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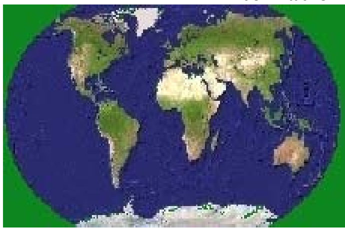

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Bright A
Asst Professor in chemistry, V V College of Engineering, Arasoor, Tisaiyanvilai-627 657, Tamilnadu, India

Michlin Ruphina Maragatham. S,
Asst Professor in chemistry, V V College of Engineering, Arasoor, Tisaiyanvilai-627 657, Tamilnadu, India

Malar vizhi.I
Postgraduate and Research Department of chemistry Sri Paramakalyani College, Alwarkurichi – 627 412, Tamil Nadu, India

Selvaraj. S
Postgraduate and Research Department of chemistry Sri Paramakalyani College, Alwarkurichi – 627 412, Tamil Nadu, India

Correspondence:
Bright A
Asst Professor in chemistry, V V College of Engineering, Arasoor, Tisaiyanvilai-627 657, Tamilnadu, India

Inhibitive effect of *Cnidoscolus chayamansa* leaves extract on Copper in Acid environment

Bright A, Michlin Ruphina Maragatham. S, Malar vizhi.I, Selvaraj. S

Abstract
The inhibition efficiency of *Cnidoscolus Chayamansa* leaves extract on the corrosion of Copper in 1.0N Hydrochloric acid environment in various concentration with temperature and period of contact has been investigated by mass loss measurement. The observed results indicate that the inhibition efficiency increased with increase of inhibitor concentration but decreased with rise in temperature and time. The inhibitor obeys Langmuir and Temkin adsorption isotherms. Thermodynamic parameters (Viz: E_a, Q_{ads}, ΔG_{ads}, ΔH and ΔS) indicates that the adsorption of the inhibitor is physisorption, exothermic and spontaneous. Corrosion product on the metal surface in the presence and absence of inhibitor is characterised by UV, FT-IR, XRD and EDX-SEM spectral techniques.

Keywords: Mass loss, Copper, Acid, Green inhibitor and spectral studies.

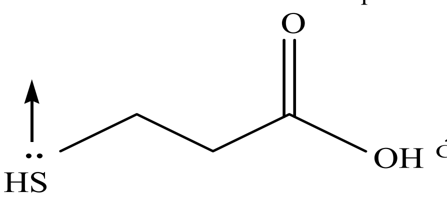
1. Introduction

Copper has been one of more important materials in various industry owing to its high electrical and thermal conductivities, mechanical workability and its relatively noble properties. It is widely used in many applications in electronic industries and communications as a conductor in electrical power lines, pipelines for domestic and industrial water utilities including sea water, heat conductors, heat exchangers, etc. Though many synthetic compounds have shown good anticorrosive activity, most of them are highly toxic to both human beings and environment[1]. The known hazardous effects of most synthetic organic inhibitors and restrictive environmental regulations have now made many researchers to focus on the need to develop cheap, non-toxic and environmentally benign natural products as corrosion inhibitors. Recent years, several green inhibitors have been used for the prevention of corrosion by most of the investigators. Few examples are Cnidoscolus *Aconitifolius*[2], *Citrullus Vulgaris* peel[3], *Albizia lebbeck* seed[4], *Hibiscus Esculenta* leaves[5], *Jatropha curcas*[6], *Eugenia Jambolana*[7], *Allium Cepa*[8], *Eucalyptus globulus*[9], *Phyllanthus amarus*[10], Carob seed oil[11], *Bacopa monnieri*[12]. Inula viscola[13] our present research work, inhibitive effect of *Cnidoscolus chayamansa* leaves extract on Copper in Acid environment have been studied with various periods of contact and temperature using the mass loss measurements and the corrosion product on metal surface is characterised by UV, FT-IR, XRD, EDX-SEM spectral studies.

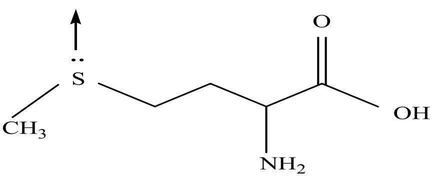
3. Materials and Methods

3.1 Properties of *Cnidoscolus Chayamansa* Leaves

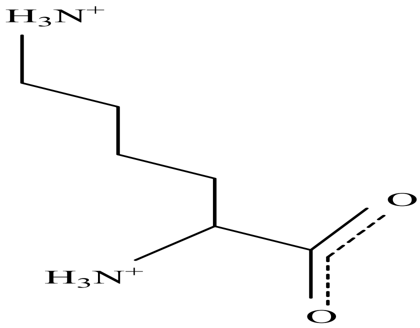
Cnidoscolus Chayamansa Mc Vaugh (Euphorbiaceae) is commonly known as 'chaya' plant. These leaves consist rich in protein, calcium, iron, carotene, and vitamins A, B and C. The leaves contain hydrocyanic glycosides, which could cause health problems if the leaves were eaten raw. It also contains Flavonoids, Terpenoids, Glycosides, Steroids, Alkaloids, Carbohydrates, Amino acid and Tannins, Chlorides, Copper, Nitrates, Potassium, Zinc, Carbonates and bicarbonates. Additionally, infusions of this plant have shown therapeutic effects in the treatment of noninsulin-dependent diabetes mellitus.



(i) Cystine



(ii) Methionine



(iii) Lysine

Fig 1: Chemical structure of the main active compounds present in CCL extract.

3.2 Stock solution of *Cnidoscolus Chayamansa* extract

Cnidoscolus Chayamansa (CCL) leaves were collected from the source and dried under shadow for about 48 hours, grinded well, then soaked in a solution of ethyl alcohol for about 48hours. Then it is filtered followed by evaporation in order to remove the alcohol solvent completely and the pure plant leaves 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.

3.3 Specimen preparation

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

3.4 Mass Loss method

In the mass loss measurements, Copper 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 303 K to 333 K 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.

