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Anti-Biocorrosive and Biocidal Efficacy of Hydroxyquinoline Derivative as Seawater Corrosion Inhibitor

Shek Dhavud S.¹, Menaha Devi A.², Raja T.³ and Syed Abuthahir S.S.^{3*}

¹PG and Research Department of Physics, Jamal Mohamed College (Autonomous), Affiliated to Bharathidasan University, Tiruchirappalli 620 020, Tamil Nadu, India

²PG Department of Chemistry, Arulmigu Palaniandavar Arts College For Women, Chinnakalayam Puthur, Palani 624615, Affiliated to Mother Teresa Women's University, Kodaikanal 624 101, Tamil Nadu, India

³PG and Research Department of Chemistry, Jamal Mohamed College (Autonomous), Affiliated to Bharathidasan University, Tiruchirappalli 620 020, Tamil Nadu, India

*Corresponding Author

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Abstract: We employed the weight-loss method to assess carbon steel's corrosion resistance in salt water with hydroxyl quinoline derivative (HQD). This system reaches 85.70% inhibitory efficacy. Potentiodynamic polarisation and electrochemical impedance spectroscopy have been used to study corrosion inhibition (EIS). According to various research, increasing inhibitor concentration improves inhibition effectiveness and corrosion rates. Metal surface chemistry has extract components. Potentiodynamic polarisation shows that the inhibitor system regulates anodic and cathodic activities as a mixed inhibitor. Inhibitors increase linear polarisation resistance and decrease corrosion current. Electrochemical impedance shows that the inhibitor system increases charge transfer resistance and decreases double layer capacitance, forming a protective covering (blanket effect) on the metal surface. Electrochemical studies described a comparable circuit. SEM examined the film's surface morphology. A comparison of carbon, blank, and inhibitor steel surface morphologies was done. This study might assist acid-pickling.

Keywords: Corrosion inhibition, Surface morphology, EIS, Carbon steel, Hydroxyquinoline derivative

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Introduction

Corrosion is a major issue in the United States. Metals and alloys may corrode when they react chemically or electrochemically with their surroundings, causing their disintegration (Angst,

2018). The vital activity of different micro-organisms utilising a metal as a culture medium or developing products which the metal causes biochemical corrosion or biocorrosion.

Biochemical deterioration advances in soils of a given composition, stagnant waterways, and certain organic compounds. Corrosion is different for every metal and may be mild or severe, depending on the conditions. Organic inhibitors are useful for little quantity of corrosive medium. In the event of substantial quantity of corrosive environment, metals may be protected by surface coatings (Abdel-Karim and El-Shamy, 2022). According to the findings of certain investigators, plant materials have been used to manage the corrosion. Nontoxic plant resources are abundant in organic chemicals, inexpensive and readily accessible (Zakeri *et al.*, 2022). Researchers are presently focusing on the need to produce inexpensive, non-toxic, and environmentally acceptable inhibitors (Obot *et al.*, 2014) due to the well-known cost impact of most synthetic organic inhibitors and rigorous environmental restrictions. Synthetic organic compounds are a renewable, low-cost, easily accessible, environmentally benign, and socially acceptable material source (Rajendran *et al.*, 2009). This study uses the mass loss technique to examine the impact of a hydroxyquinoline derivative on carbon steel corrosion in saltwater; to examine how additives such as an aqueous inhibitor affect carbon steel corrosion resistance in salt water; and to study corrosion inhibition using electrochemical methods including polarisation analysis and electrochemical impedance spectroscopy. Electrochemical tests provide a system circuit diagram. SEM can study metal's protective layer (SEM). in corrosive conditions. Examined the inhibitors' biocidal efficacy in corrosive environments.

Materials and Methods

Preparation of the carbon steel specimens:

The carbon steel specimens were chosen from the same sheet of the following composition: The carbon steel specimens compositions are Carbon - 2.0 %, Sulphur - 0.026 %, Phosphorus - 0.06 %, Nickel - 0.2%, Manganese - 0.4 % and the balance iron (Madhubala and Santhi, 2019).

As working electrodes for potentiodynamic polarisation research, specimens of carbon steel that had been encased in Teflon and had an exposed cross section of one centimetre square were employed. Following the application of trichloroethylene degreaser, the surface of the electrode was polished to a mirror sheen. It was decided to go with the medium sea water solution.

Preparation of stock solutions:

In order to make the inhibitor stock solution with the needed concentration, the inhibitor was dissolved in the smallest possible quantity of ethanol, and then the solution was brought up to the desired level with double-distilled water. To attain the appropriate concentration, the inhibitor stock solution was added to the sodium chloride solution. All experiments dissolved the inhibitor in the same amount of ethanol.

