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International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.13 No.04, pp 347-356, 2020

Synergistic Effect of Trisodium citrate (TSC) on the Inhibition Efficiency of *Sargassum swartzii* (SS) -Zn^{2+} System on Mild Steel in Aqueous Environment

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Abstract : The aquatic plant kingdom is a treasure of potential bioactive compounds. Aquatic plants contain some organic compounds that provide definite physiological actions on the human body. In the present study deals with the synergistic effect of Trisodium citrate (TSC)on the inhibition efficiency of methanolic extract of *Sargassum swartzii* (SS) and Zn^{2+} system on mild steel in aqueous environment. The corrosion monitoring techniques adopted in the study were weight-loss methods, electrochemical measurements, FT-IR and surface morphological techniques namely SEM and EDX. It has proved the formulation consisting of 100 ppm of Zn^{2+}, 120 ppm of SS and 100 ppm of TSC has 95.77% IE. The high performance of SS - Zn^{2+}- TSC system could be due to synergistic effect that covers a wide surface coverage area on the metal surface and thus retarding the corrosion. Polarization study reveals that this formulation functions as a mixed inhibitor. AC impedance spectra suggest the presence of protective film on the metal surface. FT-IR spectra reveals that the protective film consists of Fe^{2+}-SS complex, Fe^{2+}-TSC complex and Zn $(OH)_2$. SEM and EDX provide a pictorial representation on the nature of surface film in the absence and presence of inhibitors. Thus, it concluded that *Sargassum swartzii* - Zn^{2+}- TSC inhibitor system acted as a good inhibitor in aqueous medium.

Keywords: *Sargassum swartzii*, Trisodium citrate, weight-loss method, Potentiodynamic polarization, EIS, FT-IR, SEM and EDX.

Introduction and Experimental

Seaweeds are known as an excellent sources of vitamins and minerals, especially the macro level minerals include sodium, calcium, magnesium, potassium, chlorine, sulphur and phosphorous due to their high polysaccharide content which could be dietary fibers .Aquatic plants are incredibly rich naturally synthesized chemical compounds contain sulfated polysaccharides, plastoquinone, phlorotannins, flucoxanthin, fucoidans, sargaquinoic acid, sargachromenol, steroids, terpenoids and flavonoids etc. The pheaophyceae (brown algae) is a large group of marine multicelluar algae and play an important role in various sectors such as food, medicines

S. Manimegalai /International Journal of ChemTech Research, 2020,13(4): 347-356.

DOI= http://dx.doi.org/10.20902/IJCTR.2019.130403

and industrial purposes. *Sargassum* species were proven to have potential medicinal activities such as antibacterial, antiviral, antitumour, antifungal, antiprotozoal, antioxidant, mosquito and larva control, antithrombotic and anti-inflammatory activities. They are used for prevention and treatment of such widespread diseases as high blood pressure, arthritis, diabetes and obesity. Presence of heteroatoms (S, N, and O) with free electron pairs, aromatic rings with delocalized (π) electrons, high molecular weight alkyl chains and substituent groups improves inhibition efficiency. Zinc ions are frequently used as cathodic inorganic corrosion inhibitor, predominantly as sulphate salt. It also mixed with other inhibitors to obtain significant synergistic action[1] .Tri Sodium Citrate (TSC) contains three sodium salts of citric acid. It possesses a saline and mildly tart flavor. For this reason, citrates of certain alkaline and alkaline earth metals (e.g. sodium and calcium citrates) are commonly known as "sour salt". Tri sodium citrate has carboxyl and hydroxyl groups. Such compound is expected to have good corrosion inhibition efficiency. The citrate ion was the best inhibitor to prevent the pitting corrosion of tin, probably through its ability to repair defects in the oxide film. It also found that the pitting inhibition might be due to the formation of a mixed layer of tin in citric acid concentrations higher than 10^{-2} M oxide and tin citrate complexes on the electrode surfaces[2]. The study deals with the inhibition efficiency of *Sargassum swartzii*-Zn^{2+} system on mild steel in aqueous environment (60 ppm Cl^- ion) by the synergistic effect of Tri Sodium Citrate (TSC). The corrosion monitoring techniques adopted in the study are weight-loss methods, electrochemical measurements, FTIR and surface morphological techniques such as SEM and EDX.

