International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.11 No.02, pp 01-11, 2018

Evaluation of the Inhibitive Effect of *Asparagus setaceus L* + Mn^{2+} System in Neutral Medium on Carbon Steel

P. Leema Sophie*[1], Noreen Anthony[2], X. Prisil Naveentha[3]

[1]P.Leema Sophie is currently pursuing Ph.D in Chemistry in Holy Cross College (Autonomous), India,
[2]Dr. Noreen Anthony is Faculty in Chemistry in Holy Cross College (Autonomous), India,
[3]PrisilNaveentha is currently pursuing M.Phil in Chemistry in Holy Cross College (Autonomous), India

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 objective of the present set of studies has been framed to investigate in detail, the mutual influence and the compatibility of plant extract which are locally available in plenty using different techniques under different experimental conditions as inhibitor system.

The inhibition efficiency of corrosion of carbon steel in neutral, aqueous environment containing 180 ppm of Cl- ions in DD water by leaf extract of plant *Asparagus setaceus.L* which contains active constituents that exhibit synergistic property with Mn^{2+} ions has been investigated. 200 ppm of the leaf extract worked in conjunction with 10 ppm of Mn^{2+} ions in controlling the corrosion of carbon steel immersed in 180 ppm of chloride ion solution is the best system. A film is formed on the surface of the carbon steel immersed in the inhibitor system containing the extracts of the plant *Asparagus setaceus. L* and 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, polarisaion studies, surface analysis, UV, FTIR, electrochemical studies and temperature studies, a suitable mechanism for the corrosion inhibition has been proposed.

Key Words : Carbon Steel, Inhibitor, Inhibition Efficiency.

Introduction

Corrosion[1] is the deterioration of metal by chemical attack or reaction with its environment. It is an irreversible interfacial reaction of a material with its environment which develops fast after disruption of the protective barrier and are accompanied by a number of reactions that change the composition and properties of

DOI= http://dx.doi.org/10.20902/IJCTR.2018.110201

both metal surface and the local environment. A corrosion inhibitor[2] is a chemical which, when added in small concentration to a system, minimizes or prevents corrosion. Green inhibitors[3] enhance the formation of a protective oxide film through an oxidizing effect and those that inhibit corrosion by selectively adsorbing on the metal surface and creating a barrier that prevents access of corrosive agents to the metal surface[4].

The present study aims to develop a suitable corrosion control method using the plant extract which are readily and locally available for acid pickling and cooling water system with a view of their application in industrial plants. The plant extract chosen as inhibitor for the present study is *Asparagus Setaceus.L* whose botanical name is *Asparagus Setaceus.L* belonging to the family Asparagaceae and locally called as Asparagus Fern, Lace Fern, Climbing Asparagus, or Ferny Asparagus. *Asparagus setaceus. L*[5] is a scrambling perennial herb and an ornamental plant, hardy and adapts readily to cultivation.

The results of the screening of ethanol extracts of the leaves of *Asparagus Setaceus.L* (ASLE) for the phytochemical constituents has alkaloids, tannins, saponins, flavones and flavonoids and these active constituents present in the extract are responsible for the inhibition efficiency of the carbon steel immersed in 180 ppm of chloride ion solution.

Methodology

Table 1 – Best environment chosen for surface examination studies

Inhibitor	**Environment chosen**	
Asparagus setaceus.L	Chloride ions *Asparagus setaceus.L* Mn^{2+}	180 ppm 200 ppm 10 ppm

Mass Loss Method

Polished specimens were initially weighed in an electronic balance. Weighed samples were immersed in 100 ml of the D D water with and without the different concentrations of the inhibitor for various intervals of time. They were then taken out and then washed thoroughly with tap water, rinsed with distilled water, dried, stored in desiccators and reweighed.

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

$$\text{Corrosing rate} = \frac{W}{A \times T} \text{ (mdd)}$$

W = Loss in weight in mg
A = Surface area of the specimen (dm^2)
T = Period of immersion (days)

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 the inhibitor and

W_2 = corrosion rate in the presence of the inhibitor.

Inhibition efficiencies (IE) of carbon steel in aqueous environment (Cl^-= 180 ppm) in the presence and absence of the inhibitor system and the inhibition efficiencies obtained by the mass-loss method.

Inhibitor system:*Asparagus setaceus.L* -Mn^{2+} Immersion period: 1 day

Table 2 – Effect of inhibitor on corrosion rate

Conc of plant extract	**Conc of Mn^{2+}**	**Corrosion rate**	**θ**	**Inhibition efficiency**
0	10	20.56	.4728	47.28
50	10	16.23	.5838	58.38
100	10	13.79	.6464	64.64
150	10	9.61	.6766	67.66
200	10	5.48	.8594	85.94

From the Table 2, it is observed that IE is maximum for 10 ppm of Mn^{2+} with the inhibitor of 200 ppm. Table 2 clearly states that Corrosion Rate is minimum for this same system which is shown in Figure 1.

