

# The use of *Syzygium Jambos* leaf extract as a green corrosion inhibitor for carbon steel in aqueous medium

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**ABSTRACT:** This research work is concerned with the development of new ecofriendly inhibitor system which functions efficiently as green inhibitor for the corrosion control of carbon steel in aqueous environment. The inhibition efficiency of corrosion of carbon steel in neutral, aqueous environment containing 180 ppm of  $\text{Cl}^-$  ions in DD water by leaf extract of plant *Syzygium Jambos* (SJLE) which contains active constituents<sup>1</sup> that exhibit synergistic property with  $\text{Mn}^{2+}$  ions has been investigated. A film is formed on the surface of the carbon steel immersed in the inhibitor system containing the extracts of the plant *Syzygium Jambos* and  $\text{Mn}^{2+}$  ions. In order to investigate the nature of the protective film, UV-visible spectroscopy, scanning electron microscopy, FTIR spectroscopy and electrochemical studies have been used in the present study. Polarisation techniques have been used to determine the nature of inhibitor. Based on the results obtained from the mass-loss method, polarisation studies, surface analysis, UV, FTIR, electrochemical studies, a suitable mechanism for the corrosion inhibition has been proposed.

**Key Words:** Carbon Steel, Inhibitor, Inhibition Efficiency, UV, FTIR.

## I. INTRODUCTION

The use of inhibitor is one of the best methods in preventing the carbon steel against corrosion. Corrosion inhibitors are organic compounds containing oxygen, sulphur and nitrogen atoms containing multiple bonds in their molecules through which they can adsorb on the metal surface. The present study investigates the potential of the extract of *Syzygium Jambos* as an inhibitor against corrosion in ethanol extract at different concentrations.

## II. METHODOLOGY:

### 2.1 Corrosion inhibitive action of extract of the leaves of *Syzygium Jambos* + $\text{Mn}^{2+}$ system

#### Analysis of the results of the mass-loss method

The inhibition efficiencies (IE) of extract of the leaves of *Syzygium Jambos* (SJLE) in controlling the corrosion of carbon steel in 180 ppm chloride ion solution in the absence and presence of  $Mn^{2+}$  by the mass-loss method<sup>2,3</sup> are given Table – 2.1. and in Figure - 2.1.

**Table – 2.1**

**Inhibition efficiency (IE) of carbon steel in aqueous environment (Cl<sup>-</sup> = 180 ppm) in the absence and presence of different concentrations of the inhibitor system by the mass-loss method**

Inhibitor system: SJLE +  $Mn^{2+}$

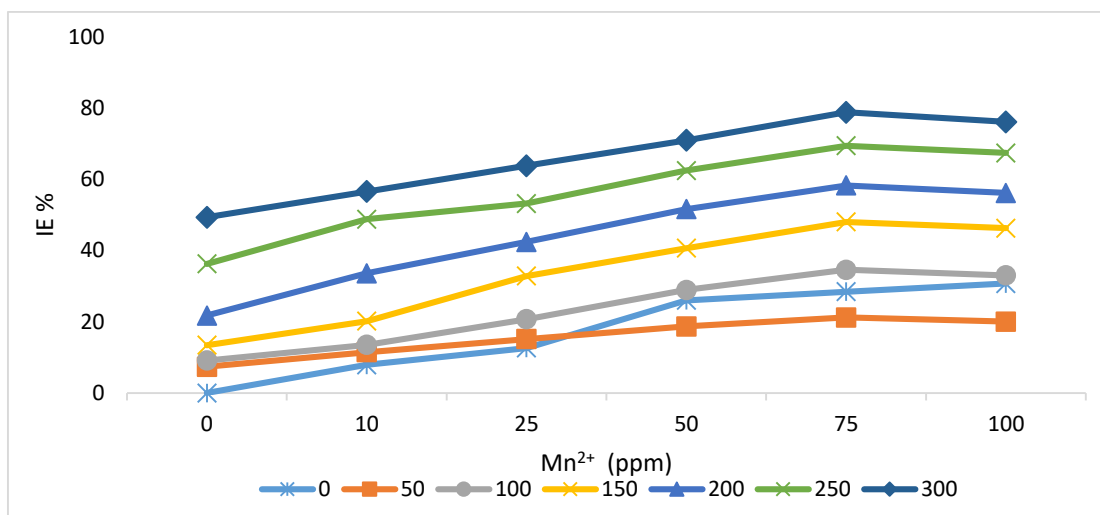
Immersion period: 1 day

SJLE (ppm) ↓ Mn <sup>2+</sup> (ppm) →	Inhibition efficiency (IE) %					
	0	10	25	50	75	100
0	-	7.9	12.6	26	28.4	30.7
50	9.01	15.23	19.67	27.63	28.36	26.37
100	15.73	18.67	24.54	30.16	32.54	31.41
150	19.61	23.96	30.67	36.56	35.61	33.72
200	23.33	28.17	39.51	49.85	47.68	41.52
250	26.54	31.62	42.62	61.37	63.87	58.45
300	33.68	48.36	63.47	<b>76.8</b>	71.2	62.56

