

Corrosion Behaviour of Mild Steel in Putrid Seaweed System at Thondi Coastal Area-(Palk Bay) Southeastern Coast of India

¹M. Jaikumar, ²R. Ramkumar, ³L. Kanagu, ³P. Senthil, ³C. Stella and ⁴Hari Muraleedharan

¹Department of zoology, Marine Biology Laboratory, Andhra University, Visakhapatnam-3, India

²Suganthi Devadason Marine Research Institute, Tuticorin, 44, Beach Road, Tamilnadu, India

³Departments of Oceanography and Coastal Area Studies,
Alagappa University Thondi Campus, Thondi, Tamilnadu, India

⁴Mio Bio, Biological Research Laboratory, Trivandrum, Kerela

Abstract: This paper reports result of putrid system seaweeds in Thondi coast (Latitude 90° 44'N and Longitude 79° 00'45'') natural seawater. Observation made weight loss measurement in room temperature, polarization technique and Impedance measurement. Three seaweeds were taken up for present study *Ulva*, *Hypnea* and *Gracillaria*. The bacteria counts of the Heterotrophic bacteria in the putrid system were very high in the range 5.5*10⁶ CFU/cm² to 5.9*10⁷ CFU / cm², Initially there is no sulphate reducing bacteria, after 30th day can observed blackening in the putrid seawater, Hence we can observed high bacteria count in the putrid seawater system. The corrosion rates by weight loss measurement mild steel in Thondi seawater and its control system corrosion rate was high at 0.0332 gms to 0.0509 gms observed in the 75 days in the immersion period, where as in the putrid system the corrosion was less in the range of 0.0222 gms to 0.1750 gms and the electro chemical polarization study indicated that icorr values were same in the putrid system and the control system but Less weight loss reducing corrosion current and increasing resistance has been observed in the putrified seaweed system. It is concluded that margacite sulphide films to form a productive coating on mild steel during putrification were observed during the study.

Key words: Mild steel Corrosion • Putrid seaweed system • Heterotrophic Bacteria • Polarization technique • Impedance measurement

INTRODUCTION

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals [1]. The most widely used metal is iron (usually as steel) and the following discussion is mainly related to its corrosion. Corrosion is usually through of as strictly a metallic phenomenon. However, all materials (Plastic, Fibre, glass, concrete, etc) can suffer from deterioration cause by corrosive environment. Mild steel is one of the major construction materials, which is extensively used in chemical and allied industries for the handling of acid, alkali and salt solutions [2]. The corrosion of metals exposed to the atmosphere is governed by the interplay

of the resistance of the metal to corrosion and the corrosivity of the aqueous electrolyte on substances on the material surface [3]. The traditional material used in the strengthening of concrete structures is steel [4].

Corrosion has a huge economic and environmental impact on virtually all facets of the world's infrastructure, from highways, bridges and buildings to oil and gas, chemical processing and water and wastewater systems. In addition to causing severe damage and threats to public safety, corrosion disrupts operations and requires extensive repair and replacement of failed assets. The annual cost of corrosion worldwide is estimated to exceed \$U.S.1.8 trillion, 2 which translates to 3 to 4% of the Gross Domestic Product (GDP) of industrialized countries Fortunately, there are highly experienced corrosion professionals using innovative and long-

proven technologies who can effectively control the effects of corrosion when given the proper resources[6]. However, many decision-makers in industry and government do not understand the consequences or extent of corrosion and how critical it is to control it. They also do not appreciate the need for ongoing research and development (R and D) to further reduce the effects of corrosion on people, assets and the environment. In the United States, 3.14% of the GDP—equal to \$276 billion—is lost annually to corrosion. Corrosion costs worldwide are therefore on the order of \$U.S. 552 billion.² Energy Production and Storage Worldwide energy production is based overwhelmingly on fossil fuels that include coal, oil and gas [7]. In the United States, the cost of corrosion related to bridges alone amounts to about \$ 8.3 billion per year. In India Corrosion reduces the life of rail to nearly half its expected life. The annual loss due to pre-replacement of corroded rails is significant (about Rs. 440 crores) [11]. The corrosion process of mild steel pipelines in gas and oilfield mining induced by the presence of carbon dioxide, acid and water has been a serious problem, economically and environmentally, in the oil and gas industries for decades [6-8,10]. In Indonesia, the gas and oilfield mining are vital industries that give valuable commodity and income to the nation. Meanwhile, the loss caused by corrosion in Indonesia was estimated 1-1.5 % of GDP (Gross Domestic Production) or approximately trillion of dollars have been spent to overcome the corrosion problems [3] Heavy metals found in wastewaters are harmful to the environment and their effects on biological systems are very severe (5)

