



INHIBITION EFFECT OF ARECA CATECHU EXTRACT ON ZINC IN 0.5M HYDROCHLORIC ACID SOLUTION

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Abstract:

The extract compositions of boiled aqueous extract of tender areca nut were investigated by GC-MS and FTIR studies. Its corrosion inhibition efficiency on zinc was studied in 0.5M HCl solution using gravimetric and electrochemical methods of corrosion analysis. Ten distinct compounds were identified from GC-MS analysis. And these identified phytochemicals were further confirmed by FTIR investigations. All the studies uncover that the extract contains hydroxyl, amine, carboxyl, double bonds in it. The gravimetric studies revealed that aqueous tender areca nut extract is effective additive for the corrosion of zinc at all the concentrations. Inhibition efficiency of the extract increments with increment in the concentration of the extract. The electrochemical strategies, such as polarization study indicate that extract inhibit both anodic and cathodic corrosion reaction. From the Nyquist plot clearly indicate that charge transfer resistance increases and double layer capacitance diminishes as ascend in extract concentrations. This is a direct result of the adsorption of the active chemical compounds present in the extract on to the surface of the zinc metal there by it reduces the corrosion rate and act as a green corrosion inhibitor. This process of inhibition was additionally affirmed by SEM results.

Key words: Tender areca nut extract, Adsorption, Corrosion inhibition, polarization method, gravimetric method

Introduction

Corrosion is defined as physicochemical interaction between a metal and its surrounding environment which results in changes in the properties of metal and which may often lead to impairment of the function of metal, the environment or the technical system of which these form a part^{I-V}. Disadvantages of corrosion are, loss in efficiency of the materials, shutdown of the plant in industries because of failure of equipment's, due to corrosion of metal, the product being transported, stored, processed or packed in a metallic content can pick up metallic salts. Which results in contamination of the products. Many time corrosion results in leakage, this leakage occurs in pipe lines which in turn cause loss of product^{IV-VIII}.

Despite of all these limitations imposed by corrosion of materials, proper maintained protection system with well-designed structures, will give long life for materials. Methods of

preventing corrosion, could be summarized as follows, 1. Methods of modification of procedure- by attention to design. 2. Methods based on the modification of the environments- by addition of the corrosion inhibitors. 3. Method based on the modification of the metal- by addition of alloying element. 4. Methods based on protective coatings- by paints, resins etc.^{IX-XI}

Different methods have been developed to control and prevent corrosion. Inhibitors is one of the most pragmatic strategies to prolong corrosion progress which has become wide spread recently.

Corrosion inhibitor is a substance which retards corrosion when added to an environment in small concentrations.^{XII, XIII}. Inhibitor is divided into organic and inorganic inhibitors.

Inorganic substance such as phosphates, vanadate, chromates, dichromate and arsenate are found to be effective inhibitors. But being highly toxic, their use as inhibitor was restricted. Among the alternative inhibitors organic compounds containing polar functional groups with N, O and S atoms in a conjugated system have been found to possess good inhibiting properties. But, unfortunately, most of these compounds are not only expensive but also toxic to living beings. Hence significance of plant extract as corrosion inhibitors becomes more as they are ecofriendly, biodegradable, cheap, easily available and safe inhibitors^{XIV-XX}. Hence, different parts of plants such as roots, leaves, barks, flowers and fruits extracts were used to reduce the corrosion^{XXI-XXVII}.

The objective of the present work is to evaluate the inhibitory action of aqueous tender areca nut extract as a corrosion inhibitor for zinc metal in 0.5M HCl media. Analysis of corrosion inhibition property has been conducted by using weight loss measurement, polarization technique and electroscopic impedance spectroscopy. Result showed that inhibition efficiency increases with increase in the concentration of extract and decrease with increase in temperature. Polarization study indicates that the corrosion current density reduces as concentration of the extract increases. EIS analysis reveals that charge transfer resistance increases as concentration of the extract increases. Corrosion inhibition occurs due to the adsorption of the extract molecule on the surface of the metal.

Experimental Methods

1. **Specimen preparation:** Zn (IS: 13229) metal was used as a test electrode with chemical composition (weight%) was Pb- 1.36%, Cd-0.05%, Fe- 0.05%, Sn- 0.02%, Cu- 0.02% and remainder Zn^{XXVIII}. The oxide layer likely to be formed on the metal was removed by abrasive paper with 200 to 2000 grades. It was followed by washing with distilled water, further it was degreased with acetone and dried.