Collection and identification of the *Sargassamswartzii* (SS) (Brown algae)

The study was carried out on the seaweeds were collected from Mandapam coastal regions, South East Coast of India. The seaweeds were spread on blotting paper to remove excess water and dried. Further, the seaweed sample was authenticated namely ***Sargassum swartzii***, **C.Agardh,** Botanical Survey of India, Coimbatore, Tamilnadu, India.

Preparation of inhibitor solution - *Sargassum swartzii* (SS), Zinc ion and TSC

The 400g of *Sargassum swartzii* material was transferred to 2000 ml round bottomed flask, directly heated in a mantle with water condenser for about six hrs at room temperature. The resulting solution was concentrated and evaporated to dryness under vacuum using rotatory evaporator. This dried extract of *Sargassum swartzii* was used as corrosion inhibitor. The methanol was used to prepare the extract and to get a fine powder of *Sargassum swartzii* (SS). It was used for the corrosion inhibition monitoring techniques. The stock solution of 1g of powdered *Sargassum swartzii* (SS) is dissolved in methanol in 100 ml standard measuring flask as stock solution. Dilution of various desired concentrations (0 to 120 ppm) are made from the above stock solution.The preparation of synergists,TSC and zinc ions were used by inhibitor .1g of TSC are dissolved in double distilled water and then made up to 100ml in a standard measuring flask. One ml of this solution was diluted to 100ml, which yield exactly 100 ppm of TSC. Exactly 1.1g of zinc sulphate was dissolved in double distilled water and made upto 250ml in a standard measuring flask. A hundred fold dilution yields exactly 10ppm of Zn^{2+} ion concentration. The environment chosen is an aqueous solution containing low concentration of chloride ions; say 60 ppm because in most of the industries demineralised water containing chloride concentration not exceeding 60 ppm is used as cooling water.

Weight loss method

Weight loss measurements were performed with dried rectangular strips following ASTM Standard Procedure[3].In the present study, weighed test pieces were immersed, in triplicate in aqueous medium with various concentrations of inhibitor. They removed after a particular period of immersion, washed, dried and reweighed. The specimens were abraded with abrasive emery papers with Grid Numbers: 320, 400, 600, 800, and 1000 grade, washed in acetone, degreased with trichloroethylene, dried at room temperature and stored in the moisture free desiccators before they are used for corrosion studies. The specimens are weighed before immersion inthe test solutions and reweighed after immersion. From the initial and final masses of the specimen, the weight losses of metal specimens were calculated. The experiments wereperformedfor evaluating the effect of concentration on inhibition efficiency for mild steel in aqueous media was carried out in the concentration range 0 - 120 ppm.

Synergism parameter

Synergism is a combined effect of compounds greater in total effect than the sum of individual effects. Synergism parameters are indication of synergistic effect existing between two inhibitors. Synergism parameters were calculated using the relation[4],

$S_1 = [1-\theta_{1+2}/1-\theta'_{1+2}]$ (1)

Where,

$\theta_{1+2} = (\theta_1+\theta_2)-(\theta_1 x\ \theta_2)$

θ_1 = Surface coverage of substance 1

θ_2 = Surface coverage of substance 2

θ_{1+2} = combined surface coverage of substances 1 and 2

Surface coverage (θ) = IE%/100

Electrochemical measurements

Potentiodynamic polarization studies

Potentiodynamic polarization studies were carried out for mild steel of same composition, both in the absence and presence of inhibitor.

Electrode surface preparation

Mild steel plate was mounted with Teflon coating leaving 0.2876cm^2 of surface area exposed to the solution was used for electrochemical studies. It was then polished using 120, 200, 400, 600, 800 and 1000 Grid emery papers and finally degreased with acetone.

Polarization cell assembly

The electrochemical experiments were performed using a typical three electrodes cell at room temperature and naturally aerated conditions. The exposed area of each sample was 0.2876cm^2 and the rest being covered by Teflon coating. A glass carbon rod was used as counter electrode and saturated calomel electrode (SCE) as reference electrode. The polarization and impedance studies were conducted in an aqueous solution using computer controlled potentiostat (Model : SOLARTRON ECI – 1286) and the data was analyzed using frequency response analyzer (SOLARTRON (FRA – 1286). The data was performed using HFimpoin 2.1 software. All the experiments were carried out after the stabilization of the system (i.e.) open circuit potential (OCP) after half an hour of electrode immersion. The inner polarization experiments were carried out from cathode potential of - 0.02 V versus OCP to an anodic potential of +0.02 V versus OCP at a sweep rate 0.125 mV/s to study the polarization resistance (Rp).The values of inhibition efficiency (%) were determined from equation (2).Where, R_p^i and R_p^o are the polarization resistance with and without addition of inhibitor[5].

