CORROSION INHIBITION OF ZIZIPHUS TRINERVIA EXTRACT ON OIL AND GAS PIPELINE STEEL IN ACIDIC ENVIRONMENT

P. Bala[1*], K. Kalirajan[2]

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Abstract

The inhibitive effect of Ziziphus Trinervia extract on the dissolution of oil and gas pipeline steel in 1.0N hydrochloric acid was examined using mass loss and electrochemical techniques. The inhibition efficiency increased with increase of inhibitor concentration and decreased with rise in temperature. The thermodynamic parameters were computed and suggested the adsorption process is spontaneous and exothermic. Various adsorption isotherms were examined hitherto, Langmuir, Temkin, Freundlich and El-Awady and it has been found to follow Langmuir adsorption isotherm. The electrochemical studies revealed that ZT extract behaves as a mixed type inhibitor.

Keywords: Adsorption, Half-life, 1.0N Hydrochloric acid, Impedance, Langmuir isotherm, Ziziphus Trinervia, Oil and gas pipeline steel, Polarization

[1*]Associate Professor, Sri Parasakthi College for Women, Courtallam, 627802, Tamilnadu, India

[2]Post Graduate and Research Department of Chemistry, Sri Paramakalyani College, 627802, Tamilnadu, India (Affiliated to Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli - 627012, Tamilnadu, India)

*Corresponding Author: [*1] P. Bala, Research Scholar, Reg.No:17221232032012, Sri Parasakthi College for Women, Courtallam, 627802, Tamilnadu, India, Affiliated to Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli - 627012, Tamilnadu, India

Email id: [1*]Pbalaspc1996@gmail.com

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1. Introduction

Corrosion is a constant and frequent problem, often difficult to eliminate completely. currently, it has become significantly important, due to the high budgetary problems caused for industrialized countries to innovate and protect materials from damage and loss. Their consequences are important in various fields and especially in industry: production loss [1-3]. Metal gas pipeline is widely used in oil transportation, gas industry, petroleum industry, on the way from oil field to refinery passing through different environments. Many environmental parameters and factors affect the corrosion of pipe materials, such as temperature, pH, salinity, etc. These factors play an important role in the corrosion of building materials. Corrosion can be minimized by adjusting for sometimes difficult-to-control environmental factors or by treating the piping yourself [4-7]. However, pipe metal corrosion is minimized by using inhibitors. Various inhibitors such as green and synthetic inhibitors. The use of inhibitors is one of the most practical methods of corrosion protection to prevent metal dissolution. Inhibitors have been extensively studied in many industries to reduce the rate of corrosion of metal surfaces when exposed to corrosive environments [8-10]. In general, plant extracts are considered environmentally acceptable and environmentally friendly inhibitors. Plant products are an inexpensive, readily available, and renewable source of raw materials. Therefore, it is non-toxic to humans and the environment. Their leaf, bark, seed, fruit, and root extracts consist of a mixture of organic compounds containing nitrogen, sulfur and oxygen atoms. Some have been reported to be metal corrosion inhibitors. effective in different aggressive environments [11-12]. In general, the inhibitory effect of plant extracts is due to the adsorption of organic substances on the metal surface, blocking active sites and forming a protective barrier. Therefore, in recent years, research has been directed toward finding green corrosion inhibitors. The plant extract(s) can be called as “green (corrosion) inhibitors” since the use of plant extracts are not only eco-friendly but also economical, renewable and readily available sources[13-15]. Jyothi et al. have reviewed the use of green inhibitors [16]. Rajendran et al. have explained green solution to corrosion problems and also discussed the various methods employed in corrosion field [17]. This inhibitor act as good inhibition character at the present work.

2. Materials and Methods

Electrode

The selection of commercially available steel pipes for corrosion testing is very important since slight variation in chemical composition or presence of impurities during molding and/or fabrication cause significant impact on corrosion. The most common and easily accessible high strength low carbon steel of API-5L-Grade X 52 was used in the present studies.

Table-1. Chemical compositions of API- 5 L Grade X52 steel pipeline

Element	**C**	**Mn**	**Si**	**P**	**S**	**Cr**	**Ni**	**Mo**	**Cu**	**V**	**W**	**Fe**
Percentage	0.2	0.9	0.3	0.02	0.02	0.12	0.02	0.07	0.07	0.01	0.02	Balance

Electrolyte

1.0N Hydrochloric acid of Analar Grade reagent was prepared using Triple distilled water and used as an electrolyte.

Inhibitors

The description of novel plants used as inhibitors are given below

Ziziphus Trinervia

Ziziphus Trinervia belongs to buckthorn family, Rhamnaceae and found in warm-temperate, sub-tropical and tropical regions of the world. As its fruit is non-edible, it is generally known as **kattu ilandai** in Tamilnadu. Ziziphus Mauritiana in Ziziphus family exhibited antioxidant activity. Different types of secondary metabolites are present that have effective functions on different type of diseases. The GC-MS analysis of methanolic extract of ziziphus trinervia fruit indicated the presence of three compounds namely Benzenemethanol.alpha. .alpha.-dimethyl- (31.06%); n-Hexadecanoic acid (21.30%) and 2, 3, 4, 6-Tetrafluorophenyl isothiocyanide (44.64%) (Kokkaiah Irulandi et, al,2016) The phytochemical analysis of ziziphus Trinervia seed showed that it is rich in alkaloids, flavonoids, phenols, saponins and quinones but complete screening of phyto constituents in ZTS is not yet investigated and reported

Fig.1. Ziziphus Trinervia Fruit / Seed

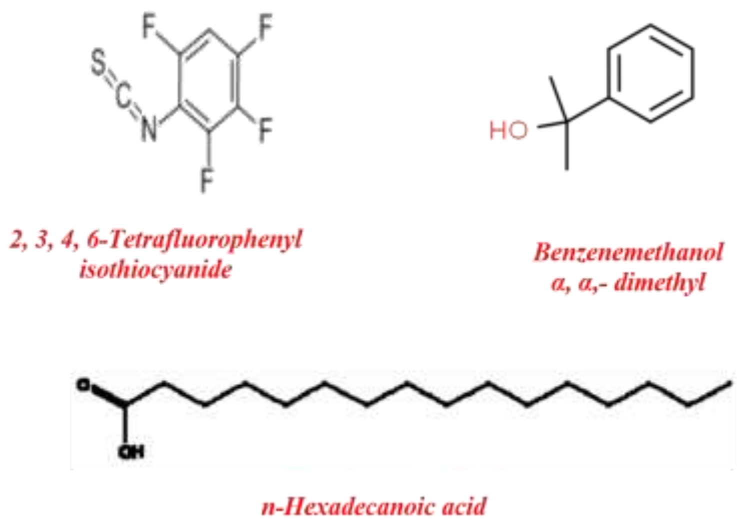


Fig.2. Common active compounds in Ziziphus Trinervia Seed

Preparation of Extract

About 20 kg of the above-mentioned plants / seeds were collected in and around Western Ghats area. The collected materials were allowed to dry (at 20^0C) in natural air bath up to 15– 20 days under sunshade environment, and then smashed into small cuts, grained well into fine powder using mortar and pestle. Exactly weighed 200 g of finely powdered material was taken in a 500 ml round bottom flask, added required quantity of ethyl alcohol and immediately covered to avoid the evaporation. and kept nearly 48 to 62hrs. Then the extract was filtered using Whatman No.1 filter paper and evaporated to get the solid mass. The obtained residue was stored in air tight bottle for investigation

Preparation of Test Specimen for Electrochemical Studies

The material used for constructing the working electrode was oil and gas pipeline steel. The steel was encapsulated in epoxy resin in such a way that only one surface was left as free surface. The exposed area (1cm2) was mechanically abraded with a series of emery papers from1/0 to 6/0 of variable grades. The samples were thoroughly washed with double distilled water, followed by A.R. ethanol and finally with distilled water, just before insertion in the three electrode cell.

