

Corrosion Effect of Cu-30Zn Alloy Using *Cnidoscopus Chayamansa* Leaves Extract In Acid Media

Bright. A^{*1}, Michlin Ruphina Maragatham. S^{*1}, Malar vizhi.I², Dr. Kalirajan. K², Dr.Selvaraj. S²

Asst. Professor, Dept. of Chemistry, V V College of Engineering, Arasoor, Tisaiyanvilai, Tamil Nadu, India^{*1}

Postgraduate and Research, Dept. of Chemistry, Sri Paramakalyani College, Alwarkurichi, Tamil Nadu, India²

ABSTRACT: The inhibitive nature of *Cnidoscopus chayamansa* leaves extract on Cu-30Zn alloy in 1.0 N HCl has been investigated by using mass loss measurements with various periods of contact as well as temperature. The observed result reveals that the percentage of inhibition efficiency increased with increase of inhibitor concentration, period of contact and temperature. Thermodynamic parameters (Viz; E_{a} , Q_{ads} and ΔG_{ads}) suggests that the adsorption of CCL extract was endothermic, spontaneous and chemisorptions. It obeys Langmuir and Temkin adsorption isotherm. The corrosion product formed on the metal surface may also be confirmed by the spectral studies such as UV, FT-IR, XRD and SEM-EDX.

KEYWORDS: Brass, Corrosion inhibition, *Cnidoscopus chayamansa*, Adsorption, Spectral studies

I. INTRODUCTION

Brass is a binary alloy composed of copper and zinc that has been produced for millennia and is valued for its workability, hardness, corrosion resistance and attractive appearance. However, their exhibition in acid media creates problems of corrosion [1-3]. Acid solutions are often used in industry for cleaning, descaling and pickling of metallic structures which are normally accompanied by considerable dissolution of the metal. A useful method to protect metal and alloys in aggressive environments against corrosion is addition of organic and inorganic species to the solution in contact with the surface in order to inhibit the corrosion reaction and hence reduce the corrosion rate. However most of these synthetic chemical inhibitors are toxic to the environments. In an attempt to find corrosion inhibitors which are environmentally safe and easily available, there has been a growing trend in the use of natural products such as leaves or plant extracts as corrosion inhibitors for metals in various environment, because they are inexpensive, readily available, renewable sources of materials and ecologically acceptable [4]. They are rich enough source of active molecules, which have noticeably high inhibition efficiency and hence termed as “Green Inhibitors” [5]. Some investigators namely Ebenso et al. [6], Abiola et al. [7], Bendahou et al. [8], Odiongenyi et al. [9], Eddy et al. [10-12], Deeparani et al. [13-16], Petchiammal et al. [17-19], and A.Sharmila et al. [20], Bright et al. [21,22], have been reported the successful use of naturally occurring substances to inhibit the corrosion of metals in various environment. In continuity of our research work the present study is aimed at investigating the inhibitive and adsorption properties of ethanolic extract of *Cnidoscopus Chayamansa* leaves for the corrosion of Cu-30Zn alloy in HCl on using mass loss measurements with different time and temperature, and the corrosion product on metal surface is characterised by UV, FT-IR, XRD, EDX-SEM spectral studies.

II. MATERIALS AND METHODS

Properties of *Cnidoscopus Chayamansa* Leaves

The tree spinach (*Cnidoscopus chayamansa*), called “Chaya” in south Texas, is popular in Mexico and Central America and now presently available in and around southern part of India. The Atomic Absorption Spectroscopy(AAS) study showed the presence of chloride, copper, calcium, iron, magnesium, nitrate, phosphate, potassium, sodium, zinc, carbonate and bicarbonate in leaf extract of *Cnidoscopus chayamansa* but below the WHO permissible limit and therefore safe to use. It also contains medicinally active constituents like Alkaloids, Carbohydrate, Amino acids,

Protein, Tannins, Flavanoids, terpenoids, Glycosides and steroids. Chaya traditionally has been recommended for a number of ailments including diabetes, obesity, kidney stones, hemorrhoids, acne, and eye problems. Chaya shoots and leaves have been taken as a laxative, diuretic, circulation stimulant, to improve digestion and to harden the fingernails.

Stock solution of *Cnidioscolus Chayamansa* extract

Cnidioscolus 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 48 hours. 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.

Specimen preparation

Rectangular specimen of Cu-30Zn alloy was mechanically pressed cut to form different coupons, each of dimension exactly 20 cm² (5x2x2cm) with emery wheel of 80 and 120 and degreased with trichloroethylene, washed with distilled water, cleaned and dried, then stored in desiccators for our present study.

Mass Loss method

In the mass loss measurements, Cu-30Zn alloy specimens in Triplicate were completely immersed 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 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.