2. **Electrolyte preparation:** The HCl solution was prepared by using analytical grade of HCl 33-38% SD Fine Chemicals Mumbai.

3. **Inhibitor preparation:** Aqueous tender arecanut extract was prepared by boiling the tender Arecanut with water and filtrate is collected and used as inhibitor. Aqueous tender arecanut extract was added in different concentration namely, 10%, 20%, 30%, 40% and 50% v/v to 0.5M HCl solution.

4. **FTIR Analysis:** Fourier Transformer Infrared Spectrometer (FTIR) is the most powerful tool for identifying the functional groups present in the extract. Powder samples of tender areca nut extract was loaded to FTIR Spectrometer (Perkin Elmer-Spectrum RX-IFTIR), with a scan range of 400-4000 cm^{-1} and resolution of 1 cm^{-1} to get the signal for the likely present functional groups.

5. **GC-MS Analysis:** The GC-MS analysis of bioactive compounds from tender areca nut extract was done using Thermo Scientific TSQ-8000 GC-MS Technique. Mass spectrometer comes paired with the TRACE 1300 GC along with auto sampler for automated sample handling. Temperature program (oven temperature) was 40°C raised to 290°C at a rate of

5⁰C/min and injection volume was 1.0 μ l with the scan range of 50-700 m/z. The results were compared with NIST library search program, to get an idea on the chemical component present in the extract.

6. Weight loss measurements: Cleaned Zn coupon was completely immersed separately in 50ml of 0.5M HCl solution without and with different concentration of areca nut extract. After 3 hours of immersion each coupon was removed from test solution. Washed in distilled water to get rid of corrosion product, dried in acetone and weighed. Weight loss measurements conducted in the absence and presence of areca nut extract at various concentrations for different temperatures ranging from 303K to 323K.

7. Electrochemical measurements: The polarization and EIS study was conducted in three electrode system. where, the saturated calomel (SCE), platinum and Zn electrodes were used respectively as reference, auxiliary and working electrode. All the three electrodes were immersed in an electrolyte solution, which in turn is connected to Gill AC.

1. Potentiodynamic polarization study: Initially working electrode was allowed to attain open circuit potential (OCP). The potential was scanned in the range of ± 250 mV around OCP (vs. SCE). With a scan rate of 1mV/s.

2. Electrochemical impedance spectroscopy (EIS): The Nyquist plot was obtained from EIS measurements in the frequency range of 100000 to 0.01Hz. the measurements were carried out for the solution with and without TACN extract.

8. SEM Analysis: Surface morphology of Zinc metal in the absence and presence of TACN inhibitor was performed by sigma series field emission scanning electron microscope (Cral Ziess Microscopy Ltd., Germany).

Result and Discussion

FTIR Analysis:

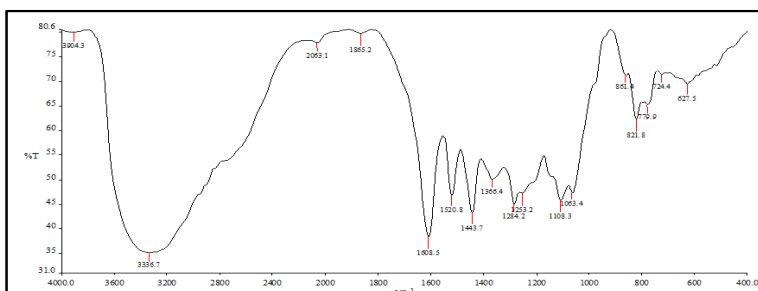


Figure:1 FTIR spectrum of Aqueous extract of tender areca nut

The FTIR spectrum of aqueous extract of tender areca nut was shown in Fig:1. The peaks at 3336.7, 1608.5 and 1443.7, 1366.4, 2184.2, 1108.3-1063.0, and 821cm⁻¹ indicates the presence of functional groups such as phenolic (-OH stretch), aromatic (C=C stretch), H-C-H bending vibration, aromatic amine (C-N stretch), alcohol, ester (C-O stretch) and NH bending vibrations (out of plane) respectively.