From the Table – 2.1, it is observed that IE (76.8%) is maximum for 300 ppm concentration of the leaf extract with 50 ppm of  $Mn^{2+}$ . It clearly states that corrosion rate is minimum for this composition of the inhibitor system and ensures that the inhibition efficiency increases as the concentration of the inhibitor increases. This may be due to the adsorption of SJLE on the surface of the carbon steel through the interaction of N, O and also  $\pi$  electrons present in it. Corrosion efficiency is supported with increase in the concentration of SJLE resulting in the increased adsorption of SJLE on the surface of the metal. As a result the metal surface is effectively separated from the corroding medium and the corrosion rate decreases when the concentration of the inhibitor system increases which is shown in Figure - 2.1. Thus, SJLE with  $Mn^{2+}$  made a positive impact in the inhibition of corrosion on carbon steel.

Figure - 2.1

**Inhibition efficiency (IE%) of SJLE on carbon steel immersed in 180 ppm of Cl<sup>-</sup> ion solution with inhibitor system, SJLE + Mn<sup>2+</sup>**

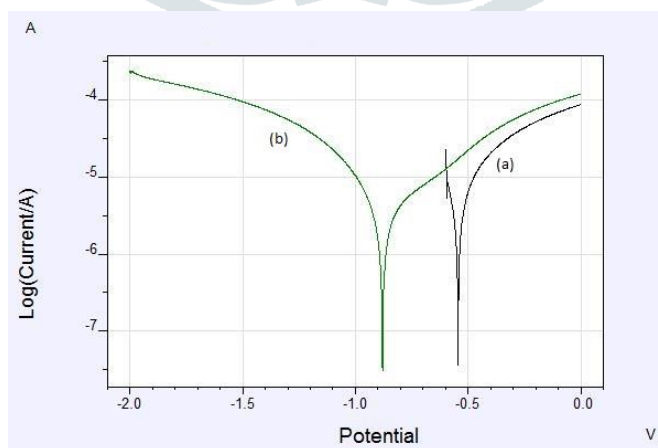


**2.2 Analysis of the Results of Potentiodynamic Polarization Studies**

The potentiodynamic polarization curves of carbon steel immersed in 180 ppm chloride ion in the presence of Mn<sup>2+</sup> and SJLE are given in Figure 2.2. The corrosion parameters of carbon steel immersed in 180 ppm Cl<sup>-</sup> ion solution in the presence and absence of Mn<sup>2+</sup> and SJLE are given in Table – 2.2

Figure- 2.2

**Polarization curves for carbon steel for inhibited and uninhibited system**



(a) Chloride ion solution (180 ppm) in DD water

(b) 300 ppm of SJLE + 50 ppm of Mn<sup>2+</sup> + 180 ppm Cl<sup>-</sup> ion in DD water

Table- 2.2

## Results of potentiodynamic polarization studies

S. NO	SYSTEM	$E_{Corr}$ (mV)	$b_a$ (mV/dec)	$b_c$ (mV/dec)	$R_p$ $\Omega(Cm^2)$	$I_{corr}$ (A/cm <sup>2</sup> )	Corrosion rate mm/y
1	180 ppm of chloride ion	-0.7789	1.459	0.385	6877	$1.923 \times 10^{-5}$	3.492
2	180ppm of Cl <sup>-</sup> +300 ppm of SJLE+50 ppm of Mn <sup>2+</sup>	-0.6292	0.502	0.997	11790	$1.23 \times 10^{-5}$	2.23

