



***Emblica Officinalis* (AMLA) leaves extract as corrosion inhibitor for copper and its alloy (CU-27ZN) in natural sea water**

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ABSTRACT

The inhibition efficacy of Emblica officinalis leaves extract on the corrosion of Copper and its alloy (Cu-27Zn) in Natural sea water environment has been studied by mass loss measurements at various time and temperature. The inhibition efficiency is markedly higher in Natural sea water environment with addition of Emblica officinalis leaves extract compared with those in the inhibitor free solution. The inhibition efficiency increased with increase of inhibitor concentration but decreased with rise in temperature and time. Corrosion inhibition may be due to the spontaneous physical adsorption of the plant constituents on the surface of Copper and its alloy. Experimental data fitted the Langmuir and Temkin adsorption isotherms. On comparing the UV and IR spectrum of alcoholic crystals of inhibitor and the corrosion product on Copper in the presence of inhibitor is reported.

Key words: Corrosion inhibition, Copper, Copper alloy, Emblica officinalis, Natural sea water.

INTRODUCTION

The protection of metal against corrosion is a major industrial problem. The use of inhibitor is one of the best options of protecting metals against corrosion. Several inhibitors in use is either synthesized from cheap raw materials or chosen from compounds having hetero atoms in their aromatic or long chain carbon system. These organic compounds can adsorb on the metal surface, block the active sites and thereby reduce the corrosion rate considerably [1]. Most of the synthetic organic compound shows good anti-corrosive activity, which are highly toxic to cause severe hazards to both human beings and the environment during its applications [2]. The safety and environmental issues of corrosion inhibitors arisen in industries have always been a global concern. The recent trend is to save human being and environment by using eco- friendly inhibitors. Some investigator [3,4] studied the plant extracts and the derived organic species become more important as an environmentally benign, readily available, renewable and acceptable source for a wide range of inhibitors. Several efforts have been made using corrosion

preventive practices and the use of green corrosion inhibitors [5]. The plant extract are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as “Green Inhibitors” [6]. These inhibitors are biodegradable and do not contain heavy metals or other toxic compounds [7]. The successful use of naturally occurring substances to inhibit the corrosion of metals in acid and alkaline environment have been presented by some research groups running through references [8 to 13]. In our present study, we have chosen eco-friendly bio-inhibitor, a green approach to prevent environmental pollution by harmful organic chemicals. The influence of *Emblica officinalis* extract in natural Sea water environment on Copper and its alloy (Cu-27Zn) using mass loss measurements with different time and temperature have been studied. The characterization of alcoholic crystals of inhibitor and the corrosion product on Copper in the presence of inhibitor is also reported by UV and IR studies.

MATERIALS AND METHODS

Stock solution of *Emblica officinalis* extract

Emblica officinalis leaves were collected in and around courtallam hills area, shade dried and ground well to powder form. Exactly 150g of dried powder with required quantity of ethyl alcohol was added to cover the powder completely in a RB flask and left it for 48 hrs. The resulting paste was refluxed for 48hrs and boiled with activated charcoal (about 1g) to remove hung and the pure plant extract was collected.

Specimen preparation

Rectangular specimen of Copper and its alloy (Cu-27Zn) were mechanically pressed cut to form different coupons, each of dimension exactly 5.0x2x2.5 Cm. The specimens were mechanically polished; a hole drilled at one end for free suspension and numbered by punching. The specimens were decreased with acetone, washed with distilled water and well polished with emery paper, cleaned, rinsed and dried then stored in desiccators for present study.

Mass Loss method

In the mass loss measurements, Copper and its alloy 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 an hour at 303K and 333K and also measured 24, 48 and 168 hrs at room temperature. 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.

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

Where, mmpy = millimeter 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.

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

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

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

RESULTS AND DISCUSSION

The corrosion and inhibition behaviour of pure Copper and its alloy in Natural sea water environment containing various concentration of Emblica officinalis leaves (EOL) extract are studied at different time (24hrs to 168hrs) and temperature (303K and 333K) respectively. The corrosion parameters of Copper containing various concentration of EOL extract at different time in natural sea water is represented in Fig. 1.