Experimental Studies - Measurement of Rate of Corrosion

Average Mass Loss Method

Commercially available oil and gas pipeline steel specimens were mechanically pressed and cut to form different coupons, each of dimension exactly 40.092 cm^2 (5.1 cm × 2.5 cm × 0.96 cm), polished with emery wheel of 80 and 120 silicon carbide mesh and degreased with trichloroethylene (TCE) then washed with distilled water, cleaned, dried and then stored in moisture free desiccator. In mass loss measurements the oil and gas pipeline steel coupons in triplicate were completely immersed in 100ml of the test solution. The metal specimens were withdrawn from the test solutions at an interval of 24 -360 hrs. (1-15 days) at room temperature. The significant change in mass was taken as the difference in weight of the specimens before and after immersion using PRECISA XR 205SM – DR (Made in Switzerland) digital balance with sensitivity of ±0.0001 mg. At the end of each experimental work, the test coupon was cleaned with pickling solution as given in table 2. The measurements were performed in triplicate to determine the results precisely and the mean of the loss in mass is taken. The same procedure was adapted to study the dissolution behavior at different temperatures such as 303K, 313K and 333k but the exposure time is 1hr.

Table-2 Pickling solution

Materials	Chemicals	Time in min.	Temperature
API -5L-Grade-X52	50g of Stannous Chloride + 20g of Antimony dioxide in 1 litre of con.HCl	1-2	Room Temperature (RT)

From the mass loss measurements, the corrosion rate was calculated using the following relation.

$$\text{Corrosion Rate}\left(\text{mmpy}\right) = \frac{87.6\times W}{DAT} \quad \text{---------- 1}$$

(Where, mmpy = millimeter per year, W = mass loss (mg), D = density (g/cm^3),A = area of specimen (cm^2),T = time in hrs.)

Potentiodynamic Polarisation

The electrochemical measurements were carried out using electrochemical analyzer CH Instrument, Inc. Model: 660E Series (Advanced electrochemical system). The electrodes of 1 cm^2 area with stem were cut from the oil and gas steel pipe and one side of the electrode and stem was masked with araldite. The electrodes were polished with 1/0, 2/0, 3/0, 4/0 emery papers and degreased with trichloroethylene. Accurately 100 ml of the test solution was taken in three-electrode cell. The working electrode was introduced into the test solution and the polarization was allowed to attain a steady potential for about 20mts. Then the electrode potential was fixed at ± 200 mV to the open circuit potential (OCP). After that the polarization measurements were carried out potentio-dynamically at a sweep rate of 1mV/sec. The potential of the working electrode was measured with respect to a saturated calomel electrode (SCE) and the platinum electrode as an auxiliary electrode. The corrosion current as well as b_a and b_c values were obtained from the polarization curves by extrapolation of anodic and cathodic curves to the corrosion potential. The E_{corr} measured as mV and I_{corr} in µA/cm^2 were recorded. The experiments were performed with and without the addition of inhibitors at room temperature.

Electrochemical Impedance Spectroscopy

Electrochemical impedance measurements of oil and gas pipeline steel in electrolyte with and without inhibitors were performed. The well-polished electrode was introduced into the test solution and measured the dielectric and transport properties as steady state potential value. To investigate the mechanism of electrochemical reactions and surface passivity, A.C. signal of amplitude 10 mV was applied to the electrochemical cell system with frequencies ranging from 100 MHz to 10 kHz using electrochemical analyzer CH660E as shown in Fig.4.9. The corrosion current was obtained by substituting R_{ct} into Stern - Geary equation.

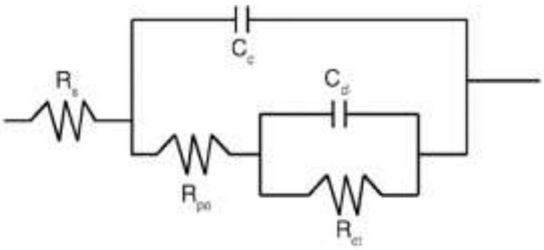


Fig. 3. Equivalent circuit of A.C. Impedance

The Nyquist plot deviating from a perfect semicircle can be attributed to frequency dispersion and in homogeneities of the metal surface. Thus dispersive behaviour is better described by the complex frequency dependent impedance (CPE). The impedance of a CPE (ZCPE) is defined as follows.

$$Z_{CPE} = \frac{1}{(J\omega)^{\alpha}}$$

Where j = -1 is an imaginary number, and $\omega=2\pi f_{max}$ and α is the correlation co efficient for the CPE (0< α<1).

The double layer capacitance (C_{dl}) was computed using the equation - 2

$$\mathbf{C}_{dl} = \frac{1}{\quad}$$

2π maxRct

Calculation of Inhibition Efficiency

Average Mass Loss Method

The average mass loss in presence and absence of inhibitors were measured. The degree of surface coverage (θ) and the percentage of inhibition efficiency (%IE) are determined using the following relations.

$$\theta = \frac{W_1 - W_2}{W_1} \quad \text{---------- } 3$$

$$\% IE = \frac{W_1 - W_2}{W_1} \times 100 \quad \text{---------- } 4$$

where W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor respectively.

Determination of the thermodynamic and activation parameters

Enthalpy of activation (ΔH) and entropy of activation (ΔS) (Suzuki et.al,1993)

The Enthalpy of activation (ΔH) and entropy of activation can be calculated by the following transition state equation - 5

$$CR = RT/Nh \exp(\Delta S/R) \ \exp(-\Delta H/RT) \quad \text{---------- } 5$$

Where **h** is the Planck's constant, **N** the Avogadro's number, Δ**S** the entropy of activation and Δ**H** the enthalpy of activation A plot of log (CR/T) vs. 1/T gives a straight line with a slope (−ΔH/R) and an intercept [log(R/Nh)) + (ΔS/R)], from which the values of ΔS and ΔH cab be calculated

Activation Energy

The activation energy (E_a) is calculated using Arrhenius of Arrhenius equation -6.

$$CR = A \exp(-E_a/RT) \quad \ldots\ldots\ldots\ldots\ldots. \ 6$$

$$\text{Log } CR = \log A - E_a/RT \quad \ldots\ldots\ldots\ldots\ldots. \ 7$$

Where E_a= activation energy, R= gas constant, T= absolute temperature, CR= corrosion rate, A= Arrhenius pre-exponential factor.

Heat of Adsorption

The formula used to calculate heat of adsorption is as follows

$$Q_{ads} = 2.303R\,[\log(\theta_2/1-\theta_2) - \log(\theta_1/1-\theta_1)] \times (T_2T_1/T_2-T_1) \quad \text{----------- } 8$$

Where θ_1 ~~and~~ θ_2 are the degree of surface coverage at two different temperatures T_1 and T_2

Free energy of Adsorption

The free energy of adsorption ($-\Delta G_{ads}$) characterize the interaction of adsorbed molecules and the adsorbent which is calculated by using the relation

$$-\Delta G_{ads} = 2.303RT\,(1.74 + \log(\theta/1-\theta) - \log C) \quad \text{----------- } 9$$

Where 'C' is the concentration of the inhibitor in % (i.e. v/V

Adsorption Studies

Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm can be expressed by the following equation.- 10

$$\log C/\theta = \log C - \log K \quad \text{----------- } 10$$

where θ is the degree of surface coverage, C is the concentration of the inhibitor in solution and K is the equilibrium constant for the adsorption of inhibitor on the metal surface.

Temkin Adsorption Isotherm

In Temkin adsorption isotherm, the degree of surface coverage (θ) is related to the inhibitor concentration (c) according to equation – 11

$$\text{Exp}(-2a\,\theta) = KC \quad \text{---------} \; 11$$

Where **K =** adsorption equilibrium constant and **a is** an attractive parameter, Rearranging and taking logarithm on both sides of equation (6.5) get equation – 12

$$\theta = (-2.303\log k/2a) - (2.303\log C/2a) \quad \text{-------------} \; 12$$

Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm is applied using equation -13

$$\theta = Kc^{1/n} \quad \text{-----------} \; 13$$

The linear form of Freundlich isotherm equation is as follows

$$\log\theta = \log K + 1/n \log C \quad \text{--------} \; 14$$

where **k** is adsorption capacity (L/mg) and 1/n is adsorption intensity and it also indicates the relative distribution of the energy and heterogeneity of the adsorbate

El-Awady Isotherm

The El-Awady adsorption isotherm is given by

$$\log(\theta/1-\theta) = \log K + y\log C \quad \text{---------------} \; 15$$

Where C is molar concentration of inhibitor in the bulk solution, 'θ is the degree of surface coverage, K is the equilibrium constant of adsorption process, $k_{ads} = k^{1/y}$ and y represents the tendency of adsorbate occupying a given active site

