



## ***Solanum Torvum* Fruits Extract as an Eco-Friendly Inhibitor on Copper in Acid Medium**

**Bright A<sup>1\*</sup>, Michlin Ruphina Maragatham S<sup>1</sup>, Malar Vizhi I<sup>2</sup>, Kalirajan K<sup>2</sup> and Selvaraj S<sup>2</sup>**

<sup>1</sup>Dept. of Chemistry, V V College of Engineering, Arasoor, Tisaiyanvilai-627 657, Tamilnadu, INDIA

<sup>2</sup>Postgraduate and Research Department of Chemistry, Sri Paramakalyani College, Alwarkurichi-627 412, Tamil Nadu, INDIA

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### **Abstract**

*The inhibition efficacy of Solanum Torvum fruits extract on Copper in 1.0 N HCl has been examined using non-electrochemical methods with various periods of contact as well as temperature. The observed result reveals that the percentage of inhibition efficacy increased with rise of inhibitor concentration, exposure time and temperature. Thermodynamic parameters (viz;  $E_a$ ,  $Q_{ads}$ ,  $\Delta G_{ads}$ ,  $\Delta H$  and  $\Delta S$ ) suggests that the surface assimilation of inhibitor is endothermic and chemisorption process. It follows both Langmuir and Temkin adsorption isotherm. The dissolution products also proved by Ultra-violet, Fourier transform infrared spectroscopy, Energy dispersion X-ray spectroscopy and Scanning electron microscope.*

**Keywords:** Copper, inhibitor, mass loss, adsorption, spectral studies.

### **Introduction**

Copper is the most important material for its excellent physical, chemical and mechanical properties<sup>1-3</sup>. The use of chemical inhibitors is the common method for the protection against dissolution in acidic media. It is revealed that the existence of heteroatoms like nitrogen, sulphur, phosphorous and olefinic double bond in the molecule enhance its action as copper dissolution inhibitor. As most efficient organic dissolution inhibitors could be toxic for the environment, contemporary studies are directed towards the search for alternative inhibitors that would be ecologically acceptable, stable, non-toxic and available at a relatively low cost. These compounds, referred as “green”, “eco-friendly”, or “environment friendly”, comprise both organic and inorganic inhibitors<sup>4-8</sup>. Recently numerous investigators have been studied the corrosion of metals using various plant extract as green inhibitors such as *Musa acuminata* peel<sup>9</sup>, orange juice<sup>10</sup>, *Strychnos nuxvomica*<sup>11</sup>, Mango Bark And Leaf Extract<sup>12</sup>, *Acacia seyal* var. *seyal*<sup>13</sup>, *Uncaria gambir*<sup>14</sup>, *Solanum melongena*<sup>15</sup>, *Punica granatum*<sup>16</sup>, *Emblica officinalis*<sup>17</sup>, *Andrographis paniculata*<sup>18</sup>, *Citrullus vulgaris* Peel<sup>19</sup>, *Anogessus leocarpus*<sup>20</sup> and *Cnidioscolus chayamansa* leaves<sup>21,22</sup>, Red onion skin<sup>23</sup>, *Ocimum Sanctum*<sup>24</sup>, *Salvia Judica*<sup>25</sup>, and Azwain seed<sup>26</sup>. Thus our aim of the present work is to investigate the effect of *Solanum Torvum* fruits extract on the corrosion behaviour of copper in 1.0 N HCl solution by mass loss measurements with various time duration and temperature by using Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), UV-Vis spectroscopy, Energy dispersive X-ray spectroscopy (EDX) and Scanning electron microscope (SEM) techniques to analyse the dissolution product formed on the copper metal surface.

### **Material and Methods**

**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. Phytochemical studies indicated that fruits of this species have good concentrations of various alkaloids, flavonoids, saponins, tannins, thiamine, niacin, solasodine and glycosides as sufficient to have pharmacological effects. The ripened fruits are used in the preparation of tonic and haemopoietic agents and also for the treatment for pain. Aqueous extract of the fruits of *S. torvum* enhanced delayed type hypersensitivity (DTH) response, increased haemagglutination antibody titer and white blood cells (WBC) count.

**Stock solution of *Solanum torvum* fruits extract:** *Solanum Torvum* (STF) fruits were collected from the source and dried under shadow for about 7 days, grinded well, then immersed in ethanol for about 48 hours. Then it is filtered followed by evaporation and the pure 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.

**Specimen preparation:** The copper specimens (5x2x2cm) were polished with different grade of emery papers and degreased with acetone, washed with distilled water, cleaned and dried, then stored in desiccators for our present study.

**Non-electrochemical method:** In non-electrochemical method, copper specimens were completely soaked in 100 ml 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 303 K to 333 K after an hour. The weight loss was taken as the difference in mass of the specimens before and after immersion using digital balance. From the non-electrochemical method, the corrosion rate was calculated using the following relationship.