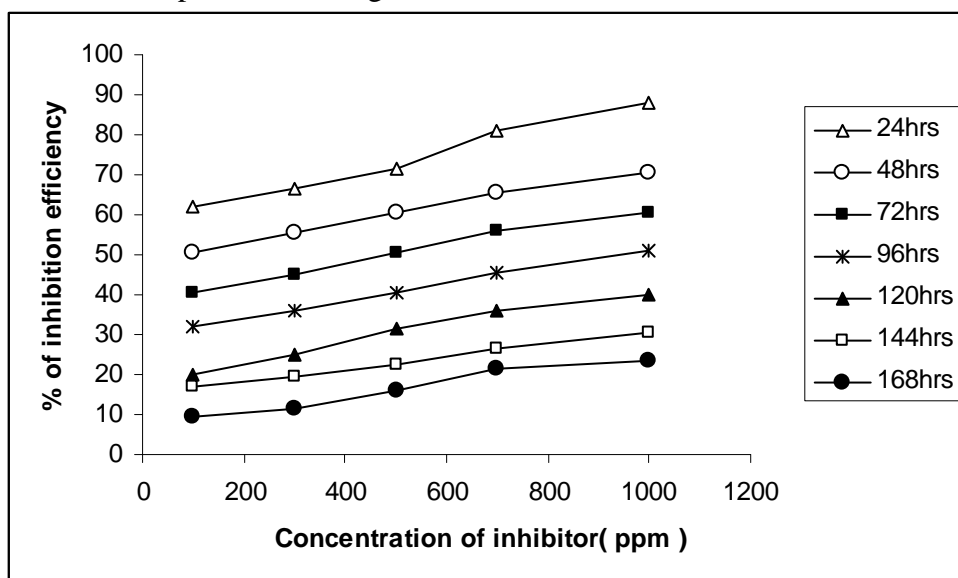


Figure : 1 Corrosion parameters of Copper containing various concentration of EOL extract at different time in Natural sea water

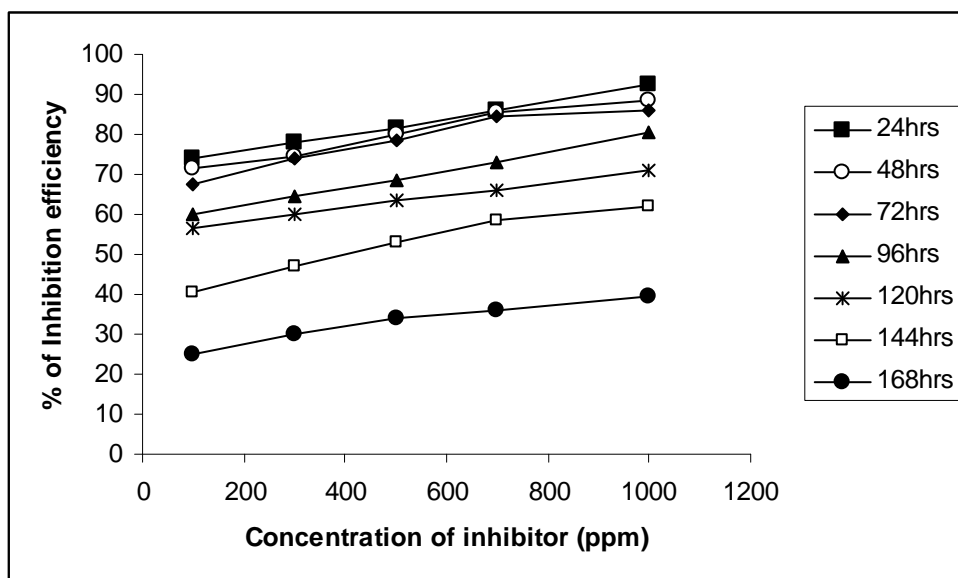


Figure : 2 Corrosion parameters of Brass containing various concentration of EOL extract at different time in Natural sea water

It is clearly indicates that the percentage of inhibition efficiency increased with increase of EOL concentration and gradually decreased with increase of exposure time. The maximum of 88.09% of inhibition efficiency is attained at higher concentration.

Fig . 2 shows that the various concentration of EOL versus percentage of inhibition efficiency of Copper alloy (Cu-27Zn) in Natural sea water environment. It is found that the percentage of inhibition efficiency increased with increase of EOL concentration. The maximum of 92.60 % of inhibition efficiency is achieved and it is almost maintained above 80% even after 96hrs exposure time. The maximum inhibition efficiency may be the adsorption of the plant constituents (Embllica A and B, phyllanththin, Punigluconin and Pedunculagin) on the Copper and its alloy by the interaction of π - electrons or lone pair electron of hetero atoms with the metal. It is reveals that the presence of phytoconstituents in the EOL extract are found to be big molecules can able to covered a large surface area on adsorption [14]. In the case of Copper alloy the maximum inhibition efficiency is arrived due to the surface area completely covered with the thin film formation rather than pure Copper because of the presence of Zinc content in Copper alloy may be preferentially co-ordinated with inhibitor than Copper [15].

