Anti-corrosive effect of *Solanum Torvum* fruits extract on Zinc in 1.0 N Hydrochloric acid

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Abstract - ***The inhibition effect of Solanum Torvum fruits extract on the corrosion of zinc in 1.0 N hydrochloric acid was investigated through mass loss measurements with various time and temperature. The observed result indicated that the corrosion inhibition efficiency was increased with increase of inhibitor concentration and temperature. The thermodynamic parameters viz; E_a, ΔH_{ads}, ΔG_{ads}, ΔS_{ads} were evaluated for corrosion inhibition process which suggests that the adsorption is endothermic, spontaneous and chemisorptions. The inhibitor follows both Langmuir, Temkin adsorption isotherm. The protective film formed on the metal surface was analyzed using spectroscopic studies viz; UV, FT-IR, XRD and SEM-EDX techniques.***

Key Words: *Zinc, Solanum Torvum fruits, Adsorption isotherm, spectroscopic studies.*

1. INTRODUCTION

Corrosion is an economic problem in world wide. Since corrosion can damage the materials which are used to construct automobiles, pipeline systems (water,oil), bridges, buildings and petroleum refineries etc[1]. Zinc is one of the most important non-ferrous metals, which finds extensive use in metallic coating. But is corroded by many agents, of which aqueous acids are the most dangerous[2]. Looking at its increasing use the study, the corrosion inhibition of zinc is of paramount importance. The dissolution behavior of zinc in acidic and nearly neutral media is known to be inhibited by nitrogen and sulfur-containing organic compounds. Such compounds contain electron-donating groups that decrease the corrosion rate by increasing the hydrogen over voltage on the corroding metal[3]. Many synthetic compounds offer good anti-corrosive action, but most of them risk being highly toxic to both humans and the environment. The recent trend is to save human being and environment by using eco-friendly inhibitors for metal in various environment such as, *Cnidoscolus chayamansa* leaves[4,5] ,*Citrullus Vulgaris* peel[6], *Albizia lebbeck* seed[7], *Hibiscus Esculenta* leaves[8], *Jatropha curcas*[9], *Eugenia Jambolana*[10], *Allium Cepa*[11], *Eucalyptus globulus*[12], *Delonix regia* extracts[13], *Rosmarinus officinalis* leaves[14], *khillah* (Ammi visnaga) seeds[15], *Carica Papaya* and *Camellia Sinensis* Leaves[16], *Ricinus communis* Leaves[17], *Justicia gendarussa*[18], *Vitis vinifera*[19] and *Punica granatum* peel[20]. In our present study, we have chosen eco-friendly bio-inhibitor, a green approach to prevent environmental pollution by harmful organic chemicals. The influence of *Solanum Torvum* fruits extract in 1.0N hydrochloric acid environment on zinc using mass loss measurements with different time and temperature have been studied. The formation of film on the metal surface may also confirmed by the spectral studies.

2. MATERIALS AND METHODS

2.1. Properties of *Solanum Torvum* fruits

Solanum Torvum is a plant growing in many parts of the world. Their fruits are edible, can withstand heavy drought and with good nutritional content. The analysis revealed the presence of phytoconstituents such as calcium, iron, carbohydrate, thiamine, niacin, solasodine, flavonoids, alkaloids, phenolic compounds, saponins, terpenoids, tannins etc.The fruits of Solanum torvum are used commonly in traditional medicine as antihypertensive and an antidiabetic.

2.2. Stock solution of *Solanum torvum* fruits extract

Solanum Torvum fruits(STF) were collected from the source and dried under shadow for about 7 days, grinded well, then soaked in a solution of ethyl alcohol for about 48 hours. Then it is filtered followed by evaporation in order to remove the alcohol solvent completely and the pure plant fruits extract was collected. From this extract, different concentration of 10 to 1000 ppm stock solution was prepared using double distilled water and used throughout our present investigation.

2.3. Specimen preparation

Rectangular specimen of zinc was mechanically pressed cut to form different coupons, each of dimension exactly 20cm^2 (5x2x2cm) with emery wheel of 80, 120 and degreased with trichloroethylene, washed with distilled water, cleaned and dried, then stored in desiccators for our present study.

