Electrochemical Studies of Mild Steel Corrosion Inhibition in Aqueous Solution by *Sargassum swartzii* Extract

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Abstract: *The Phaeophyceae or brown algae is a large group of marine multicelluar algae and play an important role in marine environments as food, medicines and industrial purposes. In the present study, the inhibition efficiency (IE) of Sargassum swartzii in controlling corrosion of mild steel immersed in an aqueous solution containing 60 ppm of Cl^- ions in the absence and presence of Zn^{2+} ions. They are environmentally suitable non-toxic compounds, biodegradable and eco friendly synergist in the corrosion inhibition process. The influence of pH on the IE of SS-Zn^{2+} system is also studied. The synergism parameters (S_I) calculated from surface coverage is given to show the synergistic effect exists between the SS and Zn^{2+} ions. The protective films formed on the metal surface analyzed by electrochemical measurements. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from weight-loss methods and the electrochemical methods. Thus, it can be concluded that Sargassum swartzii – Zn^{2+} inhibitor system acted as a good inhibitor in aqueous medium.*

Key Words: *Brown Seaweeds, Sargassum swartzii, mild steel, corrosion, Electro chemical studies.*

1. INTRODUCTION:

The aquatic plant kingdom is a treasure of potential bioactive compounds. Active constituents present in aquatic plant materials might be responsible for the benefit of humans. Aquatic plants contain some organic compounds that provide definite physiological actions on the human body and these bioactive substances include alkaloids, terpenoids, steroids,phenolic compounds, tannins and flavonoids and most of them are known to have corrosion inhibition efficiency. Presence of heteroatoms (S, N, and O) with free electron pairs, aromatic rings with delocalized (π) electrons, high molecular weight alkyl chains; substituent group in general improves inhibition efficiency. Zinc ions are frequently used as cathodic inorganic corrosion inhibitor, predominantly as sulphate salt. It is mixed with other inhibitors to obtain significant synergistic action [1].Metals acquire stability when their surfaces are isolated from the normal terrestrial environment [2]. Mild steel is used in cooling water systems where water velocity, dissolved solids and continual aeration provide conditions for continued corrosion of mild steel [3]. 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.

The study deals with the inhibition efficiency (IE) of *Sargassum swartzii* in controlling corrosion of mild steel immersed in an aqueous solution containing 60 ppm of Cl^- ions in the absence and presence of Zn^{2+} ions. They are environmentally suitable non-toxic compounds, biodegradable and eco friendly synergist in the corrosion inhibition process. The corrosion monitoring techniques adopted in the study are weight-loss methods and electrochemical measurements (Potentiodynamic polarization and EIS).

2. MATERIALS AND METHODS:

2.1 Collection and identification of the *Sargassam swartzii* (SS) (Brown algae)

The study was carried out on the seaweeds were collected from Mandapam coastal regions, South East Coast of India. Seaweed sample was picked with hand and immediately washed with seawater to remove the foreign particles, sand particles, and epiphytes. Then it was kept in an icebox containing slush ice and immediately transported to the laboratory and washed thoroughly using tap water to remove the salt on the surface of the sample. Then the seaweeds were spread on blotting paper to remove excess water and dried. Further, the seaweed sample was authenticated namely ***Sargassum swartzii***, **C.Agardh** by Dr. P. Palanisamy, Scientist-C, Botanical Survey of India, Coimbatore, Tamilnadu, India.

2.2. Preparation of inhibitor solution - *Sargassum swartzii* (SS)

The 400g of *Sargassum swartzii* material was transferred to 2000ml 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.

2.3. Preparation of synergist environment- zinc ions.

Inhibitor used the preparation of synergists, zinc ions. 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 10 ppm of Zn^{2+} ion concentration.

2.4. Weight loss method

Weight loss measurements were performed with dried rectangular strips following ASTM Standard Procedure [4].In the present work, weighed test pieces were immersed, in triplicate in aqueous medium with various concentrations of inhibitor. They were 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 in the 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 were performed for evaluating the various parameters: i) Effect of concentration on inhibition efficiency for mild steel in aqueous media was carried out in the concentration range 0 - 120 ppm. ii) Effect of time of immersion on inhibition efficiency for mild steel in aqueous media was carried out in the time range 1 hour – 24 hours. iii) Effect of   pH on inhibition efficiency for mild steel in aqueous media was carried out in the pH range 2 -11.