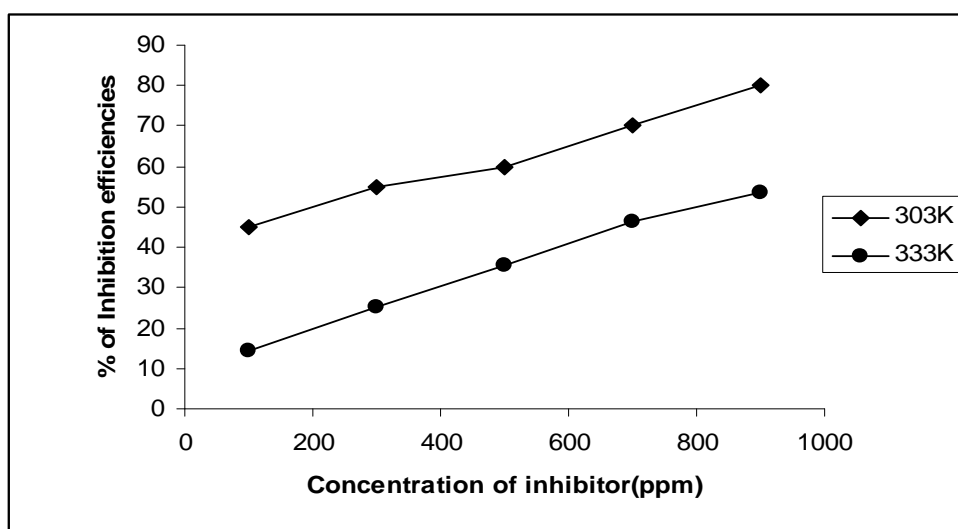


Figure : 3 Inhibition efficiencies of Copper in various concentration of Emblica officinalis extract at 303K and 333K temperature in Natural sea water

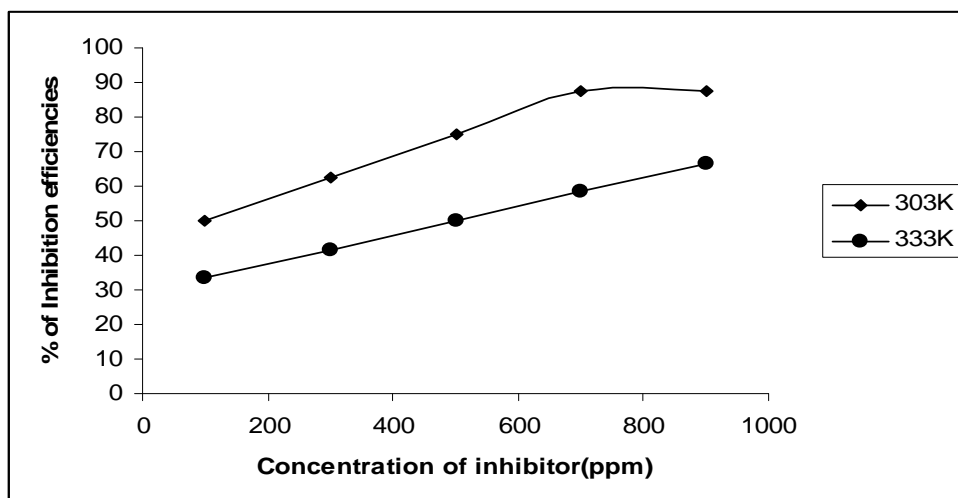


Figure : 4 Inhibition efficiencies of Brass in various concentration of EOL extract at 303K and 333K temperature in Natural sea water

Fig. 3 and 4 shows that the values of inhibition efficiency of EOL extract on the corrosion of pure Copper and its alloy (Cu-27Zn) in Natural sea water environment at 303K and 333K. It can be seen from the figures, the percentage of inhibition efficiency of EOL extract was reduced with raise in temperature for both copper and and its alloy suggesting that the mechanism of adsorption of EOL extract on the surface of copper and its alloy is physical adsorption (16).

The activation energy (E_a) for the corrosion of copper and its alloy in the presence and absence of EOL extract is calculated using Arrhenius theory. Assumptions of Arrhenius theory is expressed by equation(4) [17] .

