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Cardiospermum Halicababum Leaves Extract as Green Inhibitor for Corrosion of Brass in 1.0N Hydrochloric Acid Solution

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Abstract: Inhibition effect of Cardiospermum halicababum leaves extract on corrosion of brass in 1.0 N HCl was investigated by mass loss measurement with various period, contact and temperature. The observed result indicates that the corrosion inhibition efficiency was decreased with increase of inhibitor concentration and temperature. The thermodynamic parameters (viz; Ea, ΔH_{ads}, ΔG_{ads}, ΔS_{ads}) were evaluated for corrosion process, which suggest that the adsorption is exothermic, spontaneous and Physisorptions. The inhibitor follows Langmuir adsorption isotherm. The corrosion products are formed on the metal surface was analyzed by using various spectroscopic studies UV, FT-IR, EDX techniques and the film formation also confirmed by SEM image.

Keywords — Brass, FT-IR, adsorption, mass loss, EDX and UV

I. INTRODUCTION

Brass has been widely used as tubing material for condensers and heat exchangers in various cooling water systems. Brass is susceptible to a corrosion process known as dezincification and this tendency increases with increasing zinc content of the brass. .Brass is extensively used in various industrial operations and the study of its corrosion inhibition is of importance, most investigations on the corrosion of brass have been carried out on. The development of corrosion inhibitor based on organic compounds has much scope in several industries because of their practical usefulness[1], brass and its alloys are widely used materials for their excellent electrical and thermal conductivities in many applications and recently in the manufacture of integrated circuits [2-4]. The chemical dissolution and electro plating are the main processes used in the fabrication of electronic devices. The most widely used acid solution, so this medium has induced a great deal of research on brass [5]. Brass undergoes corrosion tremendously with environment in day to day life. To solve the above defects, it is necessary to develop cheap, non-toxic and environmentally friendly natural products as corrosion inhibitors. These natural organic compounds are either synthesized or extracted from aromatic herbs, spices and medicinal plants. Plant extracts are an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost and are biodegradable in nature. The plant extract are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as "Green Inhibitors". These inhibitors do not contain heavy metals or other toxic compounds. Recent studies using plants containing heteroatom such as oxygen, nitrogen and sulphur *like Psidium guajava[6], black pepper[7], Punica granatum[8], Ocimum viridis[9], Phyllanthus amarus[10], Annona squamosa[11], Argan[12],Mentha pulegium[13], mimusops elengi[14], Sauropus Androgynus[15], Kingiodendron pinnatum[16], Wrightia Tinctoria[17]* have also been used for inhibition of corrosion. In continuous of our research work, the present investigation is the Cardiospermum halicababum leaves extract used as corrosion inhibitor on brass in 1.0N HCl have been investigated with various periods of contact and temperature using the mass loss measurements.Also the corrosion product on the metal surface is analysed by UV, FT-IR and SEM spectral studies.

II. MATERIALS AND METHODS

2.1 SPECIMEN PREPARATION

Brass specimen were mechanically pressed cut to form different coupons, each of dimension exactly $20cm^2$ (5x2x2cm), polished with emery wheel of 80 and 120, and degreased with trichloroethylene, then washed with distilled water cleaned, dried and then stored in desicator for the use of our present study.

2.2 PREPARATION OF CARDIOSPERMUM HALICABABUM LEAVES (CHL) EXTRACT:

About 3 Kg of Cardiospermum halicababum leaves was collected from in and around Western Ghats and then dried under shadow for 5 to 10 days. Then it is grained well and finely powdered, exactly 150g of this fine powder was taken in a 500ml round bottom flask and a required quantity of ethyl alcohol was added to cover the fine powder