GC-MS Analysis:

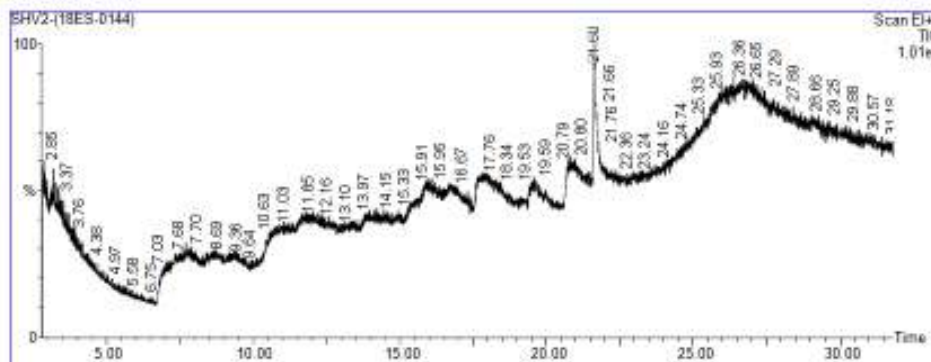
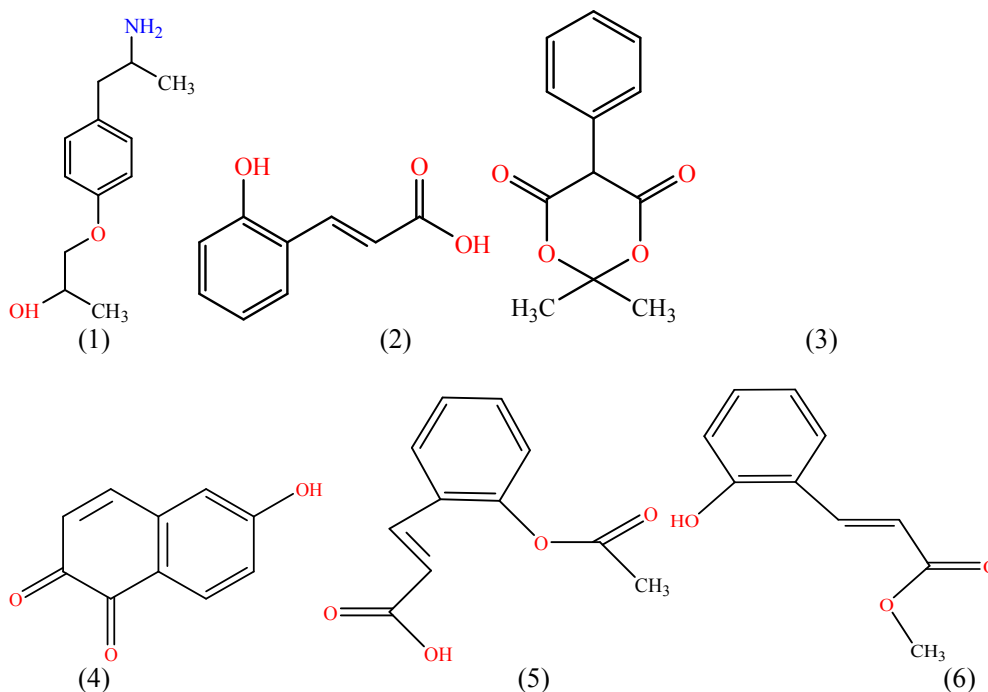
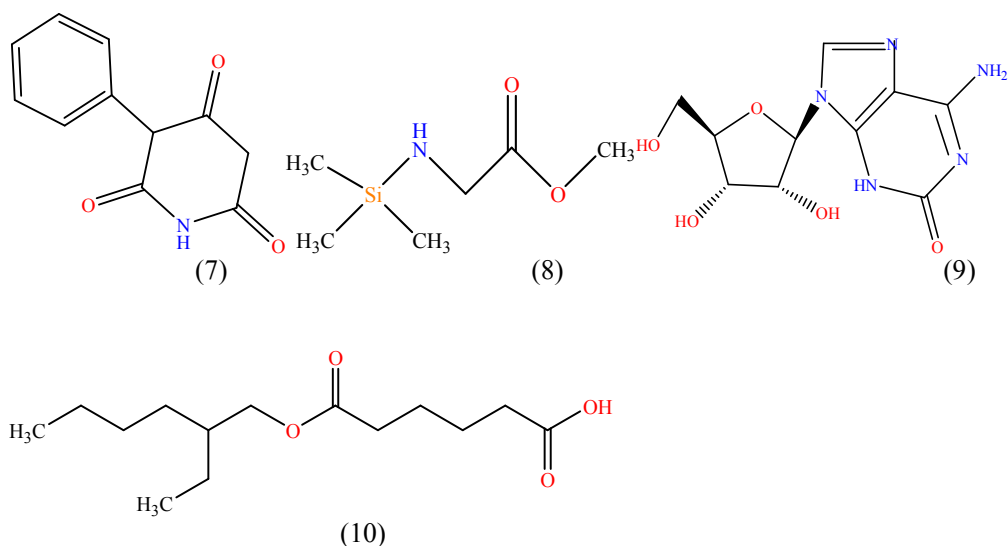