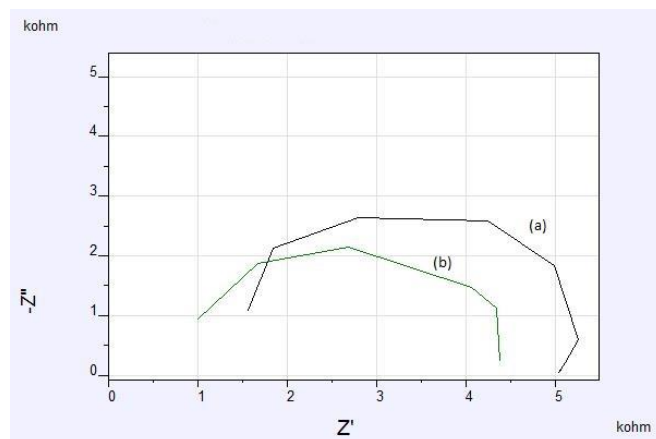
When carbon steel is immersed in 180 ppm Cl<sup>-</sup> ion solution, the corrosion potential ( $E_{corr}$ ) is -0.7786 mV and the corrosion current is  $1.923 \times 10^{-5}$  A/cm<sup>2</sup>. When immersed in inhibited system, the corrosion potential is found to be -0.6292mV and the corrosion current is  $1.23 \times 10^{-5}$  A/cm<sup>2</sup>. The decrease in the corrosion current and the change in the corrosion potential on the addition of the inhibitor system to 180 ppm of chloride ion solution indicate that the formulation reduces anodic dissolution and cathodic hydrogen evolution reaction of carbon steel immersed in 180 ppm of chloride ion solution. The anodic slope changes from 1.459 mV/dec to 0.502 mV/dec and the cathodic slope changes from 0.385 mV/dec to 0.997 mV/dec shows that the shift in the anodic slope is higher than the shift in cathodic slope. This indicates the modification of both anodic and cathodic reaction mechanism is inhibited by the inhibitor. This tells that SJLE acts as a mixed inhibitor as it is known that only when change in the value between anodic and cathodic slope is more than 85 mV/dec. It can be recognized as an evidence of a compound as an anodic or a cathodic type inhibitor. The corrosion rate decreases which indicates the adsorption of inhibitor system on the metal surface that blocks the active sites and retards the corrosion<sup>4</sup>.

### 2.3 Analysis of the Results of Electrochemical Impedance Spectroscopy

The AC impedance spectra<sup>5</sup> have been used to detect the formation of film on the metal surface. It is a rapid and convenient method to evaluate the performance of the organic coating on the metal and has been used for the corrosion studies. The AC impedance spectra of carbon steel immersed in 180 ppm chloride solution and solution containing the inhibitor formulation are shown in Figure- 2.3 The AC impedance parameters namely charge transfer resistance and the double layer capacitance are given in Table -2.3

Figure- 2.3

AC Impedance curves for carbon steel for inhibited and uninhibited system



- (a) Chloride ion solution (180 ppm) in DD water
- (b) 300 ppm of SJLE + Mn<sup>2+</sup> + 180 ppm Cl<sup>-</sup> ion in DD water

Table -2.3

AC Impedance results for carbon steel for inhibited and uninhibited system

S.No	Environment in DD water	R <sub>ct</sub> (Ohm.cm <sup>2</sup> )	C <sub>dl</sub> (μF/cm <sup>2</sup> )	Inhibition Efficiency %
1	180 ppm of Chloride ion in DD water	3.3 x 10 <sup>2</sup>	2.63 x 10 <sup>-8</sup>	82.4
2	180 ppm of Cl <sup>-</sup> + 300 ppm of SJLE+ 50 ppm of Mn <sup>2+</sup>	4.4 x 10 <sup>3</sup>	1.90 x 10 <sup>-8</sup>	