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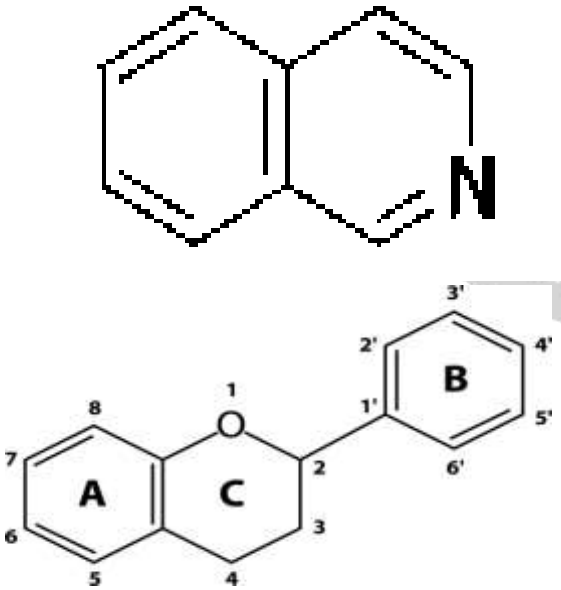
completely, and left it for 48 hrs. Then the resulting paste was refluxed for about 48 hrs, the extract was collected and the excess of alcohol was removed by the distillation process. The obtained paste was boiled with little amount of activated charcoal to remove impurities, the pure plant extract was collected and stored.

2.3 PICTURES OF CARDIOSPERMUM HALICABABUM LEAVES

2.4 PROPERTIES OF **CARDIOSPERMUM HALICABABUM LEAVES**:

It can be used to treat ear pain, menstrual cramps, general tiredness and sluggishness. The juice of this plant when combined together with pure turmeric powder and applied on the affected area treats eczema. The main phytochemical constituents present in this plant are Alkaloids, Cardiac Glycosides, Flavonoids, Saponins, Steroids and Tannins , A few structures are shown below.



Isoquinoline and flavanoids

Figure-3: Chemical structure of the main active compounds present in Cardiospermum halicababum *l*eaves extract.

2.5 MASS LOSS MEASUREMENT

In the mass loss measurements on Brass in triplicate were completely immersed in 100 ml of the test solution in the absence and presence of the inhibitor. The metal specimens were withdrawn from the test solutions after 24 to 360 hrs at room temperature and also measured 313K to 333K. The Mass loss was taken as the difference in weight of the specimens before and after immersion using LP 120 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 = millimoles 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 the following equations.

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

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

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

2.6ADSORPTION STUDIES:

2.6.1 ACTIVATION ENERGY:

The activation energy (E_a) for the corrosion of metals in the presence and absence of inhibitors in 1.0N Hydrochloric acid, natural sea water environment was calculated using Arrhenius theory. Assumptions of Arrhenius theory is expressed by equation (4).

$CR = A\exp(E_a/RT)$ ------- (4)

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

Where CR_1 and CR_2 are the corrosion rate at the temperature T_1 (313K) and T_2 (333K) respectively.

2.6.2 HEAT OF ADSORPTION*:*

The heat of adsorption on the surface of various metals in the presence of plant extract in 1.0N Hydrochloric acid, Natural sea water environment is calculated by the following equation (6).

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

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Where R is the gas constant, $\theta_1$and θ_2 are the degree of surface coverage at temperatures T_1 and T_2 respectively.

2.6.3. LANGMUIR ADSORPTION ISOTHERM

The Langmuir adsorption isotherm can be expressed by the following Equation-7 is given below.

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

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

The equilibrium constant of adsorption of various plant extract on the surface of Mild steel is related to the free energy of adsorption ΔG_{ads} by equation (8).

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

Where R is the gas constant, T is the temperature, K is the equilibrium constant of adsorption.

III. RESULT AND DISCUSSION

3.1 MASS LOSS MEASUREMENTS

The dissolution behavior of brass in 1.0N Hydrochloric acid environment containing in the absence and presence of CHL extract with various exposure times (24hrs to 360 hrs) are shown in Table-1. The observed values are clearly indicates that in the presence of CHL extract the value of corrosion rate decreased from 0.2716 to 0.0226 mmpy for 24 hrs and 0.1071 to 0.0663mmpy for 360 hrs with increase of inhibitor concentration from 0 to 1000 ppm. 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 media of chloride ion (Cl^-).