2.4. Mass Loss method

In the mass loss measurements, zinc specimens in triplicate were completely immersed in 100ml of the test solution in the presence and absence of the inhibitor. The specimens were withdrawn from the test solutions after immersion of 24 to 360 hours at room temperature and also different with temperature ranges from 303K to 333K after an hour. The mass loss was taken as the difference in weight of the specimens before and after immersion using digital balance with sensitivity of ±1 mg. The tests were performed in triplicate to guarantee the reliability of the results and the mean value of the mass loss is reported. From the mass loss measurements, the corrosion rate was calculated using the following relationship.

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

(Where, mmpy = millimetre per year, W = Mass loss (mg), D = Density (gm/cm^3), A = Area of specimen (cm^2), T = time in hours)

The inhibition efficiency (%IE) and degree of surface coverage (θ) were calculated using equation (2) and equation (3) respectively.

$$\%\,IE = \frac{W_1 - W_2}{W_1} \times 100 \quad \text{---(2)}$$

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

(Where, W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor respectively)

3. RESULTS AND DISCUSSION

Table-1 reflects that the variation of corrosion parameters with various concentration of STF extract on zinc at different period of contact in 1.0 N hydrochloric acid. It is revealed that the corrosion rate was decreased gradually with the increase of inhibitor concentration. The inhibition efficiency is attained maximum of 80.9% at higher concentration (1000ppm) after 24hrs exposure time. The inhibitive action of *Solanum Torvum* fruits extract was due to the presence of major active compounds such as thiamine and solasodine. Thiamine contains sulphur, nitrogen and hydroxyl group and solasodine contains amine, hydroxyl group respectively. These compounds can serve as a good adsorption sites onto the metal surface by inhibiting the dissolution of zinc.

Table 1: The inhbition efficiency of zinc in 1.0 N hydrochloric acid containing various concentration of STF extract with different exposure time

Con. of inhibitor (ppm)	24 hrs (%)	72 hrs (%)	120 hrs (%)	168 hrs (%)	216 hrs (%)	360 hrs (%)
10	27.1	30.0	29.0	28.2	28.5	25.6
50	50.4	49.2	49.0	46.7	46.6	43.3
100	63.9	61.0	59.2	57.8	56.6	54.9
500	72.0	69.3	68.9	65.1	61.6	60.2
1000	80.9	71.9	71.6	68.4	64.5	62.9

Table 2: The corrosion parameters of Zinc in 1.0 N hydrochloric acid containing various concentration of STF extract with different exposure temperature

Con. of inhi. (ppm)	303 K		313 K		323 K		333 K	
	C.R	% I.E	C.R	% I.E	C.R	% I.E	C.R	% I.E
0	597	-	685	-	691	-	866	-
10	496	16.9	490	28.5	483	30.1	472	45.5
50	380	36.4	375	45.3	373	46.0	405	53.2
100	289	51.6	293	57.3	268	61.2	318	63.3
500	234	60.7	256	62.7	229	66.9	255	70.5
1000	201	66.4	211	69.3	180	74.0	161	81.4

The dissolution behavior of zinc in 1.0 N hydrochloric acid containing different concentration of *Solanum Torvum* fruits extract at various temperatures such as 303K, 313K, 323K and 333K were studied and the results are shown in Table-2. It was found that the percentage of inhibition efficiency on zinc increased with increase of temperature (Fig-1). The maximum of 81.42% of inhibition efficiency is achieved at 333K. At rise in temperature, the increase of inhibition efficiency is due to strong forces of chemical adsorption on the metal surface by certain specific active molecules such as thiamine and solasodine in the extract may activate the corrosion inhibition in the different layers on the metal surface.

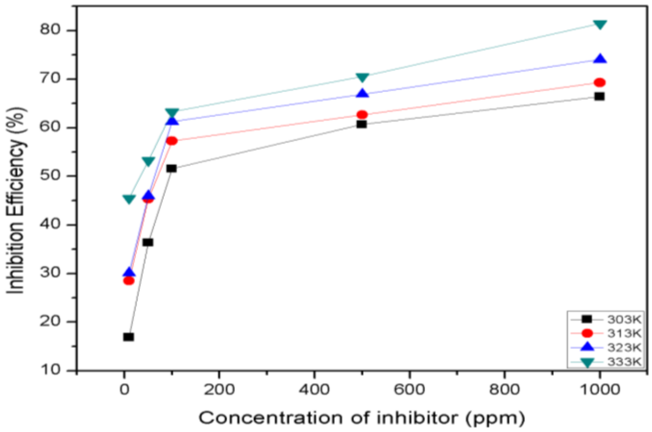


Fig 1: The corrosion parameters of Zinc in 1.0 N hydrochloric acid containing various concentration of STF extract with different exposure temperature.