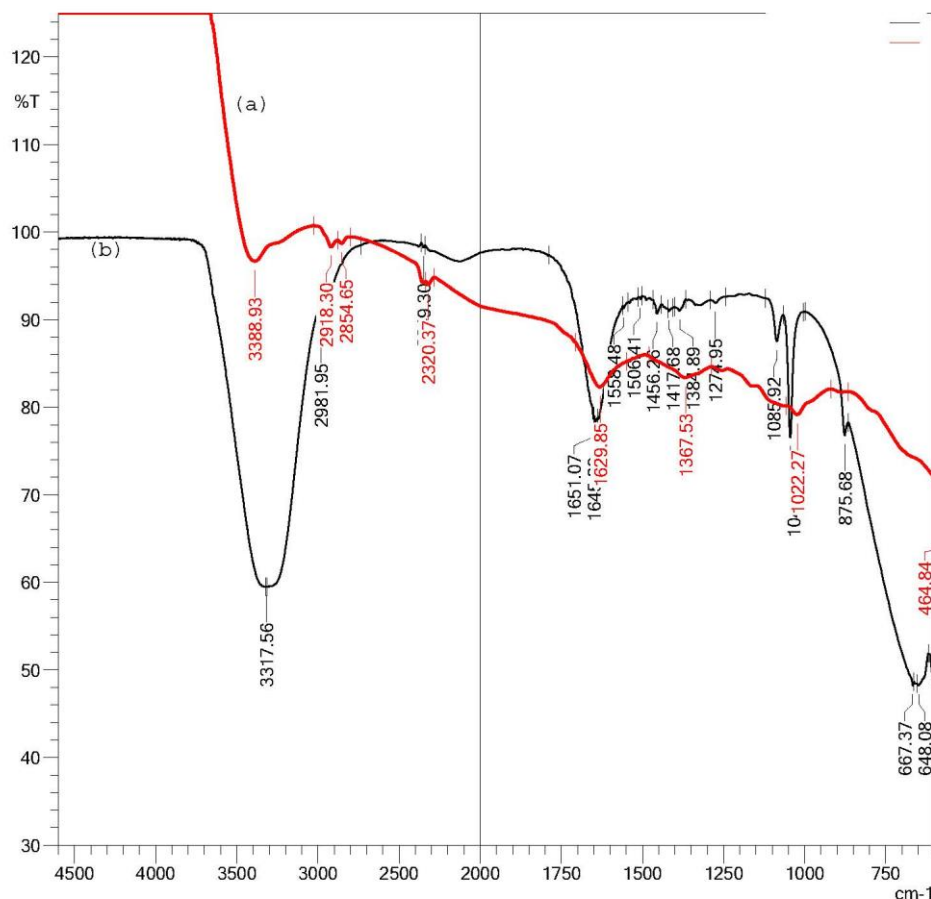
It shows clearly that in the presence of inhibitor the R<sub>ct</sub> value increases and hence inhibition efficiency increases. The decrease in C<sub>dl</sub> value can be attributed to the increase in the electrical double layer at the metal solution interface by the adsorption process. Further the decrease in the C<sub>dl</sub> value indicates the replacement of water molecules by inhibitor molecules by the process of adsorption with an increase in surface coverage. The increase in R<sub>ct</sub> values with the concentration of inhibitor tells that the charge transfer process is controlling the corrosion process. The increased R<sub>ct</sub> values and decreased C<sub>dl</sub> values from impedance studies justify the good performance of the extract with Mn<sup>2+</sup> as corrosion inhibitor in chloride ions in DD water. This behavior means that the film obtained acts as a barrier to the corrosion process and proves the existence and the formation of the film.

R<sub>ct</sub> value is used to calculate the percentage of inhibition efficiency using the equation %IE = (R<sub>ct</sub> - R<sup>\*</sup><sub>ct</sub>) / R<sub>ct</sub> X 100 where R<sub>ct</sub> and R<sup>\*</sup><sub>ct</sub> indicates the charge transfer resistances with and without the inhibitor.

## 2.4 Analysis of FTIR Spectra

The FTIR spectrum of SJLE is shown in Figure – 2.4a and FTIR spectrum of the thin film formed on the surface of the carbon steel immersed in 180 ppm of chloride ion solution containing the inhibitor system is shown in Figure-2.4b.

**Figure -2.4 FTIR spectrum (a) pure SJLE and (b) thin film formed on the surface of the carbon steel immersed in 180 ppm Cl<sup>-</sup> ion containing inhibitor system**



The -OH frequency of the extract at 3388.93 cm<sup>-1</sup> which is due to phenolic -OH is shifted to 3317.56cm<sup>-1</sup> with a sharp intense band. The bands at 2981.95 cm<sup>-1</sup> and 2918.3 cm<sup>-1</sup> are due to the H-C-H symmetric and asymmetric stretching of the extract disappear. The band at 2320 is due to C≡N stretch of the of the extract forms a broad band at 2329.30 cm<sup>-1</sup> in the thin film. A notable band at 1629 cm<sup>-1</sup> can be assigned to C=O stretching of the extract got shifted to a very intense band at 1651.07 in the film. Many small bands appear at 1384.89, 1417.68, 1456.26, 1506.41, 1558.48 of the film may be due to the presence of C-O, N=O, N-H stretch. The shifting of the bands in the thin film indicates that the carboxylate anion and the ring oxygen present in the phytoconstituents are responsible for the interaction between the phytochemicals present in the extract of the leaves of Syzygium Jambos and Fe present in the carbon steel. It could be seen that certain additional peaks had appeared and some had shifted to higher frequency region, providing information that