Conc (ppm)	Corrosion rate (mmpy)					Inhibition efficiency (%)				
	24 hrs	72 hrs	120 hrs	240 hrs	360 hrs	24 Hrs	72 hrs	120 hrs	240 hrs	360 hrs
0	0.2716	0.2036	0.1855	0.1388	0.1071	-	-	-	-	-
10	0.2036	0.1659	0.1719	0.1312	0.0965	25.03	18.52	7.32	4.92	9.85
50	0.1357	0.1282	0.1403	0.1154	0.0905	50.03	37.04	24.39	16.39	15.49
100	0.0678	0.0829	0.1222	0.1041	0.0844	75.03	59.26	34.15	24.59	21.12
500	0.0452	0.0377	0.0950	0.0973	0.0739	83.35	81.49	48.78	29.51	30.99
1000	0.0226	0.0226	0.0724	0.0792	0.0663	91.67	88.89	60.98	42.62	38.03

Table-1: The corrosion parameters of brass in 1.0N Hydrochloric acid containing different concentration of CHL extract after 24to 360 hours exposure time

3.2 TEMPERATURE STUDIES

The dissolution behavior of brass containing various concentration of CHL extract in 1.0N Hydrochloric acid with temperature ranges from 313K to 333K is investigated by mass loss method and the values are listed out in Table-2. The observed values of corrosion rate decreased from 15.2083 to 2.7157 mmpy with increase of inhibitor concentrations .the percentage of inhibition efficiency gradually is increased from 25.00 to 82.14 % with increase of inhibitor concentration. At low temperature, initially, the binding is strong and attained maximum of 82.14% IE.

Table-2: The corrosion parameters of brass in 1.0N Hydrochloric acid containing different concentration of CHL extract at 313 to 333 K

Conc. (ppm)	Corrosion rate (mmpy)			Inhibition efficiency (%)		
	313K	323K	333K	313K	323K	333K
0	15.2083	33.6755	10.8630	-	-	-
1 0	11.4062	30.9598	9.2336	25.00	8.06	14.99
50	10.3199	28.2440	8.14732	32.14	16.12	24.99
100	8.1473	27.1577	7.0610	46.42	19.35	34.99
500	4.8883	25.5280	5.9747	67.85	24.19	44.99
1000	2.7157	21.1830	4..3452	82.14	37.09	60.00

3.3 EFFECT OF TEMPERATURE:

3.3.1. ACTIVATION ENERGY:

The values of corrosion rate obtained from the mass loss measurement are substituted in equation (4) and the values of activation energy (E_a) are presented in Table-3.The observed values are ranged from -9.4104 to 13.1453 kJ/mol for brass in 1.0N HCL containing various concentration of inhibitor. The average value of Ea obtained from the blank (-9.4104) is lower than that in the presence of inhibitor and indicated that there is a strong chemical adsorption bond between the CHL inhibitor molecules and the Brass surface.

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Table -3: Calculated values of Activation energy (E_a) and heat of adsorption (Q_{ads}) of CHL extract on Brass in 1.0N HCL environment.

S.No	Conc. of inhibitor(ppm)	% of I.E		E_a ($KJmol^{-1}$)	Q_{ads} ($KJmol^{-1}$)
		30°	60°		
1.	0	-	-	-9.4104	--
2.	10	25.00	14.99	-5.9097	-17.8058
3.	50	32.14	24.99	-6.6110	-9.8360
4.	100	46.42	34.99	-4.0021	-13.3115
5.	500	67.85	44.99	5.6127	-26.5072
6.	1000	82.14	60.00	13.1453	-31.3357

3.3.2. HEAT OF ADSORPTION:

The value of heat of adsorption (Q_{ads}) on Copper in 1.0N HCl containing various concentration of CHL extract is calculated using Equation (6) and the values of Q_{ads} are ranged from -17.8058 to -31.3357 kJ/mol (Table-3). These negative values are reflected that the adsorption of CHL extract on brass follows exothermic process.

3.3.3. ADSORPTION STUDIES:

The adsorption isotherm is a process, which are used to investigate the mode of adsorption and it characteristic of inhibitor on the metal surface. In our present study the Langmuir adsorption isotherm is investigated. The straight line observed in Fig- 4 suggest that the inhibitor follows Langmuir adsorption isotherm.