The aim of this work is to investigate the corrosion behaviour of Putrid seaweeds in mild steel at Thondi natural seawater using Tafel Extra polarization studies (PAR model 173) in conjunction with potentiostatic generator and Xy recorder (Rikadenky model R 206) employing stationary electrode and electrochemical (electrochemical impedance spectroscopy, EG and G PAR model M 6310 with software M 398) methods. The morphology of mild steel surface before and after immersion in putrid seaweed solution in 1000 ml closed container was examined at every 15 days interval. However this present work deals that putrid seaweeds system in mild steel has less corrosive effect in Thondi natural seawater. Marine environments are long known to be very corrosive. Though work have been done on the nutrients and seawater corrosion and variation of putrid seaweeds from other part of India coast, no report is available from Thondi coastal area but only few reports

knowledge regarding the putrid reactions taking place in natural seawater.

Experiment Part

General Procedure

Sampling of Thondi Natural Seawater: Natural seawater sample was collected at Thondi. The collection were made for the 75 days. The water sample was collected in sterile stoppered bottle and brought to the laboratory in an Portable refrigerated to avoid microbial proliferation and contamination during transport. Physico chemical and biological characteristic of Thondi water has been analysed and water was changed for every 24 hours intervals up to 75 days in a time.

Selection of Seaweeds

Ulva

Gracillaria

Hypnea

Microbiological Analysis of Biofilm Generated on the

Metal Surface: Isolation and characterization of the microorganisms in the biofilm sample were done in the laboratory. The metallic coupon of mild steel of size 10.5cm x 5.5 cm. The metallic specimens were mirror polished and decreased by trichloro ethylene. After wards the coupons were exposed to U.V light to kill the bacteria and immersed in the natural seawater and in seeds containing.

Electrode /Coupon Design: Composition of mild steel are Sulfur 0.02-0.03%,phosphorus 0.40-0.50%,Carbon 2% and iron 97.47-97.58%.Electrodes of 1 cm² dimension, with an extended stem of 12 cm length, were used in the investigation. The connecting rod of the electrode was first wrapped with Teflon tape and coated with araldite with another wrap of Teflon tape over it exactly from the area to be exposed. The electrodes were machine polished to a mirror finish. as it was suspected that trichloroethylene or alcohol, the conventional degreasing agent, may interfere in the initial stage of corrosion or micro fouling phenomena respectively, acetone was performed and used for decreasing purposes. The electrode were placed exactly at the middle of the electrochemical cells, to avoid disturbance cause by medium of the electrochemical cells to avoid disturbances caused by medium replenishment processes, when they were near the surface or to avoid excess bacteria fouling due to nutrient accumulation when they were in close proximity with cell bottom

5cm x 1cm x 0.2cm mild steel coupons were used for the weight loss experiment. Surface preparation were done as started earlier.

Immersion Test: The studied were carried out by immersion tests are recommended in ASTM standard 931-86. The mild steel coupons of size 25 x 20 x 3 mm specimen were polished, degreased, weighed and exposed in natural sea water system, mixed culture system and a biotic system in 1 litre beaker for period of 30 days [12]. At frequent intervals the weight loss of mild steel coupons were measured. The weight loss obtained in milligram were converted to corrosion rate in mpy using the formula

$$\text{Corrosion rate (mpy)} = \frac{534 \times W \text{ (mgms)}}{\text{Density (gm/cc)} \times \text{area (inch}^2\text{)} \times \text{time (hours)}}$$

Electro Chemical Cell Design: Mild steel electrode of 1cm² dimension, with an extended stem of 12 cm length was used in impedance analysis. The connection rod of the electrode was first wrapped with Teflon tape and coated with araldite. With another wrap of Teflon tape over it exactly from its origin from area to be exposed. The electrodes were machine polished to a mirror finish and degreased with trichloroethylene. The cell assembly used for polarization impedance is become simple and single walled with 500 ml capacity. At the top three ground joints were provided to introduce working and auxiliary electrode as well as login capillary of the reference electrode. The potential of the working SCE were connected through the respective culture medium-KCL salt bridge. Studies were carried out after the corrosion potential reached as steady state value.

Tafel Extrapolarization Studies: Polarization measurement was carried out potentiodynamically using potentiostat (PAR model 173) in conjunction with potentiostan generator and Xy recorder (Rikadenky model R206) employing stationary electrode. The electrode potential was fixed at 200 mV negative to open circuit potential and allowed to attain a steady state value. The steady state polarization was carried out from -200mV to + 200mV w.r.t the OCP at a scan rate of 0.5 mV/sec. The i_{corr} values were obtained from the plot of E vs log I curve.