Table 3: Calculated values of activation energy (E_a) and heat of adsorption (Q_{ads}) of STF extract on Zinc in 1.0 N hydrochloric acid environment.

Con. of inhib. (ppm)	% of I.E		E_a (KJ mol^{-1})	Q_{ads} (KJ mol^{-1})
	30°C	60°C		
0	-	-	70.629	-
10	16.87	45.48	67.122	39.534
50	36.35	53.23	68.068	12.049
100	51.56	63.27	68.328	13.466
500	60.68	70.52	68.237	12.261
1000	66.38	81.42	65.696	22.378

3.1. Effect of Temperature

The values of E_a for the corrosion of zinc in the presence and absence of STF extract is calculated using the following Arrhenius equations (4) and its derived form equation (5).

$$CR= A_{exp} (-E_a/RT) \text{ -------------------------- } (4)$$

$$\log (CR_2/CR_1) = E_a /2.303 R (1/T_1-1/T_2) \text{ ----------------}(5)$$

Where, CR_1 and CR_2 are the corrosion rates of zinc at temperatures, T_1 and T_2 respectively, E_a is the activation energy and R is the universal gas constant. The value of activation energy for blank (70.629 kJ/mol) is higher than in the presence of inhibitors (Table-3), which is clearly indicates that adsorption process is chemisorption.

3.2. Adsorption Consideration

The heat of adsorption on zinc in the presence of inhibitor is calculated by the following equation (6).

$$Q_{ads} =2.303 R [\log (\theta_2/1- \theta_2)-\log (\theta_1 /1- \theta_1)] x (T_2T_1/T_2-T_1) \text{ ----}(6)$$

Where, R is the gas constant, $\theta_1$and θ_2 is the degree of surface coverage at temperatures and T_1 and T_2 respectively. The Q_{ads} values are ranged from 12.049 to 39.534 kJ/mol (Table-3). This value clearly revealed that the adsorption of STF extract on the surface of zinc metal is endothermic.

Table 4: Langmuir adsorption parameters of STF extract on Zinc in 1.0 N hydrochloric acid environment.

Log C	Log C/ θ			
	30°C	40°C	50°C	60°C
1	1.7729	1.5456	1.5210	1.3422
1.6989	2.1385	2.0426	2.0367	1.9728
2	2.2877	2.2418	2.2129	2.1988
2.6989	2.9159	2.9020	2.8735	2.8507
3	3.1779	3.1595	3.1307	3.0892

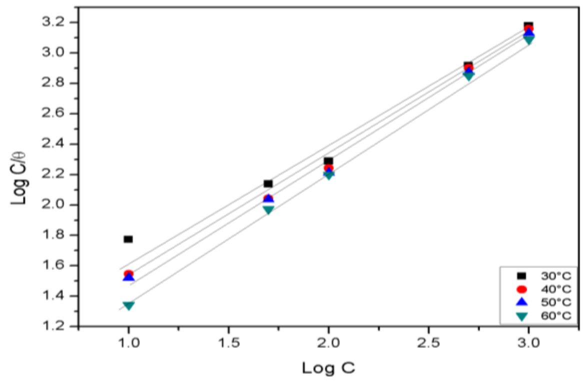


Fig 2: Langmuir adsorption parameters of STF extract on Zinc in 1.0 N hydrochloric acid environment

Table 5: Temkin adsorption parameters of STF extract on Zinc in 1.0 N hydrochloric acid environment.

