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Eco friendly extract of Banana peel as corrosion inhibitor for carbon steel in sea water

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ABSTRACT

An aqueous extract of Banana peel has been used as a corrosion inhibitor in controlling corrosion of carbon steel. The main constituent of this extract is bananadine [(3Z,7Z,10Z)-1-oxa-6-azacyclododeca-3,7,10-triene]. It has excellent inhibition efficiency (IE) of 98% at Zn^{2+} *(15 ppm) by the weight loss method. The protective film has been analyzed using Atomic Force Microscopic (AFM) and FTIR spectroscopic techniques. Protective film formed on the metal surface is confirmed by using Electro chemical studies such as potentiodynamic polarization and AC impedance techniques. Polarization study reveals that this system functions as mixed type of inhibitor.*

Key words: Carbon steel; Inhibition efficiency; Bananadine; Protective film.

INTRODUCTION

The need growing for the corrosion inhibitors becomes increasingly necessary to stop or delay the attack of a metal in an aggressive solution .Considerable efforts are made to find suitable compounds to be used as corrosion inhibitors in various corrosive media. Many works were conducted to examine extracts from naturally substances. Corrosion inhibition of carbon steel in low chloride media by an aqueous extract of Hibiscusrosa - sinensis Linn has been evaluated by mass – loss method and electrochemical studies [1] , corrosion inhibition by beet root extract in well water [2] , Electrochemical studies confirm the formation of a protective film on the metal surface by spirulina solution, this offers 90% corrosion inhibition efficiency [3] ,corrosion resistance of metals inartificial saliva in the absence and also in the presence of spirulina [4] , corrosion behavior of aluminium in various mediums has been used to control corrosion of aluminium . To prevent the corrosion of aluminium in acid medium, inhibitors such as Chlomolaena Odorata L. [5], Ananas Sativum [6], Ipomoea Invulcrata [7],

There are several reviews on the use of plant extracts as corrosion inhibitors [8].Recently aqueous extract of Cocos nucifera - Coconut Palm – Petiole [9]. Fennel (Foeniculum Vulgare) Essential Oil [10]. Pericarp of the Fruit of Garcinia Mangostana [11]. Natural Fenugreek [12]. Ethanol extract of Vernonia Amygdalina[13] Ipomoea involcrata [14]. Newbouldia leavis Leaf extract of the Corrosion of Aluminium in HCl and H_2SO_4 Solutions [15].

Emblica Officinalis (AMLA) leaves extract for copper and its alloy (CU-27ZN) [16] and Corrosion Inhibitive Properties of different plant extract[17] have been used as corrosion inhibitors.

Langmuir adsorption isotherm proved the effects of Alovera on corrosion of Zinc in HCl solution [18], in the presence of fruit peel in hydrochloric acid on carbon steel [19], and it also proved that Murraya Koenigii acts as corrosion inhibitor on mild steel in hydrochloric acid and sulphuric acid solutions [20], investigation of natural inhibitors is particularly interesting because they are non – expensive, ecologically friendly acceptable and possess no threat to the environment. The present work is undertaken

i) To evaluate the inhibition efficiency (IE) of an aqueous extract of Banana peel (BPE) in controlling the corrosion of carbon steel in sea water, in the absence and presence of Zn^{2+}
ii) To investigate the influence of immersion period on the IE of the system.
iii) To analyze the protective film formed on the carbon steel by FTIR spectra, Polarization study and AC impedance spectra, Atomic Force Microscope techniques.

MATERIALS AND METHODS

Preparation of the specimen
Carbon steel specimens of size 1.0 cm × 4.0 cm × 0.2 cm and chemical composition 0.026 % Sulphur, 0.06 % Phosphorous, 0.4 % Manganese, 0.1 % Carbon and the rest iron were polished to a mirror finish and degreased with trichloroethylene and used for the weight loss method and surface examination studies.

Preparation of Banana peel extract
An aqueous extract of Banana peel was prepared by grinding 10g of Banana peel, with distilled water, filtering the suspending impurities, and making up to 100 ml. The extract was used as corrosion inhibitor in the present study.