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

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

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

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

**Activation energy:** The activation energy ( $E_a$ ) for the dissolution of copper in acid medium was calculated using Arrhenius theory. An assumption of Arrhenius theory is expressed by equation (4) and it's derived from (5).

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

$$\log(\text{CR}_2 / \text{CR}_1) = E_a / 2.303 R (1/T_1 - 1/T_2) \quad (5)$$

**Heat of adsorption ( $Q_{\text{ads}}$ ):** The  $Q_{\text{ads}}$  on copper in the presence of STF extract in acid medium is calculated by the following equation.

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

**Langmuir adsorption isotherm:** It can be expressed by the following equation.

$$\log C / \theta = \log C - \log K \quad (7)$$

**Free energy of adsorption ( $\Delta G_{\text{ads}}$ ):** The  $\Delta G_{\text{ads}}$  on copper in the presence of STF extract in acid medium is calculated by the following equation.

$$\Delta G_{\text{ads}} = -2.303 RT \log(55.5 K) \quad (8)$$

## Results and Discussion

The dissolution parameters of copper in 1.0 N HCl with different STF concentration at various period of contact is presented in table-1. The observed values are clearly indicates that in the presence of STF extract the value of corrosion rate decreased from 6.355 to 1.528 mmpy (24 hrs) and 1.343 to 0.219 mmpy (360 hrs) with increase of inhibitor concentration from 0 to 1000 ppm. The maximum of 83.72 % of inhibition efficiency is achieved even after 360 hrs exposure time. This achievement is mainly due to the presence of active phytochemical constituents present in the inhibitor molecule which is adsorbed on the metal surface and shield completely to prevent further dissolution from the aggressive acid media. The observation of maximum surface coverage clearly indicates that the hetero atoms (such as sulphur, nitrogen and oxygen) present in the inhibitor molecules can able to bind with the metal ions from the copper surface, very strongly and protect the metal ions from corrosive environment.

**Table-1**  
**The dissolution parameters of copper in 1.0 N HCl with different STF concentration at various period of contact**

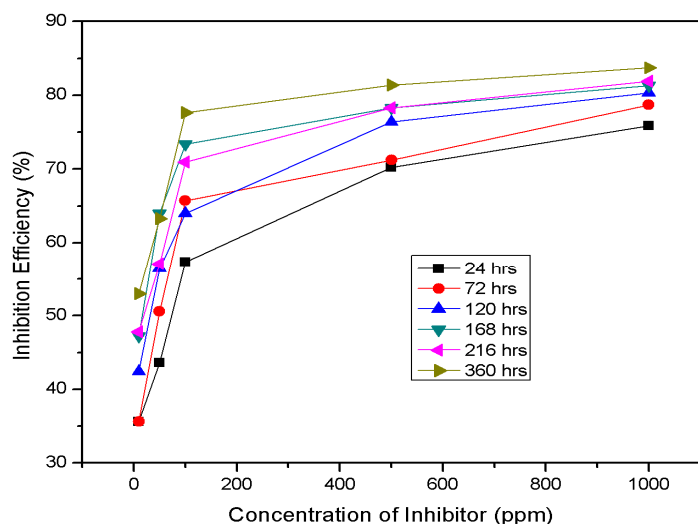
Time (hrs)	Corrosion Rate (mmpy)						Inhibition Efficiency (%)					
	0 ppm	10 ppm	50 ppm	100 ppm	500 ppm	1000 ppm	0 ppm	10 ppm	50 ppm	100 ppm	500 ppm	1000 ppm
24	6.355	4.094	3.585	2.709	1.894	1.528	-	35.58	43.59	57.37	70.19	75.87
72	3.089	1.989	1.528	1.059	0.889	0.659	-	35.60	50.55	65.71	71.21	78.68
120	2.795	1.609	1.218	1.006	0.660	0.549	-	42.42	56.41	63.99	76.38	80.32
168	2.319	1.225	0.835	0.617	0.503	0.434	-	47.18	63.99	73.39	78.29	81.30
216	2.064	1.077	0.885	0.599	0.448	0.373	-	47.80	57.12	70.94	78.29	81.91
360	1.343	0.631	0.493	0.300	0.250	0.219	-	52.98	63.29	77.65	81.39	83.72

The figure-2 reflects that the concentration of inhibitor versus the percentage of inhibition efficiency (% IE) at various temperature from 303K to 333K (table-2). The maximum of 86.22 % I.E. is reached 333K. The value of inhibition efficacy is increased with rise in temperature is suggested that chemisorption. This observed results indicate that the adsorption of main active components present in the inhibitor may shield the metal surface at higher temperature.