Impedance Study: The impedance studies were carried out using computer controlled EG and G PAR model M 6310

with software M398. A three electrode cell assembly was used for impedance measurements. Test specimen as the working electrode, a large platinum foil as counter electrode and saturated calomel electrode (SCE) as reference electrode were used. After attainment a steady value were impressed with AC signal 10 mV amplitude at frequencies ranging from 0.1 Hz to 100 KHz. The values Rct were obtained from the Rs and Rt values

Bacteria Counts: The water sample was serially diluted using 99ml and 9 ml sterile distilled water blanks. The total viable bacterial counts were enumerated using Zobell 2216 E Agar medium by pour plate method. The plating procedure for microbiological analysis should not exceed more than six hours after collecting the sample. One ml of aliquots dilution were pipetted out in to the sterile petriplates and 15 ml of Zobell 216E agar medium was added in each petriplates. The sample were mixed thoroughly by rotating the plates clockwise and anticlockwise direction and allowed solidify. Then the plates were incubated for 24 to 48 hours at 37°C. Duplicate sample were tested along with control. The plates containing bacterial colonies within 30-300 numbers were selected and total viable counts were made. The bacteria populations were expressed as colony forming units per ml (CFU/ml) of the water sample. Natural Thondi sea water was used as a Control system (with out seaweeds).

Physico-chemicals Analysis of Thondi Natural Seawater pH Measurement: pH is the negative logarithm of hydrogen ion concentration of solution and it was measured by using pH meter and standard buffers at room temperature [12].

Dissolved Oxygen: The dissolved oxygen was estimated by Winkler's iodometric method.

Total Hardness of Water: Hardness of water is generally caused by the calcium and magnesium ion present in water. 50 ml of water sample was taken in a conical flask and 1 ml of buffer solution was added and titrated against EDTA(0.01N) solution using Eriochrome black T(100-200mg) as an indicator [13]. The total hardness of water was calculated using the following formula:

$$\text{Hardness as mg/l CaCO}_3 = \frac{\text{ml of EDTA} \times 100}{\text{ml of sample}}$$

Calcium was estimated by the formula:

$$\text{Calcium mg/l} = \frac{\text{Volume of EDTA used} \times 400.8}{\text{ml of sample}}$$

Magnesium ion concentration was estimated by the formula

$$\text{Mg mg/l} = (\text{Total hardness} - \text{calcium hardness}) \times 0.244$$

Chloride Estimation: Silver nitrate reacts with chloride to form very slightly soluble white precipitate silver chloride. At the end point, the chloride gets precipitated. Free silver ion reacts with chromate to form silver chromate of reddish brown colour. 50 ml of water sample was taken in a conical flask and 2 ml of potassium chromate solution was added and titrated against silver nitrate (0.02N) for the appearance of red tinge [13]

The Chloride was calculated using the formula

$$\text{Chloride mg/l} = \frac{(\text{ml} \times \text{N}) \text{ of AgNO}_3 \times 1000 \times 355}{\text{ml of sample}}$$

Determination of Salinity: The perceptible halide ions in 10 ml volume of sea water sample were determined by titration with (standardized) silver nitrate (alpha value-0.150 to +0.145) (standardized against standard sea water obtained from National Institute of Oceanography, Goa) solution from a burette using potassium chromate as an indicator [14]. The volume of silver nitrate utilized was almost equal to salinity and the final value was obtained using the following formula and expressed as PSU (Practical Salinity Units).

Salinity (PSU) = $B \times N \times 0.03545 \times 1.80655 \times 1000 / \text{ml of the sample}$. Where B is burette reading or volume of silver nitrate used and N, the normality of Silver nitrate. After the corrosion of the titration value to obtain chlorinity, the value is obtained.

Microbiological Influenced Corrosion (MIC): Microorganisms in seawater form "biofilm" on the metal surface. Biofilm consists of population of sessile organisms and their hydrated polymeric secretion. Numerous type of organisms may exist in any particular biofilm, ranging from strictly aerobic bacteria at the water interface to anaerobic bacteria such as sulphate reducing bacteria (SRB) at the oxygen-depleted metal surface. The presence of a biofilm can contribute to corrosion in the three ways: Physical/ deposition, production of corrosive by-product, and depolarization of

the corrosion cell caused by chemical reaction. As discussed above, deposits can cause accelerated localized corrosion by creating different aeration in cells. This same phenomenon occurs with a biofilm. The non-uniform nature of biofilm formation creates an inherent, which is enhanced by the oxygen consumption of organisms in the biofilm.

Microbial Metabolisms: Many of the by-product of microbial metabolism, including organic acids and hydrogen sulphide, are corrosive. These materials can concentrate in the biofilm, causing accelerated metal attack. Corrosion tends to be self limiting due to the build up of corrosion reaction products. However, microbes can absorb some of these materials in their metabolisms, there by removing them from the anodic or cathodic site. The removal of reaction products, formed by depolarization, stimulates further corrosion. The surface exhibits scattered areas of localized corrosion, unrelated to flow pattern. The corrosion appears to spread in a some what circular pattern from the site of internal colonization.