Mass loss method:

The inhibition efficiencies were calculated from the relation.

$$IE = \frac{CR_1 - CR_2}{CR_1} \times 100 \% \quad (1)$$

Where CR_1 is corrosion rate in the absence of inhibitor and CR_2 is the corrosion rate in the presence of inhibitor.

Carbon steel samples were submerged in a static solution at room temperature for 24 h, both without and with an inhibitor. Next, the samples were taken out, cleaned, and stored in desiccators. These samples are weighed both prior to and after being submerged in the corrosive solution. The percentage of weight loss was determined by comparing pre- and post-immersion weights.

Electrochemical study:

During the course of this study, polarisation was used to evaluate the resistance to corrosion shown by carbon steel that had been subjected to a variety of test solutions. The electrochemical experiments were carried out with the assistance of a CHI 660 A electrochemical work station.

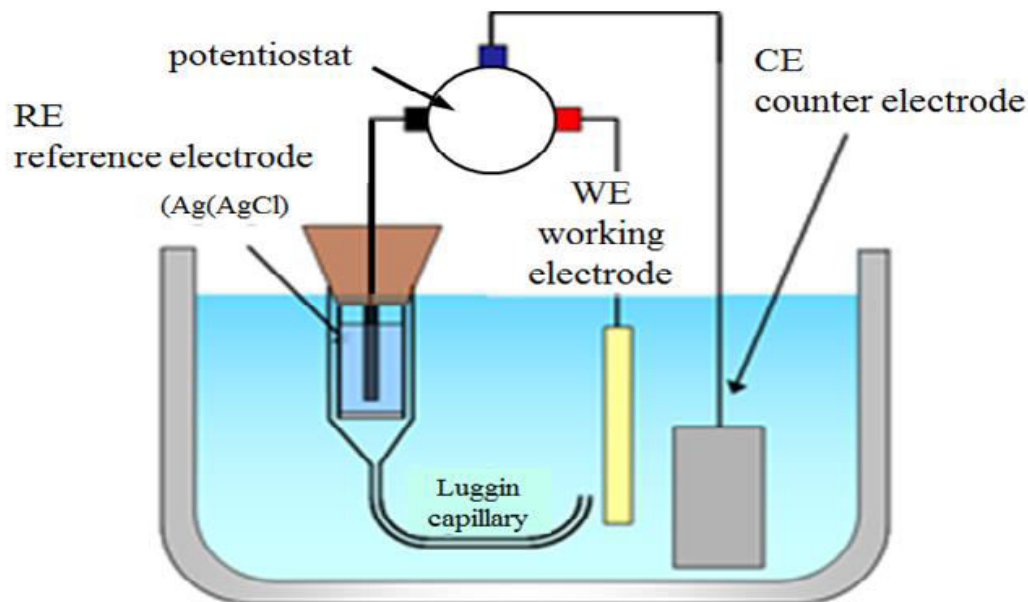


Fig. 1: Three - electrode cell assembly.

Polarization study:

In a cell assembly consisting of three electrodes, polarisation tests were performed (Fig. 1). A SCE was used as the reference electrode in this experiment. Platinum served as the counter electrode in this experiment. The working electrode was composed of carbon steel. Corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic = ba and cathodic = bc , and LPR (linear polarisation resistance) values were measured as a result of the polarisation research.

AC Impedance spectra:

The polarisation research was likewise conducted using the same equipment and in the same configuration as the AC impedance spectrum recording. The time range of 5 to 10 min was specified as the amount of time needed for the system to reach a steady state open circuit model. At a number of different frequencies, the real component of the cell impedance, denoted by Z' , and the imaginary component, denoted by $-Z''$, were both measured in ohms. The starting $E(V)$

was set to zero, the high frequency range was 1–105 Hz, the low frequency was 1 Hz, the amplitude (V) was set to 0.005 and the silent time (s) was set to 2. The values of charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were estimated based on the Nyquist plot (Mirinioui *et al.*, 2021).

Scanning electron microscopy (SEM):

One day after being immersed in various test solutions, carbon steel specimens were withdrawn, washed with double-distilled water, dried, and then submitted for surface examination (Rajendran *et al.*, 2009). The surface morphology of the carbon steel was analysed using scanning electron microscopy (SEM) of the Cartizers make type EVO-18.