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

(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)

4. Results and Discussion

4.1 Effect of time variation

Corrosion parameters of copper in 1.0 N HCL containing various concentrations (0 to 1000 ppm) of *Cnidoscolus chayamansa* leaves (CCL) extract with different period of contact are studied by mass loss measurement and the observed values are placed in Table-1. The observed result reveals that the corrosion rate increased with increase of contact period. However in the presence of CCL inhibitor, the corrosion rate reduced from 5.3976 mmpy to 1.5887 mmpy after 24 hours and 1.639 mmpy to 0.6423 mmpy even after 360 hours respectively. The maximum of 70.57 % of inhibition efficiency was obtained at higher concentration of the extract. This achievements mainly due to the presence of hetero atoms such as N, O, S present in the main phytochemicals constituent of the CCL extract.

4.2 Effect of Temperature

Corrosion parameters of copper in 1.0N Hydrochloric acid containing various concentration of CCL extract with different temperature ranges from 303 to 333 K and the observed values are listed in Table-2. The observed result indicates that the corrosion rate decreased with increase of inhibitor concentration with rise in temperature from 303 to 333K. The maximum of 74.38% inhibition efficiency is achieved at 313K. The value of inhibition efficiency is decreased with rise in temperature is suggested that the physical adsorption mechanism. This results clearly reflects that the adsorption of main active components present in the inhibitor may shield the metal surface at room temperature. However it may be deshielded from the surface with rise in temperature.

Table 1: Corrosion parameters of copper in 1.0N Hydrochloric acid containing various concentration of CCL extract with different exposure time.

S.No.	Corrosion parameters	Time (Hrs)	Electrolyte (HCl + CCL) (ppm)					
			0	10	50	100	500	1000
1	Mass Loss (mg)	24	265	251	149	108	80	78
		72	586	451	411	403	392	349
		120	543	462	305	260	255	212
		168	697	530	371	340	297	274
		216	989	695	592	489	510	536
		264	906	706	633	559	533	510
		312	995	849	749	670	630	521
		360	1207	849	763	505	496	473
2	Corrosion rate (mmpy)	24	5.3976	5.1124	3.0349	2.1998	1.6295	1.5887
		72	3.9786	3.062	2.7905	2.7361	2.6615	2.3695
		120	2.212	1.882	1.2425	1.0592	1.0388	0.8636
		168	2.0281	1.5422	1.0795	0.9893	0.8642	0.7973
		216	2.2383	1.5729	1.3398	1.1067	1.1542	1.213

		264	1.6776	1.3073	1.1721	1.0351	0.9869	0.9443
		312	1.559	1.3302	1.1735	1.0498	0.9871	0.8163
		360	1.639	1.1528	1.0361	0.6857	0.6735	0.6423
3	Inhibition efficiency (%)	24	-	5.28	43.77	59.24	69.81	70.57
		72	-	23.04	29.86	31.23	33.1	40.44
		120	-	14.92	43.83	32.12	53.04	60.96
		168	-	23.96	46.77	51.22	57.39	60.69
		216	-	29.73	40.14	50.56	48.43	45.81
		264	-	22.07	30.13	38.3	41.17	43.71
		312	-	14.68	24.73	32.66	36.68	47.64
		360	-	29.66	36.78	58.16	58.91	60.81

Table 2: The corrosion parameters of copper in 1.0N Hydrochloric acid containing various concentration of CCL extract with different exposure temperature

S.No.	Corrosion parameters	Temperature (K)	Electrolyte (HCl + CCL) (ppm)					
			0	10	50	100	500	1000
1	Mass Loss (mg)	303	103	86	69	65	51	35
		313	121	99	86	73	67	31
		323	144	131	119	97	82	53
		333	163	143	126	105	91	62
2	Corrosion rate (mmpy)	303	50.3504	42.0402	33.7299	31.7746	24.9308	17.1094
		313	59.196	48.3951	42.0402	35.6853	32.7522	15.154
		323	70.3929	64.0379	58.1719	47.4174	40.0848	25.9085
		333	79.6808	69.904	61.5938	51.3281	44.4844	30.308
3	Inhibition efficiency (%)	303	-	16.5	33.01	36.89	50.49	66.02
		313	-	18.18	28.93	39.67	44.63	74.38
		323	-	9.03	17.36	32.64	43.06	63.19
		333	-	12.27	22.7	35.58	44.17	61.96

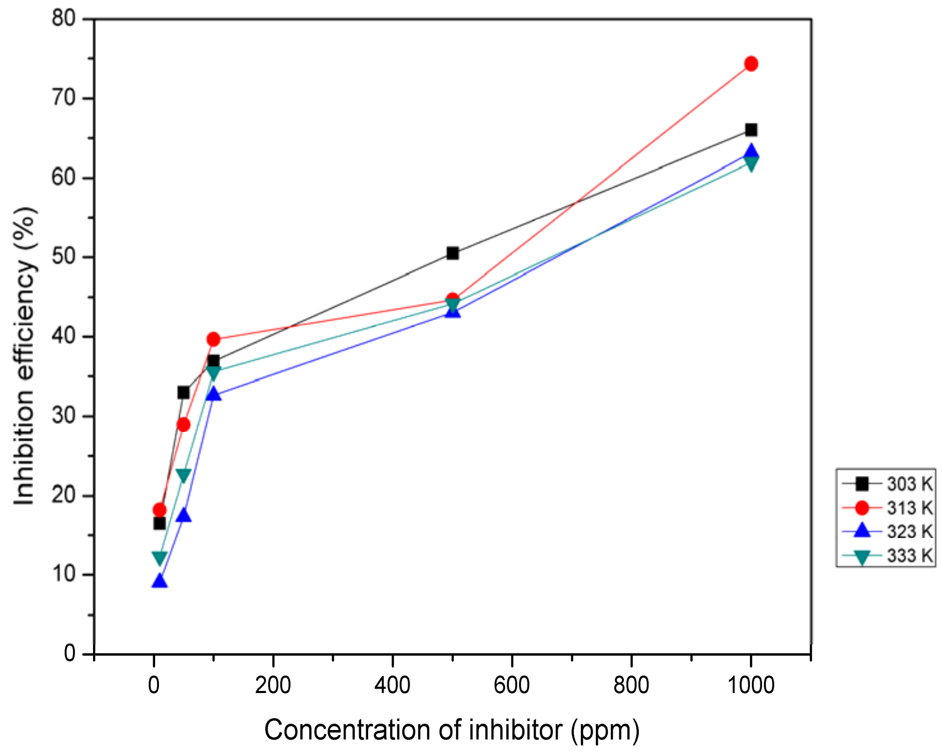


Fig 2: The corrosion parameters of copper in 1.0N Hydrochloric acid containing various concentration of CCL extract with different exposure temperature

