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WRIGHTIA TINCTORIA LEAVES EXTRACT AS EFFECTIVE CORROSION INHIBITOR ON COPPER IN ACID ENVIRONMENT

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ABSTRACT

The Inhibitive nature of Wrightia tinctoria leaves extract on copper in 1.0 N Hydrochloric acid environment contains various concentrations of inhibitor with different exposure time and temperature has been investigated by using mass loss measurements. The observed result reveals that the percentage of inhibition efficiency increased with increase of inhibitor concentration and temperature. Thermodynamic parameters Viz; E_a, Q_{ads}, G_{ads}, H and S suggests that the adsorption of WTL extract is exothermic, spontaneous and chemisorptions process. The inhibitor follows Langmuir adsorption isotherm. The corrosion product formed on the metal surface confirmed by the spectral studies such as UV, FT-IR and SEM.

1. INTRODUCTION

Copper and its alloys are commonly employed in worldwide for heating and cooling systems due to their good thermal conductivity and mechanical properties. Hydrochloric acid pickling is extensively used for the removal of rust and scale on heat transfer in several industrial processes. However, these systems should be regularly cleaned from carbonates and oxides that diminish their heating transmission[1]. Hydrochloric acid is used to clean these surfaces; a corrosion inhibitor is added to avoid the action of this acid on copper and its alloys. Corrosion inhibitor is a chemical substance when it is added with little concentration to environment effectively checks, decreases or prevents the reaction of metal with environment[2]. Most of the inhibitors have been developed by empirical experimentation. Amines and triazoles derivatives have been reported to be very effective inhibitors for copper in acidic solutions. For this reason, the corrosion behaviour of these metals has attracted more awareness of several investigators.

The heavy loss of metals is a result of its contact with the pollution environment can be minimized to a great extent by the use of corrosion inhibitors, using both organic and inorganic compounds. Pure synthetic chemicals are costly, but some of them are easily biodegradable and their disposal creates pollution problems. Plant extracts are environmentally friendly, bio-degradable, non-toxic, plenty and potentially low cost. Thus recently several efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors. Some of few studies are Beet root[3-4], Saponin[5], Terminalia bellerica[6], Oxandra asbeckii[7],Argemone

mexicana[8], Betanin[9], Henna[10], Wheat[11], Ginger[12],Marraya koeningii[13], Garlic extract[14], Ananas sativum[15] Sauropus androgynus[16], mimusops elengi[17], kingiodendron pinnatum[18] have been found effective corrosion inhibitors for copper.

In Continuous of our research work, the present investigation is the corrosion inhibition behaviour of Wrightia Tinctoria leaves on copper in Hydrochloric acid environment 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, SEM and EDX spectral studies.

2. MATERIALS AND METHODS

2.1 Specimen preparation

Copper 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 *Wrightia tinctoria Leaves (*WTL) Extract

About 3 Kg of *Wrightia tinctoria* 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 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 Properties of *Wrightia tinctoria* leaf

Wrightia tinctoria belongs to *Appocynaceae family* and it is an annual herbaceous climbing plant with a long history of traditional medicinal uses in many countries, especially in tropical and subtropical regions. The peel extract of this plant is used to regulate thyroid function and glucose metabolism. The main phytochemicals present in this plant is flavonoids, alkaloids, saponins, and triterpenes. The chemical structures are shown in Fig.1.
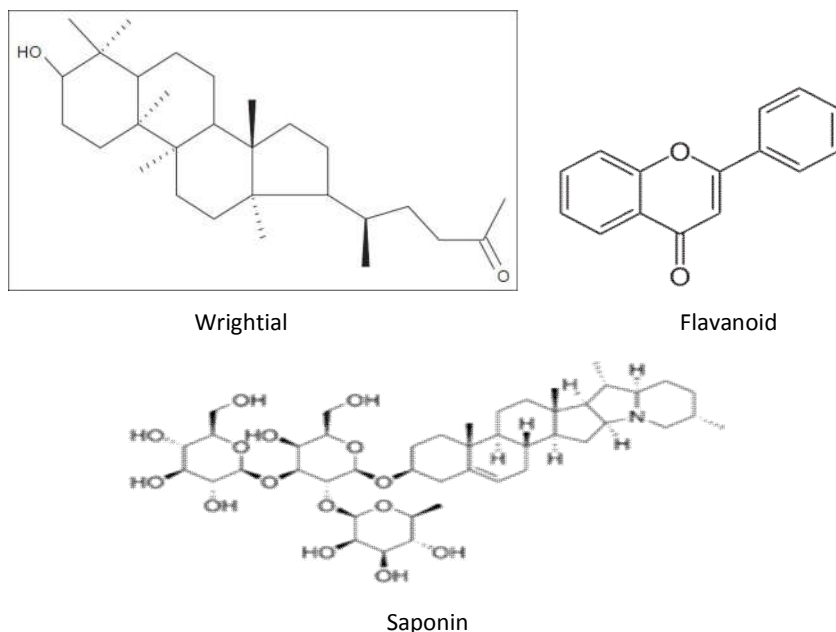