2.5. 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,

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

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

2.6. Electrochemical measurements
2.6.1. Potentiodynamic polarization studies

Potentiodynamic polarization studies were carried out for mild steel of same composition, both in the absence and presence of inhibitor. A frequency response analyzer SOLARTRON (FRA-1286) was used.

2.6.2. 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.

2.6.3.Polarization cell assembly

The electrochemical experiments were performed using a typical three-electrode 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.

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

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_{corr}^o and I_{corr}^i are the corrosion current without and with addition of inhibitor

$$IE\ (\%)\ =\ \frac{I_{corr}^o - I_{corr}^i}{I_{corr}^i}\, x100 \qquad (3)$$

2.6.4. 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).

$$IE\ (\%)\ =\ \frac{R_{ct}^i - R_{ct}^o}{R_{ct}^o}\, x100 \qquad (4)$$

Where, R_{ct} and R_{ct}^o 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).

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

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.

3. RESULTS AND DISCUSSION:

3.1. Effect of inhibitor (Sargassum swartzii) concentration and immersion time on Corrosion inhibition efficiency of mild steel in aqueous environment by Weight loss method.

Corrosion rates and percentages of corrosion protection (Inhibition Efficiencies - IE) were calculated for mild steel in aqueous environment containing 60 ppm of chloride ion in the absence and presence of inhibitor, *Sargassum swartzii*(SS) at various concentrations and immersion time obtained by weight-loss method are given in Table 1. It is found that at pH 7, SS shows a slight increase in IE. However, it decreases the corrosion rate of the metal with the increased concentration of SS at ppm level. This is due to the increase in the number of constituent molecules present in *Sargassum swartzii* (SS) adsorbed on the metal surface at 120 ppm concentration, so that the active sites of the mild steel were protected by the inhibitor molecules. The result observed from Table 1 that the maximum IE (28.83%) at 120 ppm of the inhibitor for 9 hours of immersion time. It was also noticed that a significant decrease in the corrosion rate for the first 9 hours of immersion test. It may be due to the ability of SS in forming the protective layer that covered the mild steel surface. However, after 9 hours of immersion the IE decreases. When the duration of immersion time increases, the protective film formed on the metal surface is not able to withstand the attack of aggressive Cl- ions.

Researchers investigated [5] the IE of ethanolic extract of *Gelidiella acerosa,* (red algae),Turbinaria *ornate*(brown algae), *Jania adhaerens(*red algae)on corrosion of mild steel in seawater as 76.05%, 90.70% and 69.92% respectively. The effect of inhibitor system on the IE and corrosion rate (CR) of mild steel in aqueous media shows that corrosion inhibition is taking place by adsorption mechanism.