It is also confirmed that the activation energy ( $E_a$ ) values (Table-3) gradually decreased in the presence of inhibitors which may clearly support the chemisorption process. This is because of the adsorption of active molecules on the copper surface is greater than the desorption process. The calculated  $Q_{ads}$  values (Table-3) are ranged from 8.533 to 21.663 kJ/mol. The positive values (8.533 to 21.663 kJ/mol) of  $Q_{ads}$  indicate that the adsorption of STF on the surface of copper metal is endothermic.

**Table-2**  
The dissolution parameters of copper in 1.0 N HCl with different STF concentration at various temperatures

Tem. (K)	Corrosion Rate (mmpy)						Inhibition Efficiency (%)					
	0 ppm	10 ppm	50 ppm	100 ppm	500 ppm	1000 ppm	0 ppm	10 ppm	50 ppm	100 ppm	500 ppm	1000 ppm
303	73.82	50.35	42.53	31.78	20.04	17.60	-	31.79	42.38	56.95	72.85	76.16
313	96.79	59.15	43.99	35.69	23.95	18.58	-	38.88	54.54	63.13	75.25	80.81
323	122.69	79.68	54.75	34.71	27.38	21.02	-	35.06	55.38	71.71	77.69	82.86
333	138.34	83.59	53.28	36.17	29.82	19.07	-	39.58	61.48	73.85	78.45	86.22

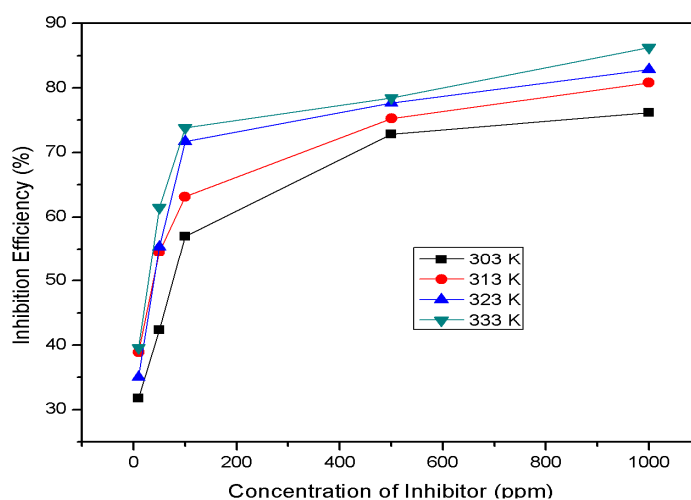


**Figure-1**  
The dissolution parameters of copper in 1.0 N HCl with different STF concentration at various period of contact

The plot of  $\log(C/\theta)$  Vs  $\log C$  yield a straight line, clearly proving that the adsorption of the used inhibitor for acid on the metal surface obeys the Langmuir adsorption isotherm (figure-3), and means that there is no interaction between the adsorbed species. The Langmuir adsorption isotherm is better fit at 313K for Copper ( $R^2 = 0.9985$ ).

The plot of  $\log C$  Vs  $\theta$  yield a straight line, clearly proving that the adsorption of the used inhibitor for acid on the metal surface

obeys the Temkin adsorption isotherm (figure-4). The negative values of  $\Delta G_{ads}$  suggested that the adsorption of STF extract onto metal surface is a spontaneous process and the adsorbed layer is more stable one (table-4).



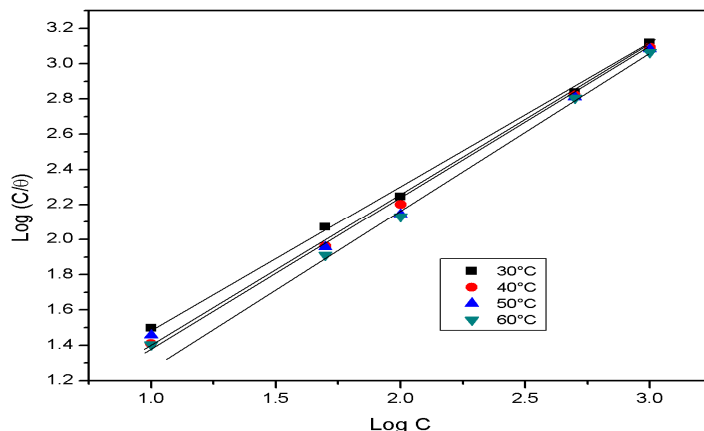
**Figure-2**  
The dissolution parameters of copper in 1.0 N HCl with different STF concentration at various temperatures

The positive value of enthalpy of activation reflects the endothermic nature of metal dissolution process means that the dissolution of metal is difficult. The increase of  $\Delta S$  is generally interpreted with disorder which may take place on going from reactants to the activated complex.