Figure:2 GC-MS spectrum of Aqueous extract of tender areca nut

Table:1 Indicates chemical species identified from GC-MS analysis

Sl.No	Retention time	Name of the compound	Chemical formula
1	15.954	2-Propanol,1-[4-(2-aminopropyl) phenoxy]-	C ₁₂ H ₁₉ O ₂ N
2	17.759	2-Proponic acid-3-(2-hydroxyphenyl)-	C ₉ H ₈ O ₃
3	17.804	2,2-Dimethyl-5-phenyl-1,3-dioxane-4,6-dione	C ₁₂ H ₁₂ O ₄
4	17.884	1,2-Naphthalenedione-6-hydroxy	C ₁₀ H ₆ O ₃
5	18.000	2-Propeonic acid,3-[2-(acetoxy)phenyl]	C ₁₁ H ₁₀ O ₄
6	18.050	2-Propeonic acid,3-(2-hydroxyphenyl)-methyl ester	C ₁₀ H ₁₀ O ₃
7	18.115	2,4,6(1H,3H,5H)-Pyrimidinetrione,5-phenyl-	C ₁₀ H ₈ O ₃ N ₂
8	18.340	Glycine-(trimethylsilyl)-methyl ester	C ₆ H ₁₅ O ₂ NSi
9	19.585	Adenosine,2,3-dihydro-2-oxo	C ₁₀ H ₁₃ O ₅ N ₅
10	21.596	Hexanedioic acid,mono(2-ethylhexyl)ester	C ₁₄ H ₂₆ O ₄





GC-MS analysis exhibited the presence of ten different chemical compounds with different retention times and are tabulated in the Table:1. Chemical structures for respective identified compounds are as shown above figures1-10. Structures shows the presence of various heteroatoms such as O, N, and aromatic rings which form the main criteria for good corrosion inhibitor. Aqueous extract contains $C_{12}H_{19}O_2N$, $C_9H_8O_3$, $C_{12}H_{12}O_4$, $C_{10}H_6O_3$, $C_{11}H_{10}O_4$, $C_{10}H_{10}O_3$, $C_{10}H_8O_3N_2$, $C_6H_{15}O_2NSi$, $C_{10}H_{13}O_5N_5$ and $C_{14}H_{26}O_4$ in 5.36, 13.10, 3.74, 6.30, 3.27,3.48, 4.52, 2.76, 3.63 and 21.60% respectively.

Weight loss measurement:

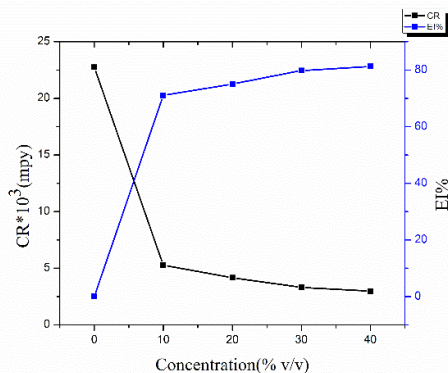


Fig:3 Variations of corrosion rate and efficiency on lead metal with respect to concentrations

Table:2 indicate the data obtained from gravimetric analysis

Sl.no	Concentration (% v/v)	Corrosion rate (CR) (mpy)*10 ³	% EI
1	Blank	22.75	-
2	10	5.26	71.04
3	20	4.15	75.07
4	30	3.30	79.80
5	40	2.97	81.28

Weight loss is determined in presence and absence of the extract by using,

$$CR = \frac{534W}{ADt} \quad (1)$$

where W is weight loss of the metal in (mg), A is area of the metal which is exposed for solution of study (square inches), D density of metal (g/cm³) and is time of exposure (hours). Efficiency of inhibitor was calculated using the formula,

$$\%EI = \frac{CR_0 - CR_{inh}}{CR_0} \times 100 \quad (2)$$

Where, CR₀ and CR_{inh} are the corrosion rate, in absence and presence of the inhibitor respectively.

