with the mass spectra from the database of National Institute of Standard Technology (NIST) library, the recorded mass spectra of the GC separated compounds are identified. The GC-MS chromatogram of the ethanolic leaves extract of *Drypetes sepiaria* (DS) showed twenty peaks which indicate the presence of twenty chemical constituents figure 3. The twenty active constituents with their retention time (RT), molecular formula, molecular weight (MW) and peak area (%) in the ethanolic leaves extract of *Drypetes sepiaria* (DS) are shown in table 4.

Weight-loss Method

The inhibition efficiency was determined for carbon steel in 0.5M HCl by using weight loss method. Inhibition efficiency of carbon steel with various concentration of *Drypetes sepiaria* (DS) ethanolic leaves extract in 0.5M HCl at room temperature are presented in the table 5. It is clear from the table that the corrosion inhibition enhances with the inhibitor concentration. The inhibitor systems that are used to determine the corrosion rate and the inhibition efficiency were DS- Zn²⁺; DS- Zn²⁺- Additives (Citric acid, tartaric acid and lactic acid). It was found that at DS-Zn²⁺

Table 4. Chemical components identified in the ethanolic extract of the leaves of *Drypetes sepiaria* (DS) by GC-MS

S.No.	RT	Name of the Compound	Molecular Formula	Molecular Weight	Peak Area (%)
1	5.811	1,1-diethoxy-3-methyl- butane	C ₉ H ₂₀ O ₂	160	1.06
2	5.843	1,1-diethoxy- pentane	C ₉ H ₂₀ O ₂	160	1.36
3	6.025		C ₈ H ₁₆ O ₃	160	1.00
		3,3-diethoxy-2-butanone			
4	7.840	1,1,3-triethoxy- propane	C ₉ H ₂₀ O ₃	176	35.82
5	16.590	2,5-dimethyl-5-hexen-3-ol	C ₈ H ₁₆ O	128	1.22
6	18.739	5-cyclohexyl- undecane	C ₁₇ H ₃₄	238	1.50
7	19.758	1,2-benzenedicarboxylic acid, diundecyl ester	C ₃₀ H ₅₀ O ₄	474	1.32
8	19.889	ethyl ester hexadecanoic acid	C ₁₈ H ₃₆ O ₂	284	5.99
9	20.851	1-hexadecanol	C ₁₆ H ₃₄ O	242	6.18
10	21.075	1-cyclopentylethyl ester pentanoic acid	C ₁₂ H ₂₂ O ₂	198	1.01
11	21.194	3,7-dimethyl-6-octen-1-ol	C ₁₀ H ₂₀ O	156	3.58
12	21.778	1,10-decanediol	C ₁₀ H ₂₂ O ₂	174	1.73
13	23.164	Hexyl (hexyloxy) methanethioate	C ₁₃ H ₂₆ O ₂ S	246	1.19
14	23.824	cis-3-hexenyl-.alpha.-methylbutyrate	C ₁₁ H ₂₀ O ₂	184	1.65
15	25.867	tetrahydro-2h-pyran-2-one	C ₈ H ₁₄ O ₂	142	2.50
16	26.158	2-(2-propenyl)-1,4-butanediol	C ₇ H ₁₄ O ₂	130	2.45
17	26.322	alpha-tocopheryl acetate	C ₃₁ H ₅₂ O ₃	472	10.72
18	26.648	(2e,6e)-1,1-dideutero-3,7,11-trimethyl-2,6,10-dodecatrien-1-ol	C ₁₅ H ₂₄ D ₂ O	224	14.38
19	28.284	10-methyl-6-trimethylsilyl-5(z),9-undecadien-1-otms	C ₁₈ H ₃₈ OSi ₂	326	1.76
20	28.757	dinonyl ester 1,2-benzenedicarboxylic acid	C ₂₆ H ₄₂ O ₄	418	3.57

**Figure 4.** GC-MS chromatogram of the ethanolic leaves extract of *Drypetes sepiaria* (DS)

(40:25) and DS-Zn²⁺ (50:50) the inhibition efficiencies were 77 and 78% respectively for 72 hours. On further addition of the additives of various concentration (10-50ppm) to the inhibitor ratio of DS-Zn²⁺ (50:50) the inhibition efficiencies of DS-Zn²⁺ -

citric acid (30ppm), DS-Zn²⁺ - lactic acid (30ppm), DS-Zn²⁺ - tartaric acid (50ppm), were found to be 90, 85 and 87% respectively.