4.3 Effect of Temperature

4.3.1. Activation energy:

The value of activation energy (Ea) for the corrosion of Copper in the presence and absence of CCL extract in 1.0N HCl acid is calculated using the following Arrhenius equation (4) and it's derived from equation (5)

CR= Aexp (-Ea/RT) -- (4)

log (CR_2/CR_1) = Ea /2.303 R ($1/T_1$-$1/T_2$) ------------------ (5)

Where CR_1 and CR_2 are the corrosion rates of Copper 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 in the ranges (71.344-72.529 kJ/mol) for copper in 1.0N HCl containing various concentration of inhibitor. The average value of E_a obtained from the blank (71.344 kJ/mol) is lower that in the presence of inhibitor and clearly suggest that there is a strong chemical adsorption bond between the CCL inhibitor molecule and the copper surface.

Table 3: Calculated values of activation energy (E_a) and heat of adsorption (Q_{ads}) of CCL extract on copper in 1.0N Hydrochloric acid environment

S. No.	Concentration of inhibitor (ppm)	% of I.E		E_a (KJ mol^{-1})	Q_{ads} (KJ mol^{-1})
		30°C	60°C		
1	0	-	-	71.344	-
2	10	16.5	12.27	71.756	-9.646
3	50	33.01	22.7	72.529	-14.470
4	100	36.89	35.58	71.514	0.186
5	500	50.49	44.17	72.338	-7.064
6	1000	66.02	61.96	72.280	-4.939

4.3.2. Heat of adsorption:

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

Q_{ads} =2.303 R [log (θ_2/1- θ_2)-log (θ_1 /1- θ_1)] x (T_2T_1/T_2-T_1) ------ (6)

Where R is the gas constant, $\theta_1$and θ_2 is the degree of surface coverage at temperature and T_1 and T_2 respectively. The Q_{ads} values are ranged from -14.470 to 0.186 kJ/mol (Table-3). This observed values clearly indicates that the adsorption of CCL extract on the surface of copper metal is exothermic followed by endothermic. In our present study the Langmuir, Temkin isotherm are investigated. The Langmuir and Temkin adsorption isotherm can be expressed by the equation (7) and equation (8) given below

log C/θ = log C – log K -------------------------------------- (7)

θ = K ln C --- (8)

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

Table 4: Langmuir adsorption parameters for the adsorption of CCL extract on copper in 1.0N Hydrochloric acid environment

Log C	Log C/ θ			
	30°C	40°C	50°C	60°C
1	1.7825	1.722	2.044	1.911
1.6989	2.1803	2.238	2.459	2.343
2	2.433	2.402	2.486	2.449
2.6989	2.996	3.049	3.065	3.054
3	3.180	3.129	3.199	3.208

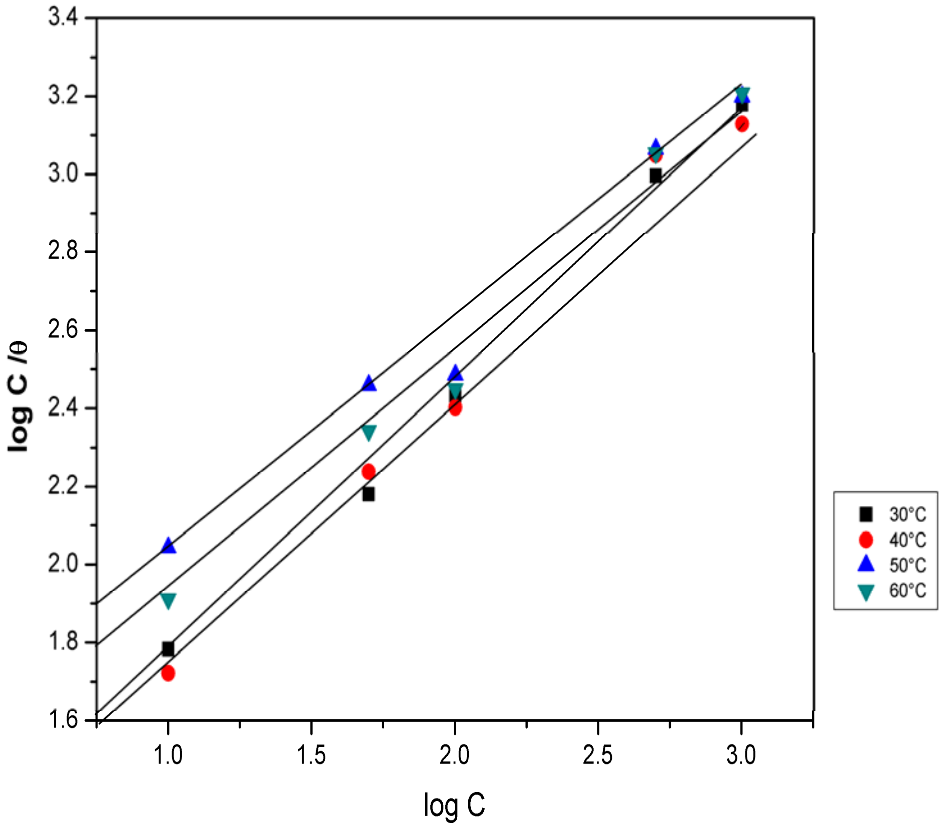


Fig-3: Langmuir adsorption isotherm for the adsorption of CCL extract on copper in 1.0N Hydrochloric acid environment

Table-5: Temkin adsorption parameters for the adsorption of CCL extract on copper in 1.0N Hydrochloric acid environment

Log C	θ			
	30°C	40°C	50°C	60°C
1	0.165	0.1818	0.0903	0.1227
1.6989	0.3301	0.2893	0.1736	0.227
2	0.3689	0.3967	0.3264	0.3558
2.6989	0.5049	0.4463	0.4306	0.4417
3	0.6602	0.7438	0.6319	0.6196