Frumkin adsorption isotherm

Frumkin adsorption isotherm is given by equation – 16

$$\log\{[C]^* (\theta/1-\theta)\} = 2.303\log K + 2\alpha\theta \quad \text{----------} \; 16$$

where k is the adsorption–desorption constant and α is the lateral interaction term describing the interaction in adsorbed layer

Flory-Huggins Isotherm

Flory-Huggins adsorption isotherm can be expressed according to equation – 17

$$\log(\theta/C) = \log K + x\log(1-\theta) \quad \text{-----------} \; 17$$

Polarization Measurements

The corrosion rates of oil and gas pipeline steel in the presence [$I_{corr}(I)$] and in the absence [I_{corr}] of the inhibitors were determined by Tafel extrapolation method. The percentage of inhibition efficiency (I.E) is calculated by the following equation.

$$\%\,I.E = \frac{[I_{corr} - I_{corr}(I)]}{I_{corr}} \times 100 \quad .... \; 18$$

Impedance Measurements

Inhibition efficiencies are also determined from R_{ct} values with and without the presence of inhibitors using the following equation.

$$\%\,I.E = \frac{[R_{ct}\text{with (I)} - R_{ct}]}{R_{ct}\text{with (I)}} \times 100 \quad \ldots\ldots\ldots \; 19$$

Where, R_{ct} with (I) = charge transfer resistance with inhibitor,
R_{ct} = charge transfer resistance without inhibitor.

Characterisation Studies of Corrosion (Adsorbed) Products

The corrosion products preferably the rust over the metal surface were subjected to various instrumental analysis. The rust generally adherent as fine form on the surface of the exposed specimen (API 5L Grade X52 pipeline steel) was removed by scrapping, and subjected to analysis by the following techniques.

Ft-Ir Spectroscopy

The rust sample was analyzed using Fourier transform infrared spectroscopy (FT-IR) model Thermo Scientific Nicolet iS5 and IRTracer-100 Shimadzu within the range of 4000 – 400cm^{-1}. This spectrometer having specially made hit for analyzing the sample directly without using KBr pellets (Highly advanced FT – IR Instrument, made of Japan).

EDX Analysis

The compositions of all elements at the surface of specimen before and after immersion were identified by Energy Dispersive X- ray spectroscopy (EDS) using the Oxford Instrument Model - INCA Penta XET. The energy of an acceleration beam employed was 20 kV.

Morphologial Studies Scanning Electron Microscope

Model: Jeol - JSM 6390, Scanning Electron Microscope was used to study the nature of the corroded surface. The dissolution of metal surface and the protective film formed by the inhibitor on the metal surface was also studied.

3. Results and Discussion

Non Electrochemical Methods

Effect of Immersion Time

The dissolution behavior of oil and gas pipeline steel in 1.0N HCl containing ZTS extract with various exposure times (24hrs. to 360 hrs.) is studied and the data are shown in Table-3**. O**bserved values indicate that, the rate of corrosion is greatly decreased from 10.9395 to 2.2464mmpy at an interval of 24 hrs and 0.7683 to 0.0569mmpy after 360 hrs exposure time with an increase of ZTS concentration from 0 to 1000 ppm. The maximum inhibition efficiency of 92.59 % is achieved with 1000ppm concentration after 360hrs exposure time. It suggests that hetero atom (N, S in addition to O) containing phyto constituents may be present in ZTS extract and are adsorbed strongly onto the pipeline steel surface thereby blocking the active sites for dissolution in acidic medium. Schematic representation of the effect of immersion time on the inhibition efficiency of ZTS extract is shown in fig. 4

Table - 3. Corrosion rate and Inhibition efficiency of oil and gas in 1.0 N HCl comprising ZTS extract with various immersion times

Con. ppm	24 hrs.		72 hrs.		120 hrs.		240 hrs.		360 hrs.	
	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	CR (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E
0	10.9395	-	3.7440	-	2.2698	-	1.1466	-	0.7683	-

10	9.3751	14.12	3.1005	17.19	1.7527	22.78	0.8459	26.23	0.5444	29.14
50	7.3827	32.51	2.4336	35.00	1.3432	40.82	0.6377	44.38	0.3916	49.03
100	5.9436	45.67	1.9578	47.71	1.0975	51.65	0.4879	57.45	0.2878	62.54
500	3.6972	66.20	1.0686	71.46	0.6014	73.50	0.2750	76.02	0.1420	81.52
1000	2.2464	79.47	0.6318	83.13	0.3299	85.47	0.1229	89.28	0.0569	92.59

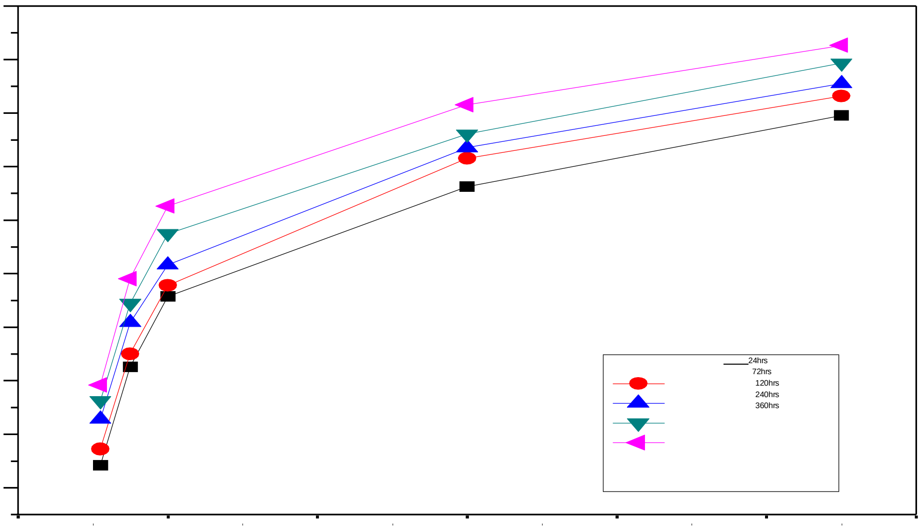


Fig: 4. Inhibition efficiency of ZTS extract on oil and gas pipeline in 1.0N HCl with various immersion times

Effect of Temperature

Influence of temperature plays an important role in understanding the inhibitive mechanism of the inhibitor in dissolution process. Dissolution behavior of oil and gas pipeline steel in 1.0N HCl containing various concentrations of ZTS extract is studied at 303K to 333K and the observed values are listed in Table – 5. The effect of temperature on the inhibition efficiency of ZTS extract is diagrammatically represented in fig.6 .The data reveal that the rate of corrosion is increased and the inhibition efficiency is decreased with increase in temperature from 303 to 333K. The maximum inhibition efficiency of 82.33% is attained at 303K. However decrease of inhibition efficiency at higher temperature suggests that adsorption followed by desorption might be occurred.

Table - 5. Corrosion rate and Inhibition efficiency of oil and gas pipeline in 1.0N HCl with ZTS extract at various temperatures

Con. ppm	303 K		313 K		333 K	
	C.R (mmpy)	**% I.E**	**C.R (mmpy)**	**% I.E**	**C.R (mmpy)**	**% I.E**
0	84.21	-	58.10	-	186.95	-
10	67.09	20.33	49.40	14.97	160.84	13.97
50	51.41	38.95	39.58	31.88	135.30	27.62
100	44.06	47.68	30.96	46.76	120.98	35.29
500	29.75	64.67	21.61	62.81	72.98	60.96
1000	14.88	82.33	12.35	78.74	41.82	77.63

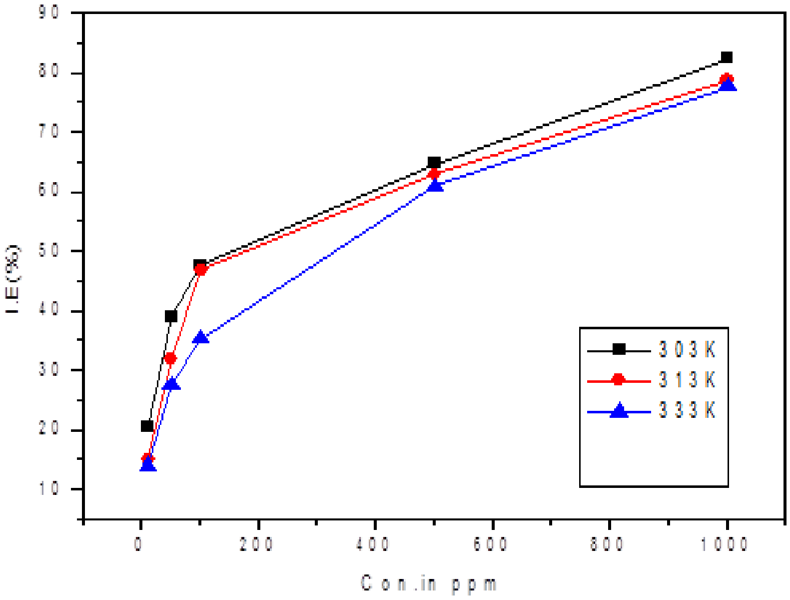


Fig: 6. Inhibition efficiency of ZTS extract on oil and gas pipeline in 1.0N HCl at various temperatures

Thermodynamic Parameters of Metal Dissolution

The transition state equation derived from Arrhenius equation is shown below - 8.1

CR=RT/Nh exp (ΔS/R) exp (-ΔH/RT) ---------- 8.1

Where **h** is the Planck's constant, **N** the Avogadro's number, **ΔS** the entropy of activation, and **ΔH** the enthalpy of activation.