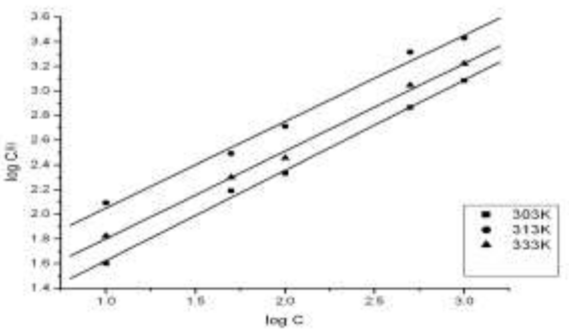

Figure -4: Langmuir isotherm for the adsorption of CHL inhibitor on Brass in 1.0N HCL environment.

Free energy of adsorption:

The standard free energy of adsorption (ΔG_{ads}) can be calculated using the Equation- (8) and the observed negative values are (Table-4) ensure that the spontaneity of the adsorption process and the stability of the adsorbed layer is enhanced.

Table-4: Langmuir adsorption parameters for the adsorption of CHL inhibitor on Brass in 1.0 N HCl environment

Adsorption isotherms	Temp (Kelvin)	Slope	K	R^2	ΔGads (KJ/mol)
Langmuir	303	0.7326	7.8058	0.9969	15.2971
	313	0.7013	22.4124	0.9908	18.5471
	333	0.7110	12.3370	0.9961	18.0791

3.3.4THERMODYNAMICS PARAMETERS

The another form of transition state equation which is derived from Arrhenius equation (4) is shown below (9)

$$CR = RT/Nh \exp(\Delta S/R) \exp(-\Delta H/RT) \text{ ----- } (9)$$

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 gives a straight line (Fig-5) 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-5. The positive value of enthalpy of activation clear that the endothermic nature of dissolution process is very difficult. The entropy (ΔS) is generally interpreted with disorder which may taking place on going from reactants to the activated complex.

Table-5: Thermodynamic parameters of Brass in 1.0N HCL obtained from mass loss measurements.

S.No	Concentration of CHL (ppm)	ΔH ($kJ\ mol^{-1}$)	ΔS ($J\ k^{-1}\ mol^{-1}$)
1	0	-7.3246	46.8965
2	10	-6.1675	49.9165
3	50	-6.5141	48.4376
4	100	-5.7540	50.3403
5	500	-2.3289	60.2940
6	1000	0.2440	67.1248

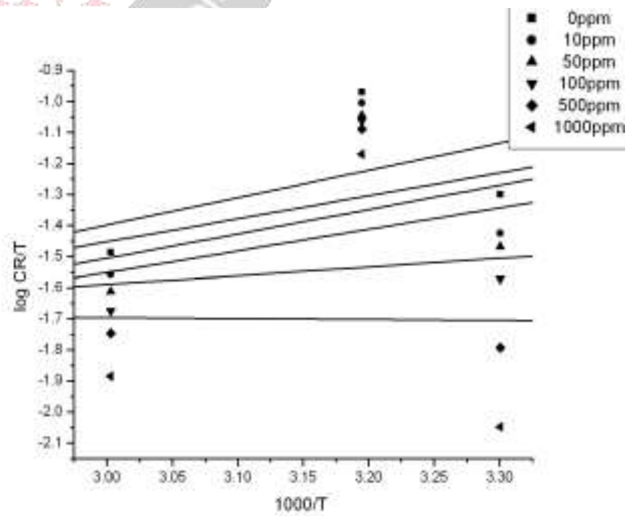

Figure-5: The relation between log (CR/T) and 1000/T for different concentrations of CHL extract