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

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

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 Tables 1 and 2. The activation energy increased with increase of inhibitor concentration i.e, 20.54 to 32.97 KJ/mol and 19.19 to 38.63 KJ/mol for Copper and its alloy respectively. The average value of E_a obtained from the blank (9.40 and 11.34 KJ/mol for Copper and its alloy) is lower than that of the values obtained in the presence various concentrations of EOL extract. Also the activation energy were found to be lower than the threshold value of 80 KJ/mol required for chemical adsorption indicating that a physical adsorption mechanism is applicable to the adsorption of EOL extract on the surface of Copper and its alloy [18].

Adsorption Considerations

The heat of adsorption on the surface of Copper and its alloy in the presence of inhibitor is calculated by the following equation (6) [19].

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

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 Tables 1 and 2.

Table 1 Calculated values of Activation energy (E_a) and heat of adsorption (Q_{ads}) of EOL extract on Copper in Natural sea water environment.

S. No.	Concentration of inhibitor (ppm)	% of I.E		E_a (KJmol ⁻¹)	Q_{ads} (KJmol ⁻¹)
		30°	60°		
1.	Blank	--	--	9.40	---
2.	100	45.00	14.28	20.54	-44.50
3.	300	55.00	24.99	23.70	-26.61
4.	500	60.00	35.71	22.66	-5.97
5.	700	69.99	46.42	25.63	-17.892
6.	1000	79.99	53.58	32.97	-33.69

These values are ranged from -44.50 to 33.69 KJ/mol for Copper and -29.03 to -34.61 KJ/mol for its alloy respectively. The negative values are indicated that the adsorption of inhibitor on Copper and its alloy surface is exothermic [20].

Adsorption isotherms are used to investigate the mode of adsorption and the adsorption characteristics of EOL extract on the surface of Copper and its alloy. A direct relationship

between inhibition efficiency and the degree of surface coverage (θ) can be observed at different concentration of the inhibitor in Natural sea water environment. The mass loss measurements are tested graphically for fitting two isotherms like Langmuir and Temkin.

Table 2 Calculated values of Activation energy (E_a) and heat of adsorption (Q_{ads}) of EOL extract on Brass in Natural sea water environment

S. No	Concentration of inhibitor (ppm)	% of I.E		E_a (KJmol ⁻¹)	Q_{ads} (KJmol ⁻¹)
		30°	60°		
1.	Blank	--	--	11.34	---
2.	100	49.99	33.33	19.19	-29.03
3.	300	62.49	41.66	23.65	-3.95
4.	500	75.00	50.00	30.72	-30.72
5.	700	87.49	58.33	45.00	-44.14
6.	1000	87.49	66.66	38.63	-34.61

The Langmuir and Temkin adsorption isotherm can be expressed by the equation (7) and equation (8) given below [21]

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

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

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

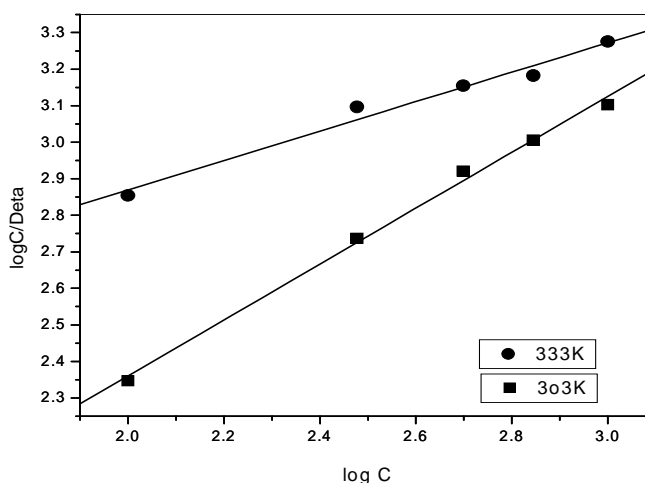


Figure : 5 Langmuir isotherm for adsorption of EOL extract on Copper in Natural sea water environment.

By plotting values of $\log C/\theta$ versus $\log C$, linear plots were generated (Fig. 5 and 6) and confirming that the experimental data fitted with the Langmuir adsorption isotherm for the adsorption of EOL extract on both Copper and its alloy mean that there is no interaction between the adsorbed species (i.e; adsorbate and adsorbent). The Langmuir adsorption isotherm is better fit at 303K for both Copper ($R^2=0.99788$) and its alloy ($R^2=0.99781$) respectively.