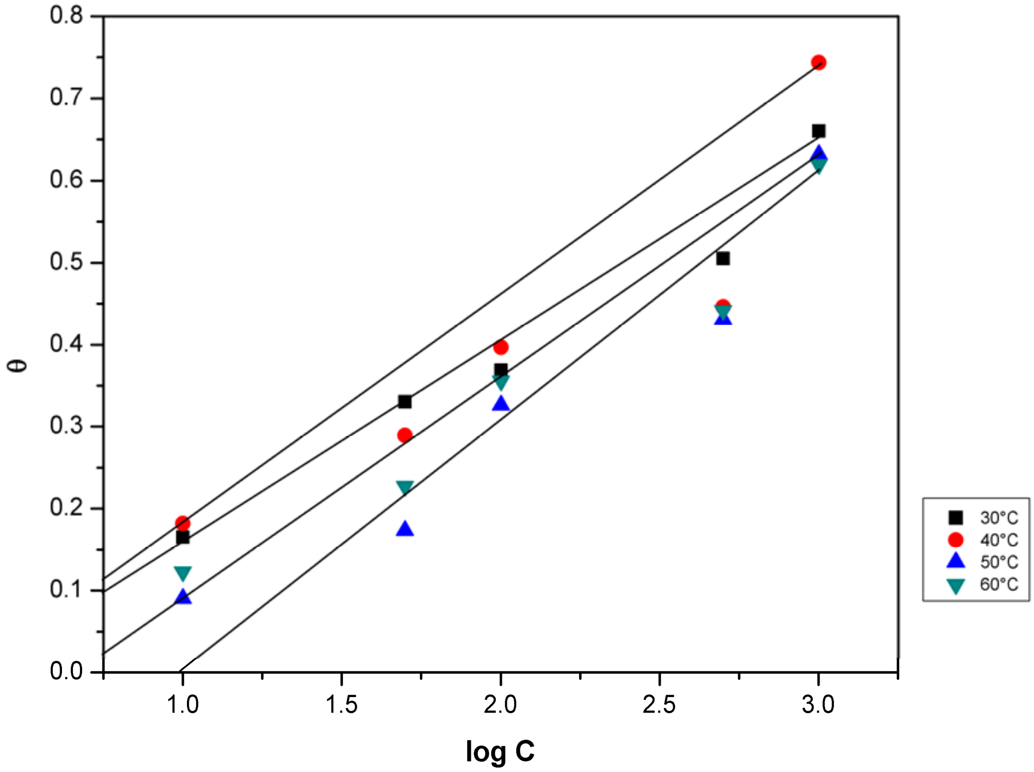


Fig 4: Temkin adsorption isotherm for the adsorption of CCL extract on copper in 1.0N Hydrochloric acid environment

By plotting the values of log(C/ θ) Vs log C, linear plots are generated (Fig-3). Inspection of this Fig. reveals that the experimental data fitted with the Langmuir adsorption isotherm, means that there is no interaction between the adsorbed species (i.e., adsorbate and adsorbent).The Langmuir adsorption isotherm is better fit at 303K for Copper (R2 =0.9925).

A plot of θ versus logC gives almost a straight line for Copper in CCL extract in acid medium (Fig-4). The straight line indicated that the inhibitor obeyed Temkin adsorption isotherm. The equilibrium constant of adsorption of CCL extract on the surface of the metal is related to the free energy of adsorption (ΔG ads) by the following equation (9)

ΔG ads = -2.303 RT log (55.5 K) ------------------------ (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 7. The negative values of ΔG_{ads} suggested that the adsorption of CCL extract onto metal surface is a spontaneous process and the adsorbed layer is more stable one. Usually the adsorption of free energy involved in a physisorption process (ΔG ads < 40 KJ/mol).

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

CR=RT/Nh exp (ΔS/R) exp (-ΔH/RT) -------------------- (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 the Table-6. The observed data shows that the thermodynamic parameters (E_a and ΔH) of the corrosion of copper in 1.0N HCl solution in the absence of the inhibitors are higher than those in the free acid solution indicating more energy barrier for the reaction in the presence of the inhibitor is attained. The positive value of enthalpy of activation reflects that the endothermic nature of metal dissolution process mean that the dissolution of metal is difficult. The increase of ΔS is generally interpreted by increase in disorder taking place on going from reactants to the activated complex

Table-6: The relation between log (CR/T) and 1000/T for different concentration of CCL extract on copper in 1.0N Hydrochloric acid environment

1000 / T	Log (CR / T)					
	0 ppm	10 ppm	50 ppm	100 ppm	500 ppm	1000 ppm
3.300	- 0.779	-0.858	-0.953	-0.979	-1.084	-1.248
3.194	- 0.724	-0.811	-0.872	-0.943	-0.980	-1.315
3.096	- 0.662	-0.703	-0.745	-0.812	-0.874	-1.096
3.003	- 0.621	-0.678	-0.733	-0.812	-0.874	-1.0409