Adding and increasing the concentration of the inhibitors markedly reduced the corrosion rate and increased inhibition efficiency of mild steel. Therefore, the significant difference between the corrosion rate of mild steel in the absence and presence of the inhibitor indicates the positive effect of the inhibitor. These   findings show that the inhibitor has the capacity to protecting the surface by forming a passive film. Figure 1 depicts   the effect of immersion time on corrosion rates of mild steel in aqueous media in the absence and presence of SS.The study clearly indicates that a strong inhibitive stable layer by adsorbed phyto constituents of *Sargassum swartzii* is formed on mild steel surface at optimum period of 9 hours.
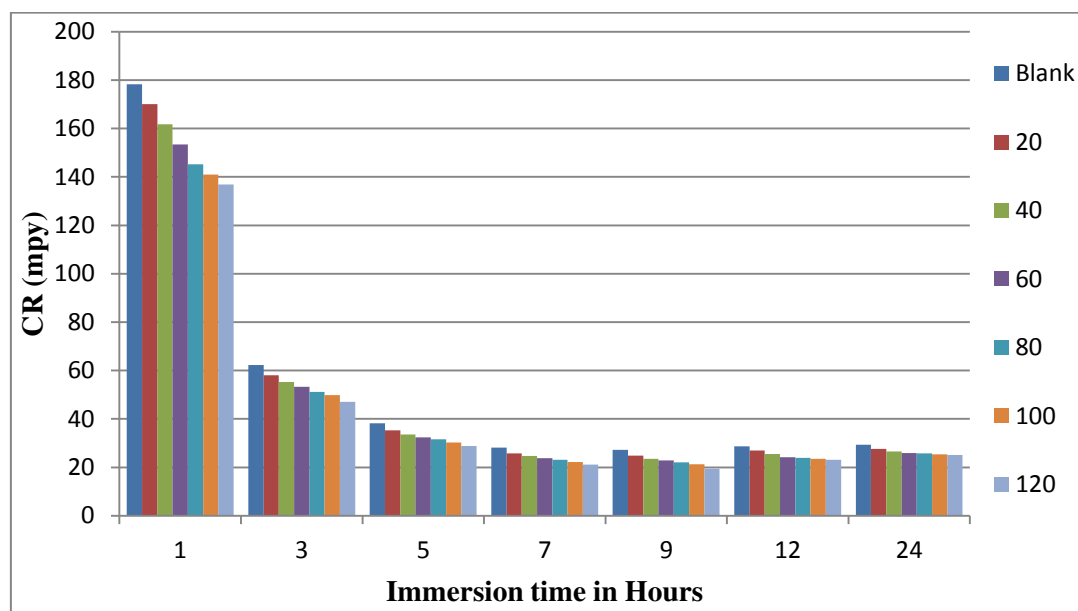
Fig. 1. Effect of immersion time on CR of mild steel in aqueous medium containing 60 ppm Cl⁻ ion in absence and presence of *Sargassum swartzii.*
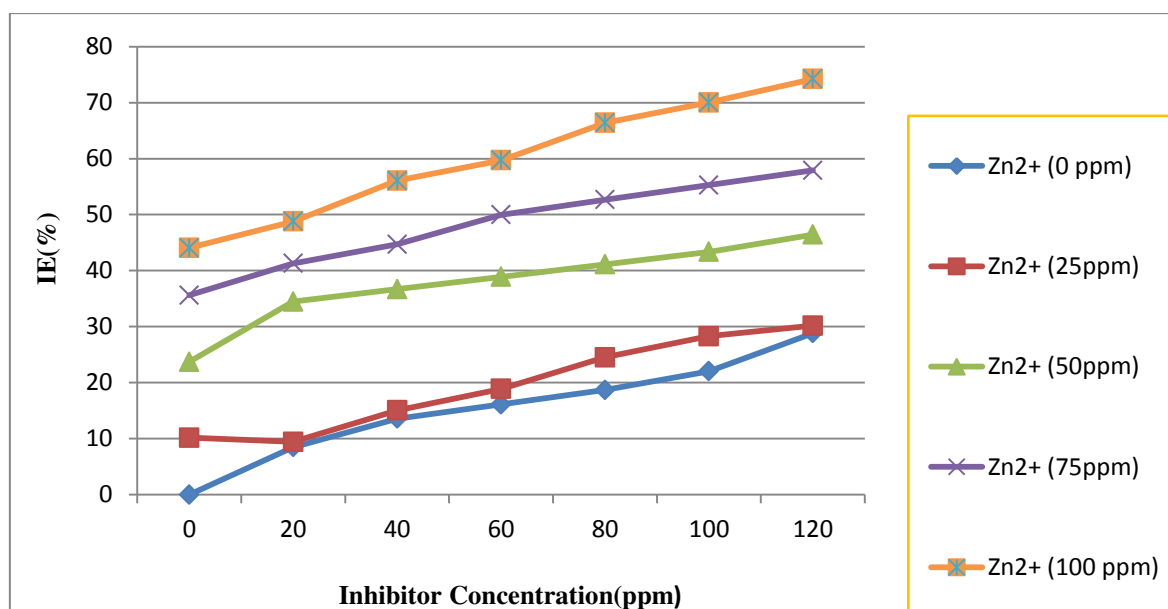

Fig.2. Effect of concentration on IE of mild steel in aqueous medium containing 60 ppm Cl⁻ ion in absence and presence of *Sargassum swartzii* – Zn^{2+} system for 9 hours by weight loss method.

3.2. Influence of Zn^{2+} on the inhibition efficiency of SS

The corrosion rates and inhibition efficiencies calculated for mild steel in aqueous environment in the absence of SS and at different concentrations of Zn^{2+} ions are given in Table 2.Zinc and calcium [6-8] salts are the most common examples of cathodic filming inhibitors. An cathodic protective film of $Zn(OH)_2$ or $Ca(OH)_2$ is formed, respectively and protects the metal from corrosion.