Wrightial   Flavanoid

Saponin

Figure-1: Chemical structure of the main active compounds present in *Wrightia Tinctoria l*eaves

2.4 Mass loss measurement

In mass loss measurements the copper specimen in triplicate were completely immersed in 50ml of the test solution in the presence and absence 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.

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

Where, mmpy = millimiles 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.

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

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

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

2.5 Adsorption studies

2.5. 1 Activation energy

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

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

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

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

2.5.2 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).

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

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.

2.5.3 Langmuir Adsorptioin Isotherm

The Langmuir adsorption isotherm can be expressed by the following Equation-4.10 is given below [38-40].

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

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.

2.5.4. Free energy of adsorption

The equilibrium constant of adsorption of various plant extract on the surface of copper, Brass and Mild steel is related to the free energy of adsorption   G $_{ads}$ by equation (8).

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

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

3. RESULTS AND DISCUSSION

3.1 Mass loss measurements

The dissolution behavior of copper in Hydrochloric acid ennvironment containing in the absence and presence of WTL extract with various exposure times (24 to 360 hrs) are shown in Table-1**.** The observed values are clearly indicates that in the presence of WTL extract the value of corrosion rate decreased from 1.3443to 0.1629 mmpy (24 hrs) and 1.0252 to 0.2131 mmpy (360 hrs) with increase of inhibitor concentration from 0 to 500 ppm. The maximum of 87.87 % of inhibition efficiency is achieved even after 24 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 media of chloride ion (Cl^{-}).

Table 1: The corrosion parameters of Copper in 1N HCl containing different concentration of WTL extract after 120 to 480 hours exposure time

Con. of inhibitor (ppm)	24 hrs		72 hrs		120 hrs		240 hrs		360 hrs	
	C.R (mmpy)	I.E (%)	C.R (mmpy)	I.E (%)	C.R (mmpy)	I.E (%)	C.R (mmpy)	I.E (%)	C.R (mmpy)	I.E (%)
0	1.3443	-	1.2967	-	1.3443	-	1.3259	-	1.0252	-
10	0.5906	56.06	0.5906	54.45	0.6314	53.03	0.6253	52.84	0.5594	45.43
50	0.4684	65.15	0.4684	63.87	0.4684	65.15	0.5193	60.82	0.4508	56.02
100	0.3055	77.27	0.3326	74.34	0.3299	75.45	0.3462	73.88	0.3652	64.37
500	0.2240	83.33	0.2376	81.67	0.2484	83.74	0.2770	79.10	0.2878	71.92
1000	0.1629	87.87	0.1833	85.86	0.1914	85.75	0.2016	84.79	0.2131	79.20

3.2 Temperature Studies

The corrosion parameters of copper in acid medium containing various concentration of KPL extract with different temperature in range from 313 to 333K is shown in Table-2. In the absence of inhibitor, the corrosion rate increased from 8.79912 to 37.6406 mmpy at 313 to 333K, but in the presence of inhibitor, the value of corrosion rate decreased from 8.7991to 2.4441mmpy and 37.6406 to 7.3325mmpy with increase of inhibitor concentration the temperature range from 313and 333K. The maximum of 80.51 % inhibition efficiency is achieved at 333K respectively. The value of inhibition efficiency is increased with rise in temperature. This results clearly reflects that component present in the inhibitor on the metal surface is higher than the desorption process. It clearly shows that the inhibitor follows chemisorptions process

Table 2: The corrosion parameters of copper in Hydrochloric acid containing different concentration of WTL extract at 313 to 333 K