Micro Organisms Associated with Corrosion: Microorganisms may be classified into three general groups namely (i) Fungi, (ii) Micro algae and (iii) Aerobic and anaerobic bacteria.

Fungi: Two forms of fungi commonly encountered are moulds (Filamentous form) and yeast's (unicellular form). The filamentous are branched and form a tangled mass referred to as mycelium. In contrast to some bacteria, fungi required oxygen for growth. Energy for growth is obtained either by release organic acid metabolism as the end product. E.g. Citric acid and oxalic acid. Since they can utilize hydrocarbon they may be active in large hydrocarbon environment.

Microalgae: Two algae are heterogeneous group of chlorophyll-containing plants found in sea and fresh waters. They are primarily autotrophic, obtaining their energy from light or by the oxidation of inorganic materials and their carbon by the assimilation of carbon dioxide. These organisms are commonly found in cooling water system. Their role is similar to that of fungi, by adhering to the metal surface they encourages the formation of differential aeration and concentration cells and there by accelerating the already existing corrosion processes.

Bacteria: These organisms can be either autotrophic or heterotrophic and either aerobic or anaerobic. Heterotrophic bacteria obtain their energy and carbon requirements from organic source. Autotrophic bacteria obtain their energy from light or by the oxidation of inorganic materials and their carbon assimilation. Anaerobic bacteria do not require oxygen for their growth. Sulphate reducing bacteria (SRB) and sulphide oxidizing bacteria are the major groups in microbial corrosion.

Mechanisms of Microbial Corrosion

Srb and Anaerobic Corrosion: The role of hydrogen activity in SRB related corrosion of mild steel is unclear. Hydrogenous positive SRB can oxidize the molecular hydrogen generated at the cathodic sites to facilitate “cathodic polarization” [15,16]. In this mechanism, where the combination of absorbed H-atoms to produce H_2 S gas is considered to be rate controlling steps, bacteria effectively increase the corrosion rate. Moreover initial corrosion rate that was accelerated by iron sulphide in a biofilm system was attributed to both anodic and cathode depolarization. However corrosion engineers should consider that the role of SRB in the corrosion process in oxygen free environments is principally dependent on their ability to produce ferrous sulphide suggested by [17]. Microbial is well known the macro organisms are closely involved in the transformation of elemental iron comparison the major material of iron and steel pipe under increased anaerobic conditions in the aquatic environment. Sulphides are formed from sulphates and organic sulphur compound present in soil / water and iron may be precipitate in nature by iron oxidizing bacterial. [18] Concluded that underground corrosion of iron and steel structure is partially due to bacteria activity. In fact the iron bacterium *Gallionella ferruginea* was isolated from corrosion products of buried steel pipes and high concentration of sulphur and organic mater in the products indicated the presence of sulphur bacteria. Thomas noted the growth and accumulation of bacteria might be the reason for the degree of corrosiveness of water.

Acid Producing Bacteria: The most direct corrosion metabolites produced by microorganisms seem to be acidic [19]. Acetic and butyric acids are example of rich corrosive microbial products. The sulphur oxidizing bacteria e.g. *Thiobacillus* spp. Produce sulphuric acid from sulphur or sulphide [20] they occur commonly in soils containing sulphide mineral [21]. Corrosion of concrete and steel pipes carrying municipal water has been resulted

to localized production of sulphuric acid by *Thiobacillus* spp [19].

Iron Reducing Bacteria: Various *Pseudomonas* spp, have been implicated of ferric (Fe^{3+}) [22] As ferric ion is insoluble except at very low pH, ferric salts protect, the metal surface from further corrosion due to chemical activity. Ferrous salt are mostly soluble and there fore of ferric salts results in the removal of the productivity layer. Thus, iron reducing *Pseudomonas* spp. Promote corrosion indirectly.

Iron Oxidizing Bacteria: The aerobic iron oxidizing namely *Pseudomonas* spp, *Gallionella* spp. Oxidise ferrous (Fe^{2+}) to ferric ion. Tubercles are initially formed by the deposition of iron and manganese oxide [19]. The tubercles have steep pH gradient, the pH inside being very low. The role of bacteria in corrosion of steel has been the subject of numerous articles and availability of a number of excellent review article on this topic show steel are the widely studied metals as far as MIC is concerned. Moreover, the first suggestion that bacteria were involved in electrochemical corrosion was made on the observation of buried iron pipelines [18]. Specific review include [23, 24]. There has been upsurge in the number of reports of various type of MIC involving iron and steel [24] and in the level of interest in the topic shown by members especially the chemical process. Petroleum and water treatment industries, [25- 28]. Effect of SRB and minimal iron / iron rich nutrients media on the weight loss of mild steel role of conversions (different forms) of bacteriogenic sulphide [17] metabolic rates of SRB and corrosion rate [29] active pitting potentials due to sulphide produced by SRB [30] adsorption of SRB to the surface and maintenance of sulphide rich layer [31] were well documented. It should be mentioned here that a major part of studies on the MIC of mild steel were attributed to SRB or bacteriogenic sulphide alone. The mechanism of steel corrosion by *Thiobacilli* spp is through H_2SO_4 production, where the local; pH around these organisms may be very low and the surrounding materials may disintegrate quite rapidly. Mechanism of steel corrosion by iron bacteria has reported through the creation of oxygen or iron concentration cells. A good example of this is the ferric hydroxide deposits produced by iron bacterial the iron water pipes [24].

