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Abstract: In the present study undergoes the corrosion behavior of benzoin oxime against corrosion of mild steel in sea water was studied using a weight loss approach. To evaluate the effectiveness of the benzoin oxime as a corrosion in terms of corrosion rates and inhibition efficiency by weight loss method. This was done in order to determine how an inhibitor adsorbs the deterioration of mild steel dished in sea water. The mechanistic aspect of corrosion inhibition has been studied by electrochemical studies, such as potentiodynamic polarization studies and alternating current impedance spectra. Potentiodynamic polarization technique reveals that the inhibitor system functions as a mixed type of inhibitor, controlling anodic and cathodic reactions. It is noted that in presence of inhibitor, linear polarization resistance value increases, and corrosion current decreases. Electrochemical impedance studies reveal that a protective film (blanket effect) is formed on the metal surface, since in the presence of inhibitor system the charge transfer resistance value increases and double layer capacitance value decreases. This is due to adsorption of the molecules of the active ingredients of the extract on the metal surface. The protective film formed over the mild steel surface has been characterized by FTIR. The smoothness of protective film has been analyzed by SEM.

Keywords: Corrosion, FTIR, Inhibitor, mild steel, Sea water and SEM.

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INTRODUCTION

Corrosion is a natural process that converts a refined metal into a more chemically stable oxide. It is the gradual destruction of materials (usually a metal) by chemical or electrochemical reaction with their environment. Corrosion engineering is the field dedicated to controlling and preventing corrosion. The study of corrosion inhibition using inhibitor in sea water is one of the most stimulating areas in the present research, due to its potential applications in industries such as acid pickling, industrial cleaning and acid descaling processes. Mild steel is one of the metals that is used the most often in construction, food processing, power generation, chemical production, and other industrial applications. This is due to the fact that mild steel may be used in a wide variety of contexts. [1 -3] Organic inhibitors have been proven to be among the most effective anti-corrosion remedies by researchers and engineers [4]. Organic inhibitors attach themselves to the surface of the metal and create a protective coating. This coating prevents oxygen and water from accessing the metal, which would otherwise lead to corrosion. The presence of p-electrons in aromatic rings and heteroatoms (N, S, O, and P) in the molecular structure of organic inhibitors is responsible for their adsorption and film-forming

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capabilities [5-7]. Corrosion inhibitor for mild steel in sea water: computational and electrochemical experiments [8,9] by Abdelshafeek et al. found that Vicia faba peel extracts containing fatty acids moieties were both cost-effective and ecologically benign. Atan et al. looked examined the usefulness of moringa leaf extract (Moringa Oleifera) as a green material [10] when it comes to reducing corrosion in carbon steel. The efficiency of a polyaspartic acid derivative composite in preventing the corrosion of carbon steel in the presence of saltwater was examined by Gao et al.[11] using a polyaspartic acid derivative composite. In a sodium chloride solution, Mohamed Kasim Sheit and his colleagues tested the anticorrosion characteristics of mild steel. [12] Researchers used a compound known as 5-acetyl-3-phenyl-2, 6-dipyridin-2yltetrahydropyrimidin-4(1H)-1 as an inhibitor. Using a thiophenol derivative inhibitor, researchers under the direction of Raja T. et al. [13] examined the electrochemical behaviour of carbon steel while submerged in a sodium chloride solution. In an experiment using simulated seawater, Bokati, K. S., et al. [14] investigated the effects of 1H-benzotriazole, sodium molybdate, and sodium phosphate on the corrosion of copper, mild steel, and copper-mild steel that had been galvanically linked. In order to determine the synergistic effect that Mangifera indica leaf extract and zinc ions have on preventing the corrosion of mild steel in simulated saltwater, Ramezanzadeh, M., et al. undertook a computational and electrochemical investigation [15]. The concept of determining the multiplicative qualities of the inhibitor is now the notion that is leading the pack. Infrared, scanning electron microscopy, electron dispersive X-ray, and atomic force microscopy were all used in the course of the research that was conducted on a specific amino benzoic acid multipart that controls the rate of zinc metal deterioration when it is submerged in seawater [16,17]. In this particular line of investigation, we made use of the mass defeat approach, electrochemical analyses, and AC impedance spectra. The objective of the present study is to investigate inhibition of corrosion of mild steel in sea water using benzoxime as corrosion inhibitor by mass loss method. And also aims to study the mechanistic aspects of corrosion inhibition by electrochemical studies such as potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS). The surface film formed over the carbon steel surface has been characterized by FTIR and SEM.