**Table-3**

Thermodynamic parameters such as activation energy ( $E_a$ ) and heat of adsorption ( $Q_{ads}$ ) of STF extract on copper in 1.0 N HCl

Concentration of inhibitor (ppm)	$E_a$ (KJ mol <sup>-1</sup> )	$Q_{ads}$ (KJ mol <sup>-1</sup> )
0	72.751	-
10	71.743	9.524
50	69.402	21.663
100	68.606	21.212
500	70.831	8.533
1000	68.193	18.804



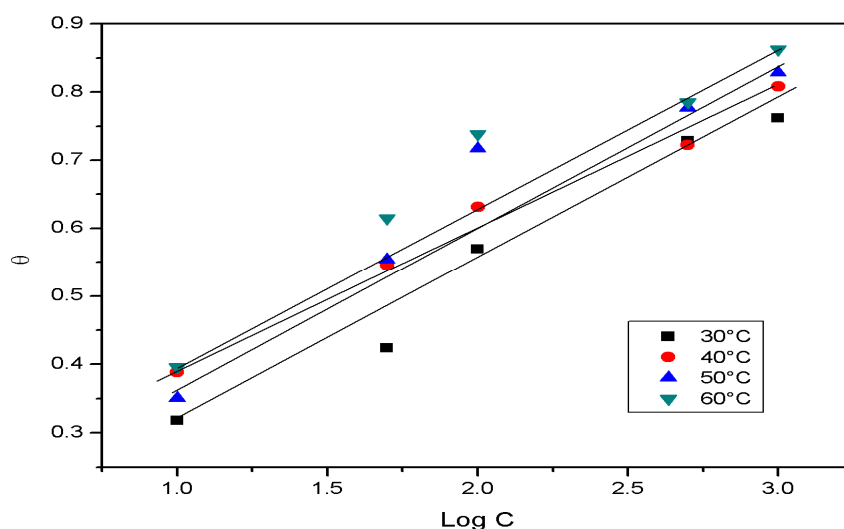
**Figure-3**

Langmuir adsorption parameters of STF on copper in 1.0 N HCl

**Table-4**

Langmuir and Temkin parameters for the adsorption of STF extract on copper in 1.0 N HCl

Adsorption isotherm	Temperature	Slope	K	R <sup>2</sup>	$\Delta G_{ads}$ (KJ mol <sup>-1</sup> )
Langmuir	303	0.8019	4.854	0.9971	-14.100
	313	0.8440	3.486	0.9985	-13.704
	323	0.8204	3.828	0.9915	-14.393
	333	0.8427	3.238	0.9937	-14.375
Temkin	303	0.2365	1.171	0.9649	-10.517
	313	0.2017	1.584	0.9817	-11.651
	323	0.2345	1.438	0.9017	-11.763
	333	0.2197	1.669	0.9026	-12.540



**Figure-4**

Temkin adsorption parameters of STF on copper in 1.0 N HCl

**Table-5**  
**Thermodynamic parameters of copper in 1.0 N HCl**  
**obtained from weight loss measurement**

Concentration of CCL extract (ppm)	$\Delta H$ (KJ mol <sup>-1</sup> )	$\Delta S$ (KJ mol <sup>-1</sup> )
0	6.376	9.735
10	5.508	9.219
50	2.126	8.038
100	0.192	7.308
500	3.711	8.299
1000	0.210	7.098

**Morphology Examination of Copper: UV Analysis:** On comparing both of these spectra (figure-5(a) and 5(b)), one absorption band is shifted to longer wavelength region (Bathochromic shift). The change of absorption band may confirmed that the strong co-ordination bond between the active elements present in the STF and the ions from the copper surface.