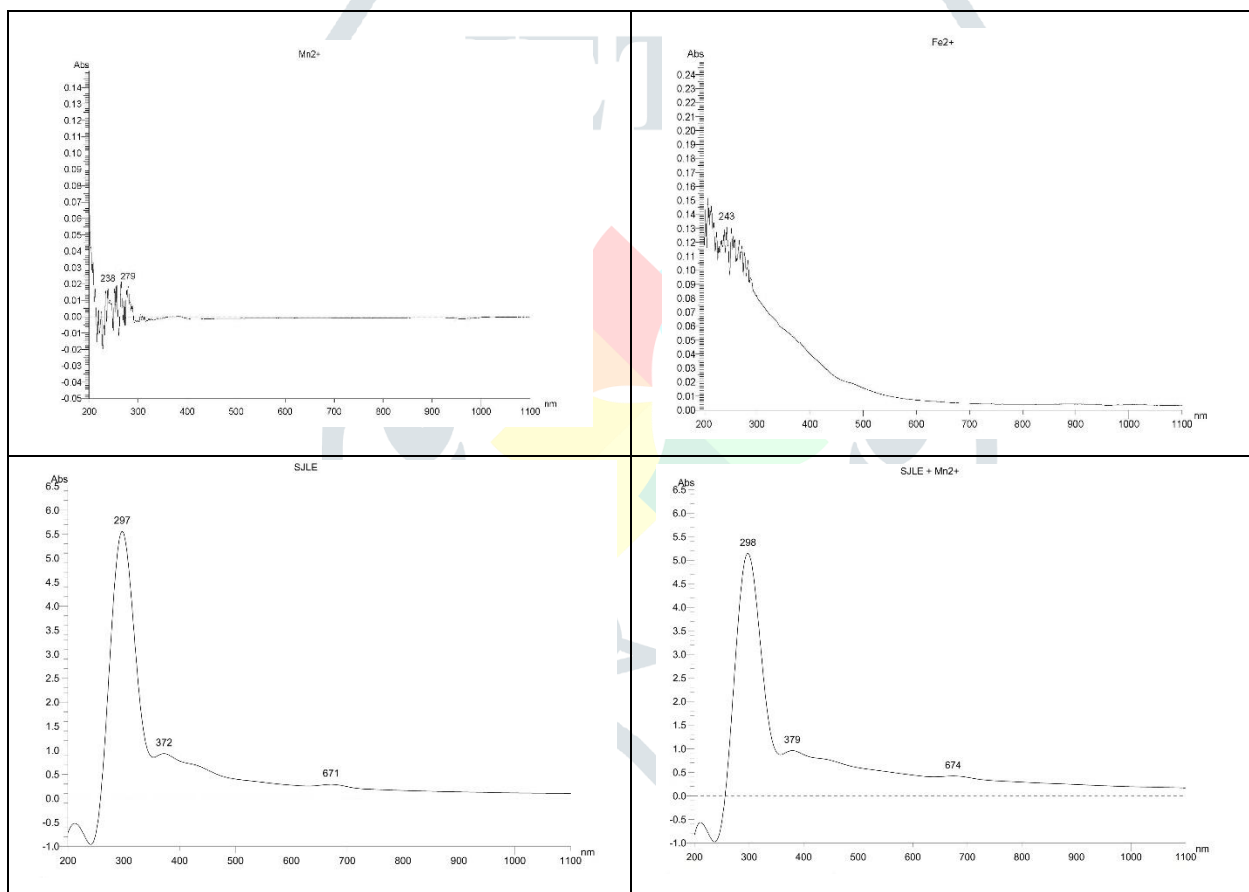
some interaction/adsorption over metal surface had taken place. The above results suggested the presence of inhibitor complex with  $\text{Fe}^{2+}$  on the surface. There is an increase in absorbance after carbon steel is immersed in the SJLE. This reveals the formation of a complex between the  $\text{Fe}^{2+}$  and the phytoconstituents of the root extract. Formation of this complex may be responsible for the observed deviation in the frequency and its intensity value and this may be responsible for anti-corrosion activity<sup>6,7</sup>.

## 2.5 UV-Visible Spectral Study

The UV-Visible spectrum of  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ , SJLE,  $\text{Mn}^{2+}$  in the presence of SJLE, and  $\text{Fe}^{2+}$  in the presence SJLE in 180 ppm  $\text{Cl}^-$  ion solution are given in Figure -2.5 a-e.