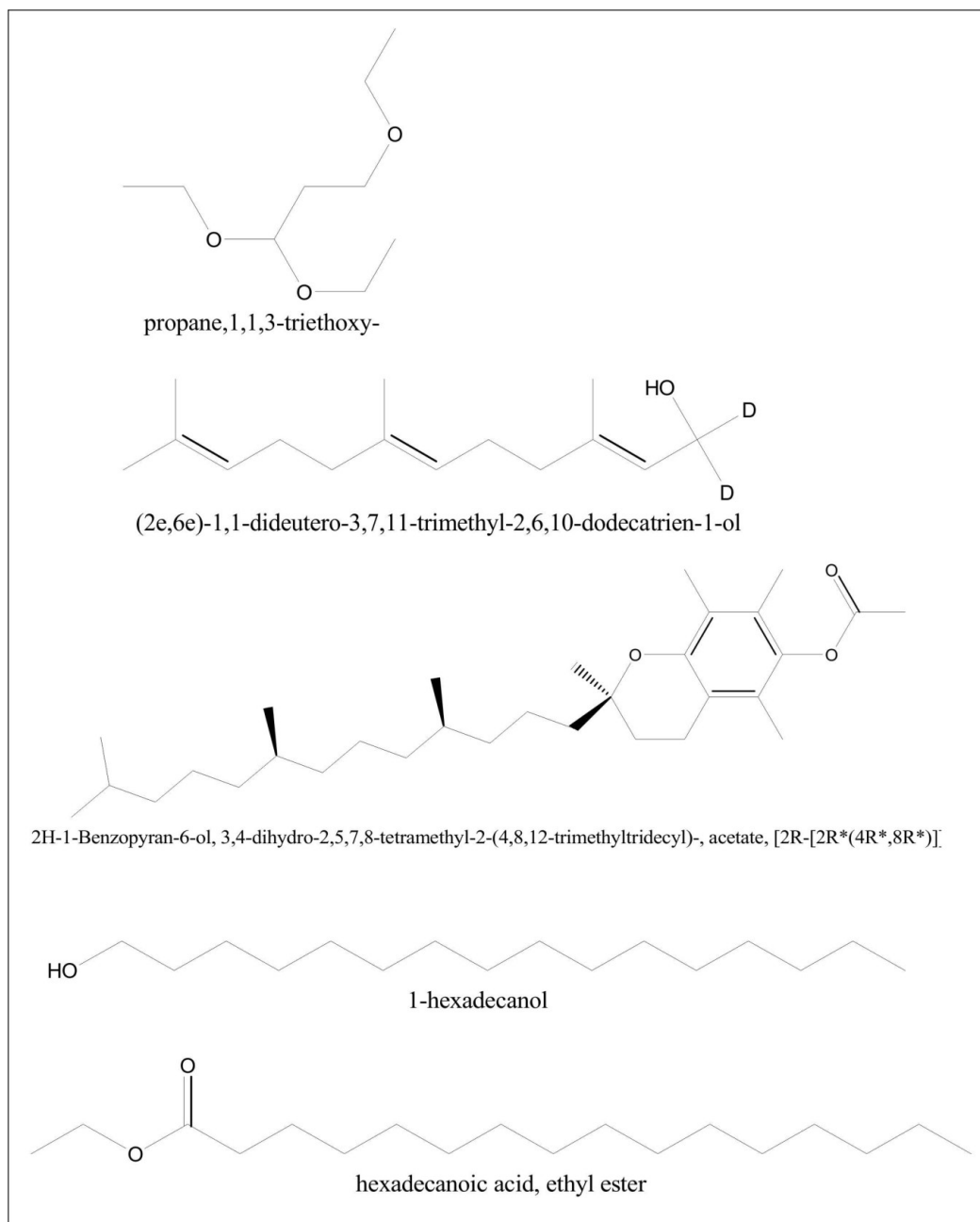


Figure 5. Predominant phytoconstituents present in *Drypetes sepiaria* (DS)