Determination of biocidal efficiency of the system:

Standard plate counts are performed to determine the total number of bacterial cells in a sample. Here are the rules and regulations that must be followed. At the bottom of each plate, write "10-2," "10-4," "10-6," and "10-8," with one plate serving as a blank or control (Wang *et al.*,

2022). Add 1 ml from each of four separate cultures to 99 ml of sterile saline blank, using aseptic procedure throughout. 1 ml from the 10-2 test tube is transferred to the 99 ml sterile saline blank designated as 10-4, and so on, all the way up to the 10-8 blank. To ensure that the germs are distributed evenly across the test tubes, shake them all. Put 1 ml of the sample onto each of the plates labelled from 10-2 to 10-8, submerge the plates in the agar medium, and incubate them at 37°C for 24 h. After incubation, choose a plate with 30–300 colonies and tally them up.

The number of CFU are calculated as--

$$\text{CFUs/dilution} \times \text{amount plated} = \text{No. of bacterial cell/ml.}$$

Results and Discussion

Analysis of mass loss method:

Before and after carbon steel was submerged in saltwater, the mass loss method was used to assess the level of corrosion inhibition achieved as well as the rates at which it was achieved. Table 1 depicts the mass loss approach to display both the inhibition efficiency (IE) and corrosion rates (CR) of carbon steel when it is submerged in sea water with or without a hydroxyquinoline derivative inhibitor. Both of these values can be found in Table 2. At a concentration of 250 ppm, the hydroxyquinoline derivative has an inhibitive activity that is 85.70 per cent. A larger concentration of the additive will result in increased resistance to corrosion. By increasing the amount of surface covering, increased amounts of inhibitor chemicals slow down the degradation of carbon steel. It is possible that the inhibitory effectiveness will improve if the hetero atoms of the hydroxyquinoline derivative combine forces with the surface metal ions of the carbon steel. Inhibitor extracts may include heteroatoms, which prevent carbon steel from corroding (Mofidabadi *et al.*, 2021).

Electrochemical studies:

Polarisation studies and AC impedance spectra have been employed in corrosion inhibition research. Corrosion resistance increases due to

the blanket effect of deposited inhibitor molecules on metal surfaces: LPR increases as corrosion current (I_{corr}) decreases. Charge transfer resistance increases impedance and phase angle but decreases double layer capacitance.

Analysis of results of potentiodynamic polarization study:

The development of a barrier coating on the carbon surface has been investigated using polarisation techniques. Carbon steel in sea water with an inhibitor is illustrated in the figure along with its potentiodynamic polarisation curves. It took 30 min of having the electrodes submerged in the test fluids to obtain the steady state potential.

Table 3 provides information on the corrosion characteristics known as corrosion potential (E_{corr}), Tafel slopes (b_c and b_a), linear polarisation resistance (LPR), and corrosion current (I_{corr}). It is shown in Figure 2a that the corrosion potential of carbon steel in sea water is -728 mV Vs SCE. This information is based on measurements taken (Saturated Calomel Electrode). There is a value of 670 Ohm/cm² for the LPR. The current due to corrosion is 7.012 times 10⁻⁶ A per cm².

When the corrosive environment described above is treated with an additive at a concentration of 250 ppm, the potential for corrosion is shifted to the less aggressive side (-740 mV / SCE) (Fig. 2b). To put it another way, a protective layer will grow on the surface of the carbon steel, changing the potential for corrosion to a side that is less anodic and more cathodic. This film governs the anodic and cathodic processes of carbon steel dissolving. It does this by forming Fe²⁺-HQ complex on the noble sites that are found on the surface of the carbon steel. This inhibitor acts as a mixed type inhibitor since the corrosion potential shift that it causes is less than the shift that occurs when the blank value is used. Readings that reveal a rising LPR and a lowering I_{corr} may be an indication of an

Table 1: Inhibition efficiency of aqueous leaves extract of *Carissa carandas* Linn on the corrosion of carbon steel in 1 N HCl

Concentration of inhibitor (ppm)	Corrosion rate (mdd)	Inhibition Efficiency (%)
blank	218.40	-
50	164.80	42.56
100	98.25	54.36
150	74.39	62.56
200	48.58	77.28
250	15.26	85.70

Table 2: Potentiodynamic Polarization parameters for the corrosion of carbon steel in sea water for the aqueous extract of hydroxyquinoline derivative system

Concentration of the aqueous extract of inhibitor (ppm)	E_{corr} mV/SCE	Tafel slope		I_{corr} A / cm ²	LPR Ω /cm ²
		ba, mV/dec	bc, mV/dec		
blank	- 728	214	145	7.012×10^{-6}	670
250	- 740	175	169	5.598×10^{-6}	780