A straight line plot is obtained by plotting log (CR/T) verses 1000/T as shown in Fig. 8.3.From the slope (−ΔH/R) and intercept [log(R/Nh)) + (ΔS/R)] of the plot, ΔS and ΔH are calculated and listed in Table-6.The negative enthalpy of activation stressed the exothermic nature of dissolution process and change in entropy (ΔS) indicates that randomness has taken place on going from reactantto the activated complex on metal surface thereby retarding further dissolution process.

Table - 6. Thermodynamic parameters of oil and gas pipeline steel in 1.0N HCl with ZTS extract

Con. ppm	-ΔH (KJ mol^{-1})	ΔS (KJ mol^{-1})
0	0.0100	0.1080
10	0.0110	0.1104
50	0.0120	0.1127
100	0.0127	0.1145
500	0.0112	0.1082
1000	0.0127	0.1106

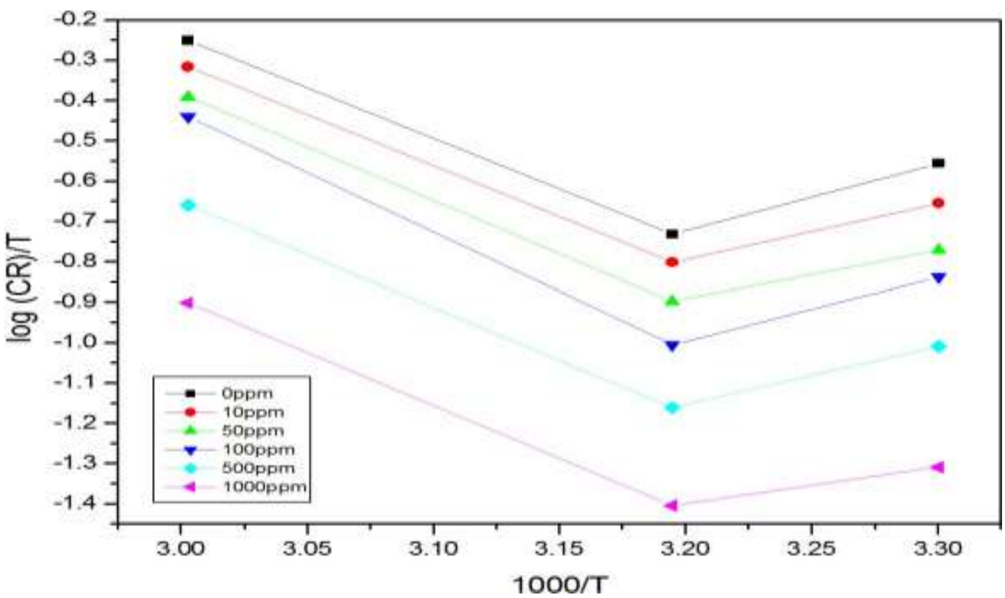


Fig: 7. Transition plot of oil and gas pipeline in 1.0 N HCl with ZTS extract

Activation Energy

The activation energy (E_a) is calculated using the following Arrhenius equation 2

$$\log (CR_2/CR_1) = E_a /2.303 R (1/T_1-1/T_2) \quad \text{-------------} \quad 2$$

Where CR_1 and CR_2 are rate of corrosion at temperature T_1 and T_2 respectively, E_a is the activation energy and R is the gas constant. The calculated values are shown in Table-8.4 and the values are ranged between 22.3022 and 28.8978KJmol^{-1} .This observation indicates that adsorption process followed physisorption. Hence the compounds in ZTS extract forms a complex through weak intermolecular forces.

Heat of adsorption

The heat of adsorption of ZTS extract on the metal surface in 1.0N HCl is calculated using the equation -3

$$Q_{ads}=2.303\ R\ [\log (\theta_2/1-\theta_2)-\log (\theta_1/1-\theta 1)]\ x\ (T_2T_1/T_2-T_1 \text{ ------- } 3$$

Where **R** is the gas constant, **θ_1**and **θ_2** are the degree of surface coverage at temperatures T_1 and T_2 respectively.

The calculated Q_{ads} values ranged from -12.6412 to -8.2365 kJ/mol are given in Table-8.4. The negative values confirmed the adsorption of ZTS extract on oil and gas pipeline steel is exothermic in nature**.**

Table - 7. Activation energy (E_a) and Heat of adsorption (Q_{ads}) of ZTS extract on oil and gas pipeline in1.0N HCl

Con. ppm	E_a ($KJmol^{-1}$)	$-Q_{ads}$ ($KJmol^{-1}$)
0	22.3022	--
10	24.4521	12.6412
50	27.0607	14.3735
100	28.2465	14.3607
500	25.0943	4.4499
1000	28.8978	8.2365

Adsorption Isotherms

Adsorption process is a very important phenomenon in determining the mechanism of the metal surface / inhibitor interaction.. Adsorption mainly depends on the charge of the ions present at the metal surface, the chemical structure of the compound in investigated, inhibitor and the aggressiveness of the electrolyte. The most frequently used isotherms viz: Langmuir, Freundlich, Temkin, El- Awady, Frumkin, and Flory- Huggins are discussed below

Langmuir Isotherm

Langmuir adsorption isotherm is expressed according to equation - 4,

$$\log C/\theta = \log C - \log K \text{ --------- } 4$$

where **θ** is the degree of surface coverage, **C** is the concentration of the inhibitor solution and **K** is the equilibrium constant of adsorption on the metal surface.

Langmuir linear isotherm is obtained by plotting log(C/ θ) verses log C, as shown in fig.8. Average regression co-efficient (R^2). is found to be 0.9991 which is nearly equal to one (unity. Hence, there is a possibility of unimolecular layered film by adsorbed species on pipeline surface and followed Langmuir linear isotherm. Moreover, its average adsorption capacity (Q_m) is found to be 10.035mg/l. It also suggests that phytoconstituents in ZTS extract adsorbed strongly on oil and gas pipeline steel as a thin protective film.

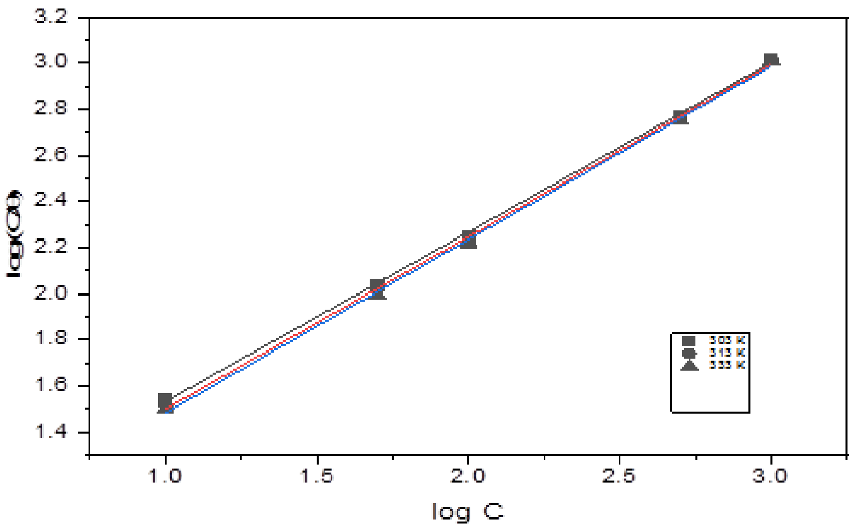


Fig: Langmuir isotherm for adsorption of ZTS extract on the surface of oil and gas pipeline in 1.0N HCl

Freundlich Isotherm

The linear form of Freundlich isotherm equation is as follows

$\log \theta = \log K + 1/n \log C$ -------- 5

The graph is plotted between log θ and log C and the derived parameters are shown in Table – 8. Average regression co-efficient (R^2= 0.9927) value is not very close to unity. Moreover, its **n** value (3.9118) lies in the range 2-10 which also suggest that compounds in ZTS extract adsorbed effectively on oil and gas pipeline steel and inhibit the dissolution process.