Log C	θ			
	30°C	40°C	50°C	60°C
1	0.1687	0.2847	0.3013	0.4548
1.6989	0.3635	0.4533	0.4595	0.5323
2	0.5156	0.5730	0.6124	0.6327
2.6989	0.6068	0.6265	0.6690	0.7052
3	0.6638	0.6927	0.7401	0.8142

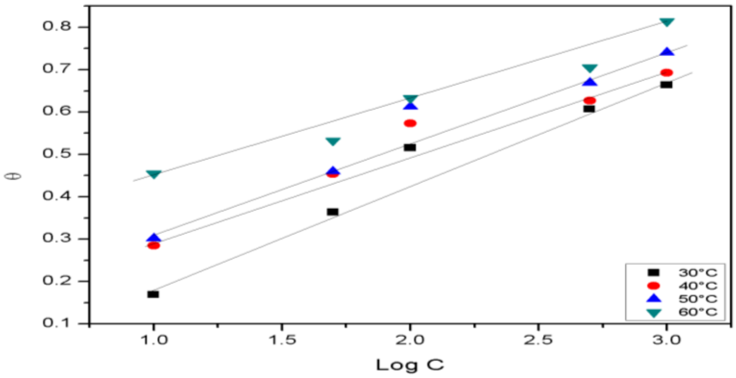


Fig 3: Temkin adsorption parameters of STF extract on Zinc in 1.0 N hydrochloric acid environment.

The adsorption isotherms are used to investigate the mode of adsorption and the characteristic of adsorption of inhibitor on the metal surface. In our present study the Langmuir, Temkin isotherms are investigated. The Langmuir and Temkin adsorption isotherm can be expressed by the equation (7) and equation (8) given below.

$$\log C/\theta = \log C - \log K \text{ ----------------------------(7)}$$

$$\theta = K \ln C \text{ ------------------------------(8)}$$

Where, θ is the surface coverage, C is the concentration of the inhibitor solution and K is an adsorption coefficient.

By plotting values of log C/θ versus log C, linear plots were generated (Fig-2) and conforming that the experimental data fitted with the Langmuir adsorption isotherm for the adsorption of STF extract on metal surface. The Langmuir adsorption isotherm is better fit at 303K for Copper (R^2 =0.9991).

A plot of θ versus log C gives almost a straight line for metal in STF extract in acid medium (Fig-3). The straight line indicated that the inhibitor obeyed Temkin adsorption isotherm.

The adsorption of STF extract on the metal surface is related to the free energy of adsorption (ΔG_{ads}) by the following equation (9)

$$\Delta G_{ads} = -2.303 RT \log (55.5 K) \text{ -----------------------(9)}$$

Where, R is the gas constant, T is the temperature and K is the equilibrium constant of adsorption. The values of intercept (K) obtained from Langmuir and Temkin adsorption isotherm is substituted in equation (9) and the calculated values of ΔG_{ads} are placed in Table-6. The negative values of ΔG_{ads} suggested that the adsorption of STF extract onto metal surface is a spontaneous process and the adsorbed layer is more stable one.

Table 6: Langmuir and Temkin parameters of STF extract on zinc in 1.0 N hydrochloric acid environment.

Adsorption isotherm	Tem.	Slope	logk	R^2	ΔG_{ads} (KJ mol^{-1})
Langmuir	303	0.715	0.972	0.973	-15.759
	313	0.817	0.680	0.993	-14.525
	323	0.812	0.667	0.993	-14.912
	333	0.877	0.467	0.999	-14.099
Temkin	303	0.246	-0.047	0.944	-9.848
	313	0.196	0.117	0.930	-11.159
	323	0.215	0.110	0.928	-11.469
	333	0.174	0.267	0.949	-12.822

Table 7: The relation between log (CR/T) and 1000/T for different concentration of STF extract on Zinc in 1.0 N hydrochloric acid environment

1000 / T	Log (CR / T)					
	0 ppm	10 ppm	50 ppm	100 ppm	500 ppm	1000 ppm
3.300	0.294	0.214	0.098	-0.021	-0.111	-0.179
3.194	0.340	0.195	0.078	-0.029	-0.087	-0.172
3.096	0.330	0.175	0.063	-0.081	-0.150	-0.255
3.003	0.415	0.152	0.085	-0.019	-0.115	-0.316

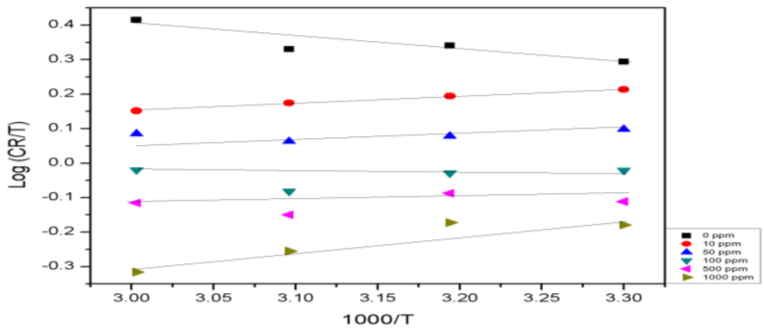


Fig 4: The relation between log (CR/T) and 1000/T for different concentration of STF extract on Zinc in 1.0 N hydrochloric acid environment