Weight-loss method
Carbon steel specimens were immersed in 100 ml of the sea water in [Nagarkovil] containing various concentrations of the inhibitor Banana peel extract (BPE) in the absence and presence of Zn^{2+} for one day. The weights of the specimens before and after immersion were determined using a Digital Balance (Model AUY 220 SHIMADZU).The corrosion inhibition efficiency (IE) was then calculated using the equation

$$IE = 100\,[1-(W_2/W_1)]\ \%$$

Where W_1 is the weight loss value in the absence of inhibitor and
W_2 is the weight loss value in the presence of inhibitor.

Surface examination study
The carbon steel specimens were immersed in various test solutions for a period of 1 day. After 1 day, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analyzed by various surface analysis techniques.

Fourier transform infrared spectra
These spectra were recorded in a Perkin-Elmer-1600 spectrophotometer using KBr pellet. The FTIR spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr and making the pellet.

Atomic Force Microscopy characterization (AFM)
The carbon steel specimen immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and subjected to the surface examination. Atomic force microscopy (Veeco dinnova model) was used to observe the samples' surface in tapping mode, using cantilever with linear tips. The scanning area in the images was 5 μm × 5 μm and the scan rate was 0.6 HZ /second.

Potentiodynamic Polarization
Polarization studies were carried out in a CHI- electrochemical work station with impedance model 660A. It was provided with iR compensation facility. A three electrode cell assembly was used. The working electrode was carbon steel. A SCE was the reference electrode. Platinum was the counter electrode. From polarisation study,

corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic = ba and cathodic = bc were calculated and polarization study was done. The scan rate (V/S) was 0.01. Hold time at (Efcs) was zero and quiet time (s) was two.

AC impedance spectra

The instrument used for polarization study was used to record AC impedance spectra also. The cell set up was also the same. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. Values of charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated. AC impedance spectra were recorded with initial E(v) = 0, high frequency (Hz) = 1x105, low frequency (Hz) = 1, amplitude (V) = 0.005 and quiet time (s) = 2.

RESULTS AND DISCUSSION

The physicochemical parameters of Sea water are given in Table 1.

Table 1: Parameters of Sea water

PHYSICAL EXAMNATION	(A)	(B)	Value
Total disolved soilds mg/L	500	2000	39824
Electrical conductivity micS/cm			58564
CHEMICAL EXAMNATION			
pH	6.5 to 9.2		6.87
Alkalinity-Ph as $CaCO_3$			0
Alkalinity Total as $CaCO_3$	200	600	136
Total Hardness as $CaCO_3$	200	600	112
Calcium as Ca	75	200	21
Magnesium as Mg	30	150	14
Chloride as Cl	200	1000	18350
Sulphate as SO_4	200	400	4354
BACTERIOLOGICAL EXAMNATION		Maximum	NT
Fecal Coliform/100ml		0 /100 ml	NT

Analysis of results of weight - loss study

The calculated Inhibition efficiencies (IE) and corresponding corrosion rates of Banana Peel Extract (BPE) in controlling the corrosion of carbon steel immersed in the presence and absence of Zn^{2+} have been tabulated in Table: 2

It is observed that banana peel only shows good inhibition efficiency (IE) (in the absence of Zn^{2+}).When Zn^{2+} (5 ppm) is added IE decreases at first and while Zn^{2+} is added IE also increases .IE increases at 4 ml of BPE and 15 ppm of Zn^{2+} it gives 98 % IE this shows that micelles forms at this condition and gives maximum inhibition efficiency when the concentration of Zn^{2+} increases from 5 ppm to 25 ppm the IE slightly decreases. This may be due to the fact that, when the concentration of Zn^{2+} increases, the Zn^{2+}-BPE complex formed is precipitated in the bulk of the solution. Hence BPE is not transported towards the metal surface. So the IE decreases [21] Hibiscus Rosa-Sinensis Al at pH 12, [22] Euphorbia, [23] Henna.