Analysis of FTIR

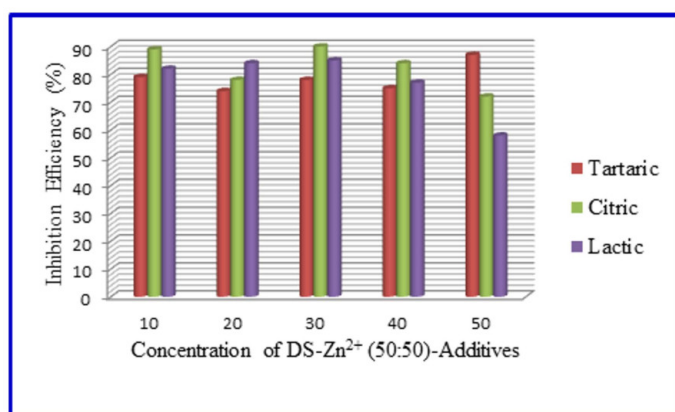
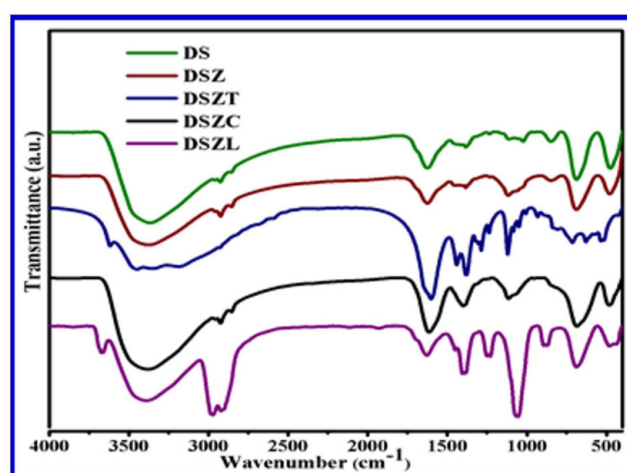
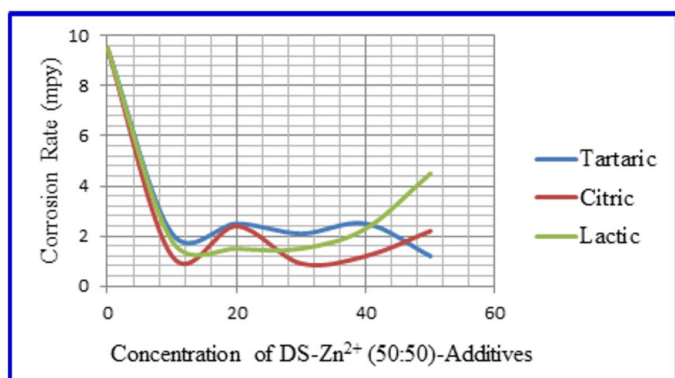
The FTIR spectrum of the extract and the film formed on the surface of the metal immersed in 0.5M HCl in the presence of the inhibitor were taken. FTIR spectroscopy has been used to analyze the protective film formed on the metal surface as investigated by (Selvi et al., 2009; Vera et al., 2007). The FTIR spectrum of the pure extract DS, DS-Zn²⁺, DS-Zn²⁺-Additives(citric, lactic and tartaric acids) as inhibitors are correlated in figure 7. For the pure extract as inhibitor the band observed at 3368.28cm⁻¹. There is a decrease in the frequency from 3600.00 cm⁻¹ to 3368.28cm⁻¹. Similar decrease pattern is observed for DS-Zn²⁺, DS-Zn²⁺-Additives (citric, lactic and tartaric acids), the bands were observed at 3379.55, 3382.44,

3389.20 and 3356.61cm⁻¹ respectively.

The bands at 1626.30cm⁻¹ and 1236.66cm⁻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 1625.48cm⁻¹ and 1384.32cm⁻¹ in DS-Zn²⁺. Similar shift in bands were observed in DS-Zn²⁺-citric acid (1612.88&1401.20cm⁻¹), DS-Zn²⁺-lactic acid (1628.57&1451.67, 1406.55cm⁻¹) and DS-Zn²⁺-tartaric acid (1602.82&1381.08, 1305.36cm⁻¹). The bands at 1022.91cm⁻¹ and 849.76cm⁻¹ (due to the ring oxygen and metal oxygen bond) are shifted to 1117.40cm⁻¹ and 851.29cm⁻¹. Similar shift in bands were observed in DS-Zn²⁺-citric acid (1115.67&685.85cm⁻¹), DS-Zn²⁺-lactic acid (1066.29, 1055.04 &893.41, 879.48cm⁻¹) and DS-Zn²⁺-

Table 5. Inhibition efficiencies and corrosion rates of carbon steel in DS-Zn²⁺, DS-Zn²⁺-(Tartaric acid, Citric acid, Lactic acid) in 0.5M HCl; Immersion Period = 72 h.