Experimental Procedure

Preparation of the mild steel specimens

The mild steel sample has the following chemical composition: 0.1% carbon, 0.026% sulphur, 0.06 phosphorus, 0.4% manganese, and the rest iron. The specimen, which measured 1 cm x 4 cm x 0.2 cm, was polished to a mirror-like finish. Before using mild steel in the weight-loss process, oil must be removed from it with acetone. Working electrodes for potentiostatic polarization experiments were mild steel samples that had been covered in Teflon. 1 square cm made up the exposed cross section. The electrode was polished to a mirror sheen, then the oil was removed from the surface using ethanol. [18,19].

Preparation of Stock Solution

At each and every location where it was required, stock solutions were prepared using sea water. Before being added to the quantity of seawater of choice, benzoxime was first dissolved in an insignificant amount of ethanol in order to make available the prerequisite concentration for the stock solution. Afterwards, the desired concentration of inhibitor stock solution had been added to the seawater solution.

Weight losss Approach

The method of mass loss was carried out in a manner that was compliant with the protocol. On the first day of the weight loss procedures, specimens of mild steel were submerged in different concentrations of seawater and benoxime for a period of one day (50 ppm -250 ppm). After being confined for a period of twenty-four hours, the subject of the test is released, subjected to a series of drenching's with water, dried off, and then weighed [20,21]. The following equation (1) is used at this point in order to estimate how effective the inhibition will be:

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IE
$$(\%) = \frac{W_0 - W_1}{W_0} X100$$
 (1)

Where,

W₁ is the rate of corrosion when there is no inhibitor. and

 W_2 is the corrosion rate when the inhibitor is present.

During 24 hours, duplicate mild steel specimens were immersed in 100 ml of sea water with varying doses of the benoxime inhibitor. The samples were removed from the water after 24 hours, cleaned with running water, dried, and weighed. The following equation (2) was used to determine corrosion rates from observations of weight changes in the specimens:

Corrosion rate = $\frac{87.6 \text{ x Loss in weight (mg)}}{\text{Surface area of the specimen (dm²)x}} \mu m / y$ (2)

Period of immersion (Hr) × Density

Electrochemical study

In the present work corrosion inhibition of carbon steel immersed in various test solutions were measured by polarization study. Electrochemical measurements were performed in a CHI- electrochemical work station with impedance model 660A.

Polarization study

Polarization studies were carried out in a three - electrode cell assembly (Figure 1). A SCE was the reference electrode. Platinum was the counter electrode. Mild steel was the working electrode. From polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic = b_a , and cathodic = b_c and LPR (linear polarisation resistance) values were measured [22].



Figure 1: Three - electrode cell assembly

AC Impedance spectra

The same instrument and set-up used for polarization study was used to record AC impedance spectra also. A time interval of 5 to 10 min was given for the system to attain a steady state open circuit model. The real part (Z') and imaginary part (-Z'') of the cell impedance were measured in ohms at various frequencies. AC impedance spectra were recorded with initial E (V) = 0, high frequency (1-10⁵ Hz), low frequency (1 Hz),

amplitude (V) = 0.005 and quiet time (s) = 2. From Nyquist plot the values of charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) values were calculated [23].

FTIR spectral analysis

Perkin Elmer FTIR spectrophotometer was used to record the FTIR spectrum from 400 to 4000 cm⁻¹. The adsorbed plant leaves extract inhibitor on mild steel surface have been analyzed by FTIR spectra. After, protective film was scratched from the carbon steel surface, which was immersed in sea water in the presence of the studied inhibitor for 24 hours at room temperature [24].

Scanning electron microscopy (SEM)

The carbon steel specimens immersed in various test solutions for 3 hours were taken out, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements of the carbon steel surface were carried out by scanning electron microscopy (SEM) using SEM instrument, JEOL MODEL JSM 6390 [25].

RESULTS AND DISCUSSION

Analysis of the weight loss technique

The corrosion rates (CR) and inhibition efficiencies (IE) of mild steel is immersed in an aqueous solution containing sea water in the absence and presence of benzoin oxime inhibitor was obtained by weight loss method and values are given in table V.1.It is observed that 85.51% of inhibition efficiency. It is observed from table 1 that benzoin oxime shows good inhibition efficiency. As the concentration of inhibitor increases, the IE increases. This is due to increase of surface coverage at higher concentration of benzoin oxime which retards dissolution of mild steel this surveillance is in good agreement with the result reported by many researches [26,27].

Table 1: Corrosion rates (CR) of mild steel immersed in sea water solution in the presence and absence of benzoin oxime systems at various concentration and the inhibition efficiency (IE %) obtained by weight loss method.