Table 2: Corrosion rates (CR) and inhibition efficiency of carbon steel immersed in an aqueous solution in the absence and presence of inhibitors Inhibitors : Banana peel extract (BPE) + Zn^{2+} Period of immersion : 1 day

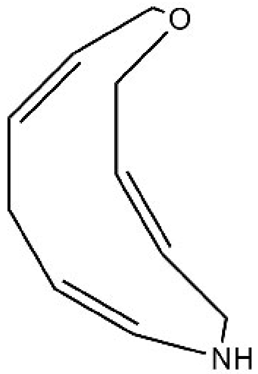
BPE (ml)	IE%				CR mdd			
	Zn^{2+} (ppm)				Zn^{2+} (ppm)			
	0	5	15	25	0	5	15	25
0	--	25	37	54	31.81	23.85	20.04	14.63
2	62	65	42	94	12.08	11.13	18.44	1.90
4	71	94	98	88	9.22	1.90	0.63	3.81
6	57	90	90	82	13.67	3.18	3.18	5.72
8	48	82	84	80	16.54	5.72	5.08	6.36

Influence of immersion period on the inhibition efficiency of BPE

The influence of duration of immersion on the IE of BPE (4ml) – Zn^{2+} (15ppm) system is given in Table 3.When the immersion period increases the inhibition efficiency decreases and the corrosion rate increases this shows that the protective film formed on the metal surface, was broken by the corrosive environment and the film was dissolved, this same result is shown in Phyllanthus amarus extract [24],

Table 3: Influence of duration of immersion on the inhibition efficiency of BPE-Zn^{2+} system.

Immersion period, day	1	3	5	7
CR in the absence of the Inhibitor, mdd	31.81	61.81	89.09	121.81
CR in the presence of the inhibitor, BPE (4ml) +Zn^{2+} (mdd)	0.63	32.75	49.89	93.79
IE,%	98	47	44	23



(3Z,7Z,10Z)-1-oxa-6-azacyclododeca-3,7,10-triene

Scheme :1

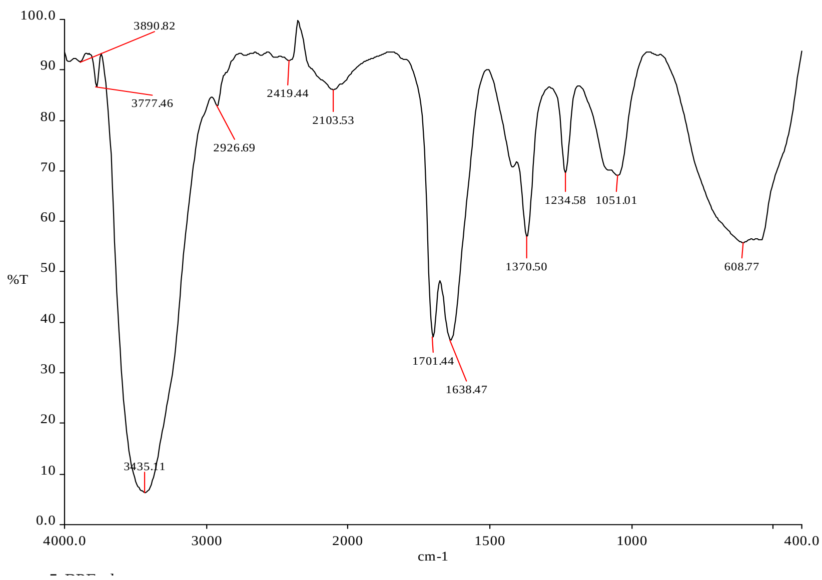


Fig :1a FTIR spectrum of pure BPE

Analysis of FTIR spectra

Earlier researchers have confirmed that FTIR spectrometer is a powerful instrument that can be used to determine the type of bonding for organic inhibitors adsorbed on the metal surface [25]. FTIR spectra have been used to analyze the protective film formed on metal surface. FTIR spectrum of pure BPE is given in Fig:1a. The FTIR spectrum of the film formed on the metal surface after immersion in the sea water for 1 day containing 4ml of BPE and 15 ppm of Zn^{2+} is shown in Fig:1b. The C=C stretching frequency has decreased from1638 cm^{-1} to 1626 cm^{-1},ring O stretching frequency has shifted from 1051 cm^{-1} to 1105cm^{-1}, NH stretching frequency has decreased from 3435 cm^{-1} to 3412 cm^{-1} [26]. This indicates that the Nitrogen atom of NH group has coordinated with Fe^{2+} formed on the metal surface resulting in the formation of Fe^{2+}- BPE complex on the metal surface. Banana peel extract contains [(3Z,7Z,10Z)-1-oxa-6-azacyclododeca-3,7,10-triene] compound this figure is shown in scheme:1.