Table 3: Electrochemical impedance parameters from Nyquist plots for the corrosion of carbon steel submerged in sea water in the absence and presence of inhibitor

Concentration of the aqueous extract of inhibitor (ppm)	Nyquist plot		Impedance Log (z/ohm)	Phase angle (degree)
	R_t , Ω /cm ²	C_{dl} F/cm ²		
blank	220.12	2.5214×10^{-4}	0.608	32.9
250	226.12	2.4978×10^{-4}	0.659	34.4

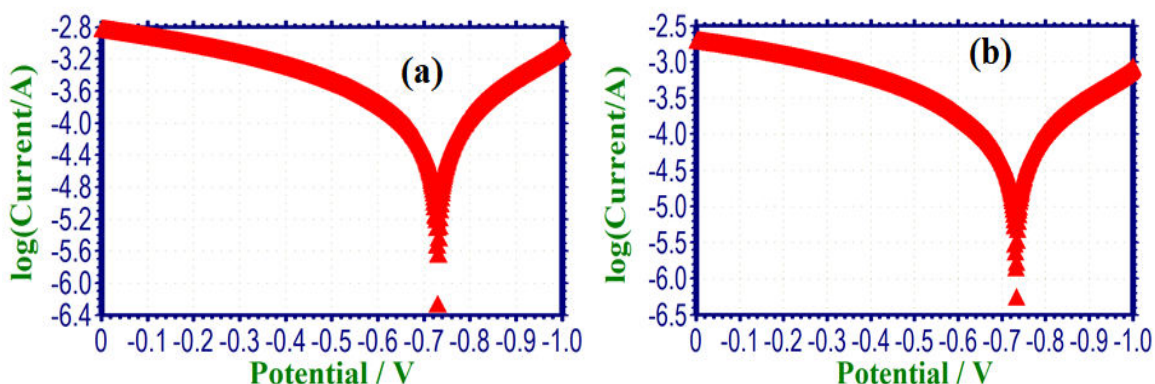


Fig. 2: Potentiodynamic polarization curves for corrosion of carbon steel in sea water in absence and presence of inhibitor. (a) Carbon steel in sea water (blank); (b) Carbon steel in sea water with 10% aqueous extract of inhibitor.

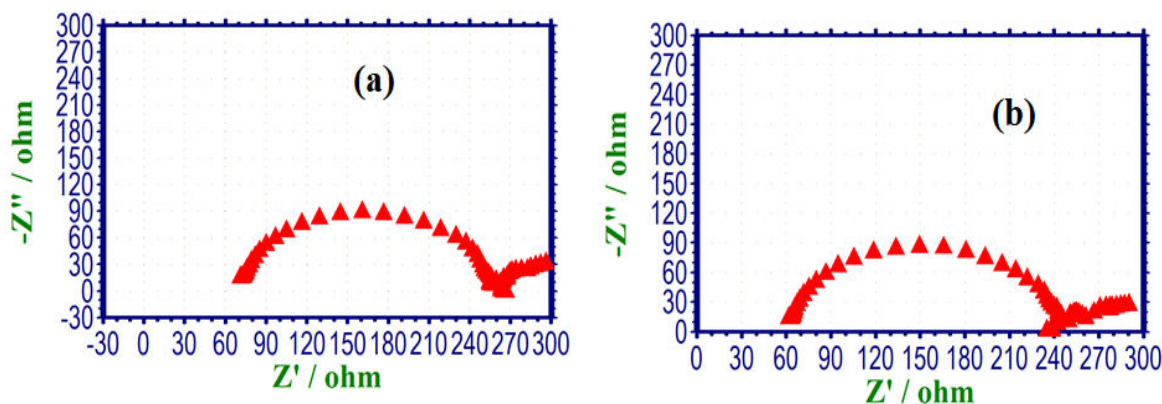


Fig. 3: AC impedance spectra for corrosion of carbon steel in sea water in absence and presence of inhibitor (Nyquist plots). (a) Carbon steel in sea water (blank); (b) Carbon steel in sea water with 10% inhibitor.