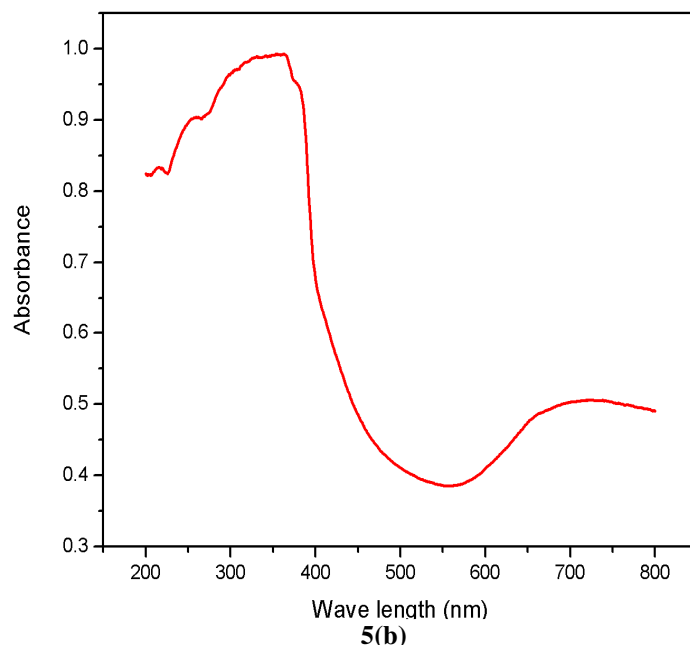
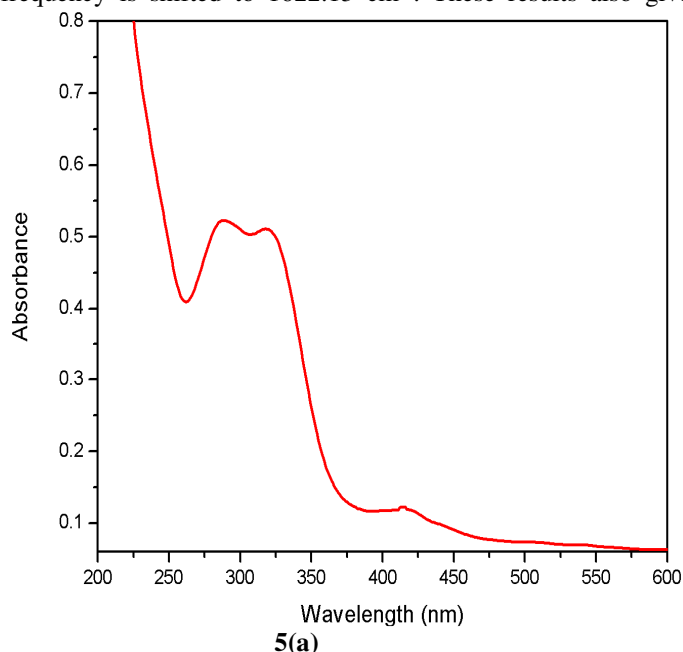
**FT-IR Analysis:** On comparing both of the spectra (figure-6 and 7) the prominent peak such as, the =N-H stretching frequency for amine is shifted from 3352.28 to 3332.99 cm<sup>-1</sup>, the C-H stretching frequency is shifted from 2974.23 to 2924.09 cm<sup>-1</sup>. 1658.78 cm<sup>-1</sup> corresponds to C=C stretching frequency is shifted to 1622.13 cm<sup>-1</sup>. These results also give

assistance to the fact that the dissolution inhibition of STF on Copper in acid media may prevent further corrosion.

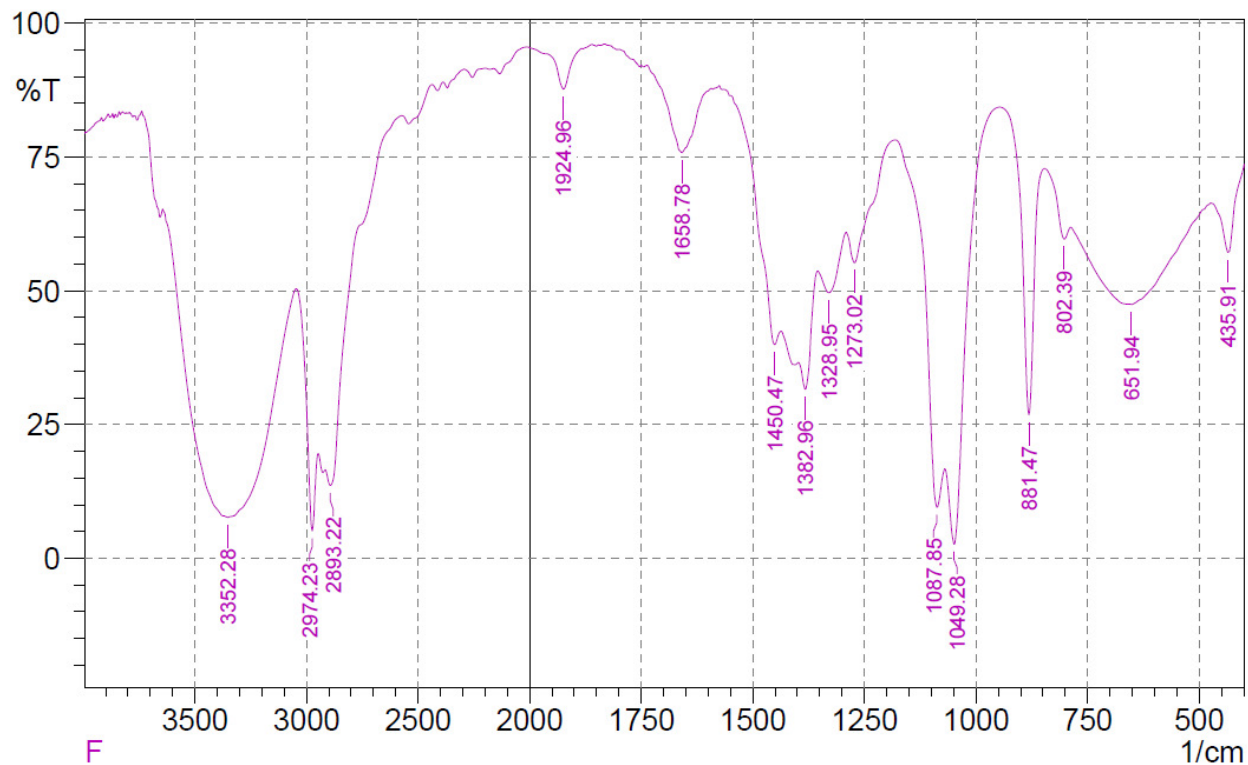
**EDX Analysis:** Energy dispersive X-ray analysis (EDAX) technique is a tool to find out the elements present in the organic and inorganic compounds. Thus we employed this technique in order to get what types of element present in the corrosion products. Figure-8 and 9 represent an EDAX view recorded for copper samples exposed in 1.0 N HCl solution in the presence and absence of optimum concentration of STF extract. In EDAX spectra of uninhibited surface (figure-8) the signal clearly indicates that the presence of copper element as a major constituent and little constituent of Cl and O elements. However figure-9 reflects that the EDAX spectra of inhibited surface clearly show the presence of Nitrogen and Sulphur element. This observation may confirm that the heteroatom present in inhibitor may be involved in the co-ordination process which suppressed the corrosion process.