$$\text{IE (\%)} = \frac{R_p^i - R_p}{R_p^i} \text{X100} \qquad (2)$$

The potentiodynamic polarization was carried out from cathode polarization of -0.25V versus OCP to an anodic potential of + 0.25V versus OCP at a sweep rate 0.5 mV/s to study the result of inhibitor action on mild steel corrosion. The linear sections of anodic and cathodic were extrapolated using Tafel technique to obtain the corrosion current densities (I_{corr}). The corrosion inhibition efficiency (%) was evaluated by equation (3). Where, I^o_{corr} and I^i_{corr} are the corrosion current without and with addition of inhibitor.

$$\text{IE (\%)} = \frac{I^o_{corr} - I^i_{corr}}{I^i_{corr}} \text{x100} \qquad (3)$$

AC Impedance Studies

The impedance studies were carried out using AC signals of amplitude for the frequency spectrum from the 100 KHz to 100 mHz. The data was performed using POWER CORE, in built software. The change transfer resistance values were calculated from the diameter of the semi-circles of the Nyquist plots. The corrosion inhibition efficiency was determined by equation (4).

$$\text{IE (\%)} = \frac{R^{i}_{ct} - R^{o}_{ct}}{R^{o}_{ct}} \times 100 \qquad (4)$$

Where, R_{ct} and R^{o}_{ct} are the charge transfer resistance in the presence and absence of inhibitor. The values of double layer capacitance(C_{dl})have been calculated by using equation (5) Where, f_{max} is the frequency at which the imaginary component of the impedance is maximum and R_{ct} is the corresponding value of charge transfer resistance.

$$C_{dl} = (2\pi f_{max} R_{ct})^{-1} \qquad (5)$$

Spectroscopic and Surface Morphological Studies

SEM, EDX and FTIR spectra were taken for mild steel specimens were carried out to study the changes that occur during the corrosion of mild steel in the presence and absence of inhibitor in aqueous medium[6] for a period of 9 hours immersion at room temperature.

Results and Discussion

Analysis of Synergistic effect of Tri Sodium Citrate (TSC) on the inhibition efficiency of SS - Zn^{2+} system on mild steel corrosion in aqueous environment by weight–loss method

The corrosion rates and inhibition efficiencies calculated for mil steel in aqueous environment containing 60 ppm of Cl^- ions and different concentrations of TSC in the presence of inhibitor SS-Zn^{2+} system at pH 7 by weight-loss method are given in Table 1. Independently, IE of 100 ppm of Zn^{2+}ion in aqueous medium is found to be 44.03% and 120 ppm SS is 28.83% (Table 1). However, their combination has 74.23% IE (Table 1). When TSC is added to this formulation, IE increases. For instance, when 100 ppm of TSC is added to this formulation consisting of 120 ppm of SS and 100 ppm Zn^{2+}, IE increases from 74.23% to 95.77% was noticed in Table 1. This result clearly indicates synergism exists between citrate, Zn^{2+} ions and SS [7].

Synergism parameter (S_I)

The synergism parameters calculated for the corrosion inhibitor system of SS- Zn^{2+} - TSC system on mild steel are given in Table 2 .The values of S_I calculated are greater than one, suggesting a synergistic effect exists between SS- Zn^{2+} - TSC in ternary inhibitor systems [8].

Table 1. Corrosion rates (CR) and inhibition efficiencies (IE) calculated for mild steel in aqueous environment (60 ppm Cl^- ion) in absence and presence of corrosion inhibitors by weight–loss method. Inhibitor system: (SS + Zn^{2+} + TSC) . Immersion time: 9 hours

Cl^- ppm	**SS ppm**	**Zn^{2+}ppm**	**TSC ppm**	**CR (mpy)**	**IE (%)**
60	0	0	0	27.19	-
60	0	100	0	15.21	44.06
60	120	0	0	19.35	28.83
60	120	100	0	3.92	**74.23**
60	120	100	10	5.90	78.30
60	120	100	20	5.07	81.35
60	120	100	40	4.70	82.71
60	120	100	50	4.47	83.56
60	120	100	75	2.30	91.54
60	120	100	100	1.15	**95.77**

Table 2. Synergism parameters derived from

inhibition efficiencies of *Sargassum swartzii* (SS) - Zn $^{2+}$- Tri Sodium Citrate (TSC) system.