An alternative formula of the Arrhenius equation is the transition state equation

$$CR = RT/Nh \exp(\Delta S/R) \exp(-\Delta H/RT) \text{ ------(10)}$$

Where, h is the Planck's constant, N the Avogadro's number, ΔS the entropy of activation, and ΔH the enthalpy of activation. A plot of log (CR/T) vs 1000/T should give a straight line (Fig-4) with a slope of (−ΔH/R) and an intercept of [log(R/Nh)) + (ΔS/R)], from which the values of ΔS and ΔH were calculated and listed in Table-8.

Table 8: Thermodynamic parameters of Zinc in 1.0 N hydrochloric acid obtained from weight loss measurement.

Con. of STF extract (ppm)	ΔH ($KJ\ mol^{-1}$)	ΔS ($KJ\ mol^{-1}$)
0	2.9489	8.195
10	1.7351	8.002
50	0.4714	8.059
100	0.4406	8.029
500	0.6285	8.014
1000	0.4107	7.871

4. MORPHOLOGY STUDIES

4.1. UV Spectrum

The Fig 5 (a) and 5 (b) shows the UV spectrum of ethanolic crystals of STF extract and the corrosion product on the surface of zinc in the presence of inhibitor. The three absorption bands are shifted from higher (288, 318, 672nm) to lower (249, 299, 668nm) region i.e., hypsochromic shift or blue shift. The results revealed that the formation of complex between the zinc and the active molecules present in the green inhibitor.

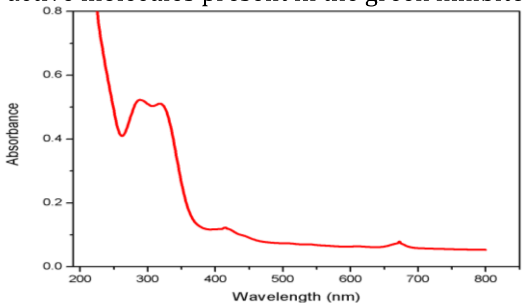


Fig 5(a)

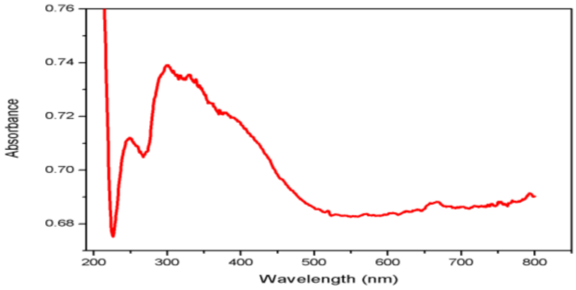


Fig 5(b)

Fig 5: UV spectrum of (a) ethanolic extract of STF, (b) the corrosion product on zinc in 1.0 N HCl in the presence of STF extract

4.2. FT-IR Analysis

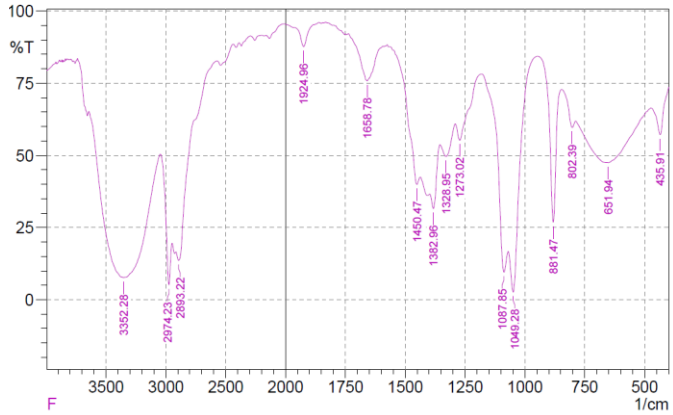


Fig 6: FT-IR spectrum of ethanolic extact of *Solanum Torvum* fruits (STF)