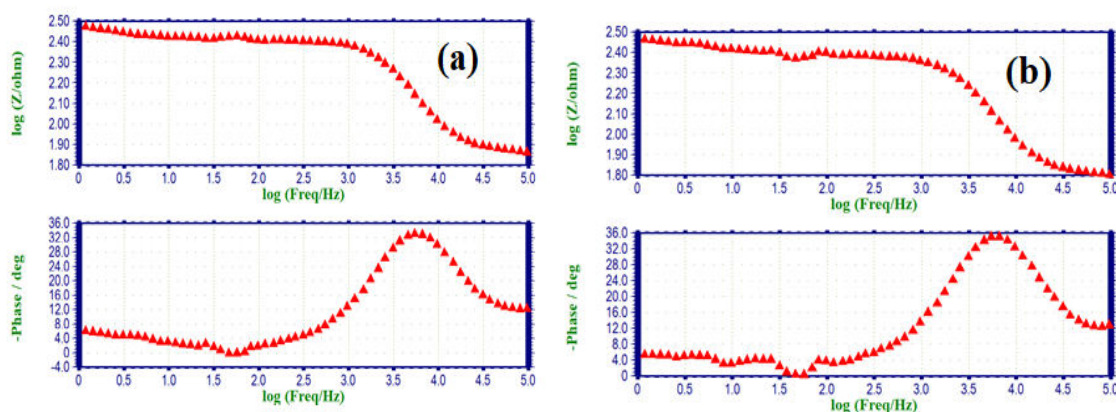


Fig. 4: AC impedance spectra for corrosion of carbon steel in sea water in absence and presence of inhibitor (Bode plots). (a) Carbon steel in sea water (blank); (b) Carbon steel in sea water with 10% inhibitor.

enhanced inhibitor system's ability to resist corrosion (Nagalakshmi *et al.*, 2014; Nagalakshmi *et al.*, 2017).

Results of alternating current impedance spectra:

Observations of electrochemical impedance spectra revealed the formation of a protective layer on carbon steel. Carbon steel that has been shielded has a greater charge transfer resistance, a lower double layer capacitance (C_{dl}), and a higher impedance $\log(z/\text{ohm})$ (R_t). The AC impedance spectra of carbon steel that has been immersed in saltwater are shown in Figures 3 (Nyquist plots) and 4 (Bode plots) (Karthikeyan *et al.*, 2021).

The alternating current impedance spectra of carbon steel dipped in various test solutions were recorded. The AC impedance parameters, namely, charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in Table 3. When carbon steel is engrossed in sea water, R_t value is 220.12 ohm cm^2 and C_{dl} value is $2.5214 \times 10^{-4} \text{ F cm}^{-2}$. R_t value increases from 220.12 to 226.12 ohm cm^2 when 250 ppm of is added to sea water blank system. The C_{dl} value also decreases from 2.5214×10^{-4} to $2.4978 \times 10^{-4} \text{ F cm}^{-2}$. The impedance value ($\log(z/\text{ohm})$) increases from 0.608 to 0.659 . Furthermore, the phase angle of inhibitor system increases from 32.9° to 34.4° when compare to the blank system. This suggests

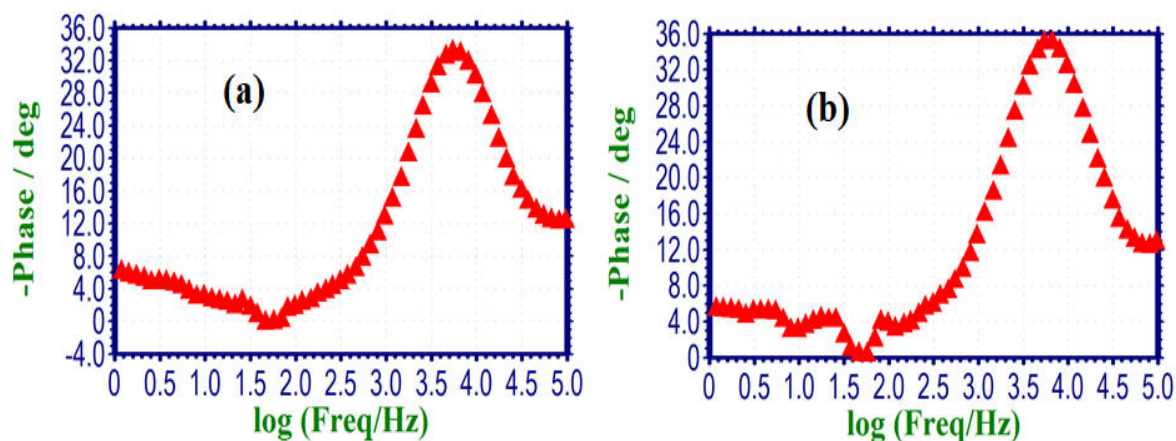
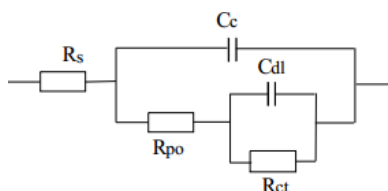