SS+ Zn^{2+} θ_2 IE (%)	TSC θ_1 IE (%)	SS- Zn^{2+}-TSC θ_{1+2} IE (%)	S_I
74.23	9.53	78.80	1.07
74.23	12.73	81.35	1.21
74.23	16.11	82.71	1.25
74.23	22.03	83.56	1.22
74.23	28.83	91.54	2.17
74.23	33.73	95.77	4.04

Electrochemical Measurements

Potentiodynamic polarization studies of SS- Zn^{2+}-TSC system

The potentiodynamic polarization curves recorded for mild steel immersed in various environments are shown in Figure 1. When mild steel is immersed in an aqueous solution containing 60 ppm Cl$^-$ ion (blank), the corrosion potential is -689.4 mV vs. SCE in Figure 1(a). The formulation consisting of 60 ppm of Cl$^-$, 120 ppm of SS, 100 ppm TSC and 100 ppm of Zn^{2+}, the corrosion potential shifts to cathodic site (–689.4mV vs. SCE to –708.9 mV vs. SCE) in Table 3 and from in Figure 1 (b), suggests this formulation effectively controls the cathodic reaction [9,10]. The anodic and cathodic Tafel slope (b_a & b_c) are found to be 99 mV and 109 mV vs. SCE and thus cathodic reaction is controlled predominantly. The I_{corr} value for this formulation is decreased from 180×10^{-6} µA/cm^2 to 35.4×10^{-6} µA/cm^2 and thereby retard cathodic reaction and suppress corrosion rate. The linear polarization resistance (LPR) value increases from 24.16 Ohm/cm ^{2} to 95.8 Ohm/cm^2.These observations suggest the formation of a protective film on the metal surface and prevents corrosion[11,12].

Table 3.Potentiodynamic polarization parameters for mild steel in aqueous medium containing 60 ppm Cl$^-$ ion in SS- Zn^{2+}-TSC system

Inhibitors system	**E corr (mV / SCE)**	**Tafel Polarisation parameters**				**Linear polarization parameters**	
		b_c (mV/dec)	**b_a (m V /dec)**	**I corr (µA / cm^2)**	**IE (%)**	**Rp (Ohm / cm^2)**	**IE (%)**
Cl$^-$ ion (60 ppm)	-689.4	218	98	180	-	24.16	-
SS (120ppm) + Zn^{2+} ion(100 ppm) + SPT (100ppm)	-708.9	109	99	35.4	**80.33**	95.8	**74.78**

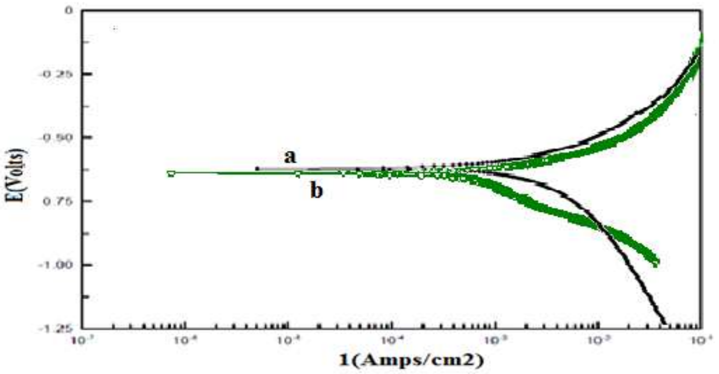

Figure1.Potentiodynamic polarization curves recorded for mild steel immersed in SS - Zn^{2+}-TSC system .(a) Cl^-ion (60 ppm) (b) Cl^-ion (60 ppm) + Zn^{2+} (100 ppm)+ SS (120 ppm) +TSC (100 ppm)