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

(Where, mmpy = millimetre per year, W = Mass loss (mg), D = Density (gm/cm³), A = Area of specimen (cm²), T = time in hours)

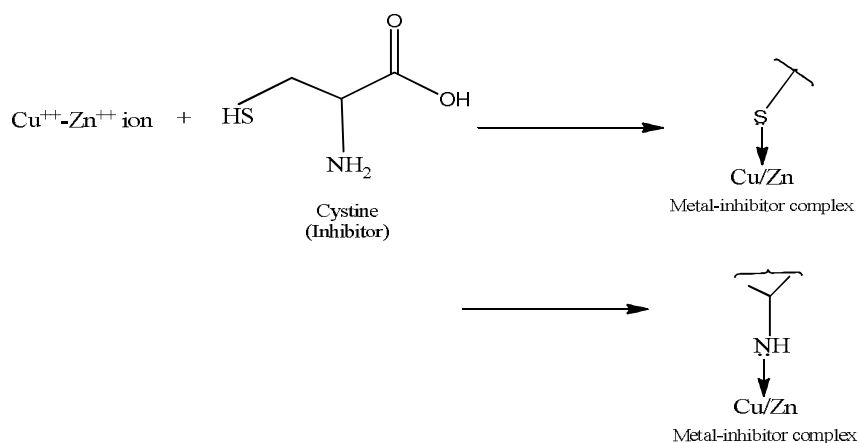
The inhibition efficiency (%IE) and degree of surface coverage (θ) were calculated using equation (2) and equation (3) respectively.

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

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

(Where, W₁ and W₂ are the corrosion rates in the absence and presence of the inhibitor respectively)

Proposed mechanism:



III. RESULTS AND DISCUSSION

The observed results (Table-1) clearly indicate that the percentage of inhibition efficiency and the degree of surface coverage (θ) increased with increase of inhibitor concentration. The maximum of 85.98% inhibition efficiency is achieved even after 360 hrs exposure time. The maximum inhibition efficiency may be predominantly by the adsorption of the plant constituents on the metal surface by the interaction of π - electrons or lone pair of hetero atoms with metal. The main phytoconstituents like Alkaloids, Amino acids, Protein, Tannins, Flavanoids, Terpenoids, and Steroids etc.. are found to be big molecules capable of covering a large surface area on adsorption. These adsorbed molecules are blocks the active sites in which direct acid attack proceed and protect the metal from dissolution process. From the results, it can be noticed that the inhibition efficiency increased with increase of CCL extract concentration. It is revealed that the CCL extract retards the dealloying process of Cu-30Zn alloy in 1.0 N HCl.

Table-1: The corrosion parameters of Cu-30Zn alloy in 1.0 N HCl containing various concentration of CCL extract with different exposure time

| 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 | 1.174 | 0.875 | 0.619 | 0.469 | 0.341 | 0.299 | - | 25.46 | 47.27 | 60.00 | 70.91 | 74.55 |
| 72 | 1.159 | 0.775 | 0.598 | 0.448 | 0.320 | 0.256 | - | 33.12 | 48.46 | 61.35 | 72.39 | 77.91 |
| 120 | 1.332 | 0.858 | 0.717 | 0.478 | 0.410 | 0.265 | - | 35.58 | 46.16 | 64.10 | 69.23 | 80.12 |
| 168 | 1.213 | 0.722 | 0.582 | 0.366 | 0.299 | 0.229 | - | 40.45 | 52.00 | 69.85 | 75.38 | 81.15 |
| 216 | 1.425 | 0.761 | 0.557 | 0.417 | 0.268 | 0.232 | - | 46.59 | 60.90 | 70.71 | 81.19 | 83.69 |
| 360 | 1.370 | 0.763 | 0.514 | 0.331 | 0.265 | 0.192 | - | 44.35 | 62.52 | 75.81 | 80.68 | 85.98 |

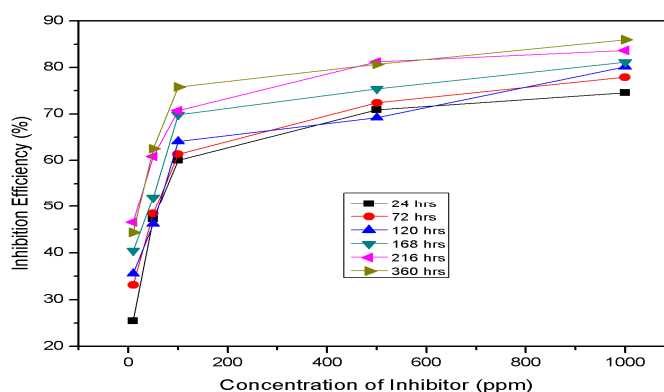


Figure-1: The corrosion parameters of Cu-30Zn alloy in 1.0N HCl containing various concentration of CCL extract with different exposure time

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 10, October 2015

The Fig-2 shows that the value inhibition efficiency versus different concentration of CCL extract on Cu-30Zn alloy at 303-333K. It can be seen from the figure that the value of inhibition efficiency of CCL extract on Cu-30Zn alloy is increased with rise in temperature. The maximum of 84.34 % of inhibition efficiency is achieved at 333 K. Thus the inhibitor efficiencies were temperature dependent and it being chemically adsorbed at all temperatures. This is due to the adsorption of active molecules on the metal surface is higher than the desorption process.