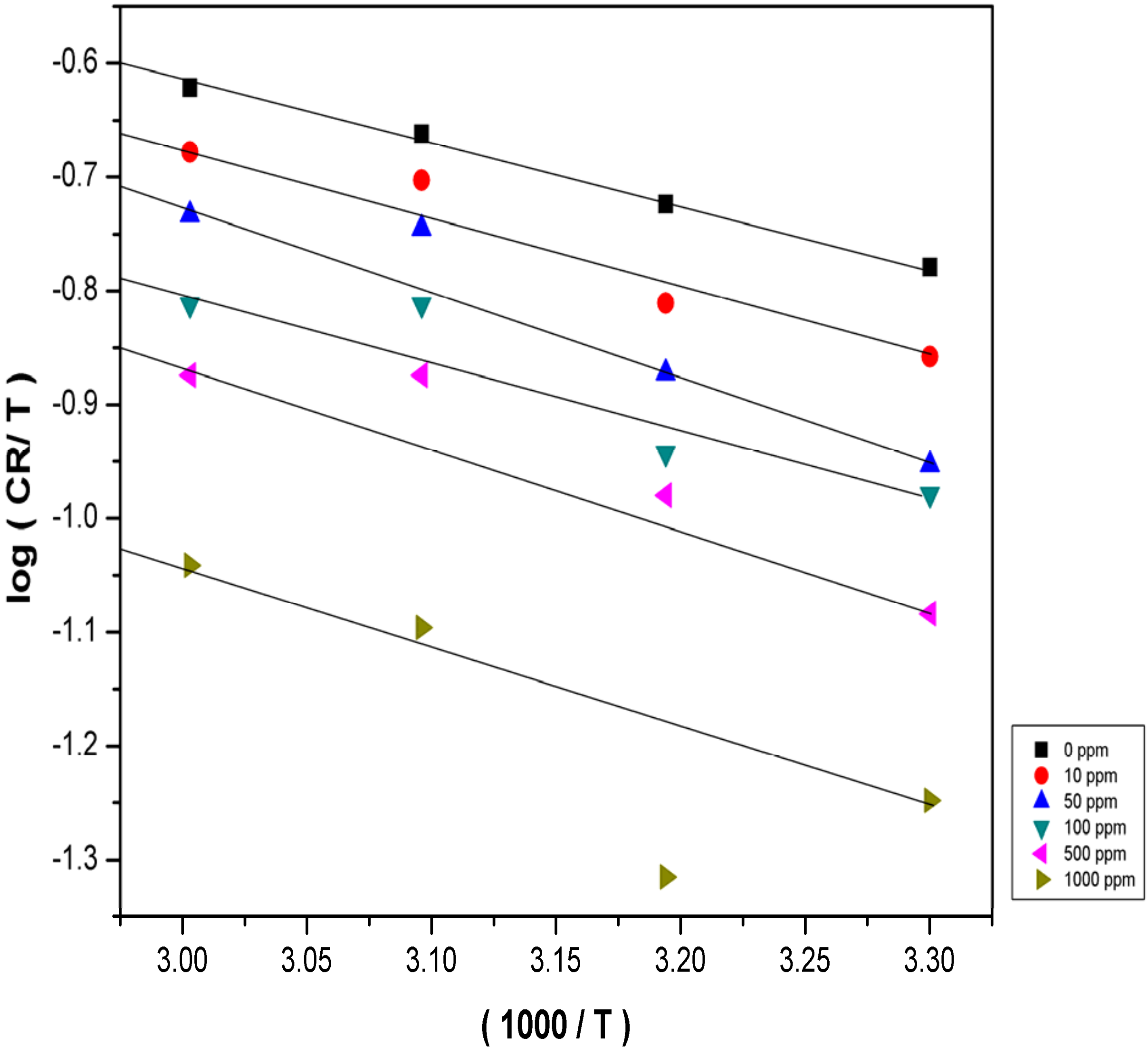


Fig 5: The relation between log (CR/T) and 1000/T for different concentration of CCL extract on copper in 1.0N Hydrochloric acid environment

Table 7: Langmuir and Temkin parameters for the adsorption of CCL extract on copper in 1.0N Hydrochloric acid environment

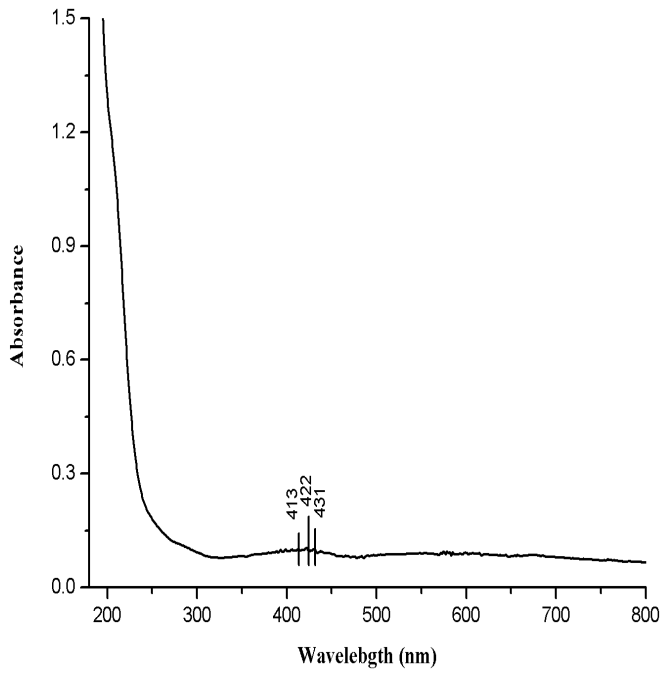
Adsorption isotherm	Temperature	Slope	K	R^2	ΔG_{ads} (KJ mol^{-1})
Langmuir	303	0.7202	10.3908	0.9925	-16.018
	313	0.7327	9.6474	0.9896	-16.353
	323	0.5897	26.560	0.9730	-19.571
	333	0.6652	1.6209	0.9859	-12.459
Temkin	303	0.2305	0.8442	0.9595	-9.693
	313	0.2446	0.7997	0.7984	-9.872
	323	0.2586	0.6206	0.9066	-9.506
	333	0.2342	0.7349	0.9269	-10.269

Table 8: Thermodynamic parameters of copper in 1.0N Hydrochloric acid obtained from weight loss measurement

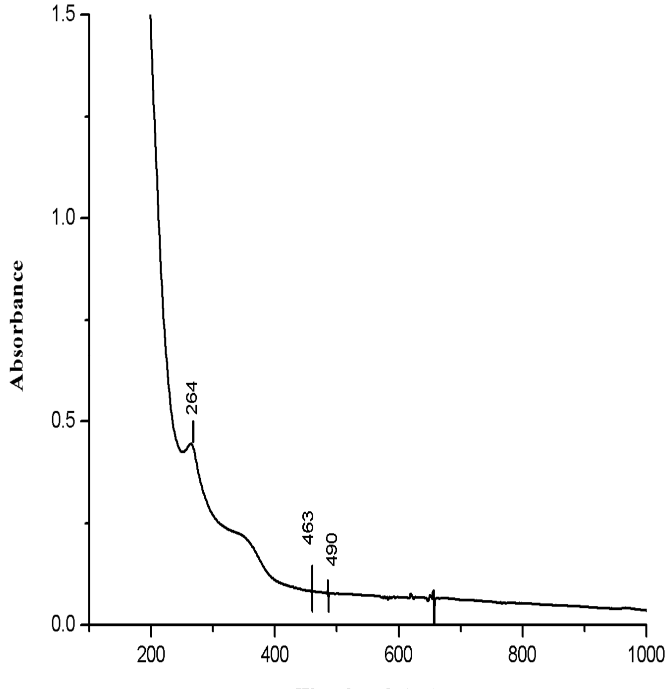
S. No.	Concentration of CCL extract (ppm)	ΔH (KJ mol^{-1})	ΔS (KJ mol^{-1})
1	0	4.5089	8.8895
2	10	5.4512	9.1312
3	50	6.6441	9.4542
4	100	5.3224	8.9876
5	500	6.2364	9.2201
6	1000	6.9789	9.2693