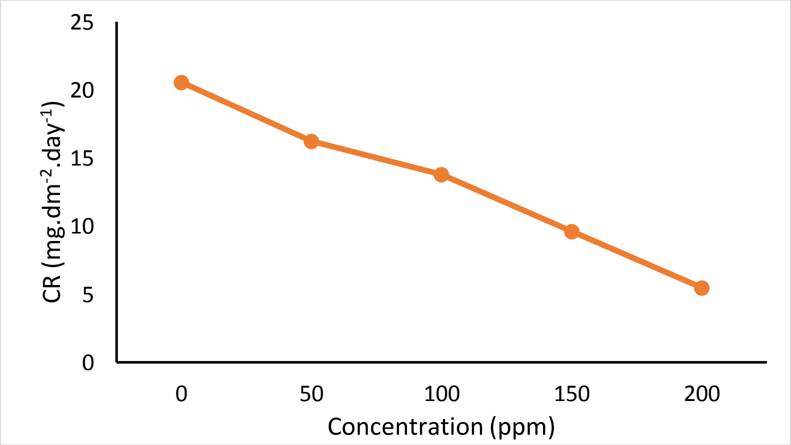


Figure1

Corrosion rates of carbon steel in aqueous environment (Cl^- = 180 ppm) in the presence and absence of the inhibitor system and the inhibition efficiencies obtained by the mass-loss method.

Inhibitor system: ASLE-Mn^{2+}

Table3 –Effect of duration of immersion on the IE of ASLE-Mn^{2+} system

S.No	**ASLE (ppm)**	**Mn^{2+} (ppm)**	**Immersion period (days)**	**Corrosion rate (mdd)**	**Inhibition Efficiency (%)**
1	200	10	1	5.39	86.1
2	200	10	3	13.61	65.10
3	200	10	5	20.57	47.25
4	200	10	7	26.35	32.43
5	200	10	15	31.16	20.10

ASLE=the extract of the leaves of*Asparagus setaceus.L.*

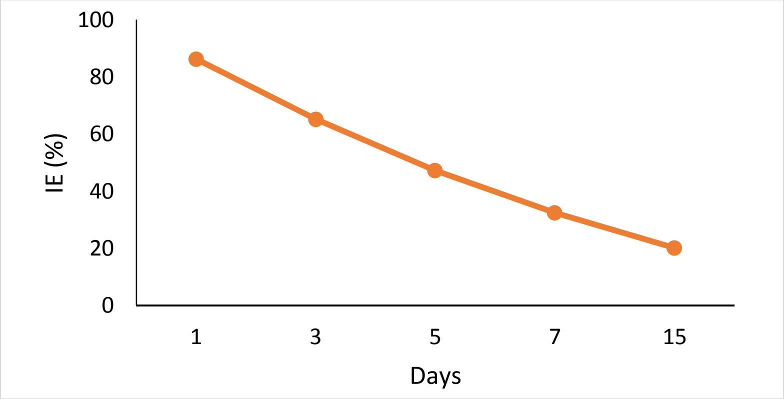


Figure2

The corrosion rates of carbon steel in the presence of the inhibitor system in 180 ppm Cl- ion solution for different durations of immersion are tabulated in Table 3 and the IE as a function of immersion period are shown in Figure 2.

From the Table 3 it is clear that the IE decreases from 86.1 % to 65.10 % from the first day to the third day and changes only slightly on increasing the days of immersion. On the fifteenth day it is found to be only 20.1%. This indicates that the aggressive chloride ions are finally able to destroy the film, formed on the surface. The film is not able to sustain their attack for a long time. It is obvious that the inhibitor system protects the carbon steel for only one day.

The decrease in IE with time may be due to the fact that the molecules are physically adsorbed on the surface and as the activation energy[6] for desorption is less for physical adsorption the molecules are easily desorbed from the surface after some time and hence the inhibition efficiency decreases on increasing the period of immersion.

Effect of pH on the IE of ASLE + Mn^{2+}System

Corrosion rates of carbon steel in aqueous environment (Cl^- = 180 ppm) in the presence and absence of the inhibitor system at different pH and the inhibition efficiencies obtained by the mass-loss method.

Table 4 Inhibitor system: ASLE + Mn^{2+}

S.No.	ASLE (ppm)	Mn^{2+} (ppm)	pH	Corrosion rate (mdd)	Inhibition efficiency (%)
1	200	10	1	30.92	8.08
2	200	10	3	15.11	61.25
3	200	10	5	9.53	75.56
4	200	10	7	5.40	86.1
5	200	10	9	10.24	73.74
6	200	10	11	27.71	28.94

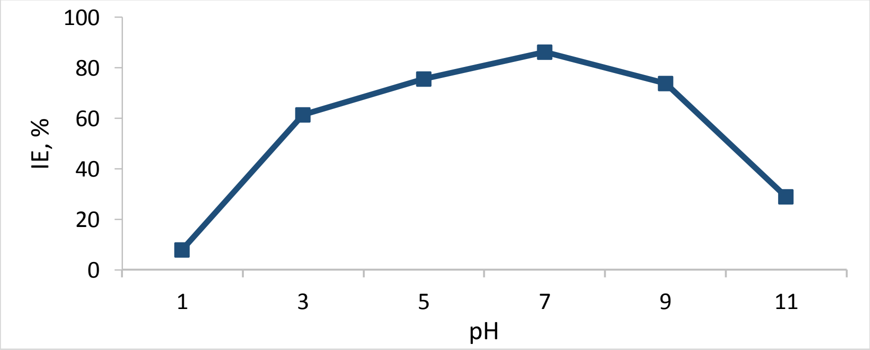


Figure3 – Effect of pH on the IE of Carbon Steel in aqueous environment (Cl^- = 180 ppm) by ASLE + Mn^{2+} system