Algae: Seaweeds are macroscopic marine algae, which form in important component of the marine living resources. In the present work three types of seaweeds

are taken (i.e) *Ulva*, *Gracellaria*, *Hypena*, these weeds are found plenty in the Thondi area. Algae play an important role in MIC by virtue of their capability to produce molecular oxygen. Two species of blue green algae have been implicated in corrosion of mild steel and stainless steel weld seam [20] various hydrogenous positive algae utilize cathodic hydrogen, During decay also it create aggressive micro environment on metal surface. They are available largely in shallow coastal waters, wherever these are the substratum on which they can grow and flourish. Based on the pigmentation the seaweeds are broadly grouped into green algae, red algae and blue green algae. The macro algae are firmly attended to the substratum by a hold fast organ [19] [32] and [33] has listed 900 chlorophyceans, 997 phaeophyceans and 2540 rhodophycean marine species worldwide. Seaweeds are known to contain more than sixty trace elements. More over seaweeds are rich in protein, fact carbohydrate, iodine, bromide, potash vitamins and minerals.

The organic and inorganic nutrients forms are the most important raw materials for plant productivity in aquatic ecosystem. It is known that the dissolved form in the water column is responsible for regulating the micronutrients required for plants and animals in the form of detritus. Many workers have reported the role of different form of nutrients as well as organic matter in aquatic productivity [34-38]. Reported the seasonal variation of nutrients like C, N and P ratio in the sediment of Vellar estuary [39].

The effect of nutrients on macro algae is governed by macro algal nutrients relationships i.e. algal uptake assimilation, storage and release [40,41].The photosynthetic production or organic matter by algae is dependent on the assimilation or organic nutrients reported [40]. In view of [29] reported that the macro algal growth was not limited by its requirements.

Nutrient concentration is usually determined by sampling the water column. These nutrients and metal concentrations can be used to predict the effects of specific pollutants on the growth of algae and aquatic plants [40]. The total nutrient content of seaweeds varies with changes in the environment [42]. Recent research by [43] and [44] has indicated the concentration of nutrients available to marine plants were ascertained by using algae, as Bioindicators. Biomonitoring involves the use of indicators, indicator species or indicator communities [45]. Generally benthic macro invertebrates, fish and algae are used. Certain aquatic plants have also been used as indicator species for pollutants including nutrient enrichment [45]. Biomonitoring is the use of biological response and to access the changes in the environment

due to anthropogenic caused and putrefied biological systems.

The detritus constitutes a significant energy source for coastal productivity and with positive impacts on fisheries and aquacultures was reported [46-48].The decomposition of leaf plays an important role in nutrient cycling and supply of organic matter to the estuarine detritus food web [46,48,49]. Algal growth is dependent as sunlight and nutrient concentration. The abundance of algae is indicative of nutrients pollution.

Putrification: Putrification process whereby heterotrophic organisms, including some bacteria, fungi, saprophytic plant and lower animals are utilize the remains of once-living tissue or dies tissue as a source of nutrition. The polysaccharides, lipids, nucleic acids and proteins of dead tissue are broken into smaller organic molecules often by enzymes that are secreted into the external environment by the bacteria and fungi that are involved. The breakdown products are readily absorbed by the heterotrophs and are used both as a source of building blocks of the synthesis of there own polysaccharides, lipids, nucleic acids and proteins. The choice of seaweed as the decomposing entity for the present study was based on Efir's observation² that the decay of plants, rather than of animals, causes little variation in pH and sulfide values during the second half of a 30-day decomposition sequence. This would permit the assessment of corrosion as a function of time in a relatively unaltered environment following oxygen depletion [49].

Physico chemical characteristics of seawater were correlated with chemical composition of marine algae [50]. The significance of bacterial grazing of mineral cycling for decomposition of particulate detritus [51]. Seaweeds gradually decomposed the organic matter under aerobic and anaerobic conditions in natural seawater. Marine Macrophytes uptake ammonium and nitrate in the seawater [52]. Microorganisms possess a remarkable adaptive capacity and may develop resistance and degradative ability to any given organic compounds. The heterogeneous micro flora exhibiting degradative enzymes, such as celluloses, amylases and pectinase[52].