Fig. 5: AC impedance spectra for corrosion of carbon steel in sea water in absence and presence of inhibitor (Phase angle). (a) Carbon steel in sea water (blank); (b) Carbon steel in sea water with 10% inhibitor.

that a defensive layer is formed on the surface of the carbon steel surface. This points to the formation of a protective layer on the surface of the carbon steel surface. Figure 5 demonstrates that when carbon steel was submerged in sea water, two semicircles could be seen developing on the surface of the steel. This is typical of a protective layer that has been produced but has since been broken. The presence of corrosive ions in the sea water, such as chloride, sulphate, and fluoride, led to the shattering of the film. These ions are found in the sea water. The schematic representation of an analogous circuit for such a system is provided in Scheme I.



Scheme 1: Equivalent circuit for a failed coating.
 C_c - The capacitance of the intact coating, R_{po} - pore resistance, R_{ct} - charge transfer resistance, R_s - solution resistance, C_{dl} - double layer capacitance

Two of the semicircles disappeared when the carbon steel was soaked in saline water, but one of them was left in its place. This is a characteristic of a process that has diffusion as

one of its controlling factors. That carbon steel submerged in salt water developed a porous inhibitive layer is now beyond reasonable doubt. As a result of this coating, the carbon steel was protected against rust. This suggests that a higher inhibitor concentration in sea water will decrease the porosity of the inhibitor film, among other implications. This control method, known as diffusing control, is compatible with the properties of the resulting curve. This suggests that the inhibitor (HQD) began diffusing constantly in the pores of the film and on the damaged region of the inhibitor film after the salt water solution was added (Subbiah *et al.*, 2021).

Surface examination of carbon steel by SEM:

Carbon steel is soaked in inhibitor-treated salt water for 24 h. SEM analysis follows after the material is removed, dried, and examined. Figure 6a (control) shows clean, freshly cut carbon steel with no corrosion inhibitor. Figure 6b shows salt water corroding carbon steel's surface. Empty diagrams demonstrate this procedure. A heavily corroded area has a rough carbon steel surface. Figure 6c shows saltwater-inhibited carbon steel. We are monitoring this process. The smaller damaged zones show that an inhibitor (250 ppm) slows corrosion.

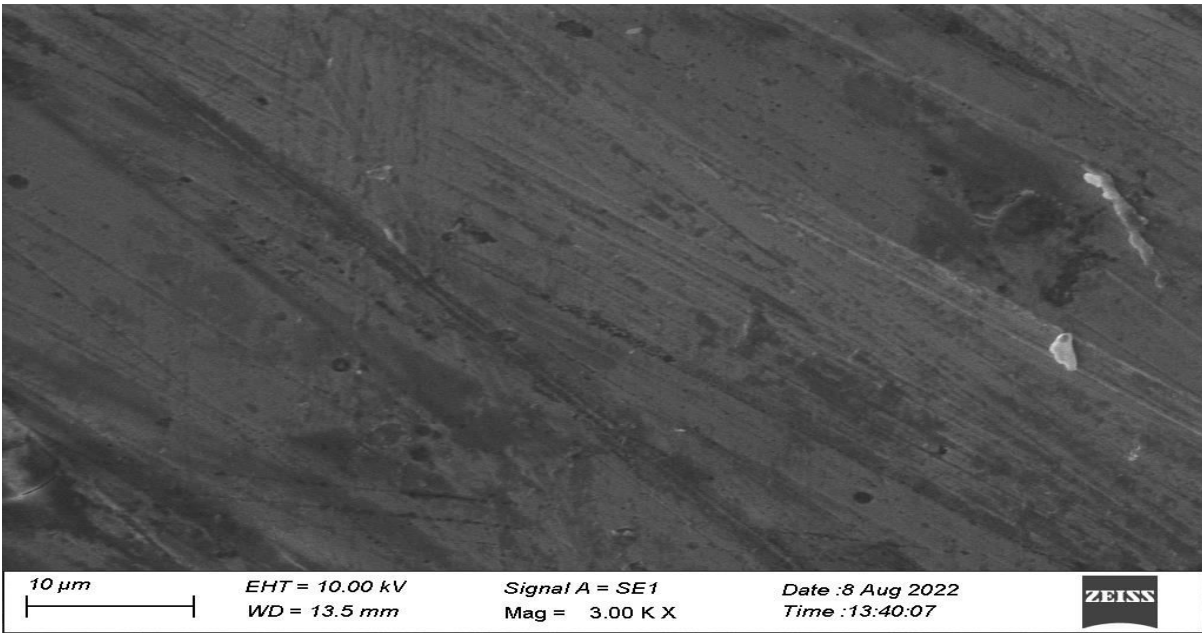


Fig. 6a: SEM image of polished carbon steel specimen before immersion in sea water (control).