Electrochemical Impedance Spectroscopy (EIS) studies of SS- Zn^{2+}-TSC system

The AC impedance parameters calculated for mild steel immersed in various test solutions are tabulated in Table 4. A perfect semicircle curve in Figure 2 (a), with low polarization resistance value (Rp = 24.16 Ohm/cm^2) is noticed for mild steel immersed in 60 ppm chloride solution (blank). For mild steel immersed in a mixture of inhibitor solution 100 ppm SS, 100 ppm Zn^{2+} and 100 ppm TSC, a distinct semicircle in Figure 2(b) with high polarization resistance (Rp = 95.8 Ohm/cm^2) is noticed. When mild steel is immersed in an aqueous solution containing 60 ppm Cl^-, the charge transfer resistance (R_{ct}) for the blank found to be 388.2 Ohms and the double layer capacitance (C_{dl}) is found to be 89.41 X 10^{-6} F/cm^2. However, R_{ct} value increases from 388.2 Ohms (blank) to 4758 Ohms for the inhibitor system(SS- Zn^{2+}-TSC) and the C_{dl} value decreases from 89.41 X 10^{-6} F/cm^2 (blank) to 8 X 10^{-6} F/cm^2 for the inhibitor system ,SS- Zn^{2+}-TSC.These results suggest that a protective film is formed on the metal surface[13].

Table 4. Impedance parameters for mild steel in aqueous medium containing 60 ppm Cl^- ion in SS-Zn^{2+}-TSC system

Inhibitor system	**C_{dl} or CPE (F/cm^2)**	**C_{dl} θ**	**R_{ct} (Ohms)**	**R_{ct} (%)**
BlankCl^- ion(60 ppm)	89.41X10^{-6}	-	388.2	-
SS(120ppm) +Zn^{2+} ion (100 ppm) + TSC (100ppm)	8 X 10^{-6}	0.9105	4758	91.84

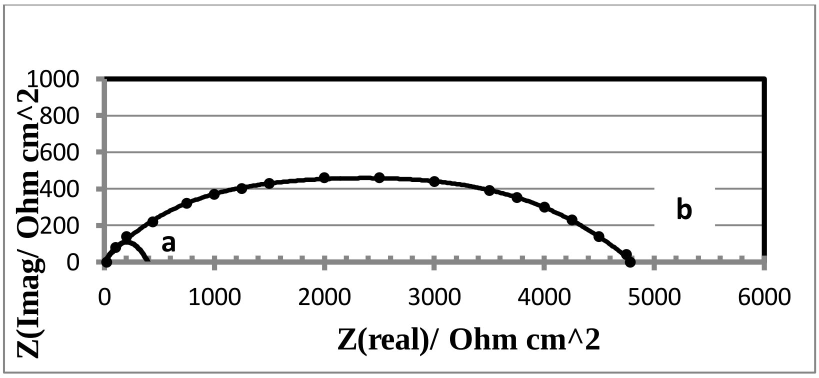

Figure 2. AC Impedance curves recorded for mild steel immersed in SS- Zn^{2+}-TSC system(a) Cl^-ion (60 ppm) (b) Cl^- ion (60 ppm) + Zn^{2+} (100 ppm)+ SS (120 ppm)+TSC (100 ppm)

FT-IR Spectroscopic studies of SS- Zn^{2+}- TSC system

The FT-IR spectrum of pure SS is also traced and shown in Figure 3 (a). The FT-IR spectrum of the film (KBr) formed on the surface of mild steel after 9 hours immersion in the test solutions containing SS (120 ppm), TSC(100 ppm) and Zn^{2+}(100 ppm) is shown in Figure 3 (b) . The N-H stretching vibrations have shifted from 3371.57 cm^{-1} to 3325.28 cm^{-1}. The C-H stretch in alkanes has shifted from 2924.09 cm^{-1} to 2970.38 cm^{-1}. The C=0 stretch in amide I-band has shifted from 1627.92 cm^{-1} to 1658.78 cm^{-1}. This suggests the formation of Fe^{2+}-SS complex and also Fe^{2+}- TSC complex on the anodic sites of the metal surface. Further hetero atoms such as N,S and O atoms present in *Sargassum swartzii* has co-ordinated with Fe^{2+} through O /S/N atom of carboxyl group. The $-N_3$ stretching has shifted from 1211.30 cm^{-1} to 1203.58 cm^{-1}. The C-H out of plane bending has shifted from 879.54 cm^{-1} to 840.96 cm^{-1}. The peaks such as 3410.65 ,2854.65 cm^{-1}, 1165 cm^{-1}, 1072.42 cm^{-1} and 694.4 cm^{-1} (O-H , N-H, S=0, C-H or C-C and C-S groups) were missed and/or formed new bands as shown in Fig.3 (b). It indicates that there is a strong interaction between inhibitor system and the surface of mild steel. The peak at 1350 cm^{-1} is due to Zn $(OH)_2$ at the cathodic site [14,15], which controls the cathodic reaction.The FT-IR study suggests that the hetero atoms like N,O and S confirmed in *Sargassum swartzii* has co-ordinated with Fe^{2+} to form Fe^{2+}-SS and Fe^{2+}- TSC complexes on the metal surface which prevents corrosion.