RESULTS

Physico-chemical Characteristic of Thondi Natural Seawater: Physico-chemical characteristic of Thondi natural seawater was analysed (Table 1) salinity, dissolved oxygen, pH, chloride concentration etc. in the range at 35 psu, 6.83 ml /litre 8.2 and 17 ppt respectively (Fig. 3).

Table 1: Physico Chemical Characteristic of Thondi Natural Seawater

S.NO	Properties	Value
1	Salinity	35 psu
2	D.O	6.83 ml/litre
3	PH	8.2
4	Chloride	17ppt
5	Inorganic phosphate	2.2348µg/litre
6	Total phosphorus	4.22141µg/litre
7	Calcium	480 mg/litre
8	Magnesium	1584 mg/litre
9	Alkalinity due to OH	8 ppm
10	Alkalinity to CO ₃	16 ppm
11	Alkalinity due to HCO ₃	107 ppm
12	Temperature	28°C
13	Light penetration	2 meters

Table 2: Bacteria Counts, Ph, and Do Concentration on (Ulva, gracillaria and Hypnea) Sea Weeds on Mildsteel

No of Days	Bacteria counts in seawater (CFU/cm ²)	Heterotrophic Bacteria (CFU/cm ²)	Sulphur reducing Bacteria	PH	DO(ppm)
15	4.5 x 10 ⁵	5.6 x 10 ⁶	Absent	8.6	5.6
30	5.1 x 10 ⁵	6.2 x 10 ⁶	Present	8.2	5.2
45	5.2 x 10 ⁵	5.9 x 10 ⁷	Present	8.2	5.1
60	4.9 x 10 ⁵	6.2 x 10 ⁶	Present	7.4	3.98
75	4.6 x 10 ⁵	5.5 x 10 ⁵	Present	6.9	3.06

Table 3: Weight Loss Measurement in Putrified Ulva, Gracillaria and Hypnea Seaweeds on Mild Steel

No of Days	Weight in putrified seawater	Corrosion Rate (mmpy)	Weight loss in Normal seawater (gms)	Corrosion Rate (mmpy)
15	0.0222	0.2059	0.0332	0.0379
30	0.0277	0.1052	0.034	0.0518
45	0.03	0.0927	0.0356	0.11
60	0.0297	0.0688	0.421	0.0976
75	0.175	0.3246	0.0509	0.0944

Table 4: Corrosion Rates of Mild Steel in Putrified Seaweeds in Natural Seawater by Polarization Technique and Impedance Analysis

No of Days	OCP (mv/SCE)	Putrified seaweeds ICORR (µA/cm ²)	Rt(ohm.cm ²)	OCP (mv/SCE)	Natural seawater ICORR (µA/cm ²)
15	-700	6	46	5	50
30	-720	8	71	9	56
45	-734	9	80	15.5	94
60	-702	12	124	35.5	98
75	-688	15	232	15.4	125

Bacterial Counts, pH and Dissolved Oxygen on (Ulva, Gracillaria and Hypnea) Seaweeds on Mildsteel: Bacteria counts on mild steel in Thondi seawater during putrification (Table 2). The bacteria count of heterotrophic bacteria in putrified system were very high in the range at 5.5*10⁶ CFU/cm² to 5.9 * 10⁷ CFU/cm² in control system i.e natural seawater the bacteria colonies were less in the range of 4.5 * 10⁵ CFU/cm² to 5.2 * 10⁵ CFU/ cm² during immersion period. Initially there is no sulphate reducing bacteria. After 30th day we can observed blackening in the putrified seawater. Here we can observed high bacteria count in the putried seawater system.

Weight Loss Measurement in Putrified Seaweeds System (Ulva, Gracillaria and Hypnea on Mildsteel: The corrosion rate by weight loss measurement on mild steel in Thondi putrified seawater system (Table 3) and its control corrosion rate were high at about 0.0332gms to 0.0509 gms during 75 day immersion period where as in putrified system the corrosion was less in the range 0.0222 gms to 0.1750 gms. The ammonium and nitrate uptake by the marine seaweed in the seawater. The less weight loss in the putrified system due to the presence at nitrogen based compound in the natural seaweeds [52]. (Fig. 1).