**XRD Analysis:** The dissolution product liberated from copper in the presence of STF examined by XRD (figure-10). It exhibits that the film may be mainly combine with Copper chlorate [Cu (ClO<sub>4</sub>)<sub>2</sub>], Copper azide [Cu(N<sub>3</sub>)<sub>2</sub>], Copper sulfide [CuS] and Copper chloride[CuCl] with inhibitor.

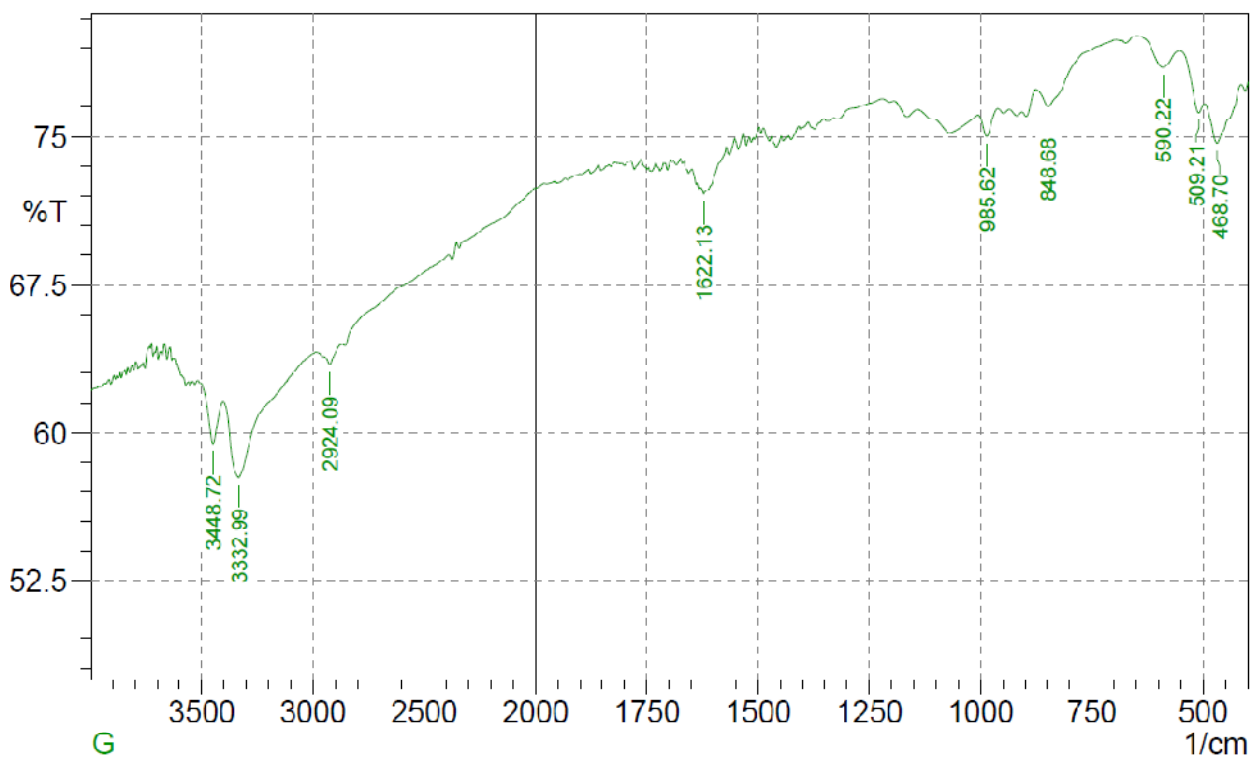
**SEM Analysis:** The SEM photographs (figure-11(a)) showed that the surface of metal has number of pits visible in the surface, but in presence of STF they are reduced on the copper surface. It is clearly implies that the development of spongy mass covered completely on the entire metal surface to reduce further dissolution of the metal.