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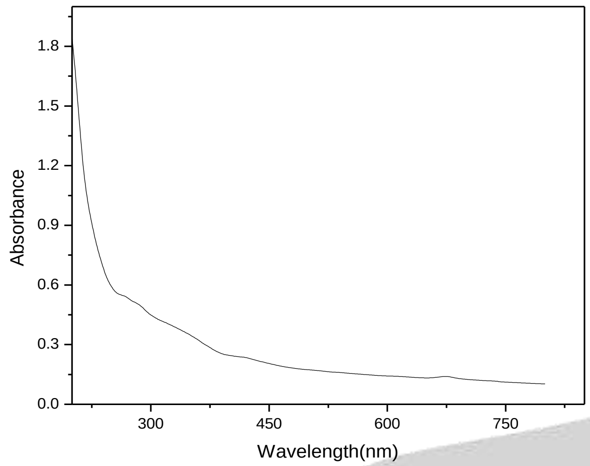
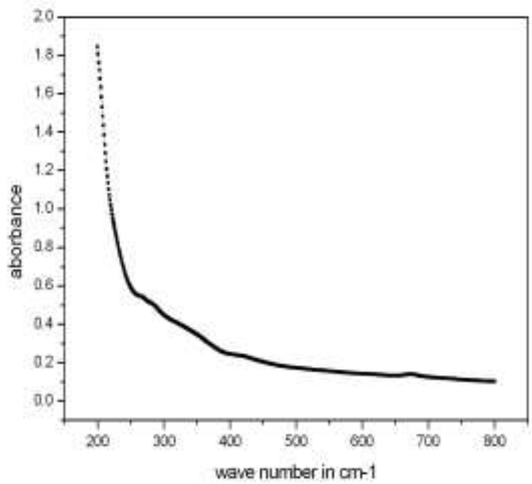
IV. MORPHOLOGY STUDIES

4.1UV SPECTRUM:



(a)



(b)

Figure-5 :UV spectrum of ethanolic extract of CHL (a), the corrosion product on Brass in 1.0N HCL in the presence of CHL extract (b).

Figures-5 (a) & (b) shows that the UV visible spectrum of ethanolic extract of CHL and the corrosion product on the surface of Brass in the presence of CHL extract in 1.0N HCL respectively. In this spectrum, the one broad absorption band around 300nm were noticed (Fig-5(a)) and in the presence of inhibitor only one broad bands was appeared (350nm) which indicates the band is shifted to longer wavelength region (Bathochromic shift (or) Red shift). The change of absorption band may confirmed that the strong co-ordination bond between the active group present in the inhibitor molecules and the ions from the metal surface.

4.2 FTIR SPECTRUM

FT-IR STUDIES OF CHL EXTRACT ON BRASS SURFACE IN 1.0N HYDROCHLORIC ACID

The figures-6(a) and (b) reflect that the FTIR spectrum of the ethanolic extract of inhibitor and the corrosion product on copper in the presence of CHL extract in1.0N HCL. On comparing both of the spectra the prominent peak such as, the –OH stretching frequency for carboxylic acids is shifted from 2920.23 to 3446.79 cm^{-1}, the –N-H stretching in amine is shifted from to 2852.72 cm^{-1} to 3358.07 cm^{-1}. The =C-H stretching frequency for alkene is shifted from 794.67 to 825.53 cm^{-1}. These results also confirm that the FTIR spectra support the fact that the corrosion inhibition of CHL extract on Brass in 1.0N HCL may be the adsorption of active molecule in the inhibitor and the surface of metal.

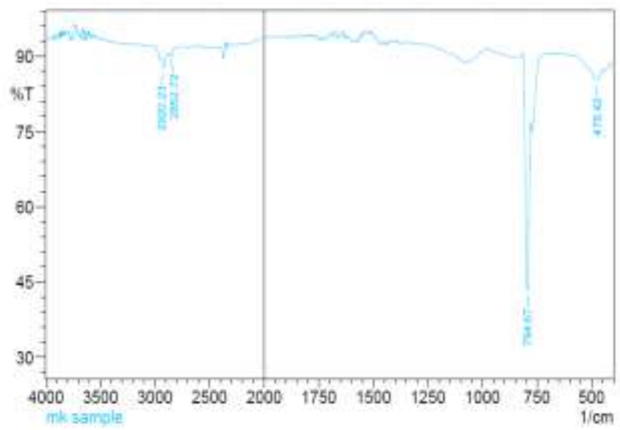


Figure 6(a): FT-IR spectrum of ethanolic extact of Cardiospermum halicababum *leaves* (CHL)