Corrosion inhibition studies were carried out at different concentrations as indicated in fig:3.. Obtained results are tabulated in the above table:2. Values indicates that corrosion rate decreases with the increase in concentrations of the extract and hence shows the raise incorrosion inhibition efficiency. Corrosion rate was suppressed because of the adsorption of chemical constituents present in the extract on metal/acid interface, which efficiently minimizes the uncovered surface area of zinc metal in acid solution. Greater inhibition efficiency is due to the high adsorption of extract molecules on metal surface.

Effect of inhibitor concentration on activation parameters:

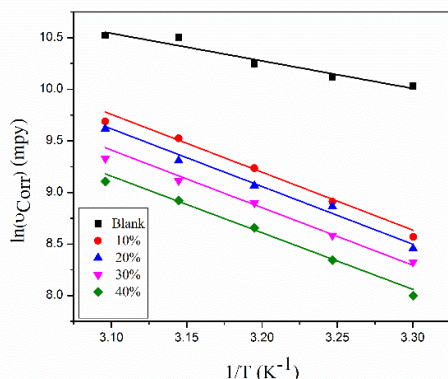


Figure: 4 Arrhenius plot (Zn metal in 0.5M HCl with and without inhibitor)

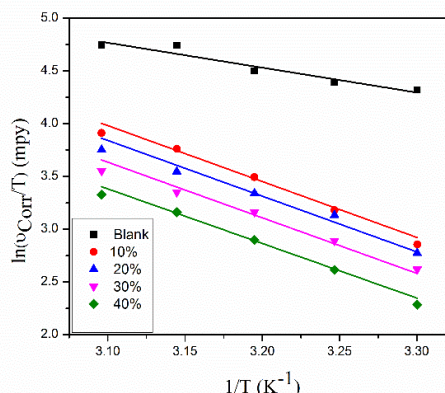


Figure: 5 Transition state plot

Table:3 Activation parameters

Sl.no	Concentration (% v/v)	E _a [*] (kJ/mol)	ΔH [*] (kJ/mol)	ΔS [*] (J/mol.K)
1	Blank	22.20	19.60	-97.14
2	10	45.62	43.02	-36.05
3	20	46.40	43.80	-31.54
4	30	46.51	43.91	-29.47
5	40	46.64	44.05	-27.89

Activation parameters concerned with the corrosion inhibition efficiency such as Energy of activation (E_a^{*}), Enthalpy of activation (ΔH^{*}) and entropy of activation (ΔS^{*}) were calculated in the absence and presence of aqueous tender arcanut extract by using the Arrhenius plot(eqn-3) and transition state plot (eqn-4) respectively

$$\ln C_R = \ln A - \left(\frac{E_a^*}{RT} \right) \quad (3)$$

Where, E_a^* is the apparent activation energy for corrosion of metal, R is the universal gas constant, A is the Arrhenius pre exponential factor and T is absolute temperature.

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \quad (4)$$

Where h is planks constant, N is the Avogadro's number, ΔS^* and ΔH^* is entropy and enthalpy of activation respectively. Fig: 4 and 5 represents the plot of $\ln(V_{corr})$ versus $10^3/T$, appears to be straight line with slope of E_a^*/R . Plot of $\ln(V_{corr}/T)$ versus $10^3/T$ the slope and intercept of linear plot represents $\frac{-\Delta H^*}{R}$ and intercept $\ln \frac{RT}{Nh} + \frac{\Delta S^*}{R}$ respectively, from which ΔH^* and ΔS^* were obtained. Table:3 contains the activation parameters for the corrosion of zinc metal in HCl solution in absence and presence of different concentrations of aqueous tender arecanut extract. from the data it was observed that addition of the aqueous tender arecanut extract leads an increase in the activation energy to value greater than that of the uninhibited solutions. This increment is due to the adsorption of the chemical constituents of the extract on the metal surface forming the protective barrier against the corrosive environment. Positive sign of the enthalpy reflects the endothermic nature of metal dissolution process. Negative values of the entropy suggest that the activation complex formed during the rate determining stage follows dissociation instead of association showing decrease in the disorderness of the species on the surface or increase in the stability of the species on the surface.