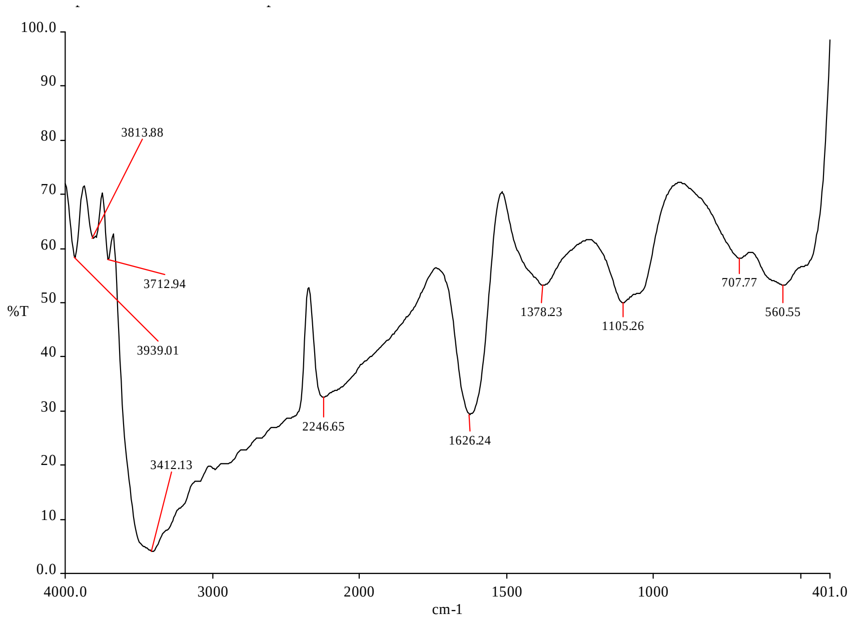
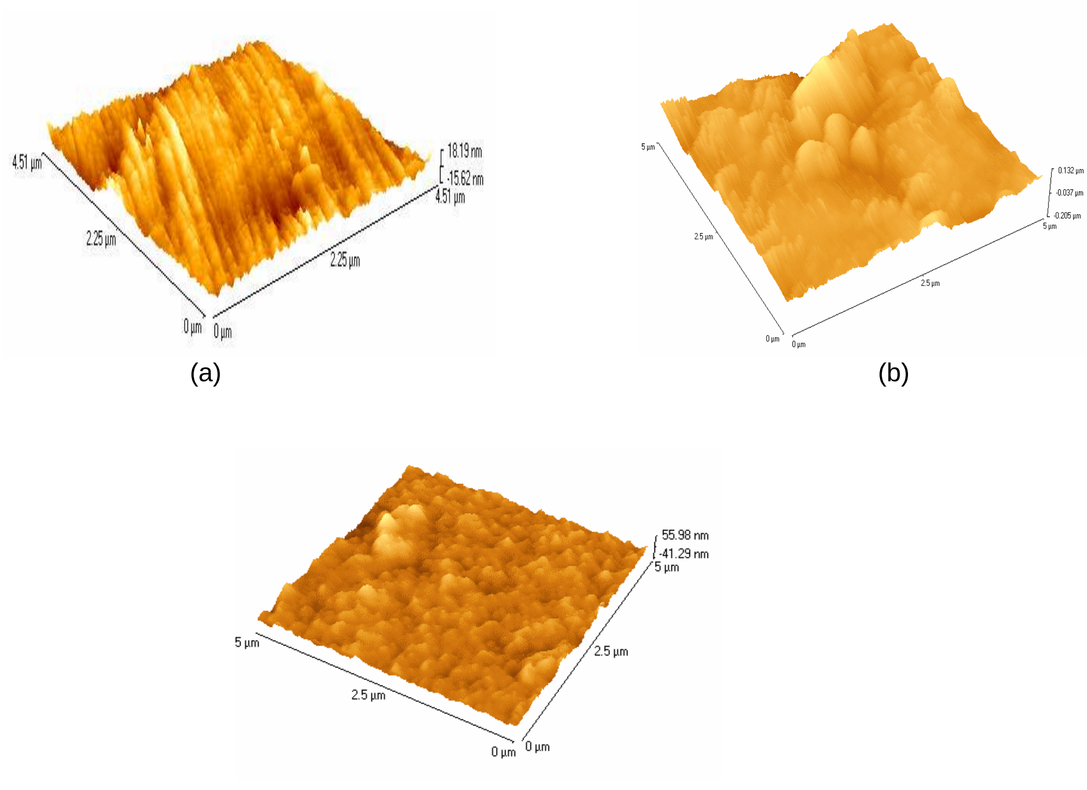