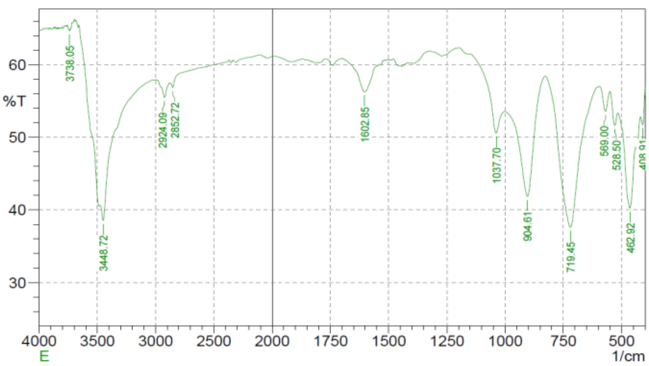


Fig 7 : FT-IR spectrum for the corrosion product on Zinc in the presence of STF extract with 1.0 N hydrochloric acid

The Fig-6 and 7 reflect that the FTIR spectrum of the ethanolic extract of inhibitor and the corrosion product of zinc in the presence of STF extract in 1.0 N HCl. On comparing both spectra, We found that -OH stretching was shifted from 2974.23 to 2924.09 cm^{-1}, the –C=C stretching frequency was shifted from 1658.78 to 1602.85 cm^{-1}, the -C-N stretching in aliphatic amine was shifted from 1087.85 to 1037.70 cm^{-1}, and the -S-OR stretching in ester was shifted from 881.47 to 719.45 cm^{-1} indicates that the binding between metal and inhibitor takes place through ester group. Thus the FT-IR spectra support the fact that the corrosion inhibition of STF inhibitor on Zinc in 1.0N hydrochloric acid may be the adsorption of active molecule in the inhibitor and surface of the metal.

4.3. XRD Analysis

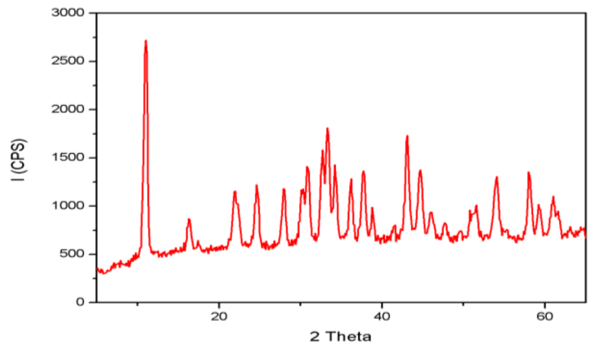


Fig 8: XRD spectrum of Zinc in 1.0 N hydrochloric acid environment

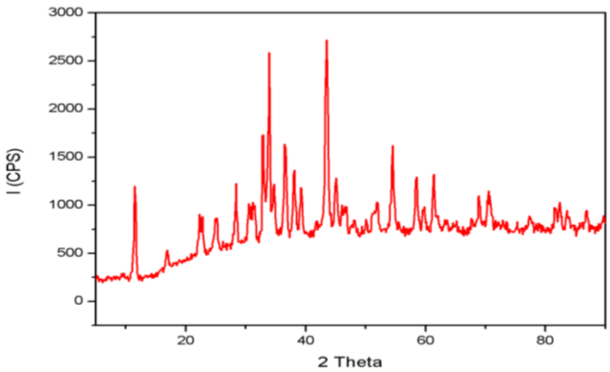
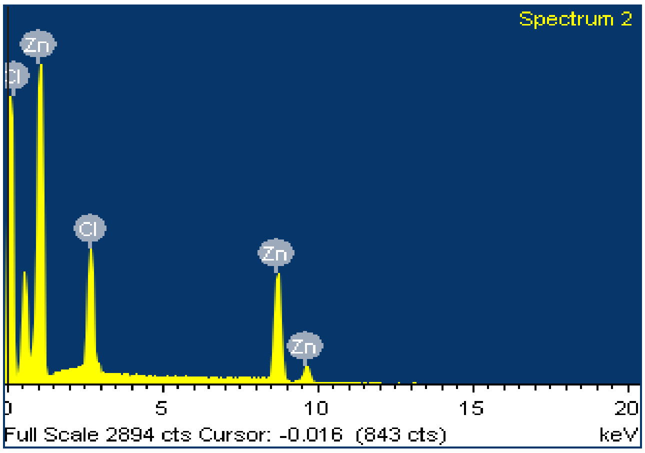