Table-2: The corrosion parameters of Cu-30Zn alloy in 1.0 N HCl containing various concentration of CCL extract with different exposure temperature

| 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 | 33.29 | 26.12 | 22.02 | 16.39 | 10.24 | 7.17 | - | 21.54 | 33.85 | 50.77 | 69.23 | 78.46 |
| 313 | 36.36 | 27.14 | 20.99 | 14.85 | 10.75 | 6.66 | - | 25.35 | 42.25 | 59.15 | 70.42 | 81.69 |
| 323 | 38.92 | 27.65 | 20.99 | 15.36 | 9.73 | 6.15 | - | 28.95 | 46.05 | 60.53 | 75.00 | 84.21 |
| 333 | 42.50 | 30.21 | 22.53 | 15.88 | 10.24 | 6.66 | - | 28.91 | 46.99 | 62.65 | 75.90 | 84.34 |

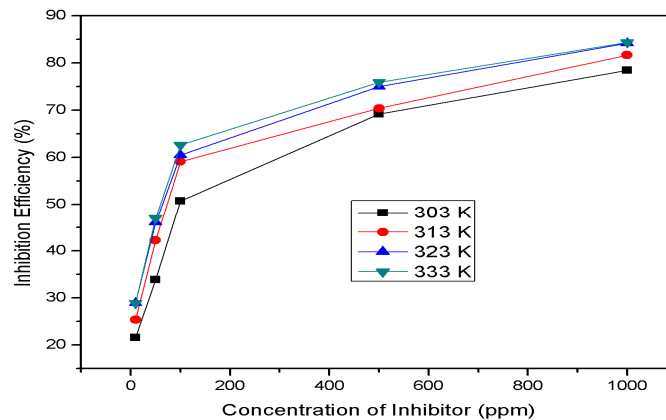


Figure-2: The corrosion parameters of Cu-30Zn alloy in 1.0 N HCl containing various concentration of CCL extract with different exposure temperature

The activation energy (E_a) for the corrosion of Cu-30Zn alloy in the presence and absence of CCL extract is calculated using Arrhenius theory. Assumptions of Arrhenius theory is expressed by equation (4) and from its derived form (5).

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

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

Where, CR_1 and CR_2 are the corrosion rate at the temperature T_1 (303K) and T_2 (333K) respectively. The values of Corrosion rate obtained from the mass loss measurements are substituted in equation (4) and the calculated values of activation energy are presented in Table-3. The activation energy decreased with increase of inhibitor concentration i.e,

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 10, October 2015

69.560 to 66.911 KJ/mol for Cu-30Zn alloy. The value of activation energy for blank (69.560 KJ/mol) is higher than in the presence of CCL extract with rise in temperature is suggested that Chemical adsorption mechanism.

Adsorption consideration

The heat of adsorption on Cu-30Zn alloy in the presence of inhibitor is calculated by the following equation (6)

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

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. The calculated values of Q_{ads} are reported in Table-3. These values are ranged from 9.402 to 15.365 kJ/mol. The positive values are indicated that the adsorption of inhibitor on Cu-30Zn alloy surfaces is endothermic. The adsorption isotherms are used to investigate the mode of adsorption and the characteristic of adsorption of inhibitor on the metal surface. The mass loss measurements are tested graphically for fitting two isotherms like Langmuir and Temkin.

The Langmuir and Temkin adsorption isotherm can be expressed by the equation (7) and equation (8) given below

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

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

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

Table-3: Calculated values of activation energy (E_a) and heat of adsorption (Q_{ads}) of CCL extract on Cu-30Zn alloy in 1.0 N HCl environment

| Concentration of inhibitor (ppm) | E_a (KJ mol ⁻¹) | Q_{ads} (KJ mol ⁻¹) |
|----------------------------------|--------------------------------|-----------------------------------|
| 0 | 69.560 | - |
| 10 | 68.739 | 10.986 |
| 50 | 67.719 | 15.365 |
| 100 | 67.264 | 13.607 |
| 500 | 67.527 | 9.402 |
| 1000 | 66.911 | 10.934 |

By plotting the values of Log C/ θ versus Log C, linear plots were generated (Fig-3) and conforming that the experimental data fitted with the Langmuir adsorption isotherm for the adsorption of CCL extract on Cu-30Zn alloy means that there is no interaction between the adsorbed species (i.e; adsorbate and adsorbent). The Langmuir adsorption isotherm is better fit at 323K for Cu-30Zn alloy ($R^2=0.9953$).