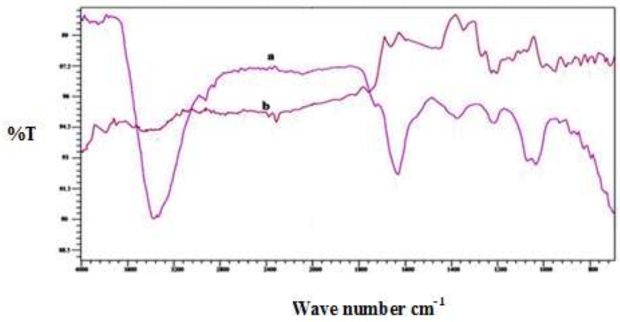

Figure 3. FT-IR spectra of a) pure SS b) Film formation on mild steel immersed in mixture of 60 ppm Cl^- ion + 100 ppm Zn^{2+}+ 120 ppm SS + 100 ppm TSC

SEM studies of SS- Zn^{2+}-TSC system

The SEM micrograph of polished mild steel surface (control) in Figure 4 (a) shows the smooth surface of the metal. This shows the absence of any corrosion products or inhibitors complex formed on the metal surface. The SEM micrographs of mild steel surface immersed in 60 ppm Cl^- ion in aqueous environment is shown in Figure 4(b) and observed the roughness of the metal surface which indicates corrosion of mild steel in aqueous environment.Figure 4(c) portrays the SEM photograph of the metal surface immersed in aqueous environment containing 120 ppm of SS, 100 ppm of $Zn^{2+}$and 100 ppm of TSC, it establishes the protective layer formation which shows the evidence for inhibition of mild steel dissolution[16,17].

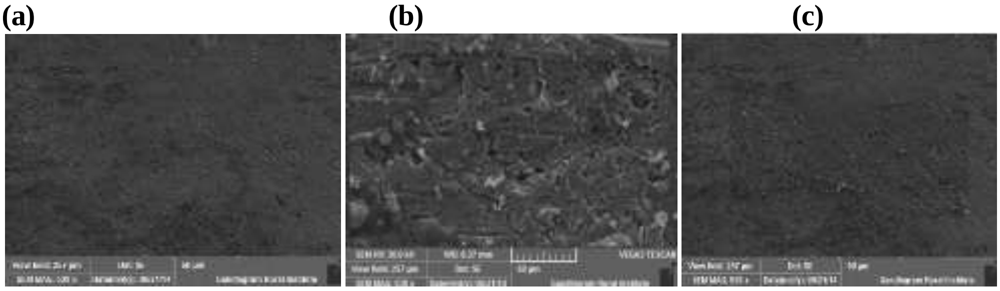

Figure 4. (a) SEM micrograph of polished mild steel (b) SEM photographs of mild steel specimen immersed in aqueous medium containing 60 ppm Cl^- ion (c) SEM photograph of mild steel exposed aqueous medium containing 60 ppm Cl^- ion and inhibitor solutions(120 ppm SS + 100 ppm Zn^{2+}ions + 100 ppm TSC).

EDX studies of SS- Zn^{2+}-TSC system

EDX spectrum of polished mild steel and it is immersed in aqueous solution containing 60 ppm Cl- is shown in Figure 5 (a) &(b). They show the characteristic peaks of some of the elements constituting the mild steel sample .The EDX spectrum of mild steel immersed in aqueous solution containing 60 ppm Cl$^-$, 120 ppm SS, 100 ppm Zn^{2+} ionand 100 ppm TSC are shown in Figure 5 (c). The weight percentage of C increases significantly from 3.88 % to 4.65%. This proves that C atoms present in inhibitor system adsorbed on metal surface to form a passive layer on the surface of mild steel [18].The weight (%) of elemental Fe atoms decreases in the inhibitor system from 94.57% to 81.37 %.This suggests that Fe form organo metallic complexes with polar groups of inhibitor system. Thus, the percentage of Fe atoms is decreased into smaller percentage [19]. Figure 5(c) showed the absence of Mn and Si peaks whereas the additional peaks were formed elements such as Na, Cl, Zn, N, P and S at a minimum percentage level. However, these elements form a passive layer in the form of organo metallic complexes on the surface of mild steel[20].