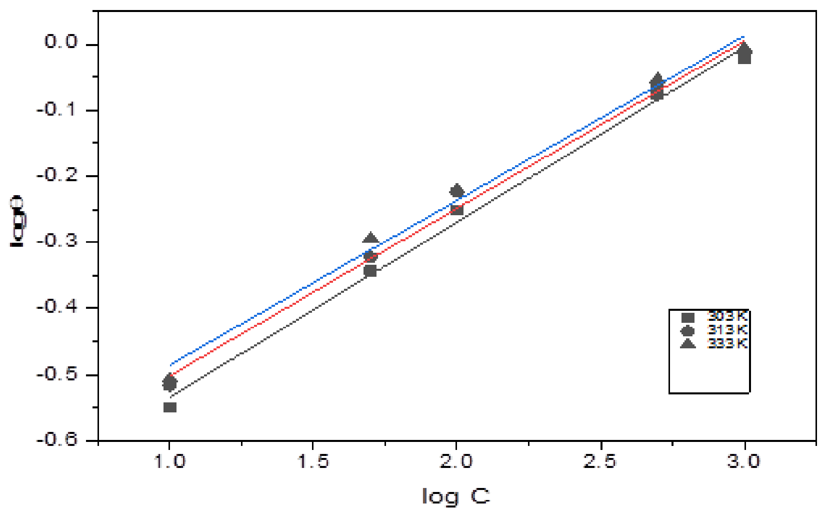


Fig: 9. Freundlich isotherm for adsorption of ZTS extract on the surface of oil and gas pipeline in 1.0N HCl

Temkin Isotherm

In Temkin adsorption isotherm, the degree of surface coverage (θ) is related to the inhibitor concentration (c)

$$\theta = (-2.303\log k/2a) - (2.303\log C/2a) \quad \text{-------------} \ 8.6$$

The surface coverage (θ) against log C is plotted and presented in Fig.– 10. Average regression co- efficient (R^2) value is 0.9908 and the parameters obtained from the plot are listed in Table-8

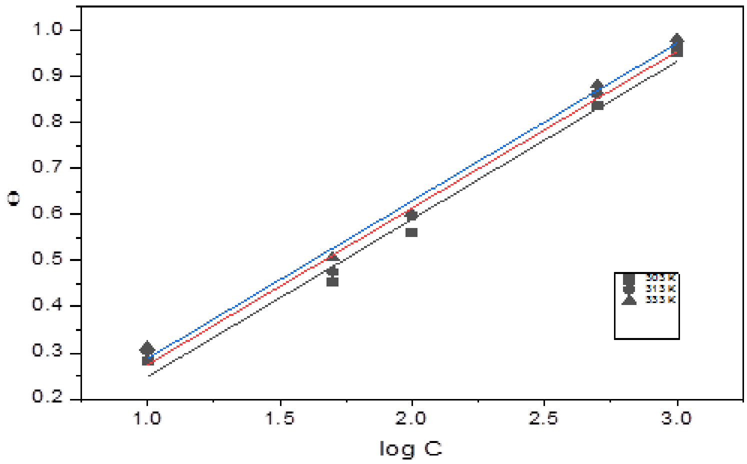


Fig: 10. Temkin isotherm for adsorption of ZTS extract on the surface of oil and gas pipeline in 1.0N HCl

El-Awady Isotherm

The El-Awady adsorption isotherm is given by

log (θ/1-θ) = log K +y log C---------- 7

where **C** is the concentration of inhibitor in the bulk solution, **θ** is the degree of surface coverage, **K** is an El-Awady isotherm constant, equilibrium constant of an adsorption process K_{ads} = K $^{I/Y}$ and y represents the tendency of adsorbate occupying a given active site. The value of log (θ/1-θ) is plotted against log C and the calculated k_{ads} and 1/y from the graph is listed in Table-8. and its average regression co efficient (R^2) is found to be 0.9714

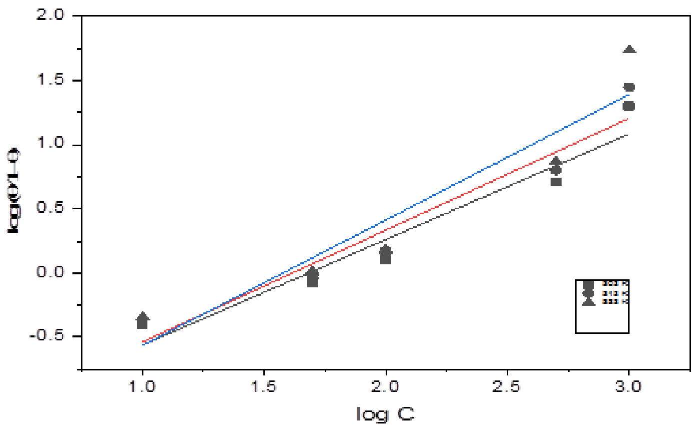


Fig: 11 El-Awady isotherm for adsorption of ZTF extract on the surface of oil and gas pipeline in 1.0N HCl

Frumkin Isotherm

Frumkin adsorption isotherm is given by equation – 8

log { [C]* (θ/1- θ)} = 2.303 log K +2αθ - --------- 8

where **k** is the adsorption–desorption constant and **α** is the lateral interaction term describing the interaction on adsorbed layers. The linear plot of log {[C]* (θ/1- θ)} versus θ is presented in fig. 12 which shows the applicability of Frumkin isotherm. The parameters derived from the above plot are recorded in Table -9. In this, average regression coefficient (R^2= 0.9912) is deviated from unity but the adsorption parameter **α** is positive which suggest that ZTS inhibitor exhibits strong attractive behavior on the surface of oil and gas pipeline steel.

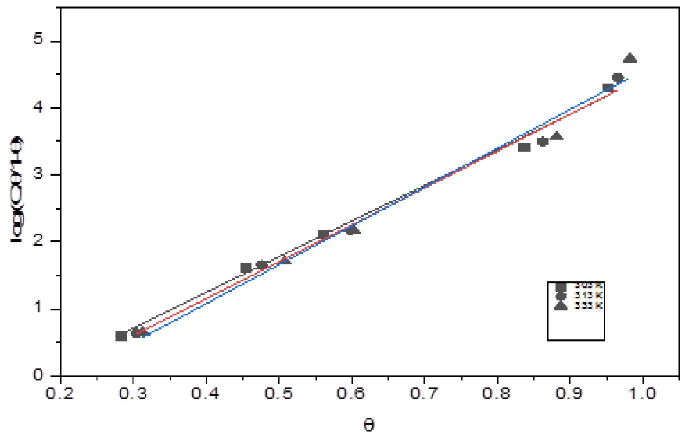


Fig: 12. Frumkin Isotherm for adsorption of ZTS extracton the surface of oil and gas pipeline in 1.0N HCl

Flory- Huggins Isotherm

Flory-Huggins adsorption isotherm can be expressed according to equation -.9

log (θ/C) = log K + x log (1- θ) ----------- 9

The plot of log (θ/C) against log (1- θ) is shown in Fig.- 13, and the obtained data are given in Table – 9. Average regression co-efficient (R^2= 0.9204) is far away from unity.