5. Morphology Examination Of Copper

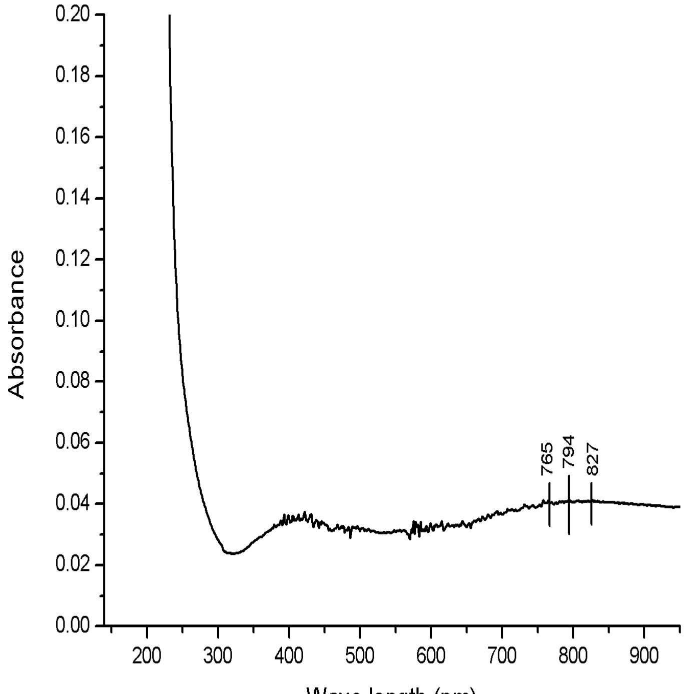
5.1 UV Spectrum:



6 (a)



6 (b)



6(c)

Fig-6: UV spectrum of ethanolic extract of CCL (a), the corrosion product on copper in 1.0N HCl in the absence of CCL extract (b), the corrosion product on copper in 1.0N HCl in the absence of CCL extract (c).

5.2 FT-IR analysis

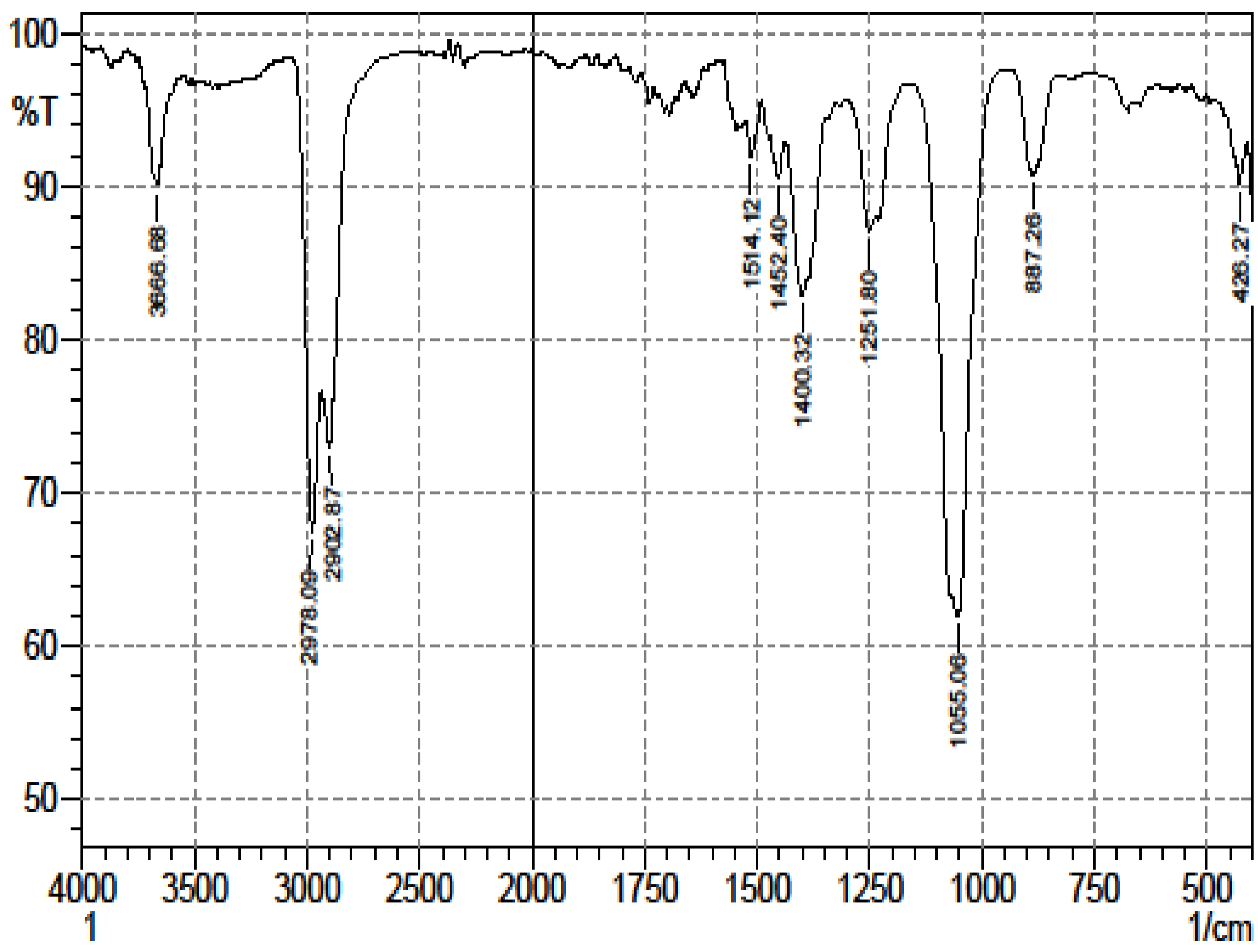


Fig 7: FT-IR spectrum of ethanolic extract of *Cnidoscolus chayamansa* leaves (CCL)