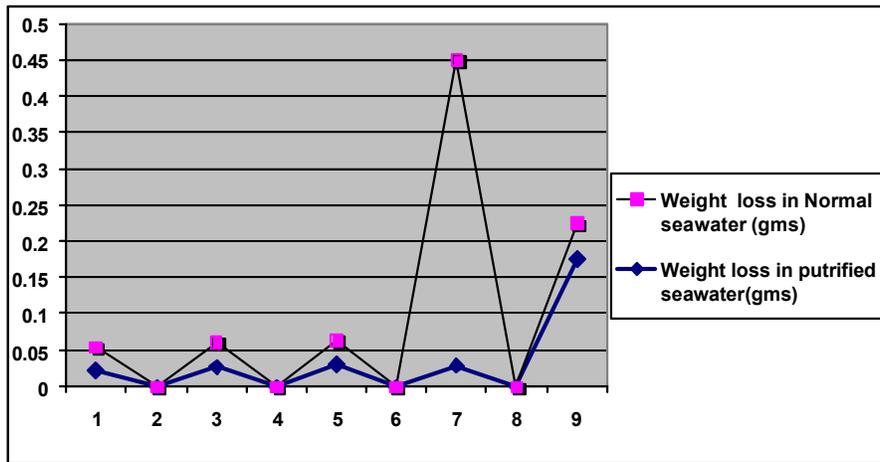


Fig. 1: Weight Loss Difference in Normal seawater and Putrified seaweed water (Putrified Ulva, Gracillaria and Hypnea Seaweeds on Mild Steel)

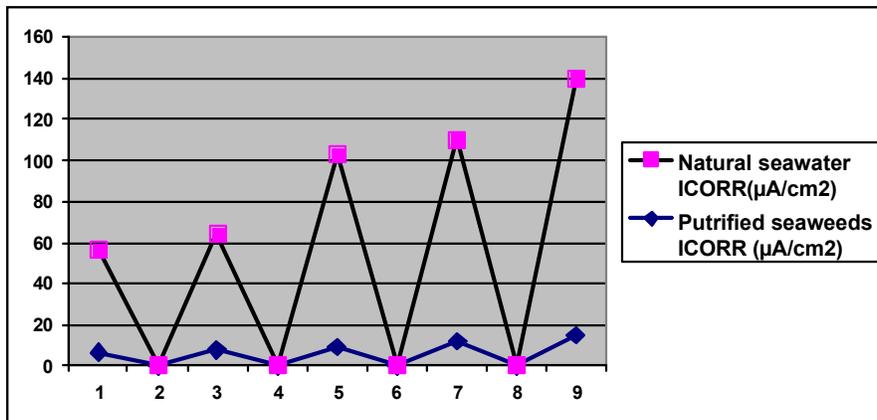


Fig. 2: Corrosion Rates of Mild Steel in Putrified Seaweeds and Natural Seawater by Polarization Technique and Impedance Analysis. [$\text{Icorr} (\mu\text{A}/\text{cm}^2)$]

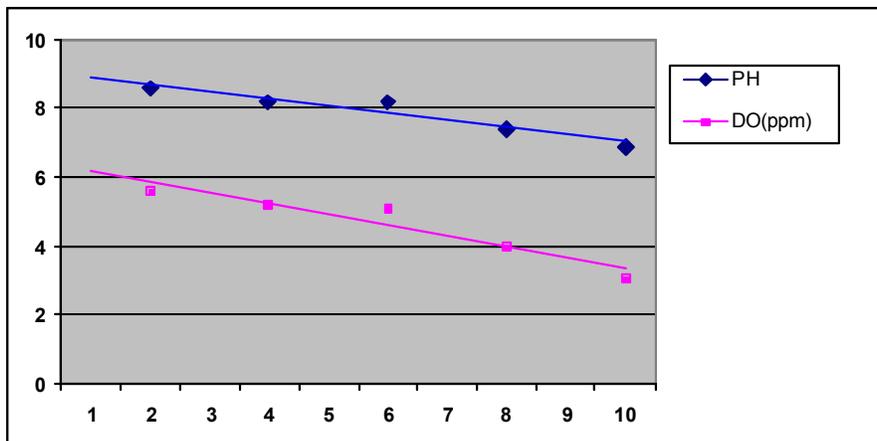


Fig. 3: Environmental Data pH and Dissolved oxygen in the study

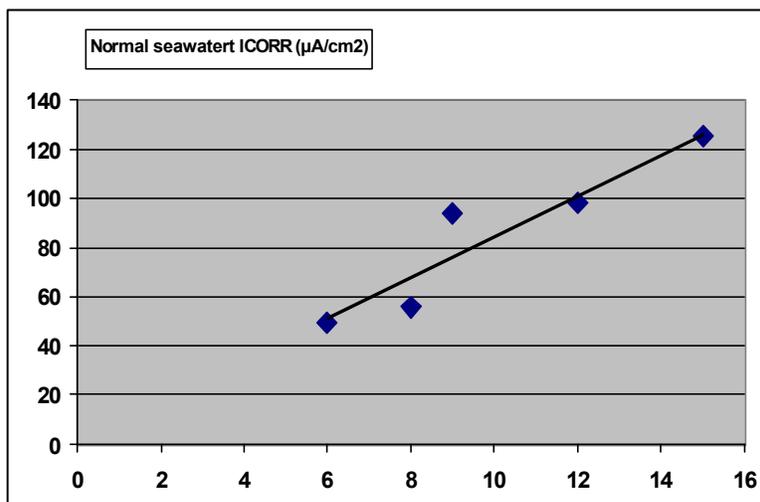


Fig. 4: Normal Seawater Icorr values $\mu\text{A}/\text{cm}^2$.