Corrosion rates of carbon steel in 180 ppm Cl- ion solution in the presence of inhibitor system at different pH and the IE are tabulated in Table 4 and IE as a function of pH is also shown in Figure 3.It is found from the Table 4 that the inhibition efficiency increases with increase in the pH, reaches maximum value at pH = 7 and then decreases. The IE at pH 5 is found to be 75.56% and at 7 pH it is 86.1. This is the highest IE obtained. This may be due to the ionization of the phytoconstituents in acid medium, resulting in the availability of the COO^- ion, for the interaction with Mn^{2+} ions[7,8]. At higher pH due to the precipitation of Mn^{2+} as $Mn(OH)_2$[9] a slight reduction in IE is noticed. The amount of Mn^{2+} ions for the transport of phytoconstituents to the surface of the carbon steel is less. Hence a reduction in the IE is noted.

Electrochemical Studies

Analysis of the Results of Potentiodynamic Polarization Studies

The potentiodynamic polarization curves of carbon steel immersed in 180 ppm chloride ion solution in the presence and absence of Mn^{2+} and *Asparagus setaceus.L* leaf extract are given in Figure4.The corrosion parameters of carbon steel immersed in 180 ppm Cl^- ion solution in the presence and absence of 10 ppm of Mn^{2+} and 200 ppm of *Asparagus setaceus.L* leaf extract are given in Table5.

When carbon steel is immersed in 180 ppm Cl^- ion solution, the corrosion potential (Ecorr) is -671.9 mV and the corrosion current is 7.779 x 10-6 A/cm^2. When 10 ppm of $Mn^{2+}$and 200 ppm of *Asparagus setaceus.L* extract are added to 180 ppm Cl^- ion solution the corrosion potential is found to be -592.8 mV. The corrosion current is 6.175×10^{-6} A/cm^2. The decrease in the corrosion current on the addition of the inhibitor and the change in the corrosion potential indicate that the formulation functions as a cathodic inhibitor and controls the cathode reactions and reduces the corrosion of carbon steel in 180 ppm of chloride ion solution. The anodic slope changes from 636 mV/dec to 513mV/dec. The change in cathodic slope from 290 mV/dec to 348 mV/dec shows that the inhibitor controls the cathodic reaction predominantly and behaves as cathodic inhibitor[10-13]. The corrosion rate decreases on introducing the inhibitor system in the chloride ion solution in neutral aqueous medium.

Table5 – Resultsof potentiodynamic polarization studies
Medium: Chloride ion solution (180 ppm) in DD water
Inhibitor system: ASLE (200 ppm) + Mn^{2+} (10 ppm) + 180 ppm Cl^- ion in DD water

S. No	SYSTEM	E_{Corr} (mV)	b_a (mV/dec)	b_c (mV/dec)	R_p $\Omega(Cm^2)$	I_{corr} (A/cm^2)	Corrosion rate mm/y
1	180 ppm of chloride ion	-671.9	636	290	1.628×10^4	7.779×10^{-6}	0.5212
2	180 ppm of Cl- +plant extract+Mn^{2+}	-592.8	513	348	1.441×10^4	6.175×10^{-6}	0.4138

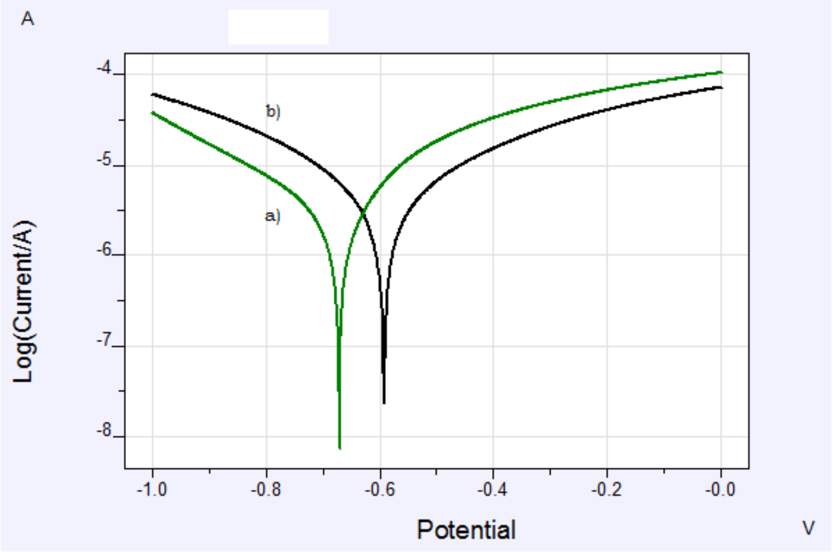


Figure 4
Medium: Chloride ion solution (180 ppm) in DD water
Inhibitor system: ASLE (200 ppm) + Mn^{2+} (10 ppm) + 180 ppm Cl- ion in DD water
(a) Chloride ion solution (180 ppm) in DD water
(b) ASLE (200 ppm) + Mn^{2+} (10 ppm)+ 180 ppm Cl- ion in DD water