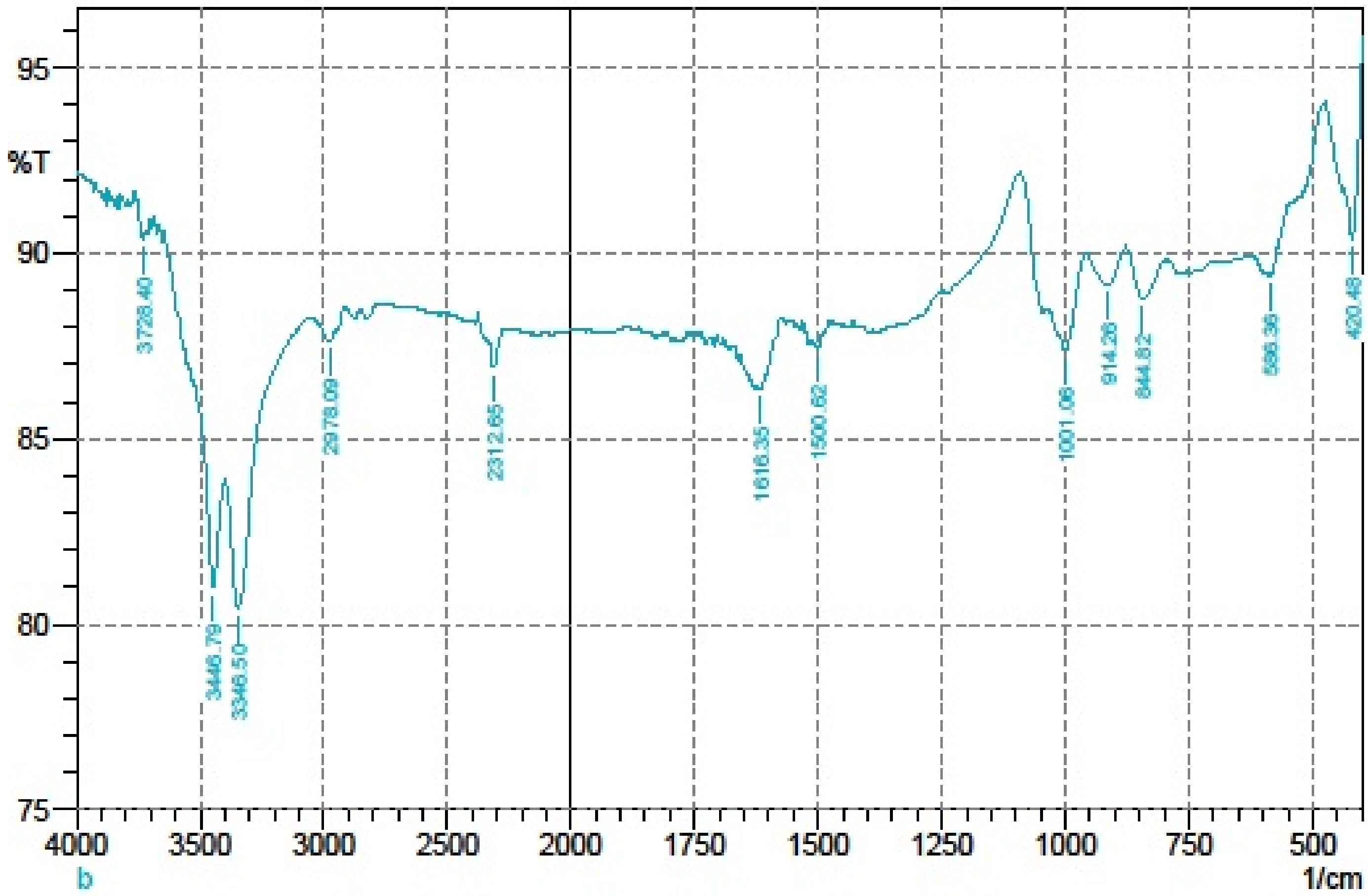


Fig 8: FT-IR spectrum for the corrosion product on copper in the presence of CCL extract with 1.0N Hydrochloric acid

The Fig-7 and 8 reflects that the FT-IR spectrum of the ethanolic extract of CCL inhibitor and the corrosion product on copper in the presence of inhibitor in 1.0N Hydrochloric acid respectively. On comparing both these spectra, the prominent peak is shifted from 1514.12 to 1500.62cm-1 for =NH group, the frequency at 1055.06cm^{-1} is attributed to –C-N stretching is shifted to 1001.06cm^{-1} and the S-OR frequency is shifted from 887.26 to 844.82 cm^{-1}. Thus the FT-IR spectra support the fact that the corrosion inhibition of CCL inhibitor on copper in 1.0N Hydrochloric acid may be the adsorption of active molecule in the inhibitor and surface of the metal.