**Figure- 2.5a-e UV-Visible absorption spectra of the test solutions in 180 ppm  $\text{Cl}^-$  ion**

**(a)  $\text{Mn}^{2+}$ , (b)  $\text{Fe}^{2+}$  ion, (c) SJLE, (d) SJLE +  $\text{Mn}^{2+}$ , and (e) SJLE +  $\text{Fe}^{2+}$**





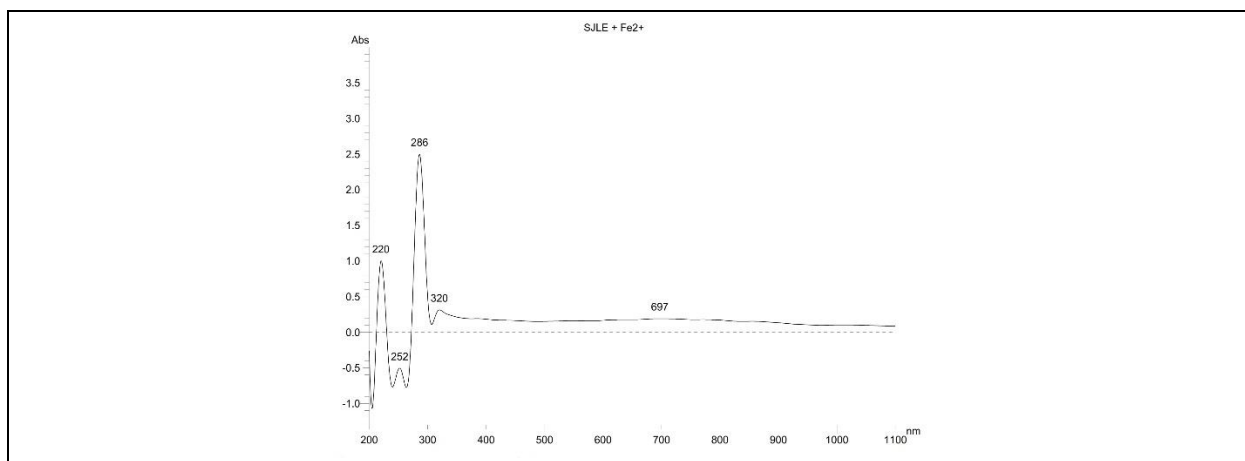


Table – 2.5

The  $\lambda_{\max}$  and absorbance values of the test solutions

S.No	Test Solutions	$\lambda_{\max}$ and Absorbance
1	Mn <sup>2+</sup>	238(0.019), 279 (0.02)
2	Fe <sup>2+</sup>	243 (0.13)
3	SJLE	297(5.7) 372(0.9) 671(0.4)
4	SJLE + Mn <sup>2+</sup>	298(5.2) 379(1.0) 674(0.5)
5	SJLE + Fe <sup>2+</sup>	220(1.0) 252(-0.4) 286(2.5) 320(0.3)

The absorbance of SJLE at 297 nm is found to be 0.57, 372nm is 0.9 and 671nm is 0.4 (Figure- 2.5c). The absorbance of Mn<sup>2+</sup> ion is found to be 0.02 at 279 nm and 238 nm at 0.019(Figure- 2.5a).The addition of 50 ppm of Mn<sup>2+</sup> to 300 ppm of SJLE changes the absorbance value. Three peaks are formed at 298,379 and 674 where absorbance has got increased. (Figure -2.5d). The change in the value of absorbance in Mn<sup>2+</sup> + SJLE constituents indicates the existence of strong interaction between Mn<sup>2+</sup> and phytoconstituents present in SJLE.

UV-visible spectrum of Fe<sup>2+</sup> (Figure-2.5 b) shows that at 243 nm the solution has an absorbance of 0.13. When Fe<sup>2+</sup> added to SJLE the peaks appear at 286,320,270,252 nm and absorbance is found to change. (Figure-2.5e). This clearly proves the existence and formation of a complex between Fe<sup>2+</sup> and phytoconstituents present in SJLE.

From the figures, the deviation is shown in absorbance values and their intensities and there is an increase in absorbance after carbon steel immersion in SJLE. This reveals the formation of a complex between the Fe ions and the phytoconstituents of the green inhibitor<sup>8</sup>. Formation of the complex may be responsible for the observed deviation in the absorbance and its intensity value and this may be responsible for

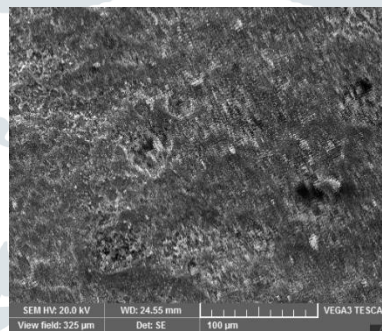


anticorrosion activity. It is also noted that there was significant difference in the shape of the spectra before and after the immersion of specimen showing the possibility of forming thin inhibitor layer over the carbon steel surface (Physisorption).