Analysis of the Results of AC Impedance Studies

The AC impedance spectra of carbon steel immersed in 180 ppm chloride solution containing the inhibitor formulation are shown in Figure5. The AC impedance parameters namely charge transfer resistance and the double layer capacitance are given in Table6. When carbon steel is immersed in 180 ppm chloride solution the Rct value is found to be $1.445\times10^{-9}\Omega cm^2$.The Cdl value is $2.423\times10^{+3}$ F/cm^2. When 10 ppm of Mn^{2+} and 200 ppm of *Asparagus setaceus.L* leaf extract are added, the Rct value is increased from 1.445×10^{-9} Ωcm2 to 3.093×10^{-9} Ωcm^2 and the Cdl value changes from $-2.423\times10^{+3}$ F/cm^2 to $-7.022\times10^{+3}$ F/cm^2. The increased Rct values and decreased Cdl values from impedance studies justify the good performance of the extract with Mn^{2+} as an inhibitor in Cl ions in DD water[14]. 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[15].

Table6 – Results of AC impedance studies

Medium: Chloride ion solution (180 ppm) in DD water
Inhibitor system: ASLE (200 ppm) + Mn^{2+} (10 ppm) + 180 ppm Cl^- ion in DD water

Environment in DD water	R_{ct}(Ohm.cm^2)	C_{dl}(μF/cm^2)
180 ppm of Chloride ion in DD water	1.445×10^{-9}	$-2.423\times10^{+3}$
Cl^- + 200 ppm ASLE+ 10 ppm Mn^{2+}	3.093×10^{-9}	$-7.022\times10^{+3}$

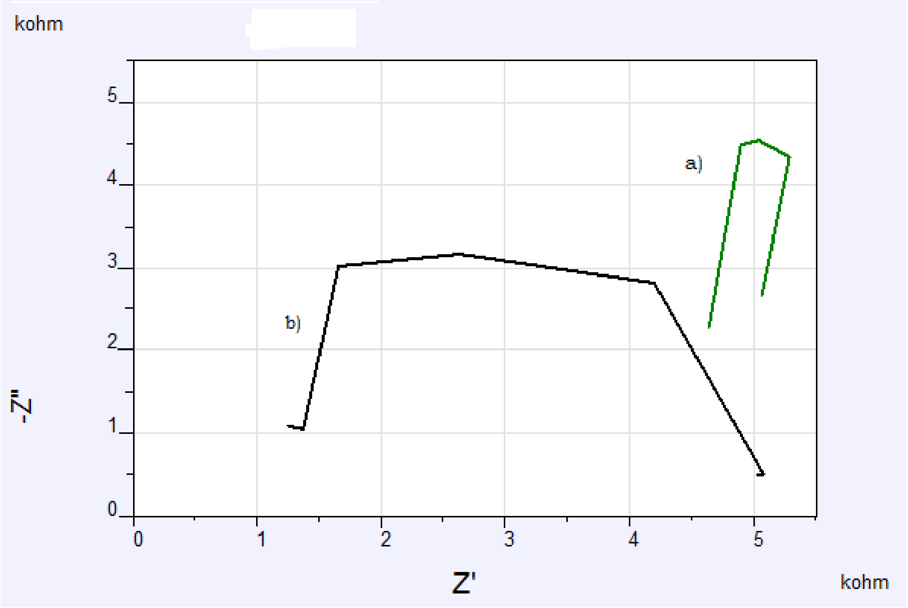


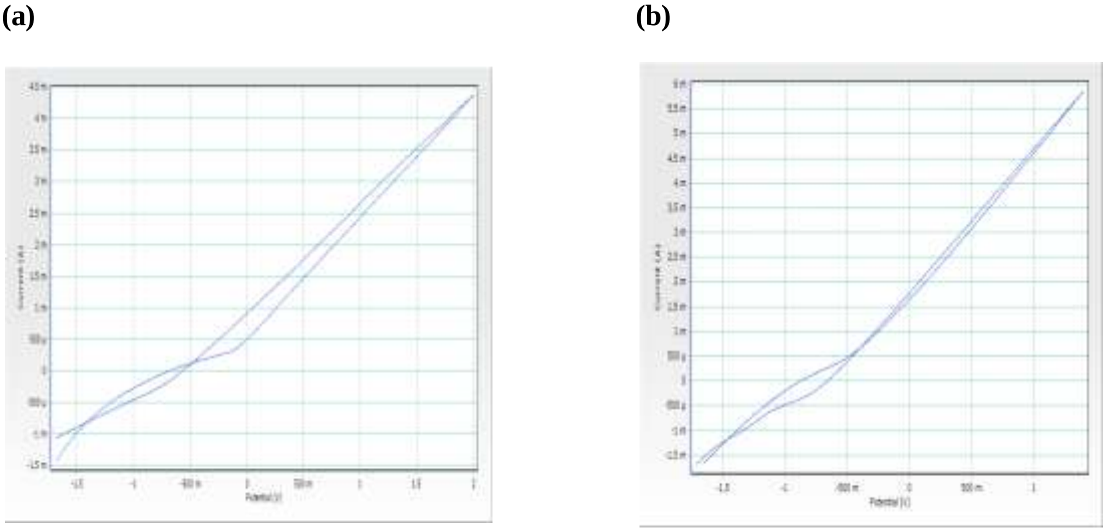
Figure5 – AC impedance of carbon steel
Medium: Chloride ion solution (180 ppm) in DD water
Inhibitor system: ASLE (200 ppm) + Mn^{2+} (10 ppm) + 180 ppm Cl^{-}ion in DD water
(a) Chloride ion solution (180 ppm) in DD water
(b) ASLE (200 ppm) + Mn^{2+} (10 ppm)+ 180 ppm Cl- ion in DD water