Edx Spectrum

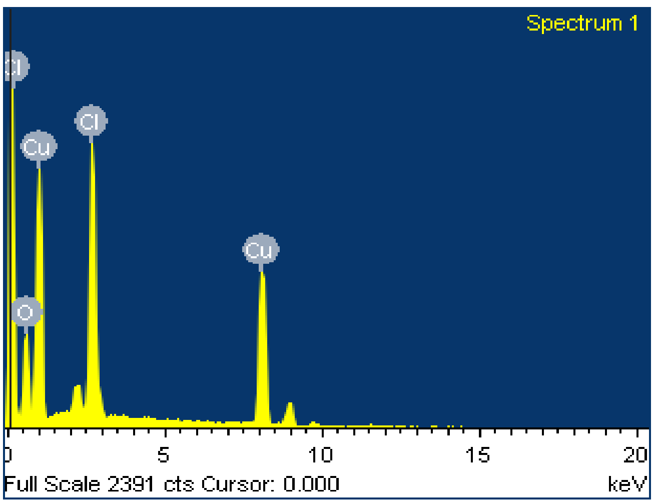


Fig- 9: EDX spectrum of the corrosion product on copper surface in 1.0N HCl

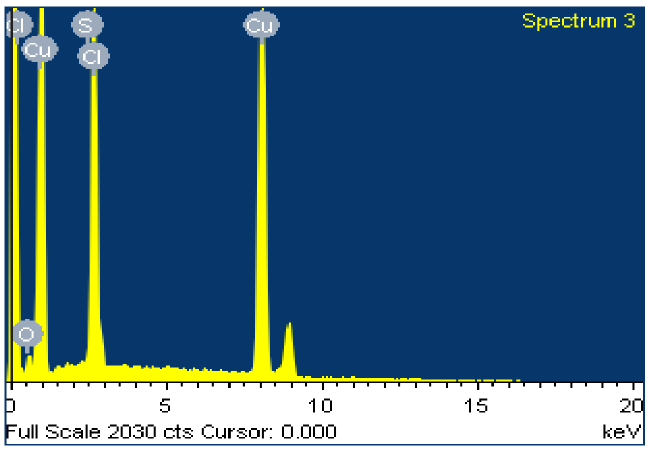


Fig 10: EDX spectrum of the corrosion product on copper in the presence of CCL extract in 1.0N HCl

EDX spectroscopy was used to determine the elements present on the copper surface in the absence and presence of inhibitor. Figs-9-10 represents the EDX spectra for the corrosion product on copper metal surface in the absence and presence of optimum concentrations of CCL extract in Hydrochloric acid. In the absence of inhibitor, the spectrum may concluded that the existence of chlorine due to the formation of metal chloride and in addition to this, spectrum consists of oxygen atom is present in the corrosion product. However, in the presence of the optimum concentrations of the inhibitors, sulphur and oxygen 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 may involve the complex formation with metal atom during the adsorption process and prevent the further dissolution of metal against corrosion

XRD ANALYSIS

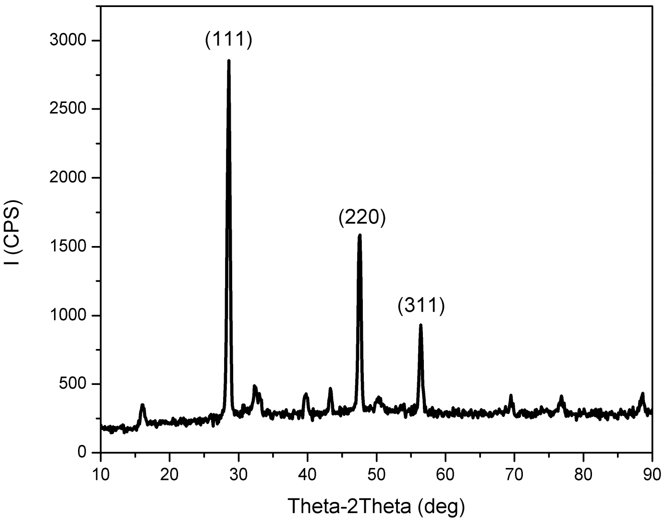
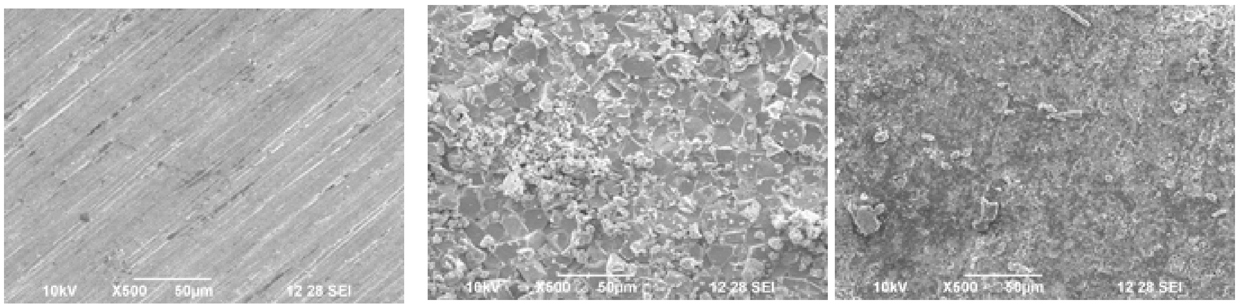


Fig 11: XRD- Analysis of Corrosion Product of the corrosion product on copper in the presence of CCL extract in 1.0N HCl

The corrosion products are scrapped from the Copper surface in the presence of CCL extract inhibitor is examined by XRD studies are shown in Fig-11. The base peak is matched with the standard peak of Copper chloride (CuCl) which has a crystal structure of Cubic with the lattice parameter values of a= 5.416, which is taken from the JCPDS File no. PDF 06-0344. Hence the present XRD pattern is indeed a CuCl compound and metal oxide and metal sulphide.

5.3 Sem Analysis

The Surface morphology of Copper was examined by scanning electron microscopy and the images are represented in fig 12(a-c). Fig-12 (a) shows that the copper sample before immersion seems smooth surface, but after careful inspection of Fig-12 (b) shows that the surface of metal has number of pits and cracks are visible in the surface. However in presence of inhibitor Fig 12 (c) the formation of protective layer can efficiently inhibit the corrosion of copper further.



(a) **(b)** **(c)**

Fig-12: SEM micrographs of copper in (a) fresh copper, (b) without inhibitor, 0 ppm (c) with inhibitor, 100 ppm

Conclusion

On the basis of the above results, it can be seen that *Cnidoscolus Chayamansa* leaves is a good inhibitor for copper in 1.0N HCl.The maxima of 70.57% inhibition efficiency was attained. The adsorption of the inhibitor is an exothermic and spontaneous process. The values of free energy suggested the physical adsorption of the inhibitor on the metal surface and it obeys Langmuir and Temkin adsorption isotherms. The corrosion product over the surface of copper is characterized by UV, FT-IR, SEM and 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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