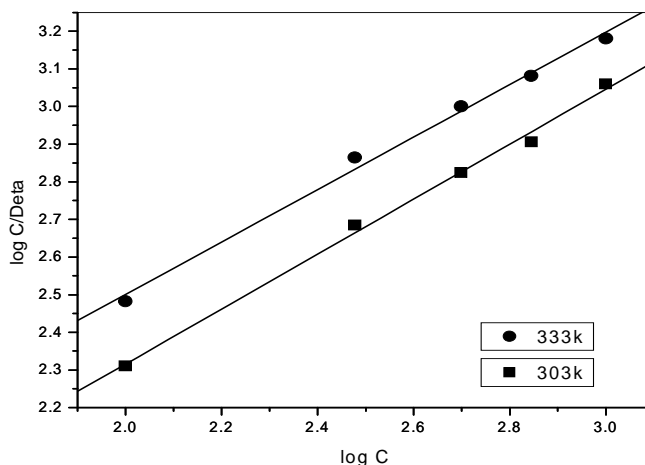


Figure : 6 Langmuir isotherm for adsorption of EOL extract on Brass in Natural sea water environment.

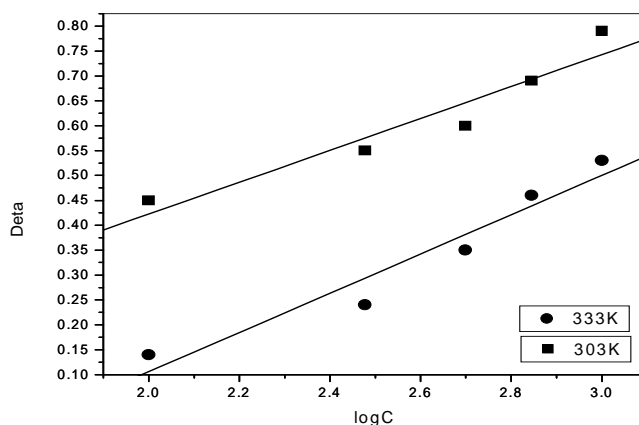


Figure : 7 Temkin isotherm for adsorption of EOL extract on Copper in Natural sea water environment

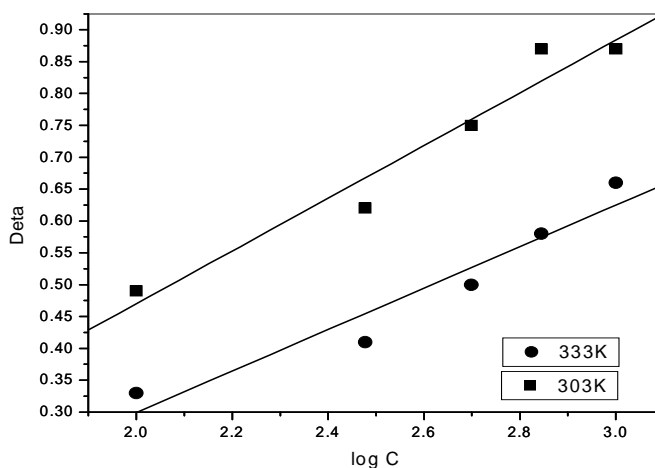


Figure : 8 Temkin isotherm for adsorption of EOL extract on Brass in Natural sea water environment.

A plot of θ versus $\log C$ give almost a straight line of both Copper and its alloy in EOL extract in sea water environment (Fig. 7 and 8). The straight line indicated that the inhibitor obeyed Temkin adsorption isotherm [22].

The equilibrium constant of adsorption of EOL extract on the surface of Copper and its alloy is related to the free energy of adsorption ΔG_{ads} by equation (9).

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

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 Tables 3 and 4.

Table 3 Langmuir and Temkin adsorption parameters for the adsorption of EOL extract on Copper in Natural sea water environment

Adsorption Isotherms	Temperature (Kelvin)	Slope	logK	R ²	ΔG_{ads} KJ/mol
Langmuir	303	0.7649	0.8306	0.9979	-31.84
	333	0.4027	2.0641	0.9887	-39.42
Temkin	303	0.3205	0.2187	0.9565	-20.76
	333	0.6833	0.3945	0.9677	-30.23

Table 4 Langmuir and Temkin adsorption parameters for the adsorption of EOL extract on Brass in Natural sea water environment

Adsorption Isotherms	Temperature (Kelvin)	Slope	logK	R ²	ΔG_{ads} KJ/mol
Langmuir	303	0.7301	0.8555	0.99781	-32.10
	333	0.6967	1.1074	0.9969	-34.24
Temkin	303	0.4133	0.3564	0.97461	-24.82
	333	0.3523	0.3511	0.96363	-24.68

The negative values of ΔG_{ads} suggested that the adsorption of EOL extract onto Copper and its alloy surface is a spontaneous process and the adsorbed layer is stable one. Usually the adsorption of free energy involved in a physisorption process ($\Delta G_{ads} < 40$ KJ/mol)[23].