Table-4: Langmuir adsorption parameters for the adsorption of CCL extract on Cu-30Zn alloy in 1.0 N HCl environment

| Log C | Log C/ θ | | | |
|--------|-----------------|--------|--------|--------|
| | 30°C | 40°C | 50°C | 60°C |
| 1 | 1.6667 | 1.5960 | 1.5384 | 1.5389 |
| 1.6989 | 2.1694 | 2.0731 | 2.0357 | 2.0269 |
| 2 | 2.2943 | 2.2280 | 2.2180 | 2.2031 |
| 2.6989 | 2.8587 | 2.8513 | 2.8239 | 2.8187 |
| 3 | 3.1054 | 3.0878 | 3.0746 | 3.0739 |

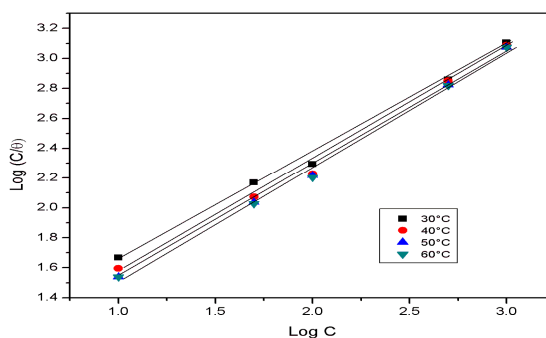


Figure-3: Langmuir adsorption parameters for the adsorption of CCL extract on Cu-30Zn alloy in 1.0 N HCl environment

A plot of θ versus Log C give almost a straight line for Cu-30Zn alloy in CCL extract in 1.0 N HCl environment (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 Cu-30Zn alloy is related to the free energy of adsorption ΔG_{ads} by equation (9).

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

Where, R is the gas constant, T is the temperature, K is the equilibrium constant of adsorption. The values of K obtained from Langmuir and Temkin adsorption isotherm are substituted into equation 9 and the calculated values of ΔG_{ads} are recorded in Table-6. 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.

Table-5: Temkin adsorption parameters for the adsorption of CCL extract on Cu-30Zn alloy in 1.0 N HCl environment

| Log C | θ | | | |
|--------|----------|--------|--------|--------|
| | 30°C | 40°C | 50°C | 60°C |
| 1 | 0.2154 | 0.2535 | 0.2895 | 0.2891 |
| 1.6989 | 0.3385 | 0.4225 | 0.4605 | 0.4699 |
| 2 | 0.5077 | 0.5915 | 0.6053 | 0.6265 |
| 2.6989 | 0.6923 | 0.7042 | 0.7500 | 0.7590 |
| 3 | 0.7846 | 0.8169 | 0.8421 | 0.8434 |

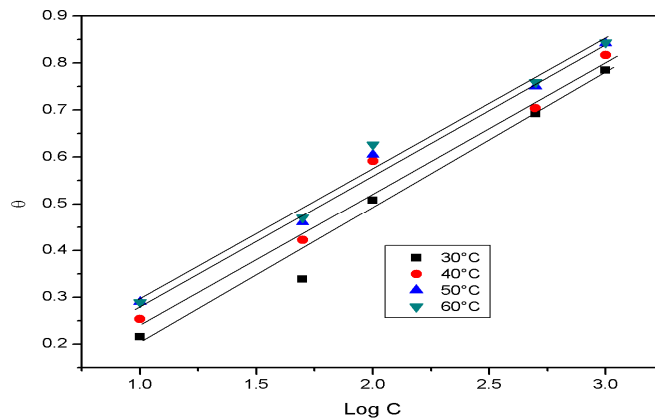


Figure-4: Temkin adsorption parameters for the adsorption of CCL extract on Cu-30Zn alloy in 1.0 N HCl environment

Table-6: Langmuir and Temkin parameters for the adsorption of CCL extract on Cu-30Zn alloy in 1.0 N HCl environment

| Adsorption isotherm | Temperature | Slope | K | R ² | ΔG_{ads} (KJ mol ⁻¹) |
|---------------------|-------------|--------|--------|----------------|--|
| Langmuir | 303 | 0.7149 | 8.555 | 0.9936 | -15.528 |
| | 313 | 0.7532 | 6.324 | 0.9916 | -15.254 |
| | 323 | 0.7720 | 5.403 | 0.9953 | -15.319 |
| | 333 | 0.7721 | 5.329 | 0.9936 | -15.755 |
| Temkin | 303 | 0.2941 | 0.7873 | 0.9733 | -9.571 |
| | 313 | 0.2773 | 0.9553 | 0.9689 | -10.335 |
| | 323 | 0.2762 | 1.0354 | 0.9857 | -10.881 |
| | 333 | 0.2770 | 1.0510 | 0.9774 | -11.259 |