**Figure-5**  
**UV spectrum of (a) Ethanolic extract of STF (b) Corrosion product on Copper in the presence of**  
**STF extract in 1.0 N HCl**



**Figure-6**  
FT-IR spectrum of ethanolic extract of STF Leaves extract



**Figure-7**  
FT-IR spectrum for the corrosion product on copper in the presence of STF extract with 1.0 N HCl



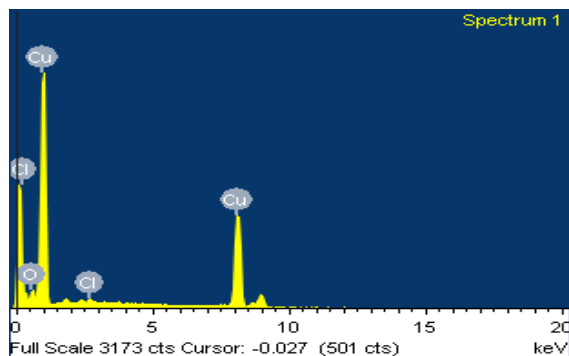


Figure-8

EDX spectrum of the corrosion product on copper surface in 1.0 N HCl

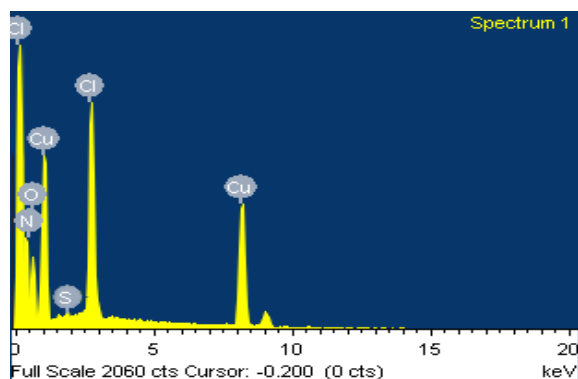


Figure-9

EDX spectrum of the corrosion product on copper in the presence of STF extract in 1.0 N HCl

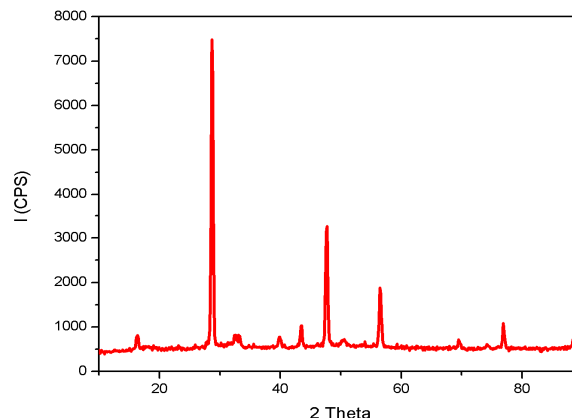
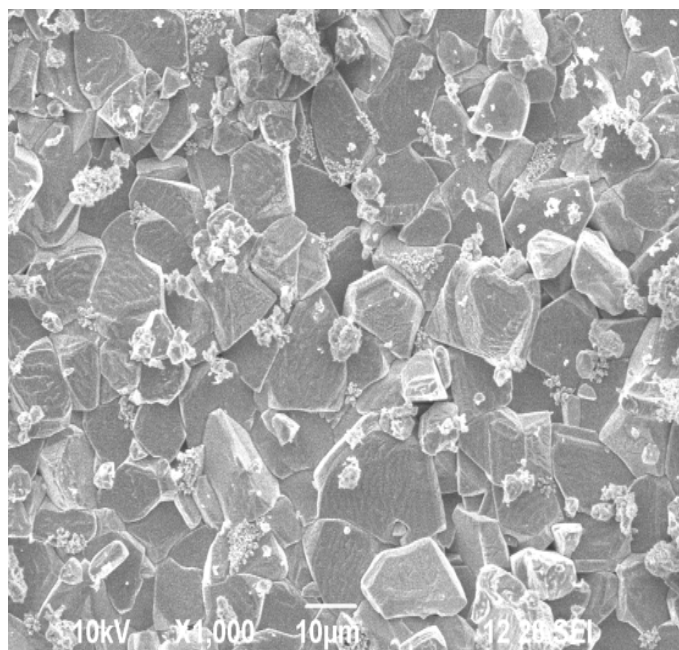