**Morphology examination of Copper
UV Analysis**

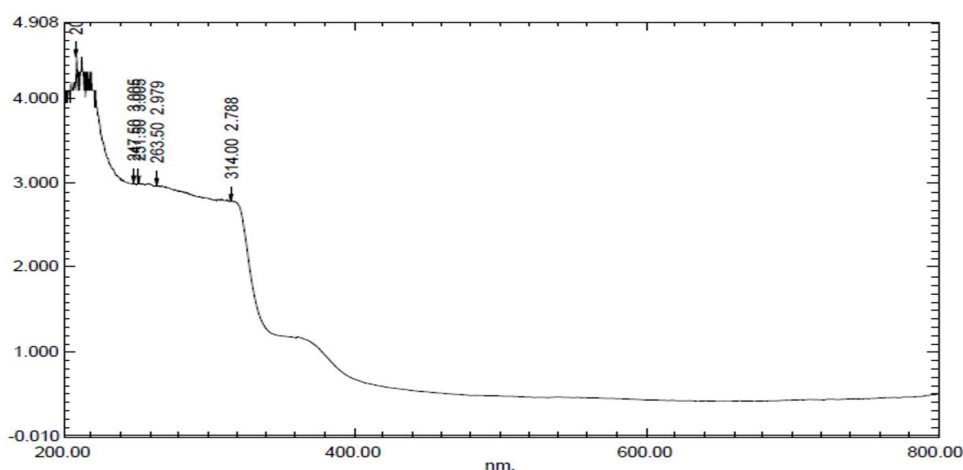


Figure : 9 UV spectrum of ethanolic crystals of EOL

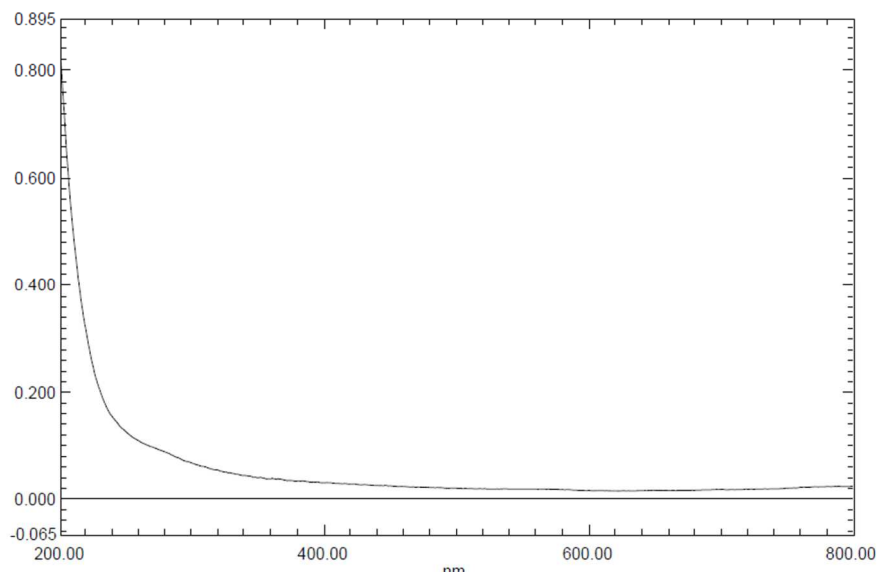


Figure : 10 UV absorption spectrum of the corrosion product of Copper in the presence of EOL extract in Natural sea water environment