IV. MORPHOLOGY STUDIES

UV Analysis: Fig-5(a) & (b) shows that the UV visible spectrum of ethanolic extract of CCL and the corrosion product on the surface of Cu-30Zn alloy in the presence of CCL extract in 1.0 N HCl. In this spectrum, only one absorption band around 265 nm was noticed (Fig-5(a)) but in the presence of inhibitor two bands were appeared (260 and 288nm) (Fig-5(b)). When compare both these spectra, the addition of absorption band may confirmed the strong coordination bond between the active group present in the inhibitor molecules and the metal surface.

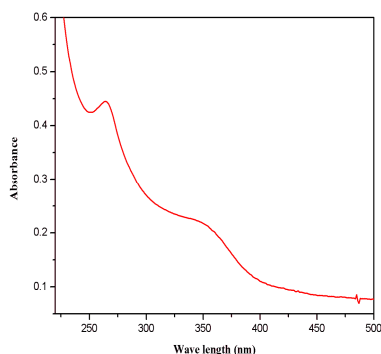


Figure-5(a)

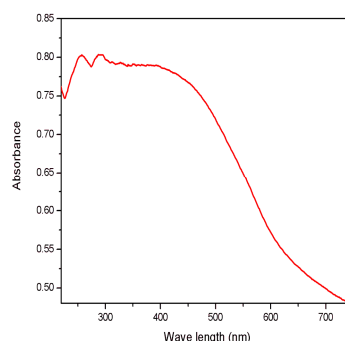


Figure-5(b)

Figure-5: UV spectrum of (a) Ethanolic extract of CCL (b) Corrosion product on Cu-30Zn alloy in the presence of CCL extract in 1.0 N HCl environment

FT-IR Analysis: Fig-6 and 7 represents that the alcoholic crystals of CCL extract and the corrosion product on the Cu-30Zn alloy surface in the presence of CCL inhibitor. On comparing these spectra, the -NH stretching frequency at 3352.28 Cm^{-1} is shifted to 3138.18 Cm^{-1} , the -CH stretching frequency at 2974.23 Cm^{-1} is shifted to 2920.23 Cm^{-1} , -CN- stretching frequency at 1087.85 Cm^{-1} is shifted to 1020.34 Cm^{-1} , clearly indicating that there is an interaction between the inhibitor and the surface of the metal. In fig-7, the appearance of few peaks and also the disappearance of some peaks are suggested that the co-ordination between the inhibitor and surface of the metal may be confirmed. The FTIR spectra also support the above fact that the adsorption between the active molecule in inhibitor and metal surface.