Fig :1b FTIR spectrum of the film formed on the metal surface after immersed in the sea water containing 4ml of BPE and 15 ppm of Zn^{2+}

Atomic Force Microscopy Characterization

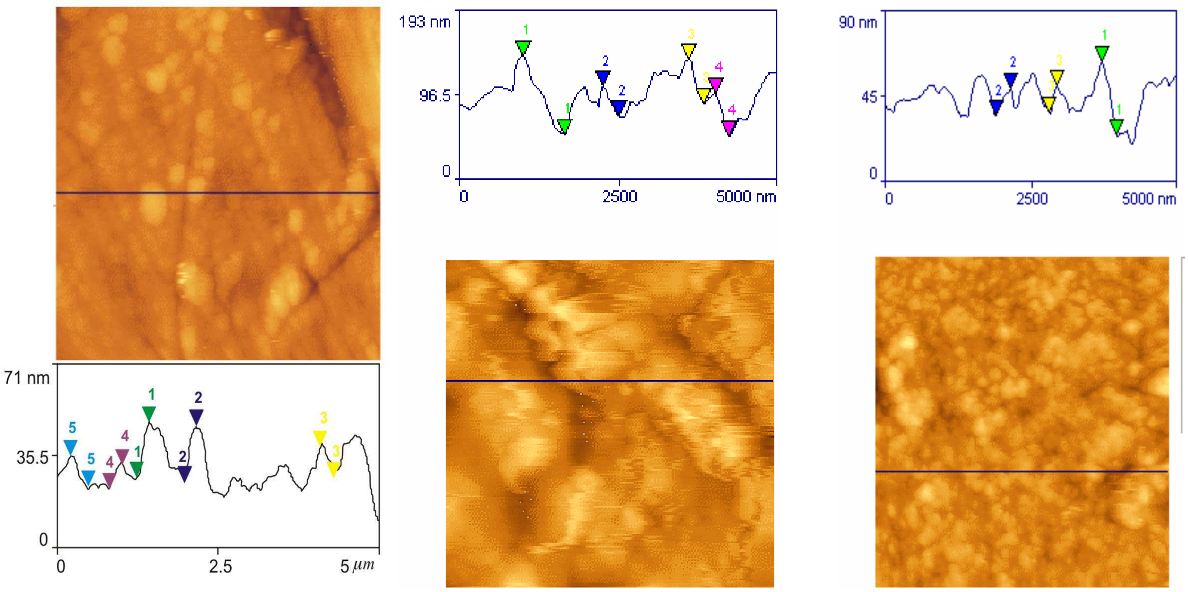
AFM is a powerful technique to investigative the surface morphology at nano- to micro-scale and has become a new choice to study the influence of inhibitor on the generation and the progress of the corrosion at the metal/solution interface [27-30]. The three dimensional (3D) AFM morphologies and the AFM cross-sectional profile for polished carbon steel surface (reference sample), carbon steel surface immersed in sea water (blank sample) and carbon steel surface immersed in sea water containing the formulation of 4ml of BPE and 15 ppm of Zn^{2+} are shown as Fig:2 images (a, d,), (b, e,), (c, f,) respectively. Root– mean-square roughness, average roughness and peak-to-valley value AFM image analysis was performed to obtain the average roughness, Ra (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness, Rq (the average of the measured height deviations taken within the evaluation length and measured from the mean line) and the maximum peak-to-valley (P-V) height values (largest single peak-to-valley height in five adjoining sampling heights) [28]. Table 4 is a summary of (Rq), (Ra), (P-V) value for carbon steel surface immersed indifferent environment. Fig:2 (a, d,) displays the surface topography of un-corroded metal surface. The value of Rq, Ra and P-V height for the polished carbon steel surface (reference sample) are 4.3 nm, 3.41nm and 35.28 nm respectively. The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion. Fig: 2 (b, e,) displays the corroded metal surface with few pits in the absence of the inhibitor immersed in sea water. The (Rq), (Ra), (P-V) height values for the carbon steel surface are 25.2nm, 19.9nm and 89.10 nm respectively. These data suggests that carbon steel surface immersed in sea water has a greater surface roughness than the polished metal surface, which shows that the unprotected carbon steel surface is rougher and was due to the corrosion of the carbon steel in sea water environment. Fig:2 (c, f,) displays the steel surface after immersion in sea water containing 4ml of BPE and 15 ppm of Zn^{2+} . The (Rq), (Ra), (P-V) height values for the carbon steel surface are 8.45nm, 6.50nm and 38.63nm respectively The (Rq), (Ra), (P-V) height values are considerably less in the inhibited environment compared to the uninhibited environment. These parameters confirm that the surface is smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+} - BPE complex thereby inhibiting the corrosion of carbon steel [28].