Adsorption isotherm:

Mechanism of adsorption process of aqueous tender arecanut extract at different temperatures on the Zn metal surface in acid media was studied by subjecting data to adsorption isotherms. On applying Freundlich adsorption isotherm to the system it forms a nonlinear plot and hence the resulted data were tried to apply to Langmuir adsorption isotherm. The plot of Langmuir adsorption found to be linear and are shown in the Fig:6 a and b.

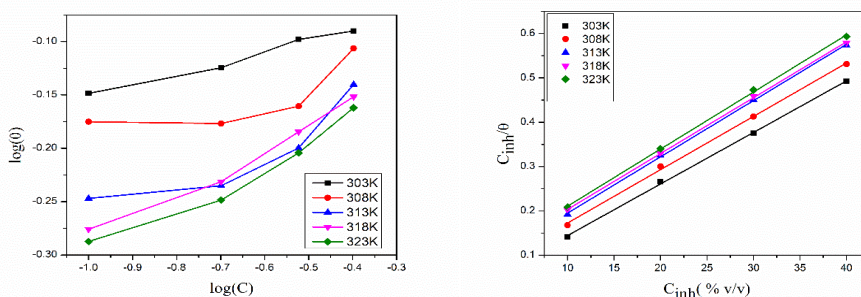


Figure: 6 a and b are Freundlich and Langmuir plots respectively

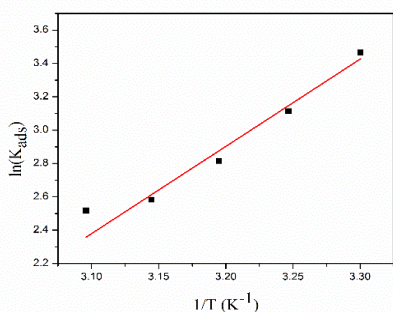


Figure: 7 plot of $\ln K_{ads}$ versus $1/T$ for adsorption of TACN on lead metal

Table: 4 Thermodynamic parameters

Sl No	Temperature (K)	K _{ads}	ΔG_{ads}^0 (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol/K)
1	303	35.84			
2	308	19.16			
3	313	14.75	-17.89	-43.51	-59.49
4	318	12.94			
5	323	12.24			

Relationship between surface coverage (θ) and the concentration of inhibitor (C_{inh}) in electrolyte can be represented by,

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh} \quad (5)$$

Where, K is the adsorption constant. Surface coverage (θ) was obtained from weight loss studies. On plotting C_{inh}/θ versus C_{inh} shown in the fig:4. The value of equilibrium constant, K_{ads} was calculated from intercept of straight line. The equilibrium constant was related to the standard free energy by following equation,

$$\Delta G_{ads}^0 = -RT \ln(55.5K) \quad (6)$$

Where, R is real gas constant, T is absolute temperature, 55.5 is molar water concentration and K is adsorption constant.

Negative sign of the ΔG_{ads}^0 indicate the spontaneity of the reaction. ΔG_{ads}^0 value is -17.89 kJ/mol indicates physisorption process, which consists of electrostatic interaction between the charged aqueous tender arecanut extract molecules with charged Zn surface. Generally, ΔG_{ads}^0 up to -20kJ/mol signifies the physisorption.