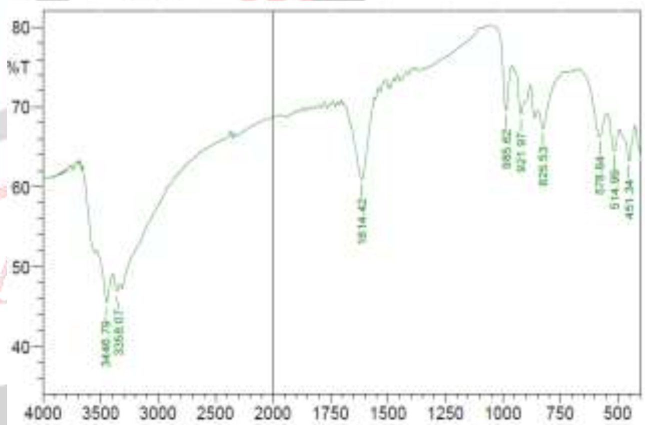


Figure 6(b): FT-IR spectrum for the corrosion product on Brass in the presence of CHL extract with 1.0N HCL.

4.3 EDX SPECTRUM

EDX spectroscopy was used to determine the elements present on the Brass surface in the absence and presence of inhibitor. Fig 7 and 8 represents the EDX spectra for the corrosion product on metal surface in the absence and presence of optimum concentrations of CHL extract in 1.0N HCL. In the absence of inhibitor molecules, the spectrum may concluded that the existence of chlorine present in the metal. 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

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such as sulfur and oxygen present in the inhibitor molecules may involve the complex formation with metal atom during the adsorption process and prevent the further dissolution of metal against corrosion**.**

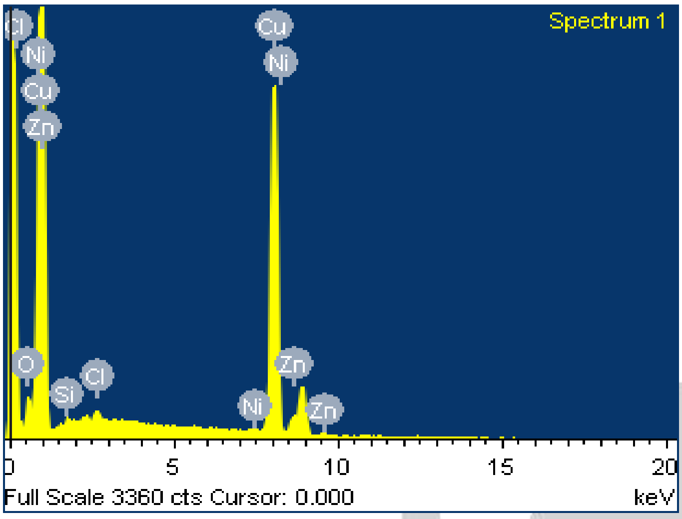


Fig-7 : EDX spectrum of the corrosion product on Brass surface in 1.0N HCL

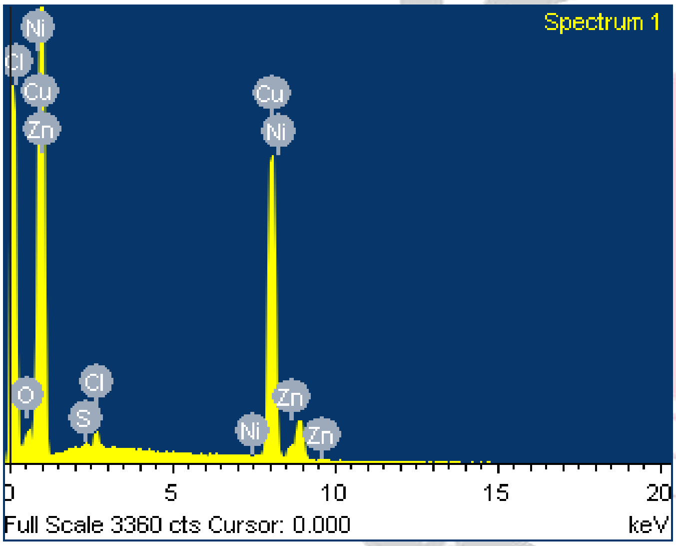
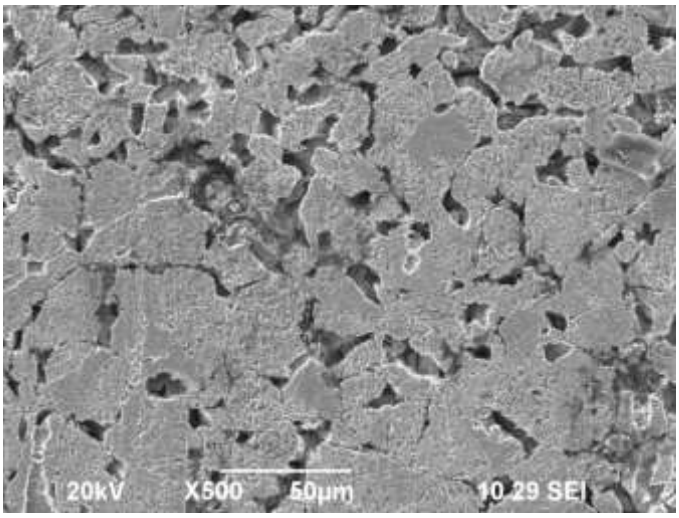