(a) (b)

(c)

Fig :2 Three dimensional AFM images of the surface of: a) As polished carbon steel(control); b) carbon steel immersed in sea water (blank); c) carbon steel immersed in sea water containing BPE (4ml) + Zn^{2+} (15ppm)



(d) (e) (f)

Fig :2 AFM cross-sectional images of the surface of: d) As polished carbon steel (control); e) carbon steel immersed in sea water (blank); f) carbon steel immersed in sea water containing BPE (4ml) + Zn^{2+} (15ppm).

Table 4: AFM data for carbon steel surface immersed in inhibited and uninhibited environment.

Samples	RMS(Rq) Roughness (nm)	Average(Ra Roughness (nm)	Maximum Peak-to valley Height (nm)
1.Polished carbon steel	4.33	3.41	35.28
2.Carbon steel immersed in sea water (blank)	25.2	19.9	89.10
3.Carbon steel immersed in sea water + BPE (4ml) + Zn^{2+} (15ppm)	8.45	6.50	38.63

Analysis of polarization curve

The potentiodynamic polarization curves of carbon steel immersed in sea water in the absence and presence of inhibitors (Banana peel extract (BPE) and Zn^{2+}) are shown in Fig:3. The corrosion parameters namely corrosion potential (E_{corr}) ,Tafel slopes (bc = cathodic ba = anodic) , linear polarization resistance (LPR) and corrosion current (I_{corr}) are given in Table 5. It is observed that in the absence of inhibitors the corrosion potential is-771 mV vs. SCE, in the presence of inhibitors (4ml BPE and 15 ppm Zn^{2+}) the corrosion potential is shifted to -769 mV vs SCE .This suggests that this formulation controls the anodic reaction and cathodic reaction to an equal extant . So we can conclude that this inhibitor acts as mixed type of inhibitor .The LPR value increases from 2378 ohm cm^2 to 5426 ohm cm^2 further the corrosion current decreases from 1.579 $x10^{-5}$ A/cm^2 to .7440$x10^{-5}$ A/cm^2 .This suggests that a protective film is formed on the metal surface [31-35].

Table 5: Corrosion parameters of carbon steel immersed in Banana peel extract obtained from polarization study.