Predominantly Zn^{2+} ions acts as strong synergists and used for corrosion inhibition with inhibitor. Table 2 depicts the corrosion rates (CR) and inhibition efficiencies (IE) of mild steel immersed in aqueous medium containing 60 ppm of Cl⁻ion in the absence and presence of inhibitor system (SS + Zn^{2+}) for 9 hours immersion time in Weight loss method . From Table 2, when zinc is added to the SS, the IE is increases at optimum concentration of 100ppm. For example, when 25 ppm of Zn^{2+} ion is added to 20 ppm of SS, the IE increases from 8.49% to 9.42%. If 50 ppm of Zn^{2+} ion concentration is added to SS, the IE is marginally increases. Therefore, the combination of inhibitor system containing 120 ppm of SS and 100 ppm of Zn^{2+} ions shows better IE (74.23%).

Table 1 Results of variation of inhibition efficiency and corrosion rate with change in concentration of the *Sargassum swartzii* for mild steel corrosion in aqueous medium containing 60ppm Cl⁻ ion.
Inhibitor system: 60ppm Cl⁻ ion + SS at pH = 7.   Immersion time:1 to 24 hours.

SS ppm	1 hr		3 hr		5 hr		7 hr		9 hr		12 hr		24 hr	
	IE (%)	CR mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR mpy)
0	_	178.33	_	62.21	_	38.15		28.14	_	27.19	_	28.69	_	29.38
20	4.65	170.04	6.67	58.06	7.60	35.25	8.42	25.77	8.49	24.88	6.03	26.96	5.89	27.65
40	9.30	161.74	11.11	55.30	11.95	33.59	11.98	24.77	13.57	23.50	10.91	25.56	9.43	26.61
60	13.95	153.45	14.45	53.22	15.20	32.35	15.78	23.11	16.11	22.81	15.68	24.19	11.78	25.92
80	18.61	145.15	17.78	51.15	17.34	31.52	17.87	23.10	18.68	22.11	16.87	23.85	12.36	25.75
100	20.93	141.00	19.98	49.78	20.63	30.28	21.04	22.22	22.03	21.20	18.09	23.5	13.55	25.4
120	23.25	136.86	24.45	47.00	24.56	28.78	24.84	21.15	**28.83**	19.35	19.28	23.16	14.70	25.06

For example, the IE exhibited by 100 ppm of Zn^{2+} shown 44.06% IE but when it is added to 120ppm of SS, it enhances the IE from 28.83 % to 74.23%. Hence, there is a synergistic effect exists between Zn^{2+} ion and the phyto constituent present in SS. On further, addition of SS, there is a gradual decrease IE was observed. Hence maximum IE offered by the inhibitor system with Zn^{2+} ions is 120 ppm SS. Interestingly, at lower concentrations a brownish green colour of Fe $(OH)_2$ or Fe$(OH)_3$ observed is changed to dark green at higher concentrations, due to the formations of inhibitive layer on the metallic surface.The result implies that the synergism is due to the complex formation between SS and Zn^{2+} ion. So, a thin film was observed on the surface of the metal. Fig.2 revealed increasing IE with increase in inhibitor concentration and reaches maximum IE of 74.23% at 120ppm SS and 100ppm Zn^{2+} ion.

3.3 Synergism Parameter (S_I)
The synergism parameter (S_I) is calculated and shown in Table 3 for different concentrations of inhibitor.
$S_I = 1-\theta_{1+2}/1-\theta'_{1+2}$
   i. If, S_I approaches 1, when no interaction between the inhibitors,
   ii. If, $S_I>1$, synergistic effect exists between the two inhibitors.
   iii. If, $S_I<1$, the negative interaction between the two inhibitors (ie) Corrosion rate increases.

The synergism parameter (S_I) values for *Sargassum swartzii* (SS) – Zn^{2+} system inhibitor system are tabulated in Table 3. It is observed that the S_I value is found to be greater than one, indicating the strong establishment of synergism exists between *Sargassum swartzii* (SS) - Zn^{2+} ions. Thus, the enhancement of the inhibition efficiency caused by the addition ofZn^{2+} ions to SS is only due to the synergistic effect [9].

Table 2 Results of corrosion rates (CR) and inhibition efficiencies (IE) of mild steel immersed in aqueous medium containing (60 ppm Cl⁻ ion in the absence and presence of inhibitors by Weight loss method.

Inhibitors system:*Sargassam swartzii (SS)*+ Zn^{2+}ion. Immersion time: 9 hours.