Con. of inhibitor (ppm)	313 K		323 K		333 K	
	C.R (mmpy)	I.E (%)	C.R (mmpy)	I.E (%)	C.R (mmpy)	I.E (%)
0	8.7991	-	21.0200	-	37.6406	-
10	4.8883	44.44	11.7321	44.18	25.9084	31.16
50	3.9107	55.55	13.1986	37.20	18.0870	51.94
100	3.4218	61.11	10.2656	51.16	14.1763	62.33
500	2.9330	66.66	8.7991	58.13	10.2656	72.73
1000	2.4441	72.22	7.8214	62.79	7.3325	80.51

3.3 Effect of Temperature

3.3.1 Activation energy

The observed values of activation energy are ranged from 30.275–46.641kJ/mol for copper in Hydrochloric acid containing various concentration of inhibitor. The average value of E_a obtained from the blank (30.275) is lower than that in the presence of inhibitor and clearly suggest that there is a strong chemical adsorption bond between the WTL inhibitor molecules and the metal surface

Table 3: Calculated values of Activation energy (E_a) and heat of adsorption (Q_{ads}) of WTL extract on Copper in 1.0N Hydrochloric acid environment.

S.No	Conc. of inhibitor(ppm)	% of I.E		E_a (KJmol^{-1})	Q_{ads} (KJmol^{-1})
		30°	60°		
1.	0	--	--	40.648	--
2.	10	44.44	31.16	46.641	-15.910
3.	50	55.55	51.94	42.831	-4.057
4.	100	61.11	62.33	39.752	1.455
5.	500	66.66	72.73	35.036	8.062
6.	1000	72.22	80.51	30.275	12.963

3.3.2 Heat of adsorption

The value of heat of adsorption (Q_{ads}) on copper in 1.0N Hydrochloric acid containing various concentration of WTL extract is calculated using Equation (6) and the values of Q_{ads} are ranged from -15.910 to -4.057 kJ/mol (Table-3). These negative values are reflected that the adsorption of WTL extract on copper is 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 work the Langmuir adsorption isotherm is investigated. The straight line observed in Fig-4 suggests that the inhibitor follows Langmuir adsorption isotherm.
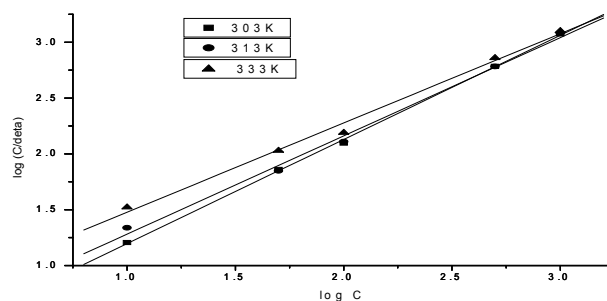
Figure 2: Langmuir isotherm for the adsorption of WTL inhibitor on Copper in 1.0N Hydrochloric acid environment.

3.3.4 Free energy of adsorption

The standard free energy of adsorption (G_{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 WTL inhibitor on Copper in 1.0N Hydrochloric acid.

Adsorption isotherms	Temperature (Kelvin)	Slope	K	R^2	G_{ads} kJ/mol
Langmuir	303	0.8998	2.7270	0.9950	-12.624
	313	0.9069	3.1318	0.9946	-13.401
	333	0.8042	4.4926	0.9982	-15.256

3.3.5 Thermodynamics parameters

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

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

where h is the Planck's constant, N the Avogadro's number, S the entropy of activation, and H the enthalpy of activation. A plot of log (CR/T) Vs. 1000/T gives a straight line (Fig. 8) with a slope of (H/R) and an intercept of [log(R/Nh)) + (S/R)], from which the values of S and H 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 (S) is generally interpreted with disorder which may taking place on going from reactants to the activated complex.

Table 5: Thermodynamic parameters of copper in 1.0N HCl solution obtained from weight loss measurements

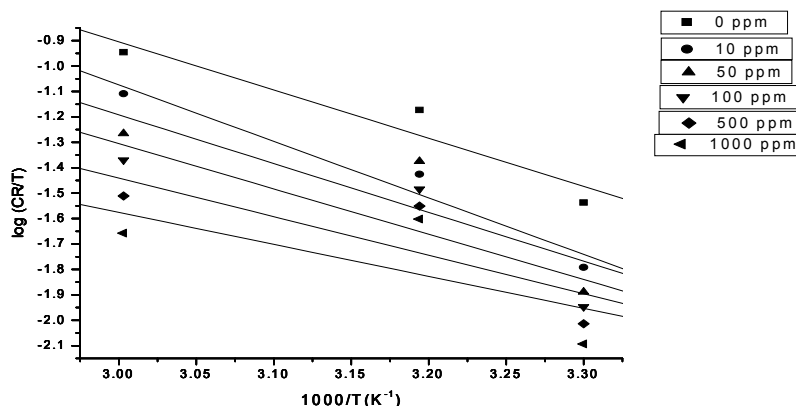| S. No	Concentration of WTL inhibitor (ppm)	H (kJ mol^{1})	S (J k^{1}mol^{1})
1	0	15.7482	12.0211
2	10	18.4838	12.7012
3	50	15.9535	11.8441
4	100	14.8156	11.4085
5	500	12.6067	10.6331
6	1000	10.4613	9.8774