System	E_{corr} mV vs. SCE	b_c mV/decade	b_a mV/decade	LPR ohm cm^2	I_{corr} A/cm^2
Sea water(blank)	-771	160	186	2378	$1.579x10^{-5}$
BPE(4ml)+ Zn^{2+}(15ppm)	-769	151	240	5426	$0.7440x10^{-5}$

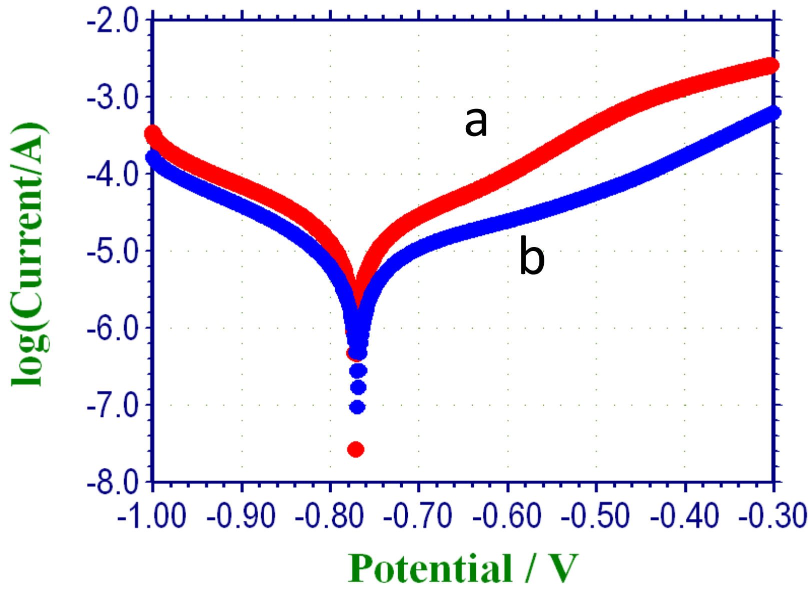


Fig:3 . Polarization curves of carbon steel immersed in various test solutions (a) sea water (blank); (b) BPE (4ml) + Zn^{2+} 15 ppm.

Analysis of AC Impedance spectra

The AC impedance spectra of carbon steel immersed in various solutions are shown in Fig:4 (Nyquist plot). The AC impedance parameters namely , charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in

Table 6. When carbon steel is immersed in sea water, the charge transfer resistance R_t is 90.32 ohm cm^2 , the double layer capacitance C_{dl} is 5.6465x10^{-8} F/cm^2 when the formulation consisting of (4 ml) BPE and 15 ppm Zn^{2+} is added , the R_t value increases to 175.25 ohm cm^2 and C_{dl} value decreases to909101x10^{-8} F/cm^2 this confirms that a protective film is formed on the metal surface the Bode plots are shown in Figs: (5a,5b). In the absence of inhibitor the real impedance value is 2.011 log (z)/ohm . In the presence of inhibitors this value increased to 2.304 log (z)/ohm , this indicates the formation of protective film on the metal surface in the presence of inhibitors [31-35].

Table 6: Corrosion parameters of carbon steel immersed in Banana peel extract, obtained from AC impedance spectral study.

System	Nyquist plot		Bode plot
	Rt ohm cm^2	Cdl F/cm^2	Impedance value log(z/ohm)
Sea water (blank)	90.32	5.6465 x10^{-8}	2.011
BPE (4ml) +Zn^{2+} (15ppm)	175.25	.9101 x10^{-8}	2.304

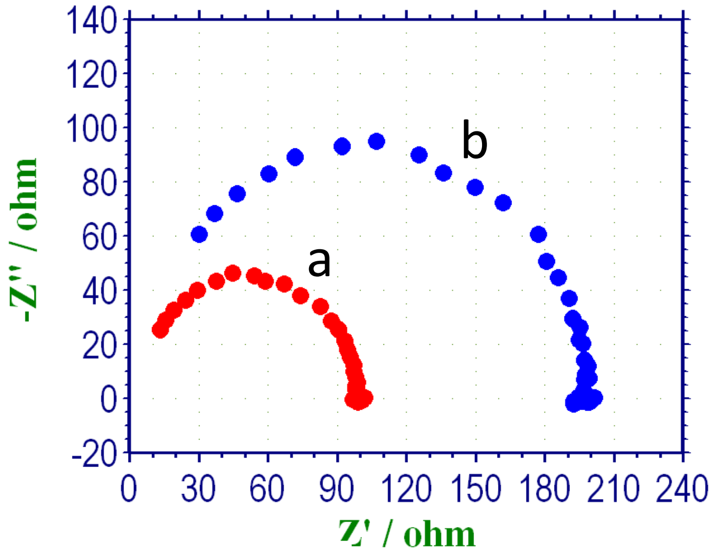


Fig:4 . AC impedance spectra of carbon steel immersed in various test solutions (Nyquist plots). (a) Sea water(blank) ; (b) BPE (4mL) + Zn^{2+} 15 ppm.