Figure-10

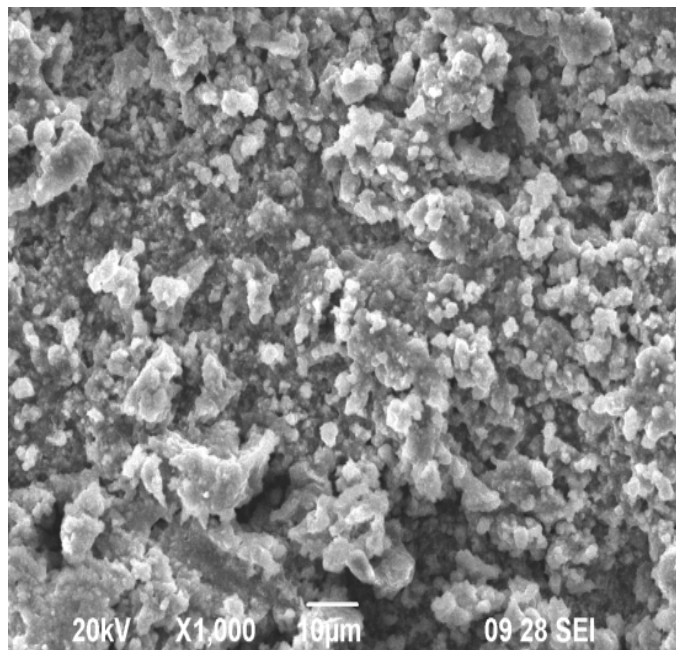
XRD spectrum of the corrosion product on copper in the presence of STF extract in 1.0 N HCl

## Conclusion

The *Solanum Torvum* (STF) fruits extract has shown excellent inhibition performance for copper in 1.0 N HCl. The maximum inhibition efficiency attained was 83.72% even after 360 hrs exposure time. The dissolution resistance of the copper increased with rise in STF concentration. The adsorption of the STF inhibitor on the copper surface in 1.0 N HCl obeys both Langmuir and Temkin adsorption isotherms and exhibits strong chemisorptions. The adsorption process is a spontaneous and endothermic process accompanied by an increase in entropy. The thin film formation on copper surface may also be confirmed by XRD, SEM-EDX studies.



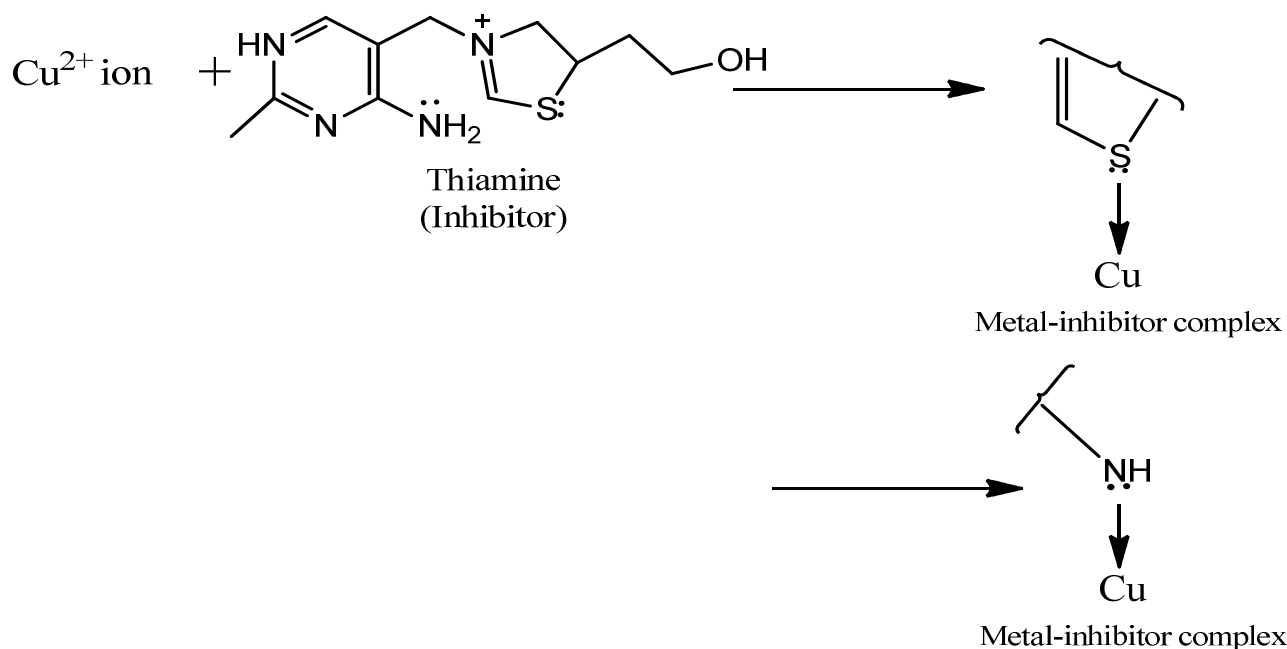
11(a)



11(b)

Figure-11

SEM micrographs of (a) copper in 1.0 N HCl without inhibitor (b) copper in 1.0 N HCl in the presence of STF extract



**Scheme-1**  
**Proposed mechanism**

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