Conc. of DS (ppm)	Conc. of Zn ²⁺ ion (ppm)				Conc. of additives (ppm)	Conc. of DS- Zn ²⁺ ion (ppm) (50:50)					
	25		50			Tartaric Acid		Citric acid		Lactic acid	
	IE%	CR (mpy)	IE%	CR (mpy)		IE%	CR (mpy)	IE%	CR (mpy)	IE%	CR (mpy)
10	73	2.7	74	2.1	10	79	2.1	89	1.2	82	1.8
20	75	2.1	73	2.2	20	74	2.5	78	2.4	84	1.5
30	72	2.7	75	2.1	30	78	2.1	90	0.9	85	1.5
40	77	2.2	76	2.0	40	75	2.5	84	1.2	77	2.3
50	76	2.3	78	1.8	50	87	1.2	72	2.2	58	4.5
Blank		8.5		8.5			9.5		9.5		9.5

**Figure 6.** Inhibition efficiencies of DS-Zn²⁺ (50:50)-Additives (ppm) in various concentration**Figure 8.** IR Spectra Correlation of DS, DSZ, DSZT, DSZC and DSZL**Figure 7.** Corrosion Rates of DS-Zn²⁺ (50:50)-Additives (ppm) in various concentration

tartaric acid (1120.26 & 807.21cm⁻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 as reported by (Epshiba et al., 2016).

Analysis of UV-Visible absorption spectra

The UV-Visible absorption spectra of the solution containing DS-50ppm, DS -Zn²⁺ (50:50ppm), DS -Zn²⁺-30ppm Citric acid, (50:50) DS -Zn²⁺-30ppm lactic acid and (50:50) DS -Zn²⁺-50ppm tartaric acid are correlated in figure 11. A peak appears at 204.50nm (3.9830au), when Zn²⁺ ion is added a peak appears at 208.20nm (3.0347au), the intensity decreases. It is observed that, when additives are added to DS- Zn²⁺ - additives (citric acid; lactic acid; tartaric acid) systems the peak appears at 205.75nm (0.1877au), 979.55nm (0.6986au); 202.00nm (3.1168au) and 208.20 nm (1.3699au), 245.25 nm (0.9440au) the intensity varies on comparing with the DS and DS-Zn²⁺ systems respectively. This indicates the complexation of DS - Zn²⁺ & Additives (Citric, lactic, tartaric acids).