Cl⁻ ppm	SS ppm	Zn^{2+} ion CR (mpy)					Zn^{2+}ion IE (%)				
		0 ppm	25 ppm	50 ppm	75 ppm	100 ppm	0 ppm	25 ppm	50 ppm	75 ppm	100 ppm
60	0	27.19	24.42	20.74	17.51	15.21	-	10.19	23.72	35.60	44.06
60	20	24.88	22.12	13.59	10.28	7.79	8.49	9.42	34.47	41.29	48.78
60	40	23.50	20.74	13.13	9.68	6.68	13.57	15.07	36.69	44.71	56.08
60	60	22.81	19.81	12.67	8.76	6.13	16.11	18.88	38.91	49.97	59.70
60	80	22.11	18.43	12.21	8.29	5.11	18.68	24.52	41.13	52.66	66.40
60	100	21.20	17.51	11.75	7.83	4.56	22.03	28.30	43.35	55.28	70.02
60	120	19.35	17.05	11.11	7.37	**3.92**	28.83	30.18	46.43	57.91	**74.23**

Table 3 Results of inhibition efficiencies and synergism parameters for various concentration of inhibitor for mild steel immersed in aqueous medium containing 60 ppm of Cl⁻ion .Inhibitor system: *Sargassum swartzii* (SS) - Zn^{2+} Immersion time : 9 hours.

SS ppm	Zn^{2+}						
	0 ppm	50 ppm	S_I	75 ppm	S_I	100 ppm	S_I
0	-	23.72	-	35.60	-	44.06	-
20	8.49	34.47	1.07	41.29	1.00	48.78	1.00
40	13.57	36.69	1.04	44.71	1.01	56.08	1.10
60	16.11	38.91	1.05	49.97	1.08	59.70	1.16
80	18.68	41.13	1.05	52.66	1.10	66.40	1.35
100	22.03	43.35	1.05	55.28	1.12	70.01	1.45
120	28.83	46.43	1.01	57.91	1.09	**74.23**	**1.55**

3.4 Effect of pH on the inhibition efficiency of Sargassum swartzii (SS) - Zn^{2+} system.

pH is an crucial factor for the determination of corrosion inhibition efficiency in neutral, acidic and alkaline media. The influence of pH on corrosion rate of mild steel in the presence of *Sargassum swartzii* (SS) – Zn^{2+} system is studied for best concentration that shows maximum efficiency.

The influence of pH is studied for pH values 2,5,7,9 and 11 on inhibition efficiency of Zn^{2+} (100ppm) – SS (120ppm) is given in Table 4. The result showed that SS – Zn^{2+} system is effective at pH 7 with IE of 74.23% .When pH is lowered to 2 and 5, the IE is decreased to 29.34%   and 59.03%. This is because the protective film is gradually broken by the aggressive ions like Cl⁻.When the pH is raised to 9 and 11, the IE is found to decreases from 42.32% and 10.24%. It may be due to the formation of Zn (OH)$_2$ in the bulk of the solution resulting in the non-availability of Zn^{2+} to form a complex with *Sargassum swartzii*. Hence, the decrease IE in more alkaline environments of *Sargassum swartzii* (SS) due to not effectively transported to the metal surface. The similar result has been observed on Uncaria gambir [10] and in ternary inhibitor system [11].

In neutral aqueous medium at pH 7 the same system shows a good IE (74.23%).This is due to the fact that in neutral solution, cathodic oxygen reduction is controlled and added Zn^{2+} ions are able to transport SS - Zn^{2+} complex from the bulk of the solution to the metal surface and prevent further corrosion. This   analysis shows that, in acidic and alkaline medium, SS- Zn^{2+} system does not show good IE. However, in neutral aqueous medium the same system shows good IE (Table 4).

Table 4 Results of corrosion rates and   inhibition efficiencies calculated for mildsteel in aqueous environment (60 ppm Cl⁻ ion) at various pH. Inhibitor System: *Sargassum swartzii (*SS)- Zn^{2+}. Immersion time: 9 hours.

System	Acidic		Neutral	Alkaline	
	pH 2	pH 5	pH 7	pH 9	pH 11
Cl⁻ ion (60 ppm) CR (mpy)	42.39	38.25	27.19	23.96	17.97
Cl⁻ ion (60 ppm) + SS (120ppm) + Zn^{2+} (100ppm) CR (mpy)	29.95	15.67	3.92	13.82	16.37
IE (%)	29.34	59.03	**74.23**	42.32	10.24

3.5 Electrochemical Measurements
3.5.1Analysis of the results of Potentiodynamic polarization studies of   inhibitor system

Electrochemical measurements were carried out to study the nature of inhibitor, mode of action and mechanism of reaction. The effect of *Sargassum swartzii*(SS) and Zn^{2+} ion on the electrochemical behavior of mild steel in aqueous medium in the absence and presence of inhibitor was studied. The electrochemical parameters such as potential (E_{corr}), corrosion current density (I_{corr}) , anodic and catholic Tafel slopes (b_a and b_c), Linear polarization resistance (Rp) and percentage inhibition efficiency based on Tafel fit and linear polarization fit are listed in the Table 5.