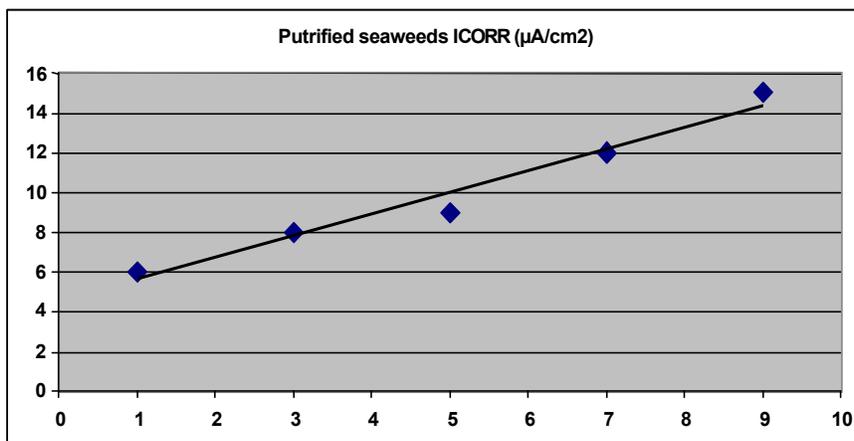


Fig. 5: Putrified Seawater Icorr values $\mu\text{A}/\text{cm}^2$.

Corrosion Rates of Mildsteel in Putrified Seaweeds by Polarizations Technique and Impedance Analysis:

The polarization studies and impedance analysis on mild steel in putrified system (Table 4). The potential were shifted from -700mV to -732 mV/SCE in putrid system. There is no much potential variation in control system. The electro chemical polarization study indicated that i_{corr} values were same in the putrified system and control system in the range of $5.0\mu\text{A}/\text{cm}^2$ to $15.4\mu\text{A}/\text{cm}^2$ during 75 days immersion period (Fig. 2). But the change transfer resistance values in putrified seaweeds system was slowly increased from 46 ohm. cm^2 to 232 ohm. cm^2 . But in the control system, vary less in the resistance values in the range 50 ohm. cm^2 to 124 ohm. cm^2 . The high resistance values observed in the putrified system in which the organic mater, varies nutrients present in the seaweeds (Fig. 4, 5).

CONCLUSION

Whatever may be the material immersed in the Ocean, sooner or later become colonized by microbes [54]. The first chemical event that takes place when solid surfaces submerged in the seawater is the accumulation of an organic ‘conditioning’ film making the surface wettable [55,56]. As a result, whether the resulting organic film in glycoprotein [59] or humic [59] in nature, its presence affects surface charge and surface wettability [58]. These properties no doubt play an important role in the subsequent attachments of bacterial to the conditioned surface [59]. Much work has been done on seawater corrosion by several groups; the details of the mechanism are still under debate for both buried soil and marine environment [60]. So we have to find out the influence of marine bacterial on mild steel surface at

Thondi seawater. During putrefication sulphide ions are released more in the putrid seaweeds. The sulphide film consists of two types one is pyrites and another one is margacite. The pyrite film actually increases the corrosion behavior of mild steel. But in margacite sulphide film to form a productive coating on mild steel. Due to the deposition of margacite film to reduce the corrosion rate of mild steel. In general, all heavy metals are inhibitory to growth, pigments, macromolecule content, nutrient uptake, ATP content, Photosynthesis and enzyme of nitrogen metabolism such as nitrogenous nitrate reeducates, glutamine synthetase, urease and alkaline phosphatase. The essential element such as Cu, Zn, Fe and Co have an important function in the micro algae. In this study we can observe less corrosion rate in the putrified seaweeds system, because of the carbohydrate, protein and minerals which are present in the seaweeds. After putrefication these elements attached on the iron oxide film and form a productive coating.

- The heretrotrophic bacteria colonies were very high in the putrified seaweed system.
- The less corrosion rate due to the presence of protein carbohydrates, enzymes, lipids and other organic nutrients which are present in *Ulva*, *Gracillaria* and *Hyphea*.
- Less weight loss reducing corrosion current and increasing resistance has been observed in the putrified seaweed system.
- The margacite sulphide film to form a productive coatings on mild steel during putrefication

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