Cyclic Voltammetry

The cyclic voltagram of carbon steel electrode, is shown in Figure 6a and Figure 6b. It is observed that during the anodic sweep, dissolution of metal does not take place. This indicates that the protective film is stable and compact. Electrons are not transferred from the metal surface, and a passive region is observed. During the cathodic sweep, the peak corresponding to reduction of pitting corrosion product appears at 571 mV. However, the peak due to reduction of iron oxide to iron appears at 1.397 V. The current density increases from 4.206 A to 5.856 A. When the electrode is immersed in the inhibitor medium, the pitting potential is shifted to the noble side, that is, 652 mV. This indicates that electro oxidation is an irreversible process[16]and the passive film found on the metal surface in the presence of inhibitors is compact and stable.

Table 7 – Resultsof Cyclic Voltammetry studies
Medium: Chloride ion solution (180 ppm) in DD water
Inhibitor system: ASLE (200 ppm) + Mn^{2+} (10 ppm) + 180 ppm Cl- ion in DD water

Sample	**EP V**	**PEAK iP A**
Blank	1.899	4.206
Inhibitor System	1.397	5.856



(a) **(b)**

Figure 6 – CV of carbon steel
Medium: Chloride ion solution (180 ppm) in DD water ……………….(a)
Inhibitor system: ASLE (200 ppm) + Mn^{2+} (10 ppm) + 180 ppm Cl^- ion in DD water……(b)

Spectroscopic Studies

Analysis of FTIR Spectra

The FTIR spectrum of the pure extract of *Asparagus setaceus.L* is shown in Figure 7. The band at 3381 cm^{-1} is due to the presence of –OH. The bands at 1594 cm^{-1} and 1398 cm^{-1} are due to the coupling of -C-O stretching and -C-O-H in-plane bending vibration of the carboxylate anion. The bands at 1057 cm^{-1} and 881 cm^{-1} are due to -C-O ring vibration.

Figure 7 shows the 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. The -OH frequency of the extract at 3381 cm^{-1} is shifted to 3353 cm^{-1}. The bands at 1594 cm^{-1} and 1398 cm^{-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 1628 cm^{-1} and 1453 cm^{-1}. The band at 1057 cm^{-1} (due to the ring oxygen) is shifted to 1119 cm^{-1}. The band at 881 cm^{-1} is shifted to 936 cm^{-1}. 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[17,18] present in the extract of the leaves of *Asparagus setaceus.L* and Fe present in the carbon steel.

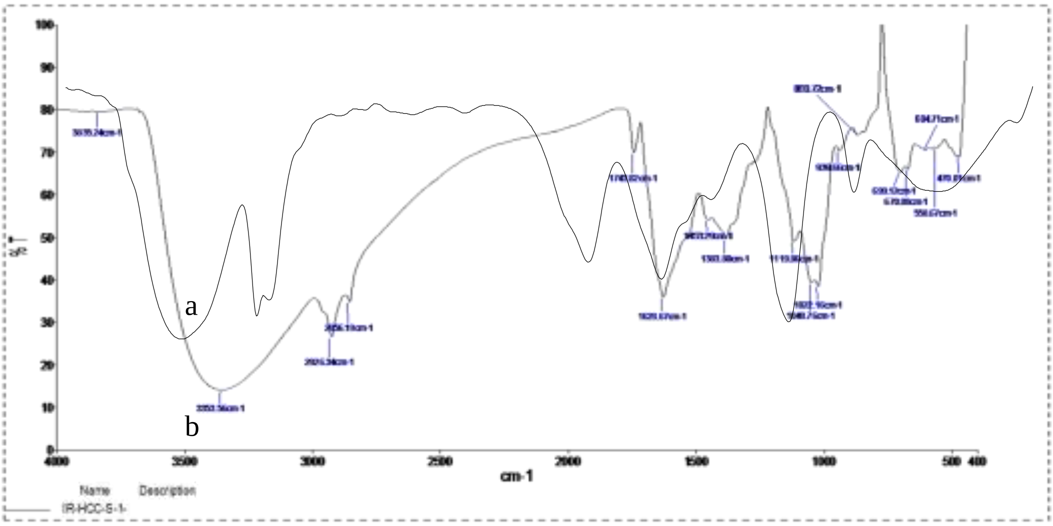


Figure 7 – FTIR spectrum (KBr) (a) pure ASLE and (b) thin film formed on the surface of the carbon steel immersed in 180 ppm Cl^- ion containing inhibitor system