## 2.6 Scanning Electron Microscopic Analysis (SEM)

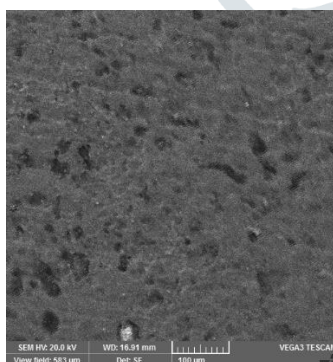
The texture and pore structure of the inhibited and uninhibited surface of the carbon steel immersed in chloride ion solution in aqueous medium in the presence and absence of the inhibitor system are shown in Figure- 2.6 a,b,c,d.

**Figure – 2.6 a**  
**SEM image of carbon steel in 180 ppm Cl<sup>-</sup> ion**

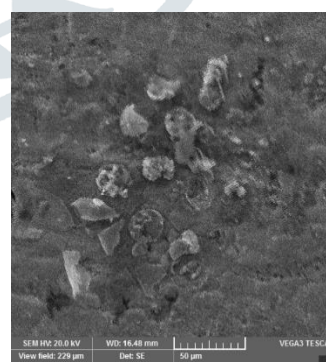


**Figure- 2.6 b, c, d Carbon steel in 180 ppm Cl<sup>-</sup> ion + 300 ppm of SJLE + 50 ppm of Mn<sup>2+</sup>**

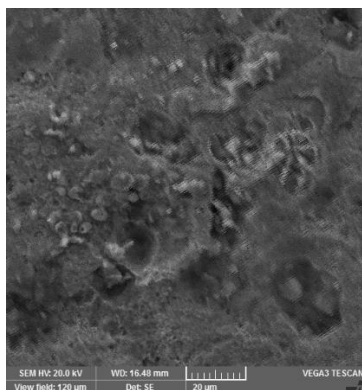
**2.6 b**



**2.6 c**



**2.6 d**



SEM Figure- 2.6 a clearly implies that the carbon steel surface is highly damaged with pitted areas in the absence of inhibitor system. But Figure- 2.6 b, c, d shows a clear, smooth deposition of SJLE on the surface of the specimen after the immersion in the inhibitor system. On viewing the images it is seen that the pits disappear and carbon steel is free from corrosion. This is because of the formation of a layer of the SJLE on the surface of carbon steel. This is also confirmed by the FTIR spectral analysis. Thus this has retarded and resisted further corrosion by forming a protective layer on the carbon steel<sup>9</sup>.

## 2.7 Energy Dispersive X-ray Spectroscopy (EDX)

The EDX spectra is used to determine the elements present on the surface of carbon steel to get a clear idea regarding the elements present. EDX spectra of the surfaces of carbon steel are recorded in order to observe changes occurred during corrosion process in absence and presence of the inhibitor. The EDX spectra of the carbon steel specimen, uninhibited specimen and inhibited specimen with the inhibitor SJLE are given in the following Figures- 2.7 a, b, c.