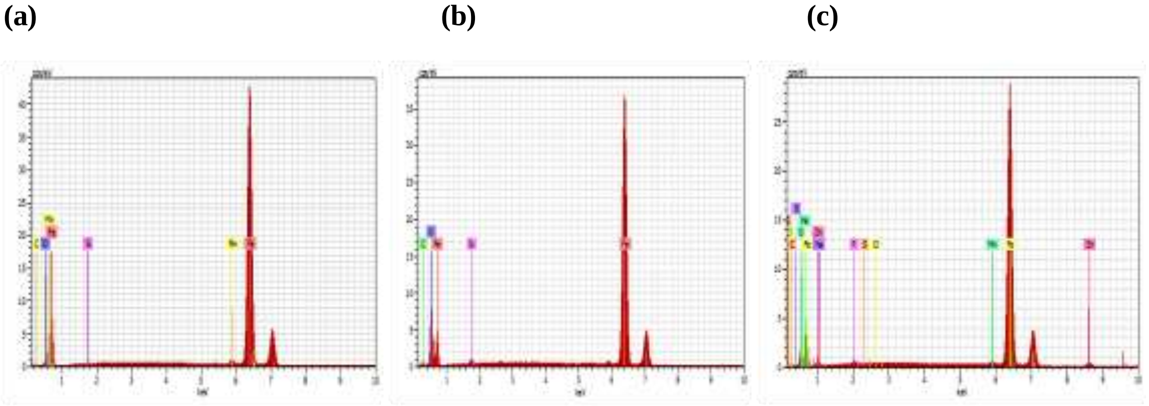
(a) (b) (c)

Figure 5.(a)EDX analysis of polished mild steel (b) EDX analysis of mild steel specimen immersed in aqueous medium containing 60 ppm Cl$^-$ ion (c) EDX analysis of mild steel exposed aqueous medium containing 60 ppm Cl$^-$ ion and inhibitor solutions (120 ppm SS ,100 ppm Zn^{2+}ions and 100 ppm TSC).

Table 5.EDX analysis of mild steel immersed in aqueous medium in absence and presence of SS - Zn^{2+}-TSC system

Inhibitor system	Element	Weight (%)	Atomic Weight (%)
Polished mild steel	Fe	94.57	81.73
	C	3.88	15.57
	O	0.49	1.48
	Mn	0.73	0.64
	Si	0.33	0.57
Blank(60 ppm Cl$^-$ion)	Fe	66.46	35.00
	C	6.34	15.53
	O	26.54	48.79
	Mn	-	-
	Si	0.66	0.69
60 ppm Cl$^-$ion + 120 ppm SS +100 ppmZn^{2+} ion + 100 ppm TSC	Fe	81.37	56.14
	C	4.65	14.92
	O	9.17	22.09
	N	1.21	3.34
	Na	1.04	1.74
	P	2.56	1.77
	Mn	-	-
	Si	-	-

Conclusion

The study proved the formulation consisting of 100 ppm of Zn^{2+}, 120 ppm of SS and 100 ppm of TSC has 95.77% IE. The high performance of SS -Zn^{2+}-TSC system could be due to synergistic effect that covers a wide surface coverage area on the metal surface and thus retarding the corrosion. Polarization study reveals that this formulation functions as a mixed inhibitor. AC impedance spectra suggest the presence of protective film on the metal surface. FT-IR spectra reveals that the protective film consists of Fe^{2+}-SS complex, Fe^{2+}-SG complex and $Zn(OH)_2$. SEM and EDX provide a pictorial representation on the nature of formed surface film. Thus, it concluded that *Sargassum swartzii* - Zn^{2+}- TSC inhibitor system acted as a good inhibitor in aqueous medium.