UV-Visible Spectral Study

The UV-Visible spectrum of Mn^{2+}, Fe^{2+}, leaves extract of *Asparagus setaceus.L*, Mn^{2+} in the presence of *Asparagus setaceus.L* leaf extract, and Fe^{2+} in the presence of *Asparagus setaceus.L* leaf extract in 180 ppm Cl- ion solution are given in Figure 8a-e. The absorbance of leaves extract of *Asparagus setaceus.L* at 256 nm is found to be 0.097 (Figure 8c). The absorbance of Mn^{2+} ion is found to be 1.554 at 291 nm and it decreases with increase in λ (Figure 8a).

The addition of 10 ppm of Mn^{2+} to 200 ppm of *Asparagus setaceus.L* decreases the absorbance value. The absorbance is found to be 0.360 at 269 nm and it decreases sharply to 0.266 at 313nm (Figure 8d). The change in the value of absorbance in Mn^{2++}*Asparagus setaceus.L* constituents indicates the existence of strong interaction between Mn^{2+} and phytoconstituents present in *Asparagus setaceus.L*.

UV-visible spectrum of Fe^{2+} (Figure 8b) shows that at 291 nm the solution has an absorbance of 1.080. When Fe^{2+} added to *Asparagus setaceus.L* the absorbance is found to be 0.506 at 257nm (Figure 8e) then decreases gradually and at 317 nm the absorbance is found to be 0.341. This clearly proves the existence and formation of a complex between Fe^{2+} and phyto constituents present in *Asparagus setaceus.L*[19].