The results revealed the strong inhibiting effect of the inhibitors. When the mild steel is immersed in an aqueous solution containing 60 ppm Cl⁻ ion (Blank), the corrosion potential (E_{corr}) for the blank value is -689.4 mV.

The value of E_{corr} for the formulation of Cl- ion (60 ppm)+ Zn^{2+} ion (100 ppm) is -712.5 mV Vs SCE. This suggests that the E_{corr} values are shifted to the more negative side with an increase in the inhibitor concentration. E_{corr} value for the best inhibitor formulation consisting of 120 ppm of(SS), 100 ppm of Zn^{2+} ion and 60 ppm Cl^- ion is -719.36 mV Vs SCE. It is noticed that the corrosion potential (E_{corr}) shift to cathodic direction from - 689.4 mV versus SCE to - 719.36 mV Vs SCE. It may be suggested that the inhibitor system act as a cathodic type and predominantly control cathodic reduction of metallic surface.

The Tafel slopes of anodic and cathodic values (b_a and b_c) of inhibitor system when compared with blank were found to be almost equal (b_a for blank=98mV /dec,b_a for inhibitor system=99 mV /dec ; and b_c for blank =218 mV /dec,b_c for inhibitor system = 238mV /dec).This results confirms the inhibitor system is a mixed type (ie) to control cathodic reactions due to the blocking of active sites on the metal surface by SS - Zn^{2+} system [12].SS extract consists of various phyto compounds like flavonoids, terpenoids, phenols and carbohydrates, all of which might act by specific mechanism and the overall effect may be a mixed mode of inhibition [13,14]

In this investigation, it is found that when concentration of inhibitor system increases, there is a regular decrease in I_{corr} from 180µA/cm^2 to 45 µA/cm^2 showing that the selected system act as an excellent inhibitor for mild steel in aqueous medium. IE calculated from I_{corr} value for inhibitor system is 75% that is an excellent agreement with mass loss experiments (74.23%). In general, lower I_{corr} values without causing any significant changes in the corrosion potential, E_{corr} suggests that the inhibitor is a mixed type inhibitor [15].The linear polarization resistance (Rp) value of the SS extract with Zn^{2+} is higher than blank value, suggests that a protective film is formed on the metal surface. The maximum inhibition efficiency of the formulation consisting of SS (120 ppm) +Zn^{2+} ion (100 ppm) + Cl^- ion (60 ppm) was found to be 74.99%, which is in good agreement from weight loss method (74.23%).

Inhibition efficiencies has been calculated by both Tafel and linear polarization method using corrosion current (I_{corr}) and polarization resistance (Rp) for the optimum concentration of 120 ppm of SS, 100 ppm of Zn^{2+} ion and 60 ppm Cl^- ion were found to be 75% and 74.99% respectively which is in good agreement from mass loss method(74.23%).The results are shown in Table 5.The polarization curves for mild steel in aqueous medium in the absence and presence of inhibitors system are shown in Fig. 3. From the figure, it can be interpreted that the addition of the inhibitor to the corrosive media changes the anodic and cathodic Tafel slopes. From the Figure 3, it is clear evident to the cathodic curves largely towards the lower current density when compared to the anodic curves.

Generally, an inhibitor can be classified as cathodic or anodic type, if the shift of corrosion potential in the presence of the inhibitor is more than 85mV with respect to that in the absence of inhibitor [16]. From the results, the changes of E_{corr} are less than 85mV (ie) 29.96mV. Hence, SS extract act as a mixed type inhibitor for the corrosion of MS in aqueous medium.

Table 5 Potentiodynamic polarization parameters for mild steel in aqueous medium containing 60 ppm Cl^- ion in the absence and presence of *Sargassum swartzii* (SS)(120 ppm) extract and Zn^{2+} ion (100 ppm).