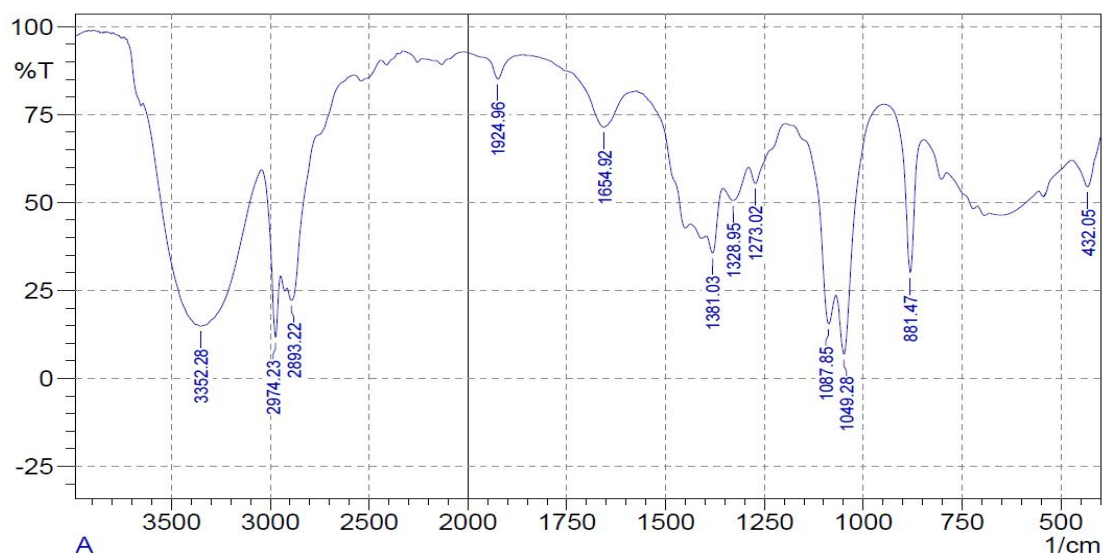


Figure-6: FT-IR spectrum of ethanolic extract of CCL extract

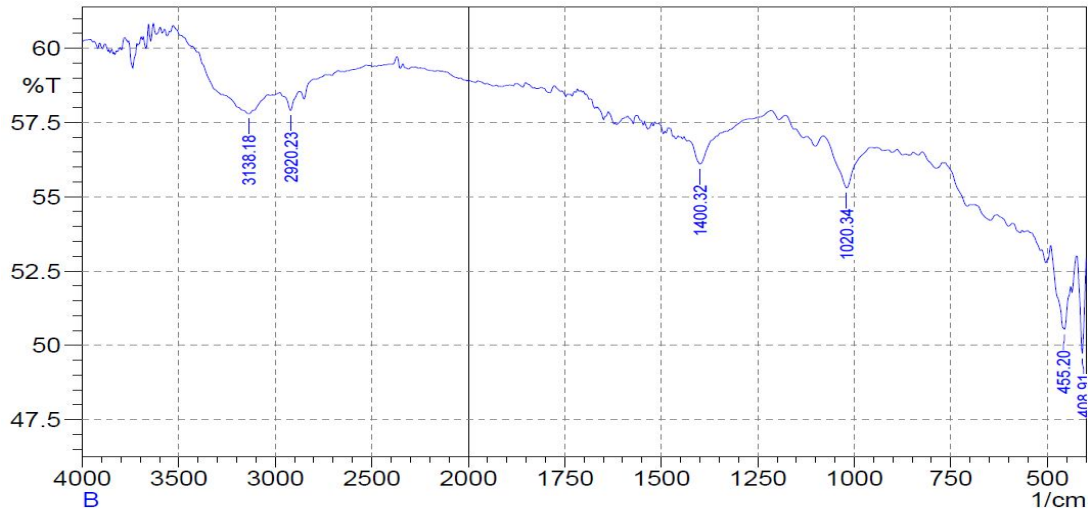


Figure-7: FT-IR spectrum for the corrosion product on Cu-30Zn alloy in the presence of CCL extract with 1.0 N HCl

DX Analysis: EDX spectroscopy was used to determine the elements present on the Cu-30Zn alloy surface in the presence and absence of inhibitor. Fig-8 and 9 represents the EDX spectra for the corrosion product on metal surface in the absence and presence of optimum concentrations of CCL extract in 1.0 N HCl. In the absence of inhibitor molecules, the spectrum may concluded that the existence of Chlorine due to the formation of metal chlorides. However, in the presence of the optimum concentrations of the inhibitors, the hetero atoms viz; Sulphur, Nitrogen 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 molecules may involve the complex formation with metal ion during the adsorption process and prevent the further dissolution of metal against corrosion.

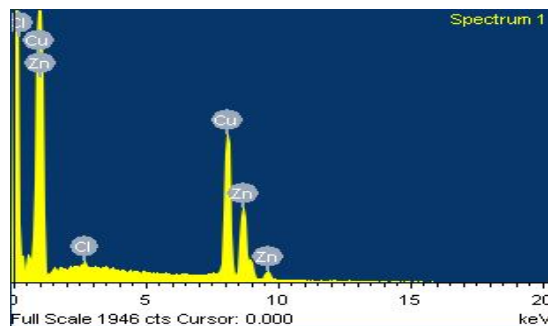


Figure-8: EDX spectrum of the corrosion product on Cu-30Zn alloy surface in 1.0 N HCl.

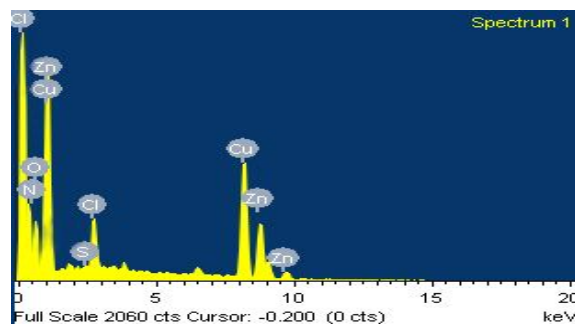


Figure-9: EDX spectrum of the corrosion product on Cu-30Zn alloy in the presence of CCL extract with 1.0 N HCl

XRD Analysis: The Corrosion product released from the Cu-30Zn alloy metal surface examined by XRD studies in the presence of inhibitor as shown in Fig-10. It reveals that the film may be mainly combine with a rich amount of $\text{Cu}(\text{OH})_2$, $\text{Cu}(\text{ClO}_4)_2$, $\text{Cu}(\text{N}_3)_2$, ZnS , Zn_3N_2 , $\text{Zn}_3\text{O}(\text{SO}_4)_2$ and ZnCl_2 etc with inhibitor.