Fluorescence study

Fluorescence spectrum is used to detect the presence of the

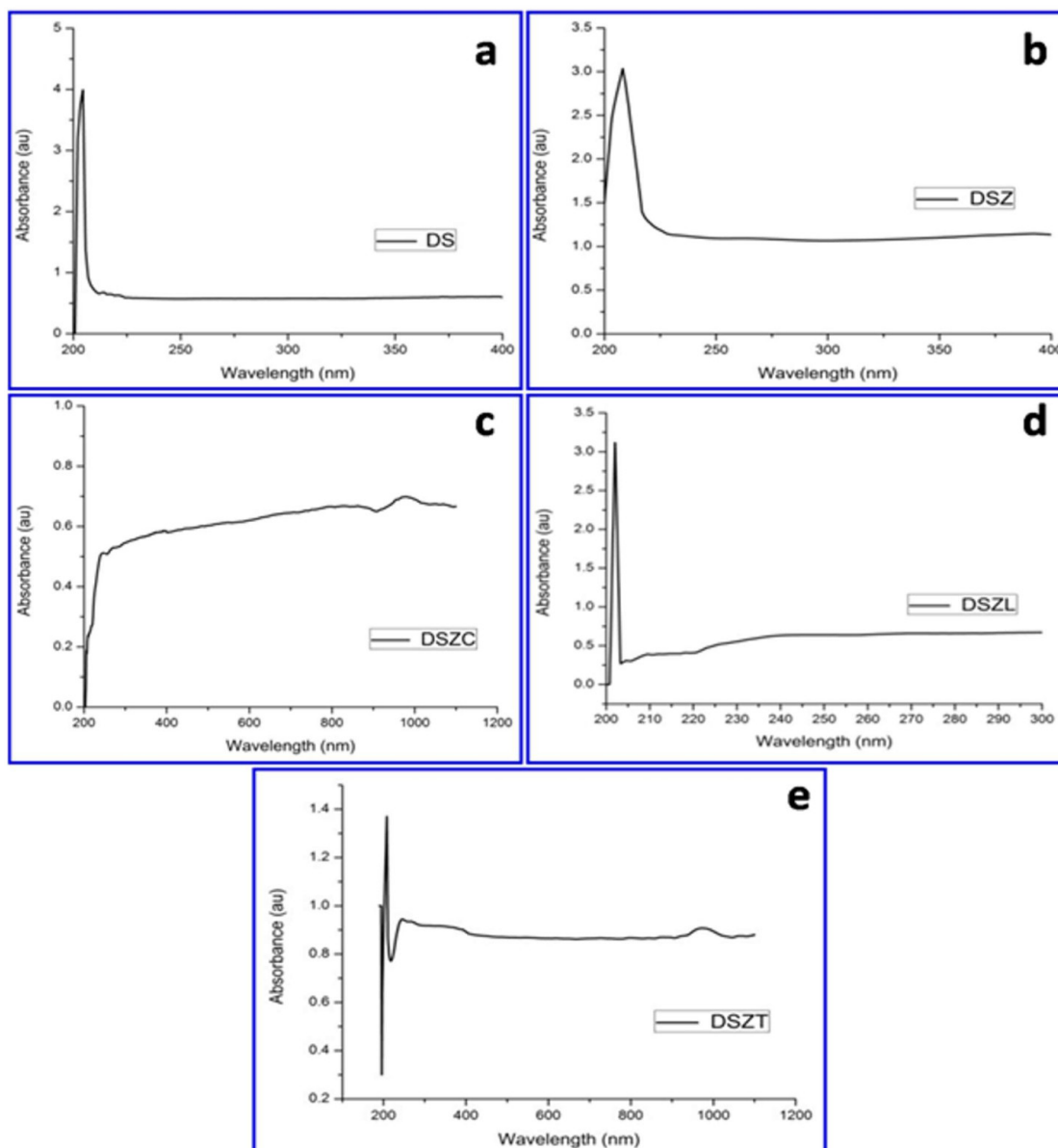


Figure 9. UV-Visible Spectra of (a) DS (b) DSZ (c) DSZC (d) DSZL (e) DSZT

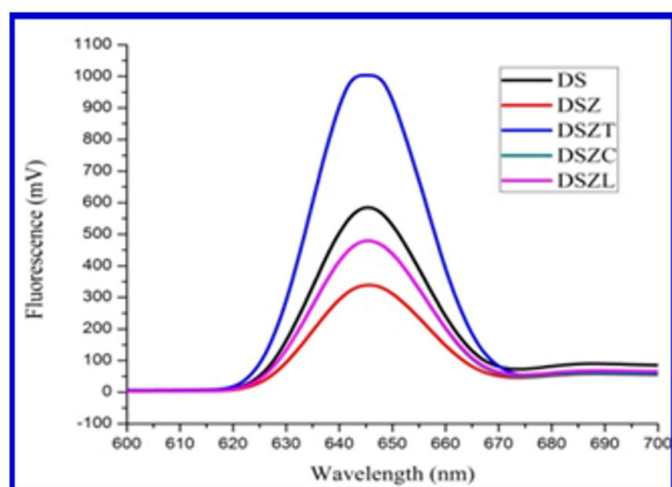


Figure 10. Fluorescence Spectra Correlation DS, DSZ, DSZT, DSZC and DSZL

inhibition complex formed on the metal surface. The λ_{ex} for the emission spectrum of the pure DS as inhibitor is found to be 645.36nm (584.80au) and for DS-Zn²⁺ the peak is obtained at 645.57 nm (339.11au). Figure 9, shows the λ_{ex} for the emission spectrum of the 50ppm DS-50ppm Zn²⁺-30ppm Citric acid, the peak is obtained at 645.34 nm (479.29au). The λ_{ex} for the emission spectrum of the 50ppm DS-50ppm Zn²⁺-30ppm Lactic acid, the peak is obtained at 645.44 nm (479.64au). Similarly, for Tartaric acid as additive the peak is obtained at 644.76 nm (1003.38 au) for 50ppm of tartaric acid. There is a shift in the intensity on comparing with the pure DS fluorescence value indicates the formation of protective film on the surface of the metal.