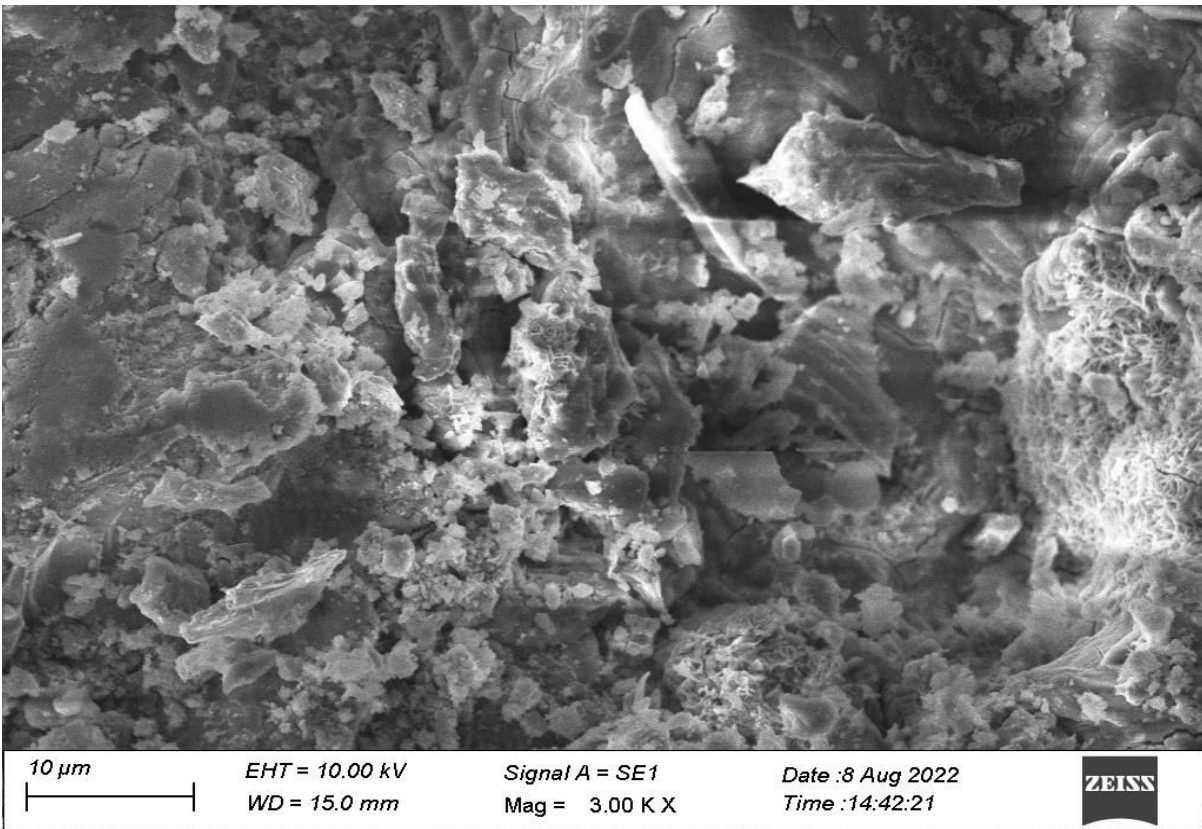


Fig. 6b: SEM image of polished carbon steel specimen after immersion in sea water (blank)