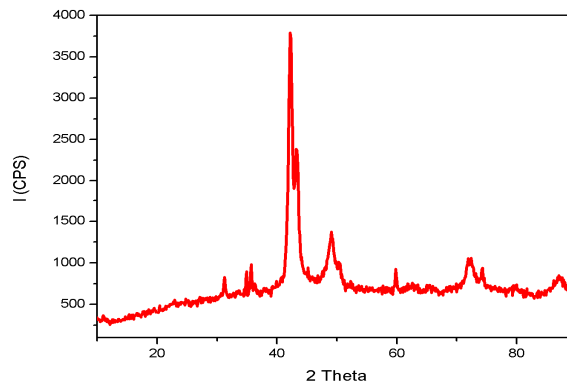


Figure-10: XRD- Analysis of Corrosion Product on Cu-30Zn alloy in the presence of CCL extract in 1.0 N HCl

SEM Analysis: The surface morphology of Cu-30Zn alloy surface was studied by scanning electron microscopy (SEM). Fig-11(a) showed that the polished surface of Cu-30Zn alloy. The Fig-11(b) shows the SEM micrograph of Cu-30Zn alloy surface immersed in 1.0 N HCl. The SEM photograph showed that the surface of metal has plug type corrosion and it is localized, but in presence of inhibitor the plug type image is minimized on the metal surface. It is clearly indicate that the formation of passive layer on the metal surface may prevent further dissolution.

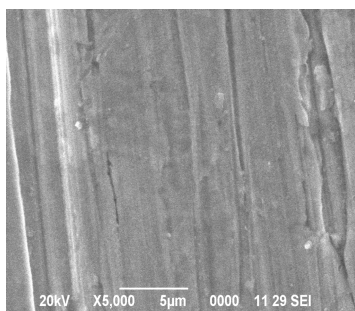
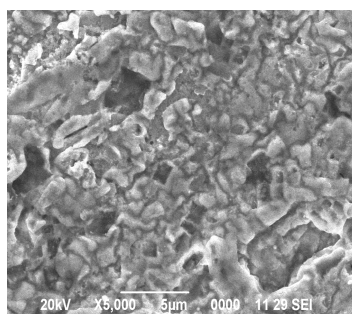
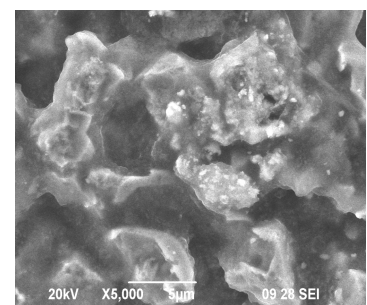


Figure-11(a)



11(b)



11(c)

Figure-11: SEM micrographs of (a) Polished Cu-30Zn alloy surface, (b) without inhibitor, 0 ppm (c) with inhibitor, 500 ppm

V. CONCLUSION

Cnidocolus chayamansa leaves extract is an effective inhibitor of the corrosion of Cu-30Zn alloy in 1.0 N HCl environment at different Temperature (303K, 313K, 323K and 333K) and exposure time (24, 72, 120, 168, 216 and 360 hrs). Even in the presence of highly corrosive media the inhibition efficiency increased with increase of inhibitor concentration and also increased with temperature and time. The hetero atom such as sulphur, nitrogen and oxygen are served as a good adsorption site onto the metal surface. They are responsible for the inhibitory action of *Cnidocolus chayamansa* leaves extract on Cu-30Zn alloy in 1.0 N HCl environment. The inhibitor obeys both Langmuir and Temkin adsorption isotherm at all temperature. The corrosion product over the surface of Cu-30Zn alloy in the presence

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 10, October 2015

of *Cnidioscolus chayamansa* leaves extract is analysed by FTIR, UV, XRD and SEM-EDX spectral studies and may conform the complex film formation on the surface of Cu-30Zn alloy.