Fig 9: XRD spectrum of Zinc in the presence of STF extract in 1.0 N hydrochloric acid environment

The corrosion products are scrapped from the zinc surface in the presence and absence of STF extract inhibitor is examined by XRD studies are shown in Fig-8 and 9 respectively. The base peak (Fig-8) is matched with the standard peak of Zinc chloride ($ZnCl_2$) which has a crystal structure of monoclinic with the lattice parameter values of a= 6.500, b=11.30, c= 12.300AU which is taken from the JCPDS File no. PDF 740518 and the second one is matched with the standard peak of Zinc oxide (ZnO) has a hexagonal structure with the lattice parameter of a= 3.253, c= 5.213AU which is taken from the JCPDS file no. PDF 891397. A peak obtained from Fig-9 is coincided with the standard peaks for zinc nitride (Zn_3N_2) with the d value of 31.703. This compound has a crystal structure of simple cubic with the lattice parameter of a=b=c=9.769 AU which is taken from the JCPDS file no. PDF 880618 and the other peak is matched with a standard peak of Zinc oxide sulphate [$Zn_3O(SO_4)_2$] has a monoclinic structure with a lattice paramater of a=7.867, b=6.700, c=7.374AU which is taken from the JCPDS file no. PDF 311469.The third one is matched with a peak of Zinc sulphate ($ZnSO_4$) has a orthorhombic structure with a lattice paramater of a=8.604, b=6.746, c=4.774 AU which is taken from the JCPDS file no. PDF 802210. It reflect that the thin film may be mainly combine with a rich amount of [$Zn_3O(SO_4)_2$], Zn_3N_2, $ZnSO_4$,ZnO and $ZnCl_2$ etc with the bio-inhibitor.

4.4. EDX Spectroscopy



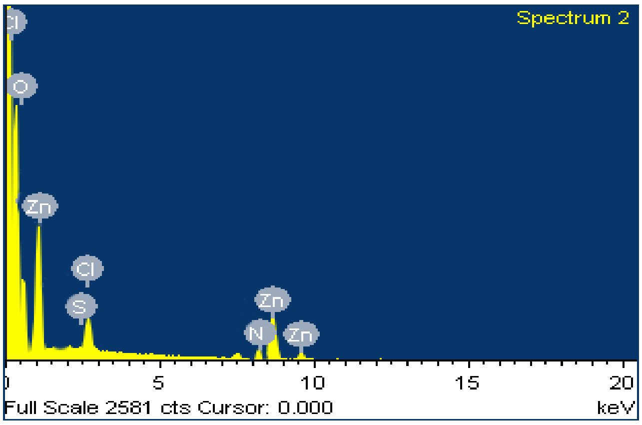


Fig 10: EDX spectrum of the corrosion product on Zinc surface in 1.0 N HCl.

Fig 11: EDX spectrum of the corrosion product on Zinc in the presence of STF extract in 1.0 N HCl

EDX spectroscopy was used to determine the elements present on the zinc surface in the absence and presence of inhibitor. Fig-10 and 11 represents the EDX spectra for the corrosion product on metal surface in the absence and presence of optimum concentrations of STF extract in 1.0 N hydrochloric acid. In the absence of inhibitor molecules, the spectrum may concluded that the existence of chlorine due to the formation of metal chloride. However, in the presence of the optimum concentrations of the inhibitors sulphur, oxygen, nitrogen atoms are found to be present in the corrosion product on the metal surface. It clearly indicates that these hetero atoms present in the inhibitor molecules may involve the complex formation between metal atom and the active species such as thiamine, solasodine etc., during the adsorption process and prevent the further dissolution of metal against corrosion.