Scanning Electron Microscope (SEM) Analysis

The texture and pore structure of the inhibited and

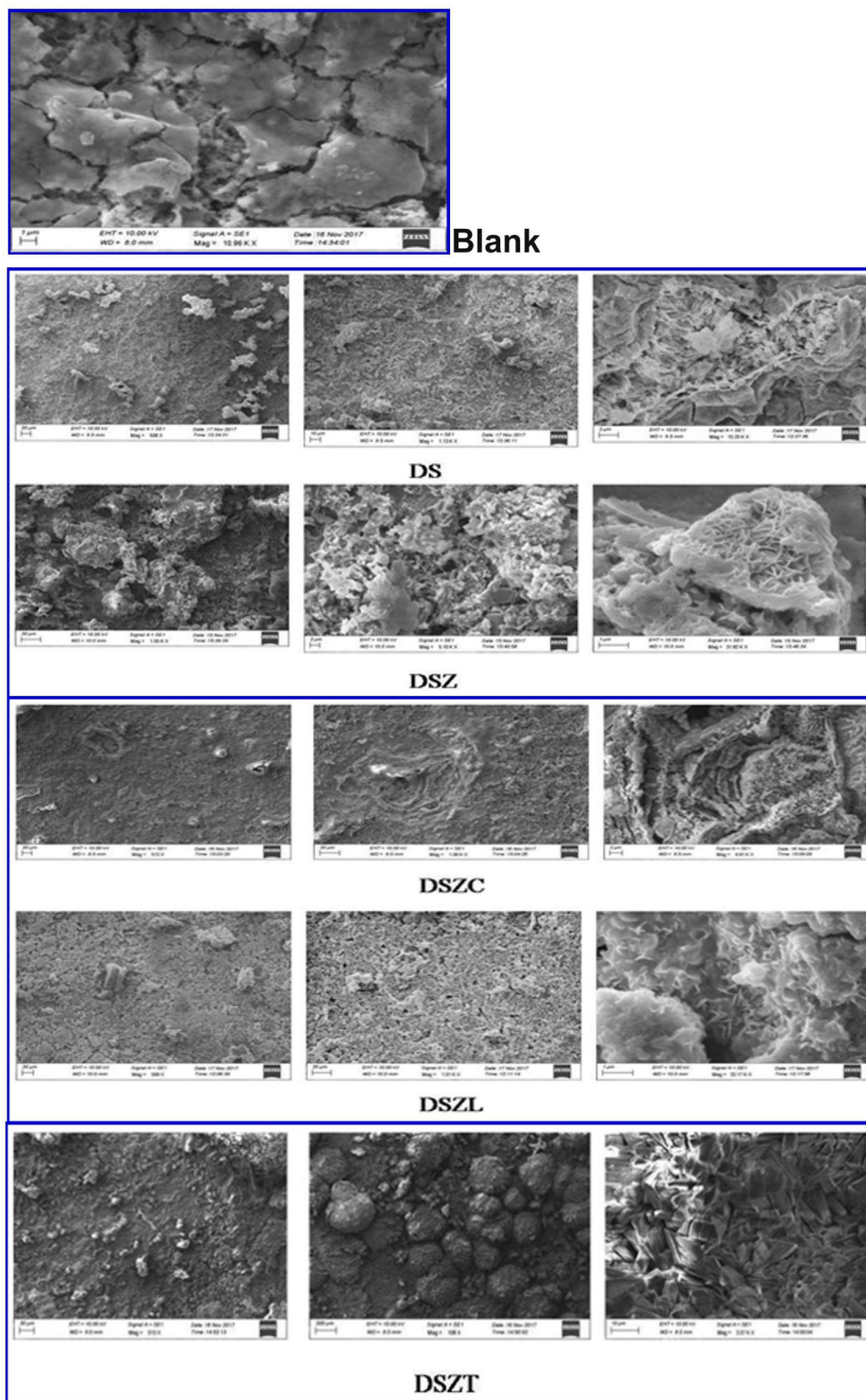


Figure 11. SEM images of blank, DS, DSZ, DSZC, DSZL and DSZT

uninhibited surface in acidic medium are shown in figure 11. It is confirmed that the inhibitor systems has formed a dense film over the metal surface.

Conclusion

From the above study it is concluded that, *Drypetes sepiaria* has a good anticorrosion ability for carbon steel in 0.5 M

HCl solution is due to the active phytoconstituents present in the plant. The maximum efficiency was found to be 78% at 50ppm DS + 50ppm Zn²⁺. And the inhibitive efficiency was found to be increased from the maximum efficiency with the additives citric acid (90%), lactic acid (85%) and tartaric acid (87%). The shift in the peaks observed in FT-IR, UV-Visible spectra proves the formation of the film on the surface of the metal. The variation in the intensities observed in the fluorescence study results the formation of the film on the surface of the metal. The protective film formed on the metal surface is found to be denser by the SEM analysis.

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