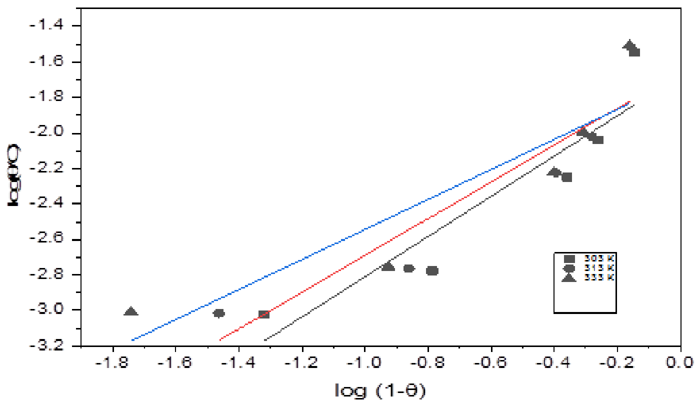


Fig: 13. Florry-Huggins isotherm for adsorption of ZTSextract on the surface of oil and gas pipeline in 1.0N HCl

Table - 9. Adsorption parameters of ZTS extract on oil and gaspipeline in 1.0N HCl

Adsorption isotherm	Tempt. In K	Intercept (k)	R^2	-ΔG KJ/mole	Variables Q_m/n/ a / 1/y/ α/x
Langmuir	303	0.9380	0.9993	9.9584	Q_m 0.9905
	313	1.1140	0.9991	10.7346	1.0020
	333	1.2031	0.9990	11.6336	1.0179
Freundlich	303	-0.9381	0.9949	10.7886	n 3.7750
	313	-1.1139	0.9920	10.9146	3.9526
	333	-1.2081	0.9911	11.6120	4.0177
Temkin	303	-0.1065	0.9882	14.6596	a 3.7658
	313	-0.1775	0.9910	14.4361	3.9247
	333	-0.2287	0.9933	14.8873	4.0216
El-**Awa**dy	303	-1.2004	0.9602	10.4852	1/y 1.2170
	313	-1.3819	0.9787	10.7024	1.1499
	333	-1.4941	0.9754	11.3263	1.0245
Frumkin	303	0.11444	0.9945	10.4852	α 2.6578
	313	0.08522	0.9905	10.7024	2.7492
	333	0.05637	0.9886	11.3263	2.8937
Flory- Huggins	303	-1.86585	0.9263	10.4852	X 1.1324
	313	-1.77779	0.9084	10.7024	1.0351
	333	-1.93743	0.9265	11.3263	0.8455

Electrochemical Methods
Polarization Studies

Potentiodynamic polarization curve for oil and gas pipeline steel in1.0N HCl in the absence and presence of ZTS extract are shown in Fig-14. The various electrochemical parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), and Tafel constants (b_a and b_c) are given in Table – 8.6. It is observed that the presence of ZTS extract lowered the corrosion current density (I_{corr}) from 3097 to 121.8μA/cm^2. This significant reduction in corrosion current density indicates that the compounds in ZTS get adsorbed over the surface of specimen more easily and rapidly thereby hindered the dissolution process. The reduced density of anodic and cathodic current also reveals the inhibitive capacity of ZTS. The corrosion potential (E_{corr}) is shifted to a nobler direction -477 to -454mV. The maximum displacement in E_{corr} is found to be 23 mV which is less than ±85mV. It suggests that inhibitor has an inhibitive effect on both anodic dissolution and cathodic hydrogen evolution. Thus the ZTS extract functioned as mixed type inhibitor.The percentage of inhibition efficiency is increased with increase of inhibitor concentration and maximum of 96.07% is obtained. This may attribute to the formation of thin barrier film resulted by adsorption involving interactions between π- electrons of phytocompounds in inhibitor and vacant d-orbitals of metal ion present at the surface of steel pipes.

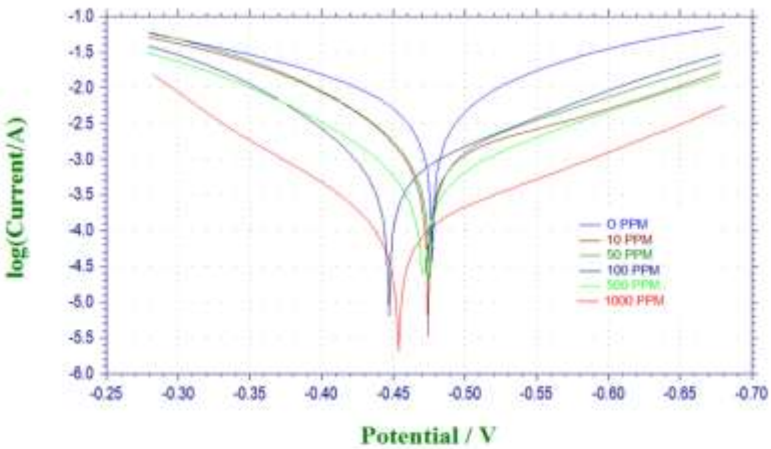


Fig: 14. Polarization curve for oil and gas pipeline in 1.0NHCl containing ZTS extract

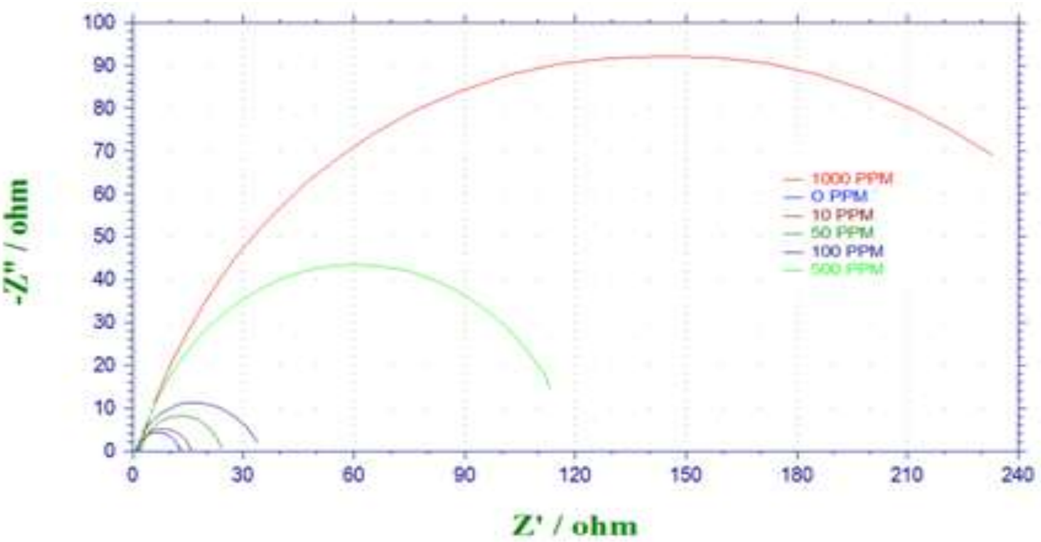
Table - 11.Parameters derived from electrochemical measurements of oil and gas pipeline in 1.0N HCl with ZTS extract.

Con. inppm	Polarization measurements					Impedance measurements		
	$-E_{corr}$ mV/dec)	b_a (mV/dec)	b_c mV/dec)	I_{corr} mAcm ^{2}	% I.E	R_{ct} (cm^2)	C_{dl} 10^{-4} Fcm^2	% I.E
0	477	166.28	153.63	3097	-	11.99	18.94	-
10	474	113.20	183.12	1655	46.56	14.56	13.74	17.65
50	476	107.56	153.28	1583	48.89	22.29	5.813	46.21

100	447	92.89	126.52	783.9	74.69	33.71	2.710	64.43
500	471	99.41	132.52	607.7	80.38	120.05	0.2218	90.01
1000	454	86.38	134.84	121.8	96.07	233.6	0.0571	94.86

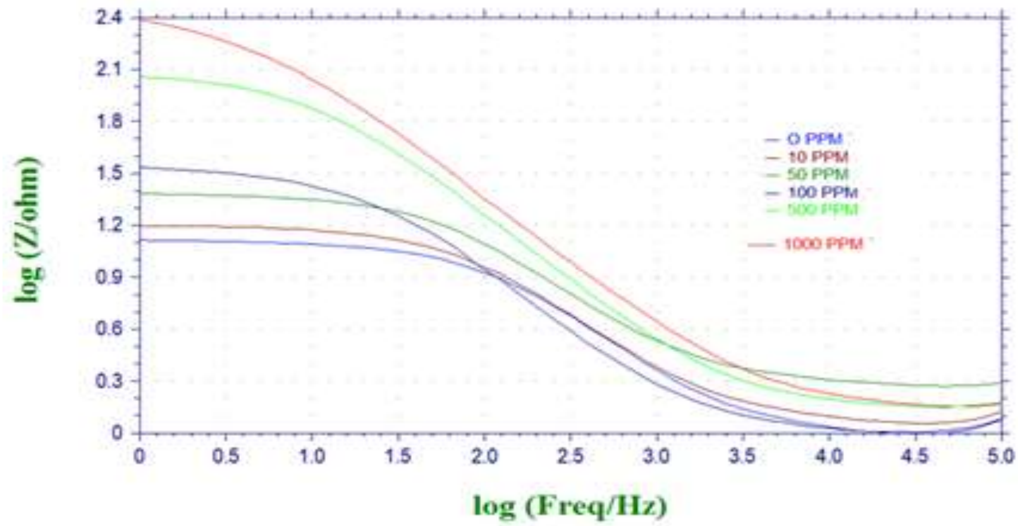
Electrochemical Impedance Studies (EIS)