Values of ΔH_{ads} and ΔS_{ads} can be calculated by using following formula

$$\ln K = \frac{-\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R} - \ln 55.5 \quad (7)$$

The value of ΔH_{ads} and ΔS_{ads} were evaluated from slope and intercept of plot $\ln K_{ads}$ versus $1/T$ ^{XXIX, XXX} and in the present work, values are found to be -43.51 kJ/mol and -59.49 J/mol/K. Negative value of ΔH_{ads} indicate that the adsorption is exothermic process indicating the role of physical adsorption. If ΔH_{ads} is 100kJ/mol then it is said to chemisorption process. ΔS_{ads} was found to be negative for zinc metal. The reason could be interpreted as follows, the adsorption of organic molecule from the aqueous solution can be considered as a quasi-substitution process between the organic compound in aqueous phase and water molecules at the electrode surface. The adsorption of inhibitor molecule was followed by desorption of the water molecule from the surface. The negative sign of entropy means the adsorption of the inhibitor was accompanied by less desorption of water molecule from the surface of the metal.^{XXXI}

Polarization study:

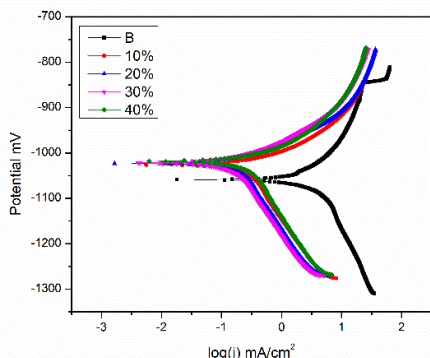


Figure: 8 Polarization curves for zinc metal in 0.5M HCl solution in the absence and presence of different concentration of aqueous extract of tender areca nut extract Table:5 indicate the results obtained from polarization study of zinc metal in 0.5M HCl solution in the absence and presence of aqueous extract of tender areca nut extract

Sl.No	Concentration (% v/v)	E _{corr} (mV)	i _{corr} (mA)	β _a (mV/decade)	β _c (mV/decade)	%EI
1	Blank	-1058.8	5.9251	239.18	270.11	-
2	10	-1026.1	1.6091	57.56	191.82	72.84
3	20	-1023.4	1.2958	52.19	189.14	78.13
4	30	-1021.8	1.0617	51.79	178.11	82.08
5	40	-1018.1	1.0231	45.05	175.89	82.73

Polarization curves of metal in acid solution absence and presence of different concentration of the extract are shown in the above fig:8 it could be stated that both anodic and cathodic reactions (i.e. dissolution of metal and evolution of oxygen) are reduced with the addition of aqueous tender arecanut extract. Which suggest that inhibitor exert inhibitory action on both the reactions. Electrochemical parameters such as E_{Corr}, i_{Corr}, β_a and β_c and %EI are listed in table:5.

Inhibition efficiency was calculated by following equation,

$$\%EI = \frac{i_{corr(0)} - i_{corr(inh)}}{i_{corr(0)}} \times 100 \quad (8)$$

Where, i_{corr(0)} and i_{corr(inh)} are the corrosion current density without and with aqueous tender arecanut extract respectively. Result shows that significant decrease in corrosion current density (i_{Corr}) and corrosion rate after the addition of inhibitor to acid solution. The values of β_c and β_a decreases with increase in the concentration of the extract, which indicates that the extract was adsorbed on the metal surface and addition of the inhibitor hindered the acid attack on the metal electrode.

Through investigations of the result obtained from gravimetric and electrochemical measurements, it could be concluded that the results of either methods are very close to each other.

EIS study:

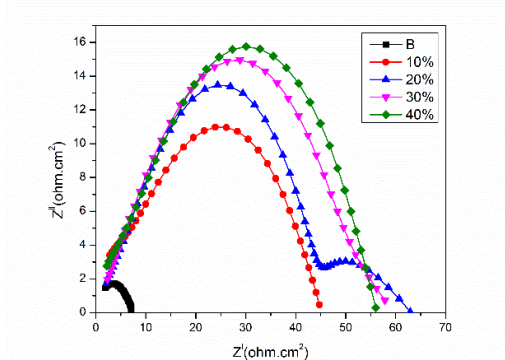


Figure: 9 Nyquist Plot of zinc metal in 0.5M HCl with and without aqueous extract of tender areca nut extract

Table: 6 Nyquist Parameters of zinc metal in 0.5M HCl with and without aqueous extract of tender areca nut extract

Sl.No	Concentration (%/ v/v)	R_s ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	R_{cdl} (F/cm^2)	%EI
1	Blank	0.68	3.86	6.345×10^{-5}	-
2	10	17.59	17.69	3.564×10^{-5}	78.16
3	20	16.43	19.18	3.287×10^{-5}	79.85
4	30	14.97	20.42	3.087×10^{-5}	81.08
5	40	11.65	22.56	2.794×10^{-5}	82.87