Inhibitor system; benzoin oxime (250 ppm)
 Immersion period: 1 day

Blank	benzoin oxime (ml)	CR (mdd)	IE (%)
An aqueous solution containing sea water	0	79.66	
	2	64.99	29.50
	4	45.33	48.20
	6	34.66	64.20
	8	27.33	76.10
	10	9.99	85.51

Analysis of the potentiodynamic polarization study

The potentiodynamic polarization curves of mild steel immersed in an aqueous solution containing sea water and 10 ml of benzoin oxime are shown in figure 2 (a & b). The corrosion parameters are given in Table 2. When mild steel was immersed in an aqueous solution containing sea water in the corrosion potential was -729 mV vs SCE. When benzoin oxime (250 ppm) was added to the above system, the corrosion potential shifted to the positive side -731 mV vs SCE. This indicates that protective film is formed on the anodic and cathodic sites of the mild steel surface. This film controls the anodic and cathodic reaction of mild steel dissolution by forming complex on the anodic sites of the mild steel surface [27,28]. The inhibitor is functioned as mixed type inhibitor.

Further, the LPR value increases from 675.0 ohm cm² to 777.7 ohm cm², the corrosion current decreases from $6.034 \times 10^{-6} \text{ A/cm}^2$ to $4.985 \times 10^{-6} \text{ A/cm}^2$. Thus polarization study confirms the formation of a protective film on the mild steel surface.

Table 2: Corrosion parameters of mild steel in an aqueous solution containing sea water in the absence
and presence of benzoin oxime system obtained by potentiodynamic polarization method.

					LPR
	E _{corr} vs	Icorr	ba	Bc	(ohmcm ²
Systems	SCE (mV)	(A/cm^2)	(mV/dec)	(mV/ec))
60 ppm of Cl ⁻					
solution	- 729	$6.034 imes 10^{-6}$	208	171	675.0
Sea water + 250					
ppm of benzoin					
oxime	- 731	$4.985 imes 10^{-6}$	179	189	777.7



Figure 2: Polarization curves of mild steel immersed in test solutions

a. An Aqueous solution containing sea water (blank)



b. An Aqueous solution containing sea water + Benzoin oxime (250 ppm)

Analysis of AC impedance spectra

AC impedance studies were conducted at a CHI- electrochemical work station utilising an impedance model 660A. The cell setup was typical for polarisation experiments. It was required that the system take between 5 and 10 minutes to achieve steady state, when an open circuit potential is present. On top of this resting potential, a 10 mV alternating current (AC) potential was applied. Alternating current (AC) frequencies between 100 kilohertz and 100 megahertz were used to determine the real and imaginary components of the cell's resistance, expressed as ohms. It was possible to calculate the double layer capacitance and the charge transfer resistance. In order to calculate C_{dl} values, the following equation (3) was used.

$$C_{dl} = \frac{1}{2 \times 3.14 \times R_{t} \times f_{max}}$$
(3)

The AC impedance spectra of mild steel immersed in an aqueous solution containing sea water in the absence and presence of Benzoin oxime are shown in figure .3 (a & b) (Nyquist plots) and figure 4 (a & b) (Bode plots). The AC impedance parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plots are given in Table V. 3. It is observed that when the be benzoin oxime (250 ppm) is added, the charge transfer resistance (R_t) increases from 223.10 Ω cm² to 228.69 Ω cm². The C_{dl} value decreases from 3.6215 × 10⁻⁵ F cm⁻² to 3.4896 × 10⁻⁶ F cm⁻². The impedance value [log (z/ohm)] increases from 0.609 to 0.657. Moreover, the phase angle increases 32.9° to 35.0°. These results lead to the conclusion that a protective film is formed on the mild steel surface [29,30].

 Table 3: Corrosion parameters of mild steel immersed in an aqueous solution containing sea water in the absence and presence of benzoin oxime system obtained from AC impedance spectra.

Concentration	Nyquist plot		Impedance Log (z/ohm)	Phase angle
of inhibitor	$R_t, \Omega/cm^2$	C _{dl} F/cm ²		(degree)
blank	223.10	3.6215×10^{-5}	0.609	3290
250 ppm	228.69	3.4896×10^{-6}	0.657	35.0



Figure 3: AC impedance spectra (Nyquist plots) of mild steel immersed in various test solutions



Figure 3: AC impedance spectra (Nyquist plots) of mild steel immersed in various test solutions

(b) An aqueous solution containing sea water⁻ + Benzoin oxime (250 ppm)



Figure. 4: AC impedance spectra (Bode plots) of mild steel immersed in various test solutions

(a) An aqueous solution containing sea water (blank)



Fig. 4: AC impedance spectra (Bode plots) of mild steel immersed in various test solutions

(b) An aqueous solution containing sea water + Benzoin oxime (250 ppm)

Analysis of FTIR spectra

FTIR spectra have been used to analyze the protective film formed on the mild steel surface [31]. The FTIR spectrum (KBr) of aqueous extract of benzoin oxime is shown in figure. 5 and the values are in the table 4. The structure of benzoin oxime is scheme I. The OH stretching frequency appears at 3435.05 cm⁻¹[32]. The C-H stretching frequency appears at 2956.20 cm⁻¹[33]. The peak due to C-C appears at 1165.88 cm⁻¹.