Figure -2.7 a Carbon steel

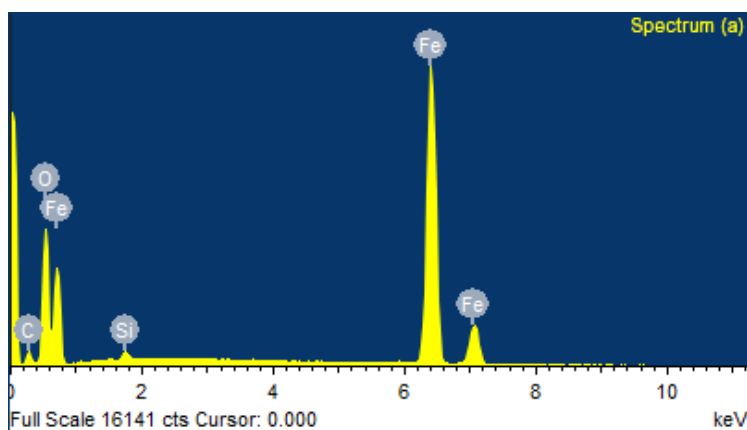
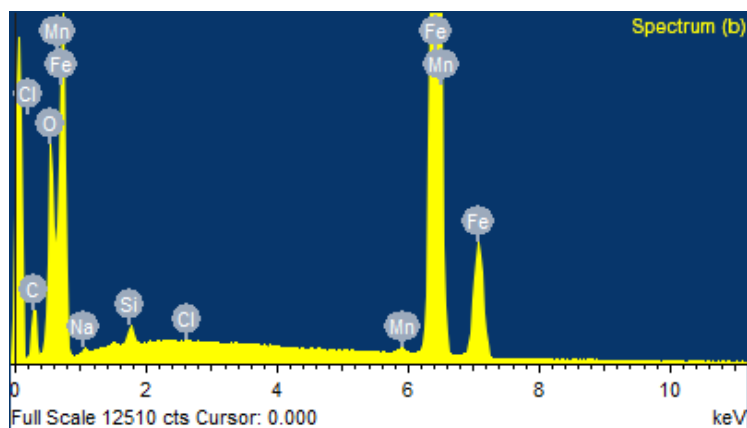
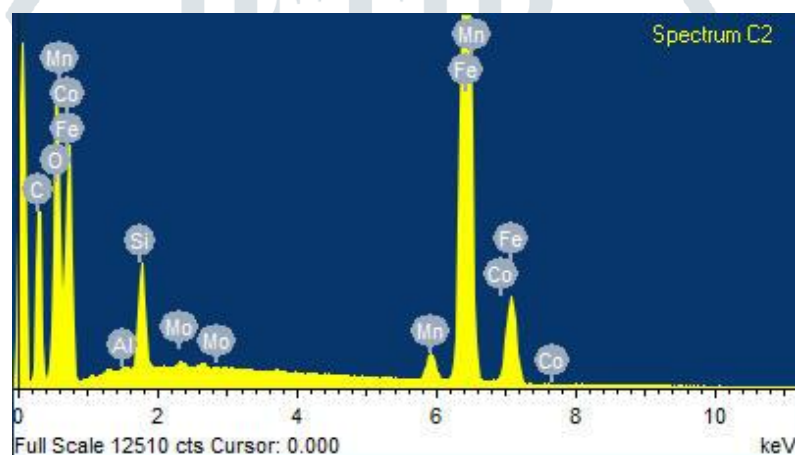


Figure -2.7 b Carbon steel in 180 ppm Cl<sup>-</sup> ionFigure -2.7 c Carbon steel in 180 ppm Cl<sup>-</sup> ion + 300 ppm of SJLE + 50 ppm of Mn<sup>2+</sup>

The EDX spectra<sup>10,11</sup> show the characteristics peaks of some of the elements constituting the carbon steel, carbon steel sample that was immersed in 180 ppm of chloride ion environment without inhibitor and in the presence of the inhibitor. The EDX spectrum of inhibited specimen show the presence of cobalt, magnesium, aluminium, manganese, iron, carbon, oxygen and silicon. Their presences are due to the phytoconstituents that are adsorbed on the surface of the specimen. There is suppression in iron peaks because of the overlying inhibitor film whereas the uninhibited specimen shows the absence of most of the elements, except Chlorine. All these confirm the presence of thin layer on the surface of inhibited specimen and SJLE to be a good and efficient, green inhibitor.

### SUMMARY AND CONCLUSION

Analysis of the results of the mass-loss method shows that the formulation consisting of 300 ppm extract of the leaves of *Syzygium Jambos* and 50 ppm Mn<sup>2+</sup> offers 76.8 % IE in controlling the corrosion of carbon steel immersed in 180 ppm Cl<sup>-</sup> ion solution. A synergistic effect exists between Mn<sup>2+</sup> and the phytoconstituents

present in the leaf extract of *Syzygium Jambos*. The inhibition of corrosion of carbon steel in aqueous chloride ion solution in the presence of the inhibitor system is due to the interaction between the lone pair of electrons present in the active constituents of the extract with the positively charged metal surface. The IE of the inhibitor formulation depends on the ability of the inhibitor to form complex with  $Mn^{2+}$  and the ability of  $Fe^{2+}$  to react with  $Mn^{2+}$  complex to form iron complex on the surface of the specimen.

Results of polarization studies show that this inhibitor controls both anodic and cathodic reactions and behaves as mixed inhibitor. AC impedance spectra reveals the formation of protective film on the metal surface. The FTIR spectra confirm the presence of active constituents on the metal surface and also the change in nature of the active constituents. The UV-visible absorption spectra indicate the possibility of formation of a film with the extract and with manganese and iron ions. The SEM micrographs confirm the formation of protective layer on the metal surface. The EDX analysis confirms the presence of a layer and reveals the existence of other ions in the inhibited specimen which are the constituents present in the inhibitor. Thus all these experiments confirms the adsorption of SJLE molecules on the carbon steel surface in aqueous medium.

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