4.5. SEM Analysis

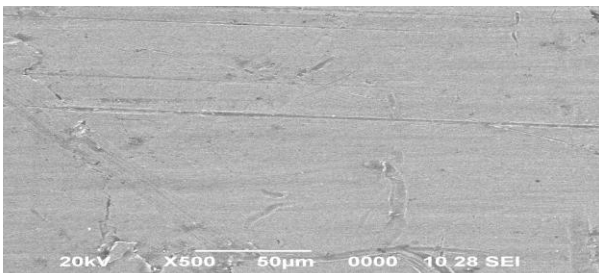


Fig: 12(a)

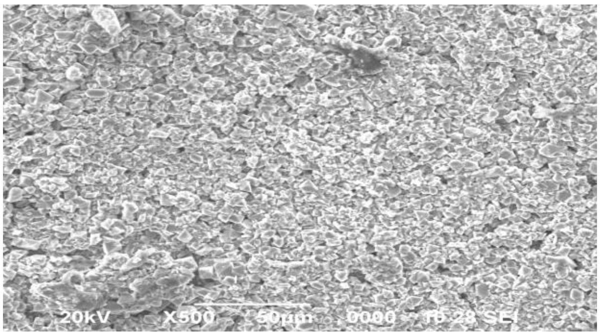


Fig: 12(b)

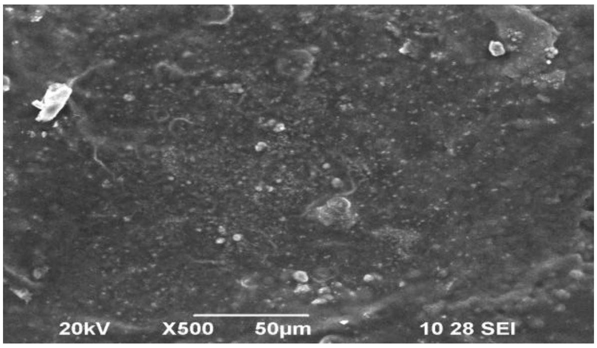
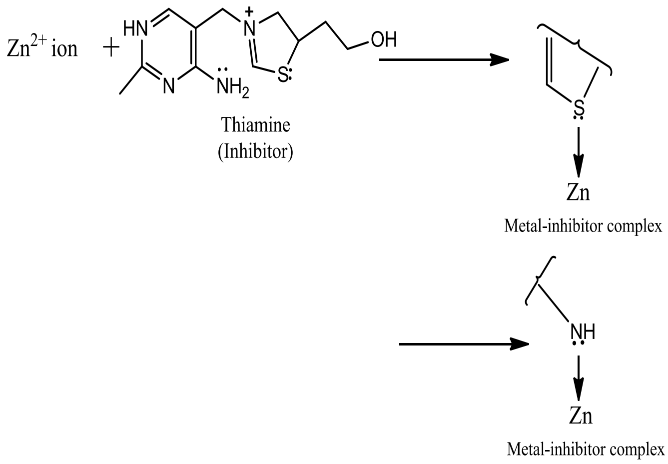


Fig: 12(c)

Fig 12: SEM micrographs of (a) polish zinc, (b) without inhibitor, (c) with inhibitor

The Surface morphology of zinc was studied by scanning electron microscope (SEM). Fig-12(a) shows that the zinc sample before immersion seems smooth surface, The SEM photograph 12(b) showed that the surface of metal has number of pits and cracks, but in the presence of inhibitor [Fig-12(c)] they are minimized on the metal surface. It is clearly indicates that the formation of spongy mass covered on the entire metal surface to reduce further dissolution of the metal.

5. Proposed Mechanism



6. CONCLUSIONS

On the basis of the above results, it can be seen that *Solanum Torvum* fruits extract is a good inhibitor for zinc in 1.0 N hydrochloric acid. The inhibition efficiency of STF attains a maximum value of 80.9%. This inhibition effect increases with the increase of inhibitor concentration and temperature but decreases with time. The hetero atom such as sulphur, nitrogen and poly hydroxyl group in thiamine and solasodine are electron rich centre and served as a good adsorption site onto the metal surface. They are responsible for the inhibitory action of *Solanum Torvum* fruits extract on zinc in 1.0 N hydrochloric acid. The value of activation energy (E_a), enthalpy of adsorption (ΔH_{ads}) and free energy changes (ΔG_{ads}) indicates that the adsorption of inhibitor on metal surface follows chemical, endothermic and spontaneous process respectively. The corrosion product over the surface of zinc is characterized by UV, FT-IR, XRD and SEM-EDX studies also confirm protective film completely shielded the entire metal surface and reduce the further dissolution of metal against corrosion.

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