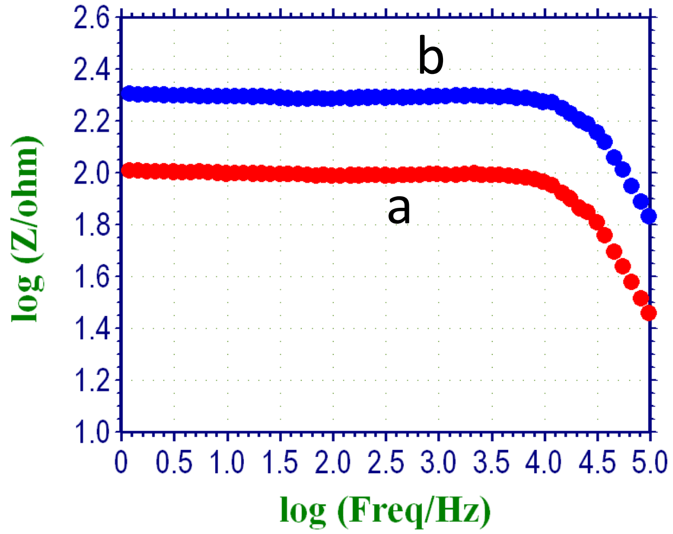


Fig:5a. AC impedance spectra of carbon steel immersed in various test solutions (Impedance-Bode plots) (a) Sea water(blank) ; (b) BPE (4ml) + Zn^{2+} 15 ppm.

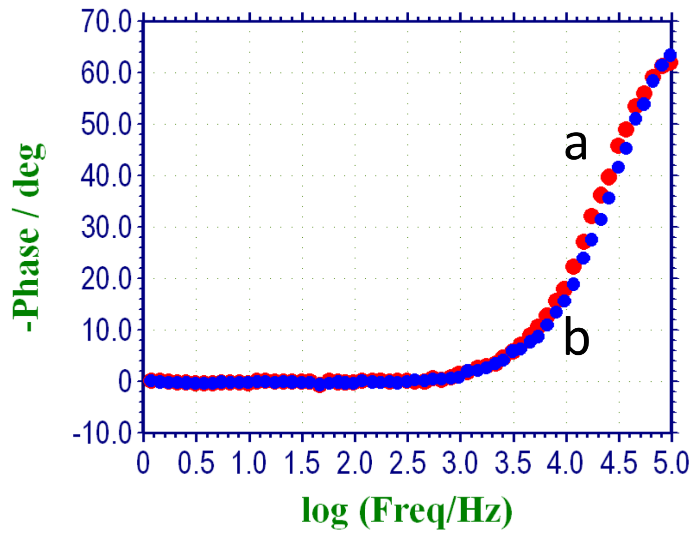


Fig:5b. AC impedance spectra of carbon steel immersed in various test solutions (phase-Bode plots) (a) Sea water (blank) ; (b) BPE (4ml) + Zn^{2+} 15 ppm

CONCLUSION

The present study leads to the following conclusions.

- The formulation consisting of 4ml of BPE and 15 ppm of Zn^{2+} offers 98% inhibition efficiency to carbon steel immersed in sea water.
- When immersion period increases corrosion rate also increases.
- Polarization study reveals that this system formulation acts as a mixed type of inhibitor.
- AC impedance spectra reveal that a protective film is formed on the metal surface.
- The FTIR spectra reveal that the protecting film consists of Fe^{2+}-Banana peel (active ingredient) complex.
- AFM studies confirm that the surface is smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+} - BPE complex on the metal surface thereby inhibiting the corrosion of carbon steel

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