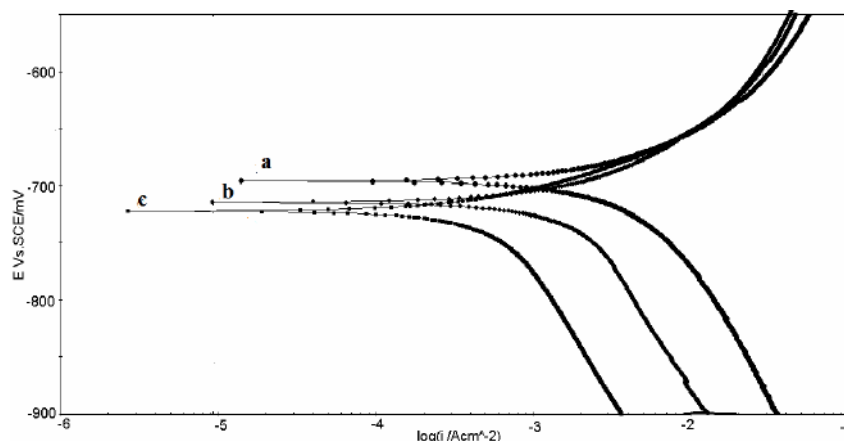| Inhibitors system	E$_{corr}$ (m V / SCE)	Tafel Polarisation parameters				Linear polarization parameters	
		b$_c$ (mV/dec)	b$_a$ (m V /dec)	I$_{corr}$ (µA / cm^2)	IE (%)	Rp (Ohm / cm^2)	IE (%)
Cl$^-$ ion (60 ppm)	-689.4	218	98	180	-	24.16	-
Cl$^-$ ion (60ppm) + Zn^{2+} ion (100 ppm)	-712.5	229	96	102	43.33	37.71	35.93
Cl$^-$ ion (60ppm) + Zn^{2+} ion (100 ppm) + *Sargassam swartzii* (120 ppm)	-719.36	238	99	45	**75.0**	96.55	**74.98**

Fig. 3. Potentiodynmicpolarization curves recorded for mild steel immersed in test solutions. (a) Cl⁻ 60 ppm. (b) Cl⁻ 60 ppm + Zn²⁺ 100ppm (c) Cl⁻ 60 ppm + Zn²⁺ 100 ppm+ SS (120 ppm)

3.4.2 Analysis of the results of Electrochemical Impedance Spectroscopy (EIS) studies of inhibitor system

The EIS technique is based on the response of an equivalent Randle circuit for an electrode solution interface [17]. The equivalent circuit consists of double layer capacitance (C_{dl}) in parallel in the charge transfer resistance R_{ct} that is in series with solution resistance Rs. Values of these components and inhibition efficiencies are derived from EIS measurements.

The corrosion behaviour of mild steel in aqueous medium containing 60 ppm Cl⁻ ion in presence of SS extract was investigated by EIS method at room temperature. The various parameters such as charge transfer resistance (R_{ct}) double layer capacitance (C_{dl}) and the corresponding IE were calculated and summarized in the Table 6 and represented in Figure 4.These plots having the shape of semicircle indicate the activation controlled nature of the reactant with single transfer process. The existence of depressed nature of semi circle with its centre below the x-axis is the characteristics of solid electrodes, it is attributed to the increased micro roughness of surface, and other in homogeneities of solid electrode during mechanism [18] .The diameter of the semicircle gives the R_{ct} equivalent to Rp that is inversely proportional to corrosion rate. The charge transfer resistance (R_{ct}) is calculated from difference in impedance at lower and higher frequencies.

In the investigation, R_{ct} value ranges from 388.2 Ohms to 1554.7 Ohms .The increase in R_{ct} value indicating the charge transfer process is the main controlling factor of the corrosion of MS. Thus, there is an increase in the surface coverage by the inhibitor molecules. The increased surface coverage led to an increase in inhibitor efficiency. The interfacial double layer capacitance (C_{dl}) decreased from 89.41 X 10⁻⁶ (F/cm²) to 22.49 X 10⁻⁶ (F/cm²) respectively. The addition of inhibitors provide decrease in C_{dl}, which can result from increase in thickness of electrical double layer, and decrease in local dielectric constant [19],suggests that the inhibitor molecular function by adsorption of metal solution interface.

The electrochemical experiments reveal that the inhibition efficiencies obtained from EIS and potentiodynamic polarization studies are in good agreement. The study evident from the data, the percentage inhibition efficiency from electrochemical measurements (approximately 75 %) are in good agreement with those obtained from weight loss method (74.23%).