The FTIR spectrum (KBr) of the film formed on the mild steel surface after immersion in an aqueous solution containing sea water⁻ + 250 ppm of benzoin oxime is shown in figure. 5b and the values are in table 4. A shift of the O-H stretching from 3436.06 to 3391.93 cm⁻¹ indicates that the molecular adsorption possibly occurs via O-H [34]. The C-H stretching frequency is shifted from 2950.10 cm⁻¹ are noticed in the region of 2982.36 cm⁻¹. The peaks at 1482.74 cm⁻¹ is noticed for O-H bending group. The shift from 1014.78 to 1165.88 cm⁻¹ is

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noticed for C-C group. The peaks at 663.92 cm⁻¹ are attributed to CH oop. The band 588.20 cm⁻¹ considerably originate mainly from Fe-complex [35]. This observation suggests that hetero atoms of organic compounds has coordinated with Fe^{2+} through the oxygen atom and nitrogen resulting in the formation of Fe^{2+} -inhibitor complex on the mild steel surface. Thus the FTIR spectral study leads to the conclusion that the protective film consists of Fe^{2+} -inhibitor complex.

 Table. 4: IR spectra of pure benzoin oxime and film formed over the mild steel surface is obtained from IR Spectra.

IR bands of crude JS	IR bands of film from	Frequency assignment to
plant leaves extract mild steel surface		functional groups
3436.05	3391.93	-OH
2950.00	2982.36	С-Н
1383.65	1482.74	O-H bending
1014.78	1165.88	C-O stretching
650.64	663.92	CH "oop"
-	588.20	Y-Fe ₂ 0 ₃



Figure 5a. FTIR spectrum of aqueous extract of benzoin oxime



Figure 5b. FTIR spectrum of film formed on mild steel surface after immersion in an aqueous solution containing sea water + 250 ppm of benzoin oxime [37].

Analysis of Scanning Electron Microscopy

The SEM images of various surfaces are shown in figure 6. The SEM image of polished mild steel is shown in figure 6(a). The SEM image of polished mild steel immersed in sea water (corrosive medium) is shown in figure 6(b). The SEM image of the polished mild steel immersed in sea water (corrosive medium) and inhibitor system is shown in figure 6(c). The SEM image of polished mild steel is smooth. The SEM image of the mild steel in corrosive medium is found to be rough and the pits are visible on the mild steel surface. The SEM image of the mild steel in corrosive medium and inhibitor system is smooth due to the formation of protective film [38,39]. Thus SEM study is useful to know the smoothness of the protective film.



Figure - 6a: SEM image of polished mild steel coupon before immersion in sea water (control)



Figure - 6b: SEM image of mild steel coupon after immersion in sea water (blank)



Figure - 6c: SEM image of polished mild steel coupon after immersion in sea water in the presence of benzoxime inhibitor.

CONCLUSION

The use of the corrosion inhibitor benzoxime to avert the corrosion of mild steel submerged in sea water solution. Increase in inhibition efficiency and decrease in corrosion rate of MS in sea water medium was observed with the increase in concentration of inhibitor. The maximum inhibition efficiency of 85.51%

was achieved for 250 ppm of organic compound as corrosion inhibitor. Based on the findings from the weight-loss method, the polarisation research, AC impedance measurements, and surface examination methods including FTIR spectroscopy and Scanning Electron Microscopy, the mechanistic components of corrosion inhibition are provided. Potentiodynamic polarization study indicates, inhibitor is mixed type. The rate of corrosion decreases with increased addition of organic compounds, likely as a result of the benzoxime adsorption on the surface of mild steel. FTIR spectra show that the protective layer is composed of Fe²⁺-2-(benzylidene-amino)-benzenethiol complex, indicating that the inhibitor is adsorbed on mild steel surface. SEM micrographs reveal the mild steel's surface's smoothness, similar to polished mild steel. The outcome of the study may find application in processing cotton fabric, metal cleaning and processing, oxide coating, electroplating, electrolytic extraction and wherever aqueous solution containing chloride ions.

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