Fig.– 8.15.(a) represents the Nyquist plot of oil and gas pipeline steel in 1.0N HCl in the absence and presence of ZTS extract as inhibitor. The impedance plot has almost a perfect semi-circular capacitive loop, and its diameter is increased with increase of inhibitor concentration. Meanwhile, C_{dl} value is decreased from 18.94 to 0.0571 x 10^{-4} Fcm^2 and its charge transfer resistance is increased from 11.99 to 233.6 cm^2 with increases of inhibitor concentration..It is clearly showed that the decrease in oxidation of the metal surface in 1.0N HCl is proportional to the increase in concentration of ZTS extract. The inhibition efficiency of ZTS in 1000ppm concentration is 94.86%. Thus the high value of R_{ct} represents a stable passive layer is formed at the (inhibitor) electrode - solution interface junction and act as an effective barrier which might be the reason for limiting diffusion of corrosive species towards the underlying metal substrate

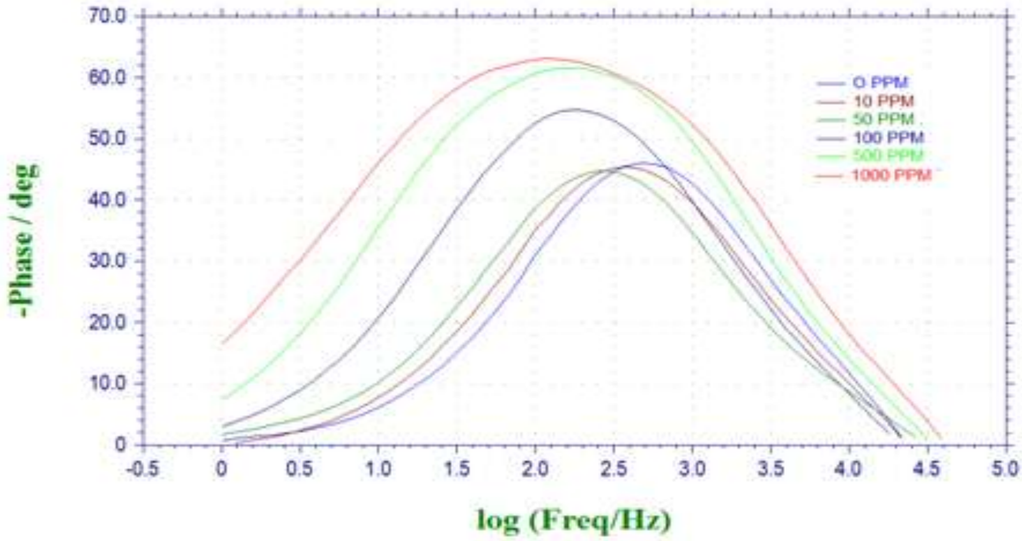


(a)

Fig.15. (b) and (c) show Bode impedance and Bode phase angle plots for adsorbed and unadsorbed oil and gas pipeline steel in 1.0N hydrochloric acid at room temperature. From Bode plot (b) it is observed that the impedance at the interface is increased with increase of inhibitor concentration and observed maximum phase angle in fig.(c) clearly indicates the dissolution process is prevented due to adsorption of molecules onto the pipeline surface



(b)



(c)

Fig: 15. (a-c) Electrochemical impedance plots, Nyquist (a), Bode impedance (b), Bode phase angle for oil and gas pipeline in 1.0N HCl containing ZTS extract

Characterisation Studies
FT-IR Spectral Analysis

The FT-IR spectrum of the purified ethanolic crystals of ZTS extract, corrosion product formed on oil and gas pipe line steel surface in the presence of ZTS inhibitor in 1.0N HCl is shown in Fig: 16 (a) and (b). On comparing FT-IR spectral data, the aromatic –CH stretch is shifted from 2921.94 cm^{-1} to 3369.71 cm^{-1}, the –C=O stretch for carbonyl groups shifted from 1731.47 cm^{-1} to 1790.67 cm^{-1}, the aromatic CH_2 bending stretch for carbonyl group shifted from 1653.10 cm^{-1} to 1656.87 cm-1, the C-O-C stretch shift of ester group 1163.45 cm^{-1} is observed. It is closely observed that certain peaks moved towards to higher frequency region and it providing that adsorption has been taken place over the oil and gas pipe line metal surface in the presence of potential green ZTS extract.

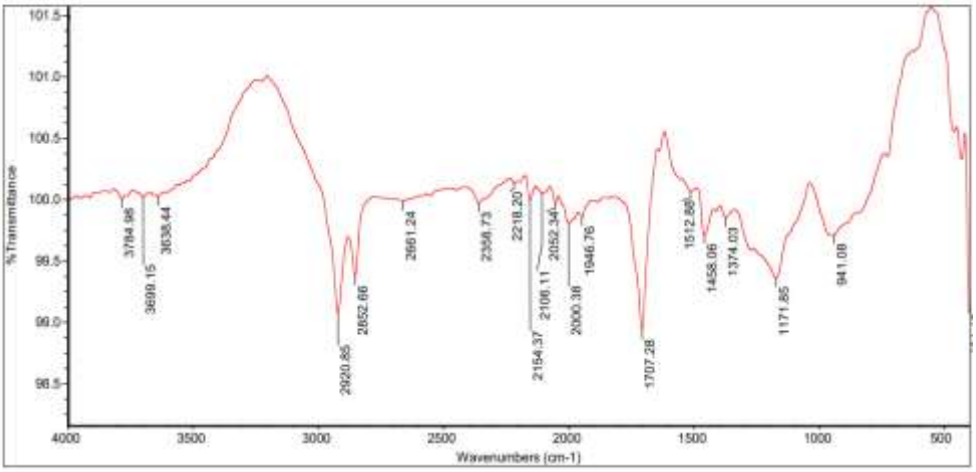


Fig: 16 (a) FT-IR spectrum of ZTS extract

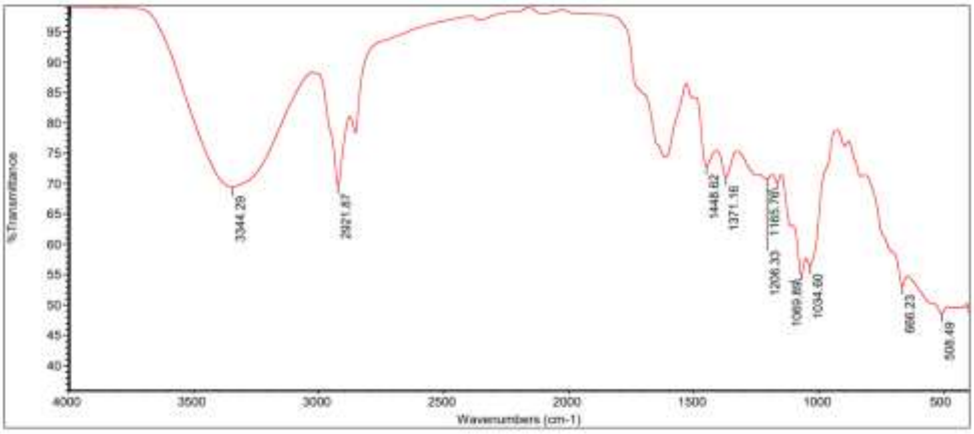


Fig: 16 (b) FT-IR spectrum of corrosion product on oil and gas pipeline in the Presence of ZTS extract in 1.0N HCl.