Impedance spectra of the sample in the absence and presence of the aqueous tender arecanut extract are shown in Fig:9. Polarization parameters such as solution resistance (R_s), charge transfer resistance (R_{ct}), double layer capacitance (R_{cdl}) and percentage efficiency (%EI) are given in Table:6. From the Nyquist plot it is concluded that curves are approximated by a single semi-circle loop, showing that corrosion process is mainly charge transfer process.^{XXXII} The shape of the curve is almost same for all the cases, indicating that there is no change in the corrosion mechanism occur during the process of addition of different amounts of inhibitor. The diameter of these loops increases with the concentration of the extract indicating that charge transfer process has retarded in the presence of aqueous tender arecanut extract. From impedance parameters listed in Table:6. It is unveiled that R_{ct} value rises while C_{dl} value decreases. An increase in the charge transfer value could be attributed to adsorption of organic groups of aqueous tender arecanut extract at metal/acid interface, which effectively prevent the transfer of charges across the interface making the corrosion efficiency to increase. C_{dl} value decrease with increment in the extract concentration, suggesting that either thickness of the protective layer increased or local dielectric constant of film decreases.

SEM Analysis:

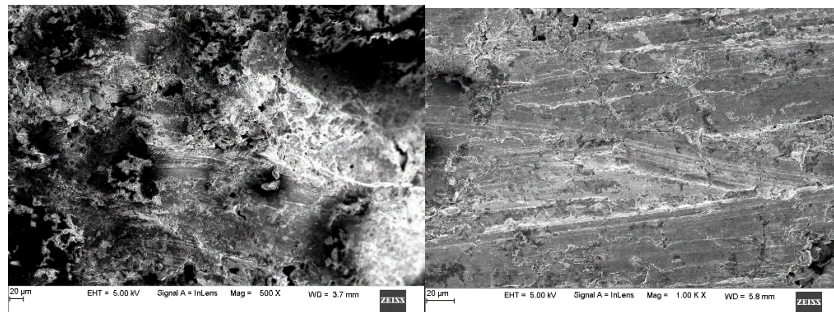


Figure:10 SEM images of Zinc metal before and after addition of aqueous tender arecanut extract respectively

SEM images of the metal sample are shown in above Fig: 10 it was observed that when the specimen is present in the absence and presence of inhibitor, the surface morphology of zinc metal was different. More cracks are observed in the surface of zinc in absence of extract while the metal surface was smoother in presence of extract. This shows that the formation of the protective film on the specimen surface by the inhibitor molecules, which in turn block the active sites on the zinc metal surface. Which result in the decrease of corrosion rate of the metal.

Corrosion Mechanism:

The weight loss and electrochemical studies revealed that the corrosion process of the zinc metal was retarded in the presence of aqueous tender arecanut extract. The GC-MS analysis of extract showed the presence of heteroatoms such as O, N, double bonds in the identified compounds. The chemical compounds present in the extract block the surface of the metal surface and protect it from corrosion through adsorption process. Generally two modes of adsorption can be considered they are,

1. The neutral inhibitor molecule may be adsorbed on the metal surface via chemisorption process i.e sharing of the electrons between metal and inhibitor molecules.
2. Adsorption occurs as a result of electrostatic force between electric charges on the metal and ionic charges or dipoles on the inhibitor molecules. The charges on the metal in the given solution can be determined from the corrosion potential (E_{Corr}) and zero current potential (ZCP). In the present study the difference between $E_{Corr} - ZCP$ was found to be negative. Hence the surface charge of the metal is negative. Therefore protonated form of the inhibitor molecules directly adsorb on to the metal surface and thereby it reduces corrosion rate. XXXIII-XXXV

Conclusion:

1. Characterization of aqueous extract of tender Arecanut reveals the presence of OH, NH, double bonds in it
2. The negative Gibbs free energy value shows that the adsorption of inhibitor on the surface of metal is spontaneous process
3. The adsorption of extract on the metal surface obeys Langmuir adsorption isotherm
4. Polarization and EIS study revealed that extract act as an effective inhibitor against corrosion of zinc metal

5. Zinc in the presence of aqueous tender arecanut extract reveals the formation of a protective film on its surface
6. SEM image discover the development of a smooth surface which support the result obtained from gravimetric and electrochemical studies

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