Figure 3: The relation between log(CR/T) and 1/T for different concentrations of WTL extract

3.4 Spectral studies

3.4.1 UV spectrum

Figure 4 & 5 shows that the UV visible spectrum of the corrosion product on the surface of copper in the absence and presence of WTL extract in 1.0N Hydrochloric acid. In the absence of inhibitor, the UV absorption maximum of around 235.54nm and 277.82nm were obtained. However in the presence of inhibitor also shows two peaks were appeared at around 222.34 & 344.12nm. The change of adsorption band from the above spectrum revealed that the strong co-ordination between the active group present in the inhibitor molecules and the metal surface.
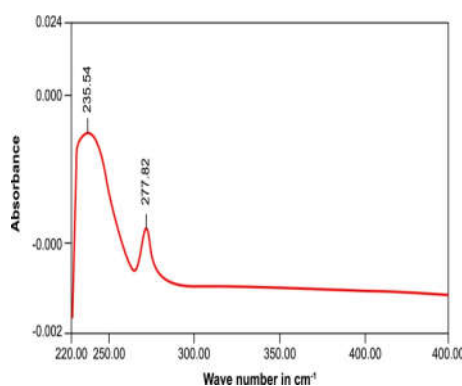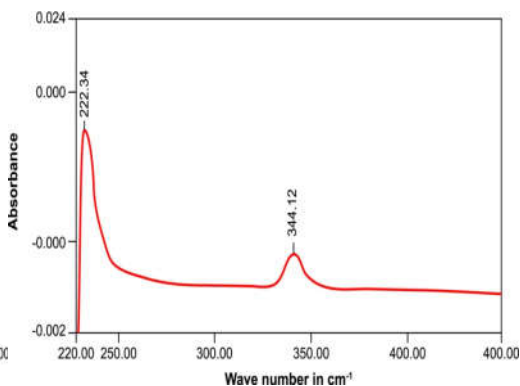
Fig-4   Fig-5

Figure 4 & 5: UV spectrum of corrosion product in the absence and presence of WTL on the copper in 1N HCL

3.5 FT-IR SPECTROSCOPY

3.5.1 FT-IR studies of WTL extract on Copper surface in 1.0 N Hydrochloric acid

The figures 6 and 7 reflect that the FTIR spectrums of the ethanol extract of inhibitor and the corrosion product on copper in the presence of WTL extract in1N HCL. On comparing both of these spectra the prominent peak such as, the –N-H stretching frequency for amine is shifted from 3446.56 to 3379.05 cm^{-1}, the –C=O stretching in carbonyl is shifted from to 1645.17 cm^{-1} to 1625.38 cm^{-1}. The C-N stretching frequency for aromatic amine is shifted from 1420.22 to 1400cm^{-1}. These results also confirm that the FTIR spectra support the fact that the corrosion inhibition of WTL extract on Copper in 1.0N Hydrochloric acid may be the adsorption of active molecule in the inhibitor and the surface of metal.
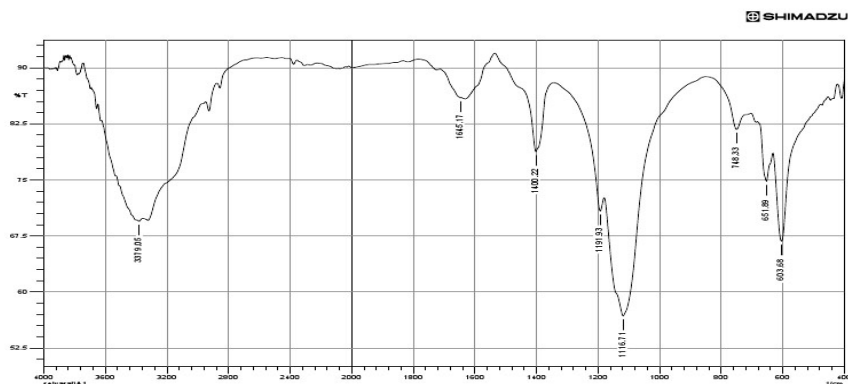
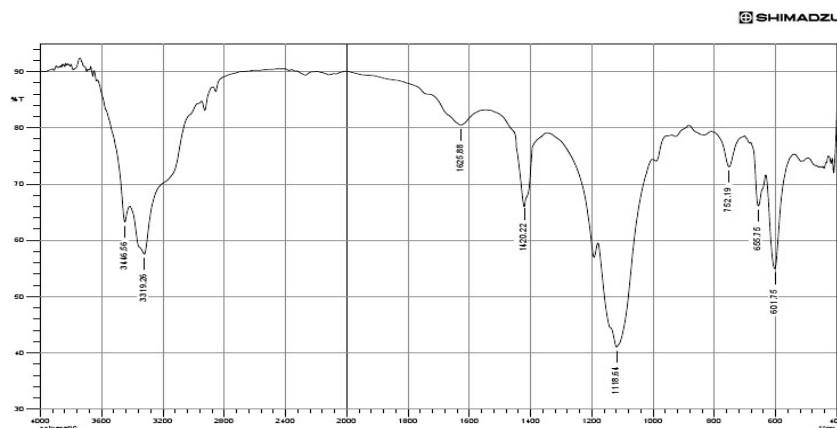**Figure 6: FT-IR spectrum of ethanolic extact of *Wrightia Tinctoria* laeves (WTL)**