References

1. Antonyraj, A. and Augustin, C.O.,Investigation of corrosion behaviour of magnesium in aqueous solutions, Bulletin of Electrochemistry, 1999, 15 , 135-138.
2. Almedia, C. M. V. B. and Giannetti, B. F., Protective film growth on tin in perchlorate and citric acid electrolytes, Materials Chemistry and Physics , 2001,69 , 261-266.
3. ASTM G1., Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.
4. Gunasekaran, G., Palaniswamy, N. and Apparao, B. V.,Synergistic effect of Zn^{2+} ions and 2-Carboxyethyl phosphonic acid on the corrosion inhibition of mild steel in neutral environment, Bulletin of Electrochemistry, 1996,12, 59-63.
5. Rajendran, S., Sathiyabama, J., Krishnaveni, A., Shanthy, P., Manimaran, N. and Shyamaladevi, B., Corrosion Inhibition by an Aqueous Extract of Phyllanthus Amarus Portugaliae Electrochimica Acta, 2011, 29 ,429-444.
6. Kalman, E., Karman, F. H., Telegdi, J., Varhegyi, B., Balla, J. and Kiss,T., Inhibition efficiency of N-containing carboxylic and carboxy-phosphonic acids, Corrosion Science, 1993,35, 1477-1482.
7. Muralidharan, V. S.,Some aspects of kinetics and mechanism of corrosion and passivation of metals in aqueous media. 1978, PhD thesis, Banaras Hindu University.
8. Bentiss, F ., Bouanis, M., Mernari, B., Traisnel, M. and Lagrenee, M., Effect of iodide ions on corrosion inhibition of mild steel by 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole in sulfuric acid solution, Journal of Applied Electrochemistry, 2002, 2, 671-678.
9. Shalaby, M. N. and Osman, M. M., Synergistic inhibition of anionic and nonionic surfactants on corrosion of mild steel in acidic solution, Anti Corrosion Methods and Materials, 2001,48 ,309-318.
10. Gunasekaran, G., Natarajan, R. and Palaniswamy, N.,The role of tartrate ions in the phosphonate based inhibitor syste*m*,Corrosion Science, 2001, 43, 1615-1626.
11. Raja, P. B. and Sethuraman, M. G., Natural products as corrosion inhibitor for metals in corrosive media –A review, Materials Letters, 2008, 62 ,113-116.
12. Rajendran, S., Ganga Sri, V., ArockiaSelvi, J. and John Amalraj, A., Corrosion inhibition by plant extracts an overview, Bulletin of Electrochemistry, 2005, 21,367-377.
13. Dhanalakshmi, J., ArockiaSelvi, J., John Amalraj, A., Rajendran, S. and Palaniswamy, N., Corrosion inhibition by an Oxyanion-Zn^{2+} system ,Transaction of SAEST, 2006,57 , 41-
14. El Azhar ,M., Traisnel, M., Mernari, B., Gengembre, L., Bentiss, F. and Lagrenee, M., Electrochemical and XPS studies of 2,5-bis(n-pyridyl)-1,3,4-thiadiazoles adsorption on mild steel in perchloric acid solution , Applied Surface Science, 2002,185, 197-205.
15. Rajendran, S., Anuradha, K., Kavipriya, K., Krishnaveni, A. and Angelin Thangakani, J., Inhibition of corrosion of carbon steel in sea water by sodium molybdate–Zn^{2+} system European Chemical Bulletin,2012, 1 , 503-510.
16. Ozyilmaz , A. T., Kardas , G., Erbil, M. and Yazici, B., The corrosion performance of polyaniline on nickel plated mild steel, Applied Surface Science, 2005,242, 97-106.
17. Shyamala, M. and Arulanantham, A., Corrosion Inhibition Effect of Centella asiatica (Vallarai) onMild Steel in Hydrochloric Acid ,Asian Journal of Chemistry, 2009,21, 6102-6110.
18. Shyamala, M. and Kasthuri, P. K. A., Comparative Study of the Inhibitory Effect of the Extracts of Ocimum sanctum, Aegle marmelos, and Solanum trilobatum on the Corrosion of Mild Steel in Hydrochloric Acid Medium, International Journal of Corrosion,2011, Article ID 129647.
19. Chigondo, and Fidelis Chigondo., Recent Natural Corrosion Inhibitors for Mild Steel: An Overview, Journal of Chemistry, 2016, Article ID 6208937 .

20. Ziad T Khodair , Anees A Khadom. And Hassan A Jas ., Corrosion protection of mild steel in different aqueous media via epoxy/nanomaterial coating: preparation, characterization and mathematical views, Journal of Materials Research and Technology, 2019,8 , 424-435.

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