EDX Spectral Analysis

EDX spectroscopy is used to predict the elements present on the oil and gas pipeline steel surface in the absence and presence of ZTS as inhibitor. Fig.17 (a) and (b) reflect the EDX spectra of corrosion product formed on metal surface in the absence and presence of optimum concentrations of ZTS extract in 1.0N HCl. In the presence of inhibitor molecules, the spectrum confirmed the existence of oxygen and sulphur due to the formation of metal oxide and sulphide in addition to iron, nickel, chromium and carbon, which is the part of composition of oil and gas pipeline steel. However in the absence of inhibitor, oxygen was not found in the corrosion product on the metal surface. It is obviously indicated sulphur containing compound in addition to oxygen containing compounds present in the inhibitor which might be involved in complex formation with metal ion. As a result of adsorption process, dissolution of metal surface is strongly prevented.

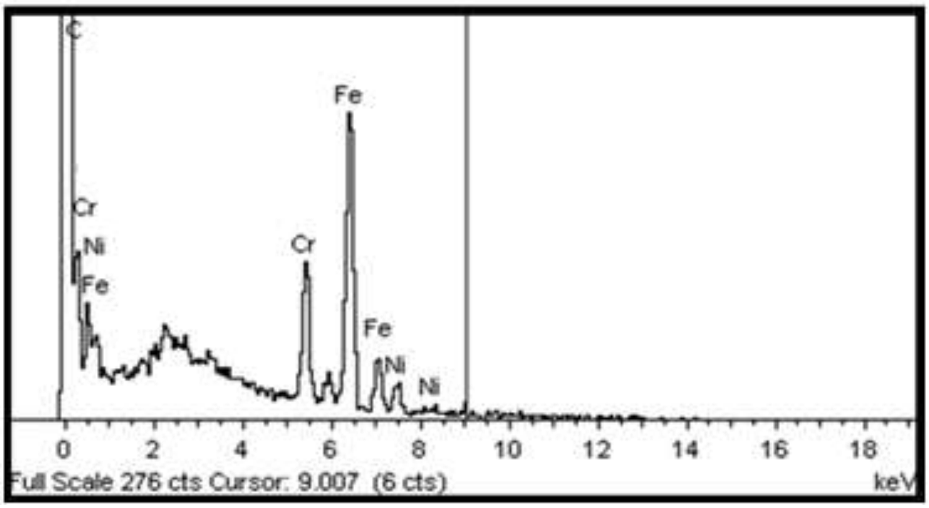


Fig: 17a.EDX spectrum of corrosion product on oil and gaspipeline steel in the absence of ZTS extract in 1.0N HCl

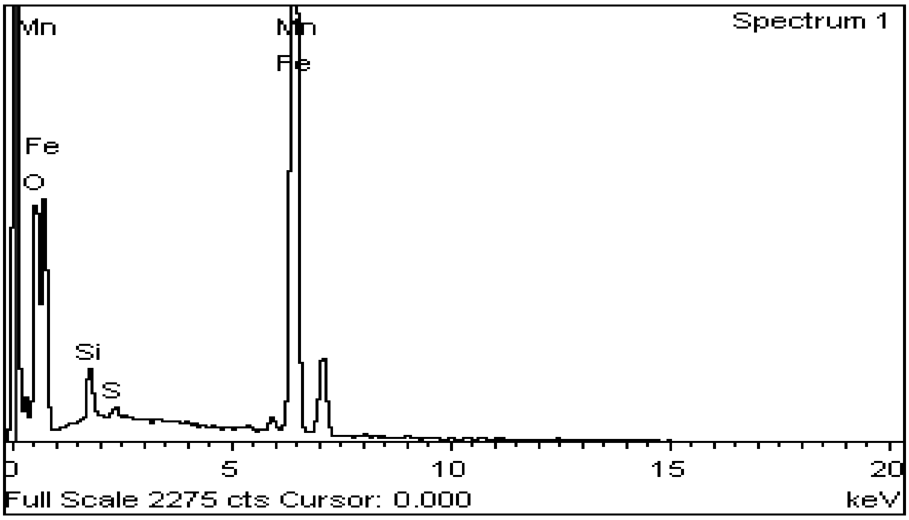


Fig: 17 .b. EDX spectrum of corrosion product on oil and gas pipe line steel in the presence of ZTS extract in 1.0N HCl

Morphological Studies - SEM Analysis

Fig. 18. (b and c) show the surface morphological view of polished oil and gas pipeline steel, in the absence and presence of ZTS extract in 1.0N HCl.The SEM image of polished mild steel surface (Fig 8.14.a) shows the smooth surface of the metal.The surface morphology of pipeline steel in the absence of an inhibitor showed the severe damage on the metal surface leading to pitting type of corrosion (Fig: 8.14. b). However, in the presence of ZTS extract (Fig. 8.14.c), almost smooth and completely covered image confirmed the film formation which could effectively shield the metal surface from corrosive environments.

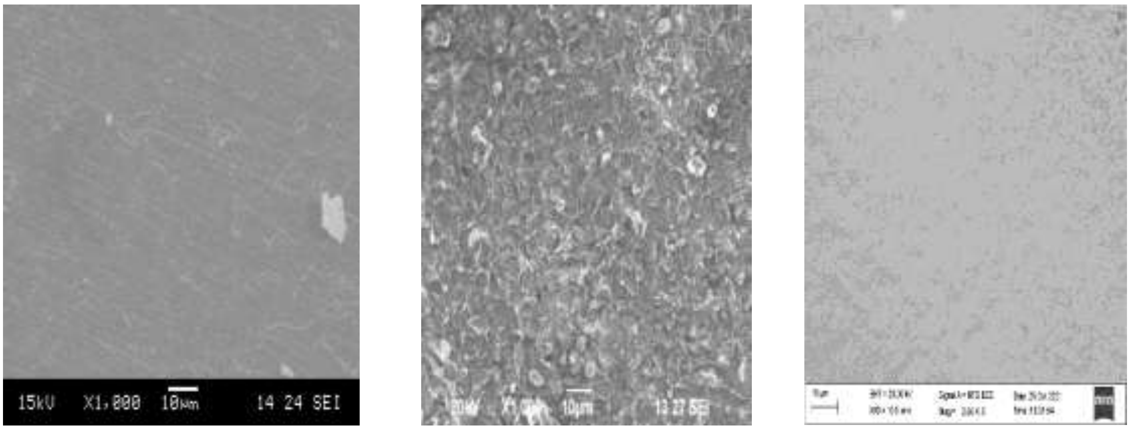


Fig: 18. (a -c) SEM image of the polished oil and gas pipeline steel surface, before and after immersion in1.0N Hydrochloric acid with ZTS extract

4. Conclusion

Ziziphus Trinervia Seed has shown excellent inhibition performance on oil and gas pipeline steel in 1.0N HCl environment. Its inhibition efficiency of 1000ppm concentrated solution is 92.59% at room temperature. It suggest that the phyto constituents present in ZTS extract are adsorbed strongly onto pipeline steel surface thereby blocking the active sites for further dissolution in acid medium. Like other chemical reactions, rate of dissolution is also increased with increase of temperature and hence inhibition efficiency is decreased. The value of activation energy (E_a), heat of adsorption (Q_{ads}) and change in free energy (ΔG_{ads}) indicate the adsorption of alcoholic extract of ZTS on metal surface followed physisorption, exothermic and spontaneous process respectively. Adsorption of phytoconstituents in ZTS extract as inhibitor on pipeline steel surface followed Langmuir adsorption isotherm which is confirmed by its average regression coefficient (R^2= 0.9991) nearly equal to one (unity). In Polarization measurements, corrosion current (I_{corr}) is decreased from 3097 to 121.8µA/cm^{2}with the increase of ZTS concentration and the maximum inhibition efficiency of 1000ppm concentrated solution is 96.07 % . E_{corr} value is shifted from-477 to -454mV, which suggest that ZTF extract behave as a mixed type of inhibitor. In Impedance studies, C_{dl} value is decreased from 18.94 to 0.0571 $\times 10^{-4}$ Fcm^2 whereas charge transfer resistance (R_{ct}) is increased from 11.99 to 233.6Ωcm^2 and the maximum inhibition efficiency of 94.86 %. Is attained. The high R_{ct} value represents a stable passive layer is formed at the (inhibitor) electrode – solution interface junction which acts as an effective barrier and hence dissolution is prevented. The corrosion composite is analysed by FT-IR and EDX which conclude that thin stable protective Fe – S film along with oxide is also formed on the surface of oil and gas pipeline. The formed film passivate the metal surface from further dissolution which is confirmed by the images of SEM.

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