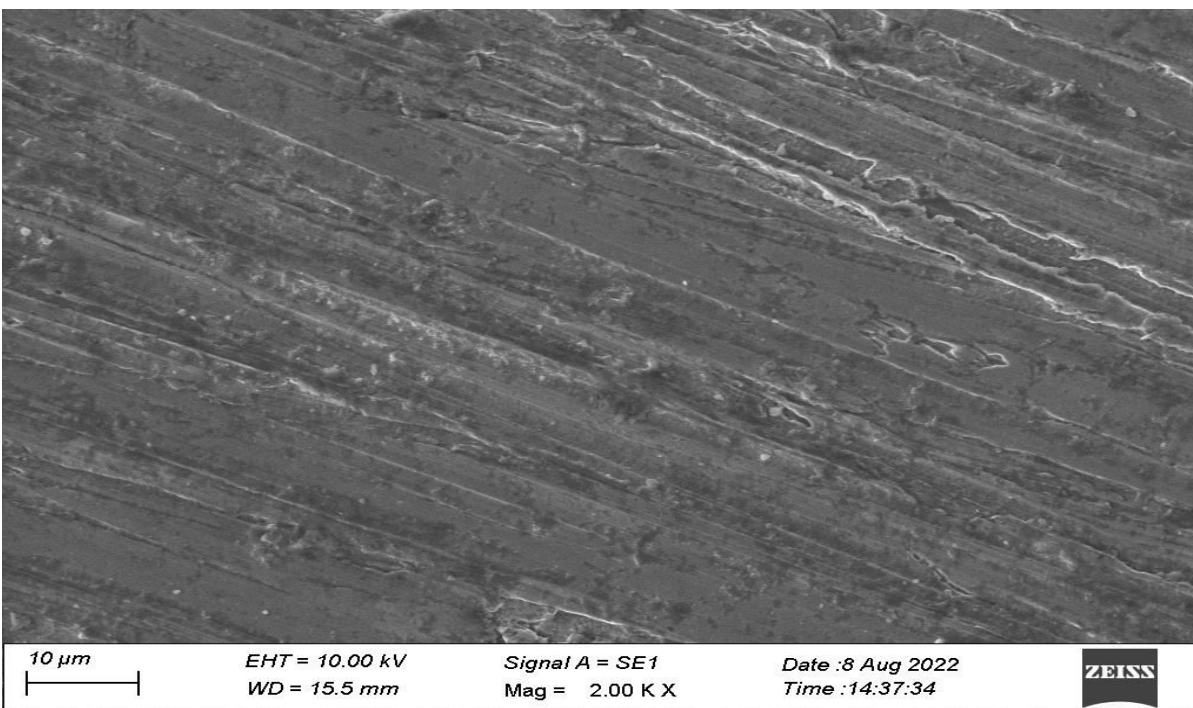


Fig. 6c: SEM image of polished carbon steel specimen after immersion in sea water in the presence of 250 ppm of aqueous extract of additive.

Table 4: Colonies forming unit (CFU) of carbon steel in an aqueous solution containing sea water in the absence and presence of HQD inhibitor obtained by bacterial enumeration count method

Systems	Colony Forming Unit (per ml)			
	<i>E. coli</i>	<i>Streptococcus</i>	<i>Pseudomonas</i>	<i>Entrobacter</i>
Sea water	150×10^7	156×10^7	140×10^7	137×10^7
Sea water + 250 ppm HQD inhibitor	78×10^7	80×10^7	66×10^7	64×10^7
Biocidal activity (%)	48.00	50.66	52.85	53.28

Analysis of biocidal efficiency of the system:

Table 4 presents the findings of bacterial enumeration counts (Pandiarajan *et al.*, 2013) conducted on an aqueous solution that was composed of sea water and HQD inhibitor. A variety of test solutions were left in contact with samples of carbon steel for a whole day. This process took up one whole day. A count of the amount of bacteria that were living in the test solutions was performed after a waiting time of 24 h. The bacterial count increases to a greater level when pathogenic bacteria like *Escherichia coli*, *Streptococcus*, *Pseudomonas*, and *Entobacter* are permitted to proliferate in an aqueous

solution consisting of sea water without the presence of an inhibitor. This results in a higher level of bacterial contamination. An inhibitor, when mixed with seawater, prevents the development of pathogenic bacteria such as *Escherichia coli*, *Streptococcus*, *Pseudomonas*, and *Entobacter*. The corrosive medium was improved by the addition of HQD inhibitor, which was ultimately responsible for the positive outcome of the experiment.

Conclusion

The mass-loss method employs a system of corrosion inhibitors made of carbon steel that utilises sea water with 250 ppm HQD. As much as

85.70 per cent of its potential is blocked by this mechanism. The molecules of the HQD extract inhibitor adsorb on the surface of the carbon steel, increasing the efficacy of the inhibition and decreasing the corrosion. Resistance to linear polarisation is increased by inhibitors, while corrosion current is decreased. Research into the electrochemical impedance of carbon steel shows that it produces a protective "blanket effect" covering on its surface. The double layer capacitance is decreased and the charge transfer resistance is increased by inhibitors. The formulation acts as a mixed-type inhibitor that controls both anodic and cathodic processes through potentiodynamic polarisation. SEM analysis of corrosion and surface layer on carbon steel with and without aqueous extract of HQD (SEM). Components on polished carbon steel before and after being treated with the inhibitor solution were characterised using SEM. Experiments were conducted on HQD inhibitory systems and biocidal carbon steel surfaces.

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