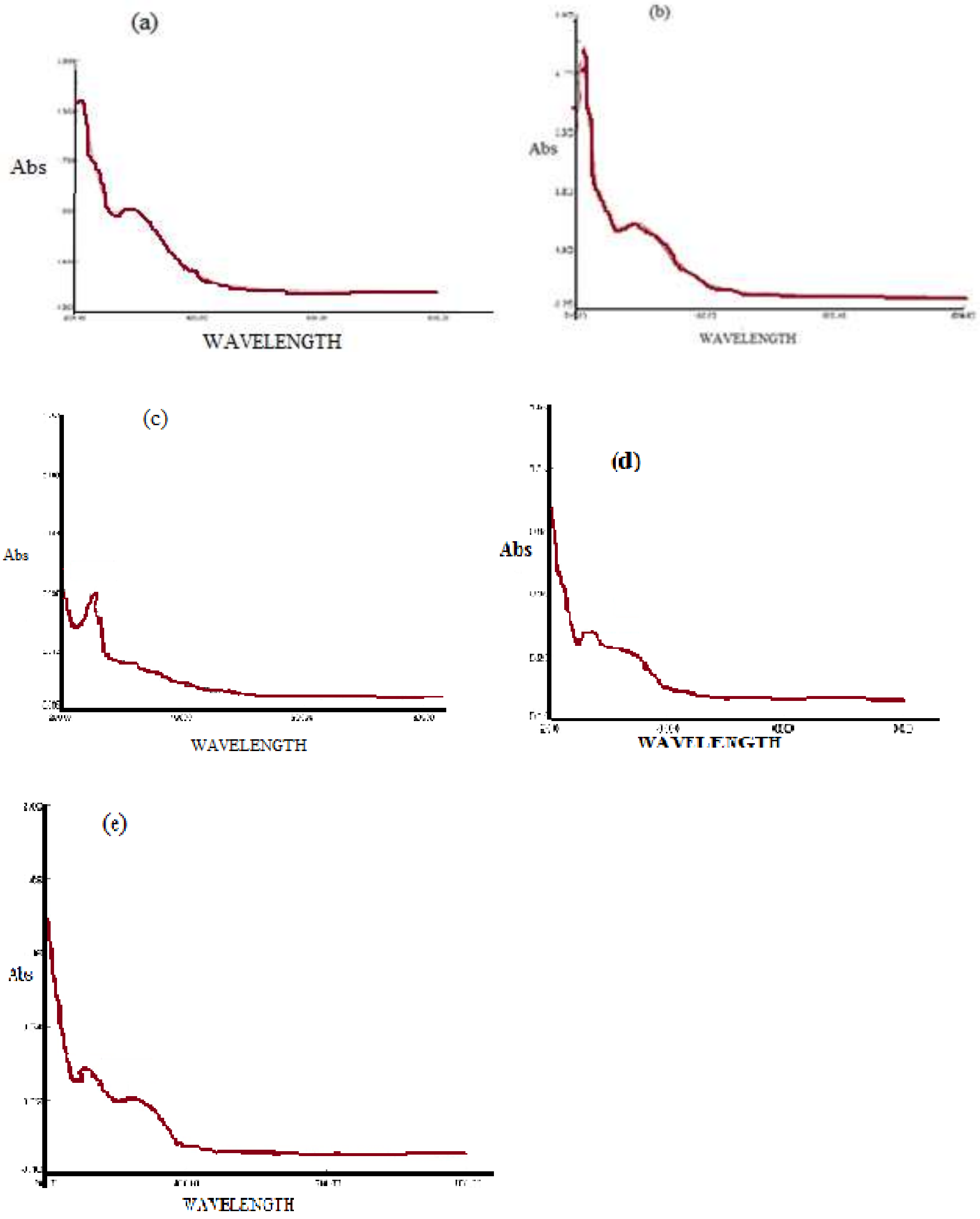


Figure 8 – UV-Visible absorption spectra of the test solutions in 180 ppm Cl^- ion (a) Mn^{2+}, (b) Fe^{2+} ion, (c) ASLE, (d) ASLE +Mn^{2+}, and (e) ASLE + Fe^{2+}

SEM Observation

The texture and pore structure of the inhibited and uninhibited surface of the carbon steel immersed in chloride ion solution in neutral medium in the presence and absence of the inhibitor system are shown in Figure 9 and 10. From Figure 10 a,b,c it is confirmed that the inhibitor system[20] has formed a dense film over surface of the carbon steel immersed in chloride ion solution in neutral medium containing 180 ppm of chloride ions.

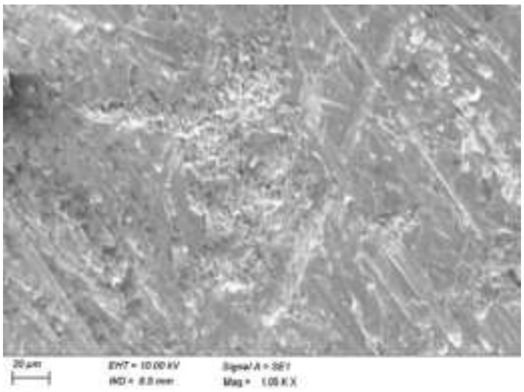
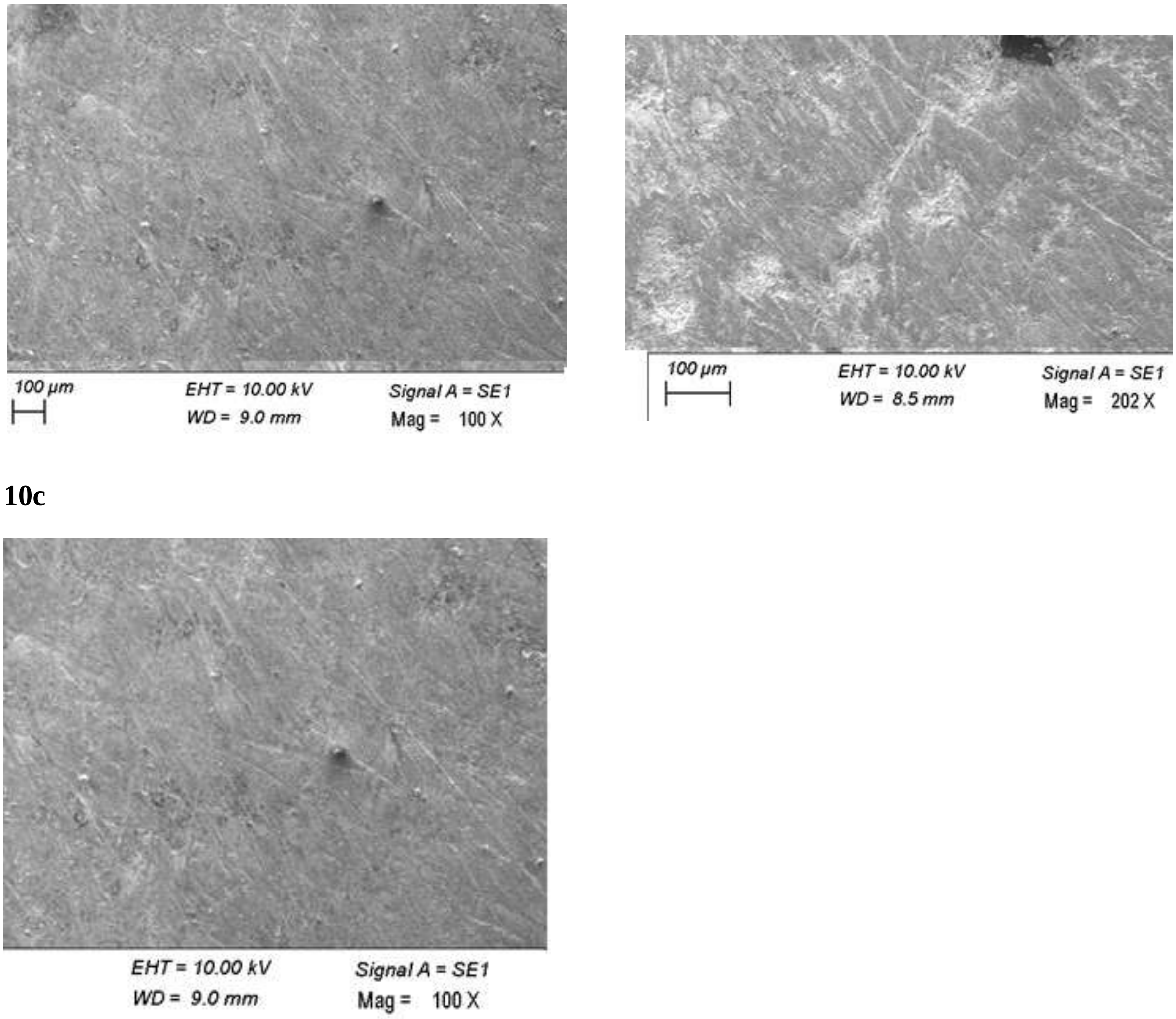