IR Analysis

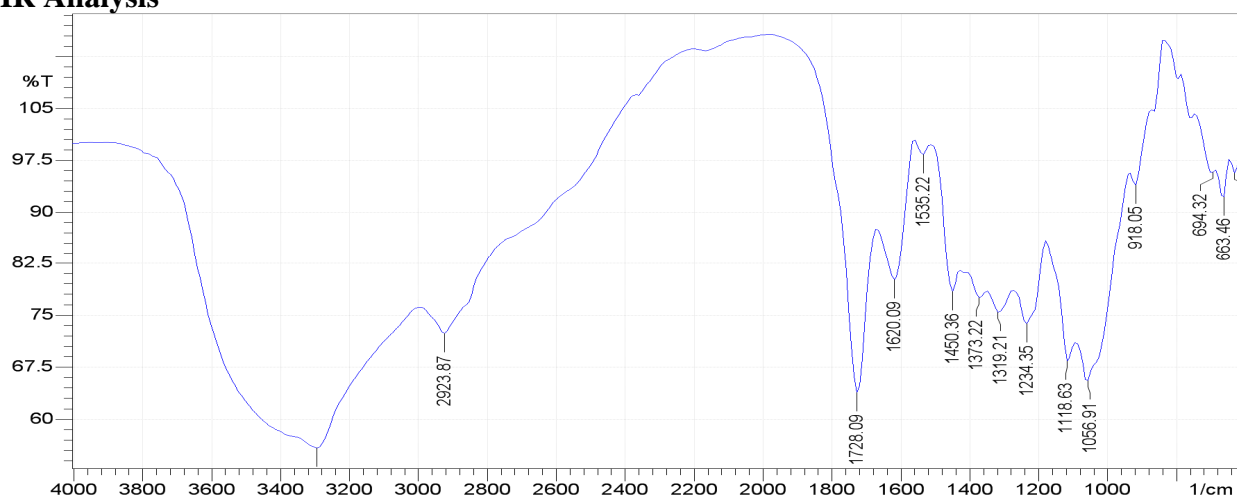


Figure : 11 IR spectrum of ethanolic crystals of EOL

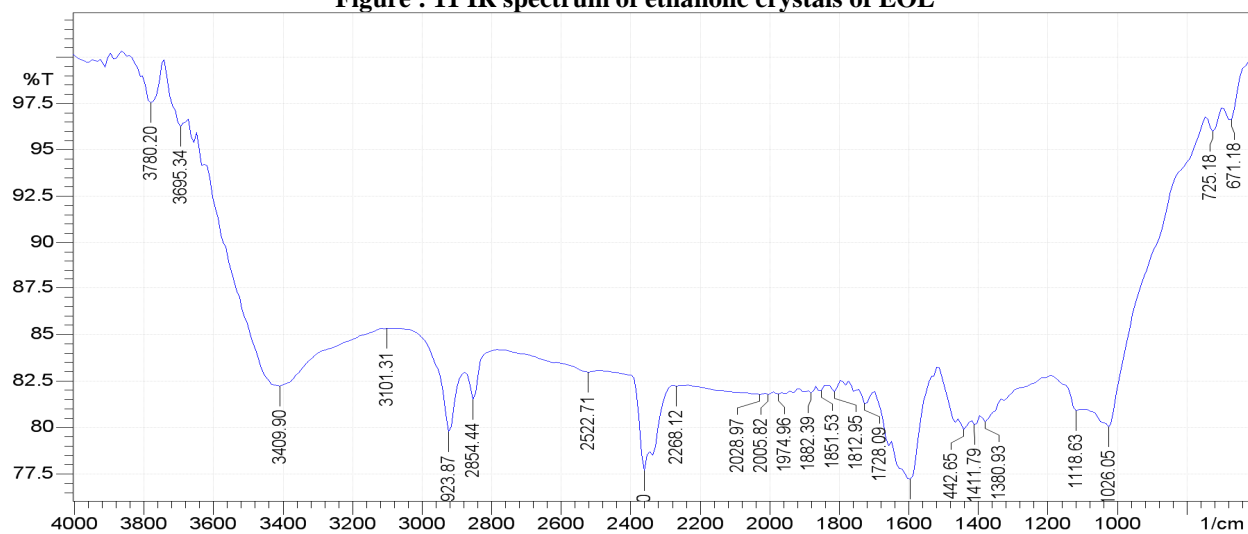


Figure : 12 IR spectrum of Copper in the presence of EOL extract in natural sea water environment

The Fig . 9 and 10 represents that the UV adsorption spectrum of alcoholic crystals of EOL extract and the corrosion product on the surface of pure Copper in the presence of inhibitor. On compared both of the spectrum, there is no adsorption peak in Fig . 10 suggesting that some olyfinic bond disappeared may be due to a co-ordination between the metal atom and the active groups present in the inhibitor.