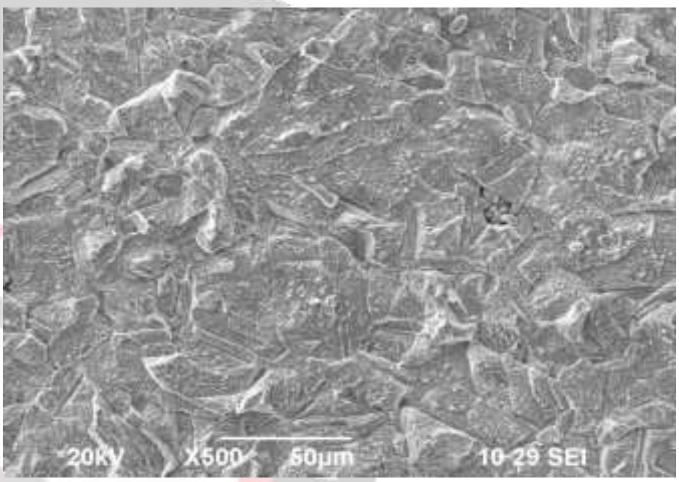
Fig-8: EDX spectrum of the corrosion product on Brass in the presence of CHL extract in 1.0N HCL.

4.4 SEM ANALYSIS

The surface morphology of Brass surface was studied by scanning electron microscopy (SEM). The Figure-9 (a) and (b) shows the SEM micrographs of Brass surface before and after immersion in 1.0N HCL respectively. The SEM photographs (a) showed that the surface of metal has number of pits and cracks are visible in the surface and belongs to plug type corrosion. but in presence of inhibitor they are minimized on the metal surface. It is clearly indicates that the formation of thin film covered on the entire metal surface.



(a)



(b)

Figure-9: SEM images of the Brass surfaces: (a) immersed in 1.0N HCL; (b) immersed in 1.0N HCL with CHL extract

V. CONCLUSION

Cardiospermum halicababum *l*eaves have shown excellent inhibition performance for Brass in 1.0N HCL environment. The inhibition efficiency increased with the increase of inhibitor concentration. The maximum inhibition efficiency was achieved 91.67%. Also, the inhibition efficiency gradually decreased with the rise in temperature ie, 82.14% to 60% for 313K and 333K respectively. It follows physical adsorption mechanism. 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 physical, exothermic and spontaneous process respectively. The inhibitor is found to obey Langmuir adsorption isotherms. UV spectrum indicates the band is shifted to longer wavelength region (Bathochromic shift (or) Red shift). The change of absorption band may confirmed that the strong co-ordination bond between the active group present in the inhibitor molecules and the ions from the metal surface

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FTIR spectra support the fact that the corrosion inhibition of CHL extract on Brass in 1.0N HCL may be the adsorption of active molecule in the inhibitor and the surface of metal. EDX Spectrum indicates that these hetero atoms such as sulfur and oxygen present in the inhibitor molecules may involve the complex formation with metal atom during the adsorption process and prevent the further dissolution of metal against corrosion.

The thin film formation on the metal surface may confirmed by SEM photographs and the corrosion products characterised by UV, FT-IR and EDX spectroscopy.

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