Figure 9 – SEM image of carbon steel in 180 ppm Cl^- ion

10a **10b**



10c

Figure 10 – Carbonsteel in 180 ppm Cl^- ion + ASLE + Mn^{2+}

Summary and Conclusion

Analysis of the results of the mass-loss method shows that the formulation consisting of 200 ppm extract of the leaves of *Asparagus setaceus.L* and 10 ppm Mn^{2+} has85.94 % IE in controlling the corrosion of carbon steel immersed in 180 ppm Cl^- ion solution. A synergistic effect exists between Mn^{2+} and the phytoconstituents present in the extract of *Asparagus setaceus.L* leaf extract.The inhibition of corrosion of carbon steel in neutral aqueous chloride ion[21,22] solution in the presence of the inhibitor system is due to the interaction between the lone pair of electron on oxygen atoms 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 cathodic reactions, but behaves predominantly as cathodic inhibitor. AC impedance spectra reveal the formation of protective film on the metal surface. Cyclic voltammetry confirms the protective nature of the film formed on the metal surface, in the presence of inhibitor system. The FTIR spectra confirms 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 the iron ions. The SEM micrographs confirm the formation of protective layer on the metal surface.

References

1. Susan Kristoff, "Introduction to Corrosion", E-Journal of Chemistry, 4 (2009) 57-59.
2. E.C. Potter, "Electrochemistry Principles and Application", Cleaver-Hume Press, London, 1961.
3. K. Anuradha, R. Vimala, B. Narayanansamy, J. ArockiaSelvi, S. Rajendran, Chem. Eng. Commun.008) 352.
4. M.G.Fontanna ,"Corrosion Engineering", McGraw hill book company(1986), Chaps.2,9&10.
5. https://en.wikipedia.org/wiki/Asparagus_setaceus
6. Prashant Tiwari, Bimlesh Kumar, Mandeep Kaur, Gurpreet Kaur and Harleen Kaur, Internationale PharmaceuticaSciencia, 1 (2011) 98.
7. M.M. Cowan, Clinical Microbiology Review, 12 (1999) 564.
8. N. Raman, Phytochemical Techniques, New India Publishing Agency, New Delhi, 2006.
9. R. Saratha and V.G. Vasudha, E-Journal of Chemistry, 6 (2009) 1003.
10. S. Mohan, M. Manimegalai, P. Rajeswari, S. Maruthamuthu and N. Plalanisamy, Bulletin of Electrochemistry, 18 (2001) 332.
11. J. ArockiaSelvi, V. SusaiRajendran, A. Ganga Sri, B. John Amalraj and Narayanasamy, PortugaliaeElectrochimicaActa, 27 (2009).
12. F. Bentiss, M. Lebrini and M. Lagrenee, Corrosion Science, 47 (2005) 2915.
13. F. Khaled, K. Babic-Samardzija and N. Hackerman, Journal of Applied Electrochemistry, 34 (2004) 697.
14. Hui-Long Wang, Rui-Bin Liu and Jian Xin, Corrosion Science, 46 (2004) 2455.
15. ZorSibel, Dogan Pinar and YaziciBirgul, Corrosion Reviews, 23 (2005) 217.
16. P. Singh, R. Shukla, B. Prakash, A. Kumar, S. Singh, P.K. Mishra and N.K. Dubey, Food and Chemical Toxicology, 48 (2010) 1734.
17. S. Gowri et al International Journal of Chemical Engineering Volume 2014, Article ID 607209, 9 pages.
18. S.C. Comerford, Economic Botany, 50(3) (1996) 327-336.
19. M. Yadav, S. Kumar, R.R. Sinha, I. Bahadur, E.E. Ebenso, New pyrimidinederivatives as efficient organic inhibitors on mild steel corrosion in acidicmedium: electrochemical, SEM, EDX, AFM and DFT studies, J. Mol. Liquids 211(2015) 135–145.
20. N. Patni, S. Agarwal, P. Shah, Greener approach towards corrosion inhibition,Chin. J. Eng. 2013 (2013) 10.
21. F. Zhang, Y. Tang, Z. Cao, W. Jing, Z. Wu, Y. Chen, Performance and theoreticalstudy on corrosion inhibition of 2-(4-pyridyl)-benzimidazole for mild steel inhydrochloric acid, Corros. Sci. 61 (2012) 1–9.
22. L. Yohai, M. Vázquez, M.B. Valcarce, Phosphate ions as corrosion inhibitors forreinforcement steel in chloride-rich environments, Electrochim. Acta 102(2013) 88–96.

*****