The Fig . 11 and 12 shows that the IR spectrum of alcoholic crystals of EOL extract and the corrosion product on the surface of Copper in the presence of inhibitor. On comparing Fig . 11 and 12 shows that the certain additional peaks have been appeared and few have shifted to higher frequency region, providing that some interaction/ adsorption has been taking place over the metal surface. The -OH stretching shifted from 3300 to 3409.90 cm^{-1} and C=O stretching shifted from 1728.09 to 1812.95 cm^{-1} may be conformed that there is an strong interaction between EOL inhibitor and the metal surface.

CONCLUSION

From our present study, the results concluded that EOL extract can be used as an inhibitor for Copper and its alloy in Natural sea water environment at different time and temperature. It has also been found that the corrosion of both Copper and its alloy in Natural sea water environment depends on concentration of inhibitor, period of contact and temperature. Corrosion inhibition may be due to the adsorption of the plant constituents on the surface of both Copper and its alloy. The adsorption of the inhibitor on the surface of Copper and its alloy is exothermic, spontaneous process and is consistent with the mechanism of physical adsorption. Langmuir and Temkin isotherms are best described the adsorption characteristics of the inhibitor.

The corrosion product over the surface of Copper in the presence of EOL extract is characterized by UV and IR studies and may conform the complex film formed between the metal and the active groups present in the inhibitor.

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REFERENCES

- [1] Pandian , Bothi Raja , Mathur Gopalakrishnan Sethuraman, *Iran. J. Chem. Chem. Eng.*, **2009**, 28, 77.
- [2] I.B. Obot , N.O. Obi-Egbedi, *Int. J.Electrochem.Sci*, **2009** ,4, 1277.
- [3] A. Mesbah., C. Juers, F. Lacouture, S. Mathieu, E .Rocca, M. Francois, J. Steinmetz, *Solid State Sciences*, **2007**, 9, 322.
- [4] P.C. Okafor, V.I Osabor, E.E. Ebenso, *Pigment and Resin Technology*, **2007**,36, 299.
- [5] K. Anuradha, R. Vimala, B. Narayansamy, J .Arockia Selvi, S. Rajendran. *Chemical Engineering Communications*, **2008** ,195, 352.
- [6] P. Bothi Raja, M.G .Sethuraman, *Materials Letters*, **2008**, 62, 113.
- [7] S.K.Sharma, Ackmez Mudhoo, Gargi Jain ,Jyothi sharma, *Rasayan Journal of Chemistry*, **2009**, 2, 332.
- [8] Muhamath, Basha Mubarak Ali, Kulanthai, Kannan, *Appl. Sci. Environ.Manage*, **2009**, 13, 27.

- [9] A.O.James, O. Akaranta, *African. J.Pure.Appl.Chem*, **2009**, 3, 262.
- [10] J. Arockia Selvi, Susai Rajendran, V. Ganga Sri, A. John Amalraj, B. Narayanasamy, *Port. Electrochemica Acta*, . **2009**, 27, 2.
- [11] A. Noor Ehteram , *Journal of Engineering and Applied Sciences*, **2008**, 3, 23.
- [12] L .Valek, S. Martinez, *Materials Letters*, **2007**, 61, 148.
- [13] A. Sharmila, A. Angelin Prema, P. Arockia Sahayaraj, *Rasayan. J. Chem*, **2010** 3, 74.
- [14] R.Saratha, Vasudha, V.G, *e-journals.net*, **2010**,7,677.
- [15] P.Deepa Rani, Selvaraj, S, *Rasayan. J. Chem*, **2010**, 3, 473.
- [16] M.Abdallah, *Corros.Sci.*2004,46,1981.
- [17] K.C. Emregul, E. Duzgun, O.Atakiol, *Corrosion Sci*, **2006**, 48 , 3243.
- [18] E.E. Ebenso, *Bull. Of Electrochem*, **2003**,19, 5, 209.
- [19] N.O. Eddy, Ebenso , *J.pure & Appl. Chem*, **2008**, 2, 6,046.
- [20] H.M. Bhajiwala, R.T. Vashi, *Bull.Electrochem*, **2001**,17,441.
- [21] T.Arslan, F.Kandemirli, E.E. Ebenso, I.Love, H.Alemu, *Corros. Sci.*, **2009**,51, 35.
- [22] M.A. Quaraishi, Sardar Rana, *Bull. Electrochem*, **2002**, 18 ,11, 515.
- [23] N.O. Eddy, S.A. Odoemelum, *J.Surface Sci. Technol*, **2008**, 24, 2, 1.