Figure 7: FT-IR spectrum for the corrosion product on Copper in the presence of WTL extract with 1.0N HCL

3.6 SEM Analysis

The surface morphology of copper surface was studied by scanning electron microscopy (SEM). The Figure-8 (a) and (b) shows the SEM micrographs of copper 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, but in presence of inhibitor they are minimized on the metal surface. It is clearly indicates that the formation of spongy mass covered on the entire metal surface.
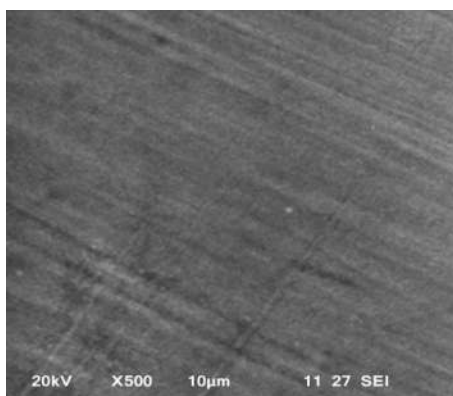
(a)
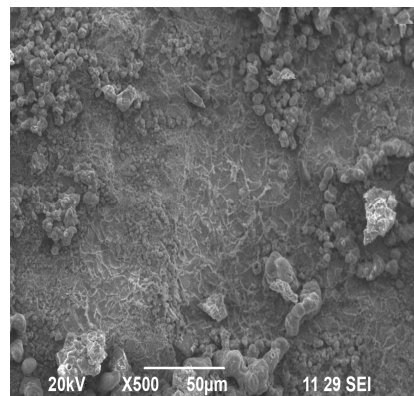
(b)

Figure 8: SEM images of the copper surfaces: (a) immersed in1.0N HCL; (b) immersed in1.0N HCL with WTL extract

4. CONCLUSION

From the above observations and findings, the following conclusions may be drawn. Using *Wrightia tinctoria* leaves (WTL) extract of copper in 1.0N Hydrochloric acid Using WTL extract on copper, the corrosion rate markedly reduced with increase of concentrations from 0 to 1000ppm. Eventhough we attained the maximum of 87.87% inhibition efficiency after 24 hours exposure time. This is due to strong bindings between the inhibitor molecule and ions from the metal surface. In temperature studies, the percentage (%) inhibition efficiency increased with rise of temperature from 303 to 333K is due to the adsorption of active inhibitor molecules on the metal surface is higher than desorption process. The maximum 80.51% inhibition efficiency is attained with increases of temperature and follows chemisorptions. The activation energy (E_a), heat of adsorption (Q_{ads}), Standard free energy adsorption (G_{ads}), enthalphy (H), entrophy (S), suggests that, strong chemical bond, endothermic, spontaneous process respectively. The WTL inhibitor obeys Langmuir adsorption isotherm. The thin film formation may also confirmed by spectral studies and morphological studies by SEM.

5. ACKNOWLEDGEMENTS

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