Table 6 AC impedance parameters for mild steel in aqueous mediumcontaining 60 ppm Cl⁻ ion in the absence and presence of *Sargassum swartzii* and Zn²⁺ ion.

Inhibitor system	R_{ct} (Ohms)	IE (%)	C_{dl}(or)CPE (F/cm²)	IE (%)	C_{dl} $\theta=1-C_{dl(inh)}/C_{dl(blank)}$
Cl⁻ ion (60 ppm)	388.2	-	89.41 X 10⁻⁶	-	-
Cl⁻ ion (60ppm) + Zn²⁺ ion (100 ppm)	682.6	43.13	27.35 X 10⁻⁶	69.41	0.6941
Cl⁻ ion (60ppm) + Zn²⁺ ion (100 ppm) +	1554.7	75.03	22.49 X 10⁻⁶	74.84	0.7484

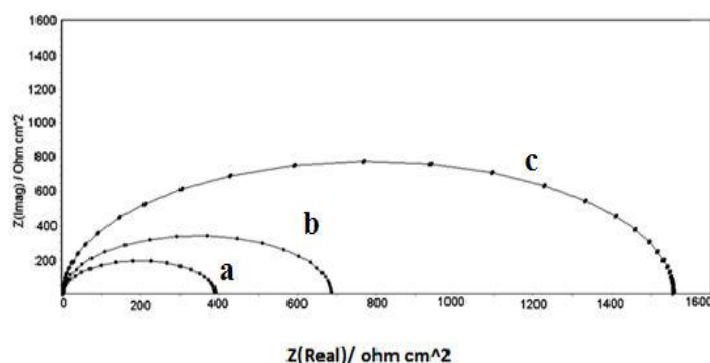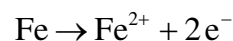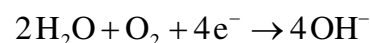| Sargassum Swartzii (120 ppm)					

Fig.4. Impedance curves recorded for mild steel immersed in test solutions. (a) Cl⁻ 60 ppm.   (b) Cl⁻ 60 ppm + Zn²⁺ 100 ppm(c) Cl⁻ 60 ppm + Zn²⁺ 100 ppm+SS (100ppm).

Mechanism of corrosion inhibition

When mild steel specimen is immersed in the neutral aqueous environment, the anodic reaction is,

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

and the cathodic reaction is,

$$2H_2O + O_2 + 4e^{-} \rightarrow 4OH^{-}$$

i)When the formulation consisting of 60 ppm of Cl⁻, 120 ppm of SS and 100ppm of Zn^{2+} is used, the Zn^{2+}-SS complex is formed in the solution .

ii) When mild steel is immersed in the solution, the Zn^{2+}-SS complex diffuses from the bulk of the solution towards the metal surface.

iii) On the metal surface, Zn^{2+}-SS complex is converted into Fe^{2+}-SS complex, and Zn^{2+}released.

Zn^{2+}- SS + Fe^{2+} --- Fe^{2+}-SS + Zn^{2+}
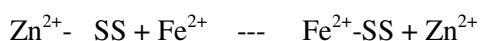
The released Zn^{2+} ions combine with OH^{-} to form Zn $(OH)_2$ precipitate on the cathodic sites.

$$Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_2 \downarrow$$
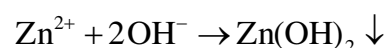
iv) Thus the protective film consists of Fe^{2+}-SS complex, $Zn(OH)_2$ and oxides of iron.Thus,these complexes might be adsorbed onto metal surface by weak Vander Waals force of attraction to form a protective film and to prevent mild steel from corrosion.

4. CONCLUSION:

The investigated aquatic plant *Sargassum swartzii*- Zn^{2+} are found to perform well as corrosion inhibitors in aqueous solution containing 60ppm Cl⁻ ion. They are environmentally suitable non-toxic compounds, biodegradable and eco friendly synergist in the corrosion inhibition process. Results of the weight-loss method reveal that the formulation consisting of 60 ppm of Cl⁻, 100 ppm of Zn^{2+} and 120 ppm of SS offers an inhibition efficiency of 74.23%.The high performance of SS - Zn^{2+} 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 shows that this formulation functions like a mixed inhibitor. AC impedance spectra indicate the presence of a   protective film on the metal surface. Thus, it can be concluded that *Sargassum swartzii* – Zn^{2+} inhibitor system acted as a good inhibitor in aqueous medium.

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