REFERENCES

1. Mihit M., Belkhaouda M., Bazzi L., Salghi R.,* El Issami E., Ait Addi; Behaviour of Brasses Corrosion in Nitric Acid with and without PMT, *Portugaliae Electrochimica Acta.*, 25 (2007), 471-480.
2. Karpagavalli R., Rajeswari S; Corrosion control of brass in groundwater by interface and interphase inhibitors, *Anti-Corrosion Methods and Materials.*, 45, (1998), 333.
3. Kertit S., Essoufi H., Hammouti B., Benkaddour M; 1-Phenyl-5-Mercapto-1,2-3,4-Tetrazole (PMT) - A New Corrosion-Inhibitor For Cu-Zn Alloy, *Chim. Phys.*, 95, (1998), 2070.
4. Abdel-Gaber A.M., Khamis E., Abo-EIDahab H., Adeel; Inhibition of aluminium corrosion in alkaline solutions using natural compounds, *Materials Chemistry and Physics.*, Vol.109, (2008), 297-305.
5. Bothi Raja P., Sethuraman M.G; Natural products as corrosion Inhibitor for metals in corrosive media- A review, *Materials Letters.*, Vol.62, (2008), 113- 116.
6. Ebenso EE., Eddy NO., Odiongenyi AO; Corrosion inhibitive properties and adsorption behaviour of ethanol extract of *Piper guinensis* as a green corrosion inhibitor for mild steel in H₂SO₄. *Afri.J. Pure and Appl. Chem.*, 4(11), (2008), 107-115.
7. Abiola OK., Oforka NC., Ebenso EE., Nwinuka NM; Eco – friendly corrosion inhibitors: Inhibitive action of Delonix regia extract for the corrosion of aluminium in acidic medium, *Anti-Corrosion Methods Mater.*, 54(4), (2007), 219 – 224.
8. Bendahou MA., Benadellah MBE., Hammouti BB; A study of rosemary oil as a green corrosion inhibitor for steel in 2M H₃PO₄, *Pigment and Resin Technol.*, 35(2), (2006), 95-100.
9. Odiongenyi AO., Odoemelam SA., Eddy NO; Corrosion inhibition and adsorption properties of ethanol extract of *Vernonia Amygdalina* for the corrosion of mild steel in H₂SO₄, *Portugaliae electrochimica acta.*, 27(1), (2009), 33-45.
10. Eddy NO., Ebenso EE; Adsorption and inhibitive properties of ethanol extract of *Musa sapientum* peels as a green corrosion inhibitor for mild steel in H₂SO₄, *Afri. J. Pure Appl. Chem.*, 2(6), (2008), 1-9.
11. Eddy NO., Odoemelam SA; Inhibition of the corrosion of mild steel in H₂SO₄ by ethanol extract of Aloe vera, *Resin and Pigment Technology.*, 38(2), (2009), 111-115.
12. Eddy NO., Odoemelam SA; Ethanol extract of *Musa* species peels as a green corrosion inhibitor for mild steel, Kinetic, adsorption and thermodynamic consideration, *Adv. Nat. Appl. Sci.*, 2(1), (2008), 35-42.
13. Deepa Rani P., Selvaraj S; Inhibitive action of vitis vinifera (grape) on copper and brass in natural sea water environment, *Rasayan J. Chem.*, 3(3), (2010), 473-482.
14. Deepa Rani P., Selvaraj S; Inhibitive and adsorption properties of punica granatum extract on brass in acid media, *J. Phytol.*, 2(11), (2010), 58-64.
15. Deepa Rani P., Selvaraj S; Comparitive account of *Jatropha curcas* on Brass(Cu- 40Zn) in acid and Natural sea water environment, *Pacific J. of Sci. and Technol.*, 2011;12: 38- 49.
16. Deepa Rani P., Petchiammal A., Piramma Rajeswari M., Rajeswari C., Selvaraj S; *Eugenia Jambolana* Used as Corrosion Inhibitor on Mild Steel in 1N Hydrochloric Acid Medium, *American Journal of Phytomedicine and Clinical Therapeutics.*, 2, (2013), 215-225.
17. Petchiammal A., Deepa Rani P., Selvaraj S., Kalirajan K; Corrosion Protection of Zinc in Natural Sea Water using *Citrullus Vulgaris* peel as an Inhibitor., *Res. J. of Chem.Sci.*, 2, (2012), 24-34.
18. Petchiammal A., Selvaraj S., Kalirajan K; *Albizia lebbek* seed extract as effective corrosion inhibitor for Mild steel in acid medium, *Bio interface res. in App. Chem.*, 3, (2013), 498-506.
19. Petchiammal A., Selvaraj S., and Kalirajan K., Influence of *Hibiscus Esculenta* leaves on the corrosion of stainless steel in acid medium, *Inter. J. of Univ.Pharm and Bio Sci.*, 2, (2013), 242-252.
20. Sharmila A., Angelin Prema A., Arockia Sahayaraj P; Influence Of *Murraya Koenigii* (CURRY Leaves) extract on the corrosion inhibition of carbon steel in HCl solution, *rasayan. J. Chem.*, 3, (2010), 74.
21. Bright A., Michlin Ruphina Maragatham S., Malar vizhi I., and Selvaraj S; Inhibitive effect of *Cnidioscolus chayamansa* leaves extract on Copper in Acid environment, *International Journal of Multidisciplinary Research and Development.*, 2(4), (2015), 35-44.
22. Bright A., Michlin Ruphina Maragatham S., Malar vizhi I., and Selvaraj S; Corrosion behavior of Zinc in 1.0 N hydrochloric acid with *Cnidioscolus Chayamansa* – A Green Approach, *International Journal of Recent Scientific Research Research.*, Vol.6(4),(2015), pp.3594-3601.