International Journal of
Chemical and Pharmaceutical Sciences
2012, Mar., Vol.3 (1)

ISSN: 0976-9390
IJCPS

Inhibitive Efficacy of Amla as Green Inhibitor for Brass in Natural Sea Water Environment

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ABSTRACT

The inhibitive effect of *Emblica officinalis* seed extract on the corrosion of Brass in Natural sea water environment has been studied by mass loss measurements at various exposure time with temperature. The inhibition efficiency increased with increase of inhibitor concentration but decreased with rise in temperature is suggestive of physisorption process. The value of activation energy (E_a), heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG_{ads}) is also support the spontaneous physical adsorption process. Adsorption of *Emblica officinalis* seed extract on Brass surface is obeyed Langmuir adsorption isothem. The alcoholic crystals of inhibitor and the corrosion products on the metal surface is analysed by UV and IR studies.

Keywords: Corrosion, Inhibition, Brass, *Emblica officinalis* and Environment.

1. INTRODUCTION

Copper and its alloy are very interesting because of its great industrial importance. However it affects severely by polluted environment. Thus recent years, most of the investigators are attempted for their research work in this interesting field. Use of inhibitors is one of the most practical methods for protection against corrosion to prevent unexpected metal dissolution [1]. The large numbers of organic compounds whose hetero atoms such as N, O ,S and olefinic double bond are being tested as corrosion inhibitor for metals in various environments. The efficient inhibitors should posses plentiful of π electrons and unshared electron pairs on hetero atoms of inhibitors which will be given to the vacant d-orbital of the metal [2-4]. Thus the corrosion process may be suppressed by the protective film of inhibitor on the metal surface [5]. Even though many synthetic organic compounds showed good anticorrosive activity, most of them are highly toxic to both human beings and the environment. Thus we have more interest only to chosen various part of green plant extract as corrosion inhibitors for metal in various environment such as, such as *Vitis vinifera* [6] , *Ocimum tenuiflorum* [7], *Punica Granatum* [8], *Emblica officinalis* [9], *Jatropha curcas* [10] and *Vinca rosea* [11]. In the continuity of our investigations of green approach, the environmentally benign Emblica officinalis seed extract as inhibitor for Brass in Natural sea water environment by using mass loss method. The alcoholic extract of the inhibitor and the corrosion product on the metal surface in the presence of inhibitor is analysed by UV and IR studies.

2. MATERIALS AND METHODS

2.1. Stock solution of Emblica Officinalis seed extract

Wastage of Emblica officinalis seed about 1 Kg collected from the source and shade dried. 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 4 hours and boiled with activated charcoal (about 1g) to remove hung and the pure seed extract was collected.

2.2. Specimen preparation

Rectangular specimen of Brass was mechanically pressed cut to form different coupons, each of dimension exactly 5.0x 2x 2.5 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 and dried then stored in desiccators for present study.

2.3. Mass Loss method

In the mass loss measurements, Brass coupon in triplicate was completely immersed in 50ml of the test solution of Natural sea water in the presence and absence of the inhibitor. The metal specimens were withdrawn from the test solutions after an hour at 303K to 333K and also measured 24, 48, 72, 96, 120,144 and 168hrs at room temperature. The mass loss was taken as the difference in weight of the specimens before and after immersion determined 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.

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

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 3, respectively.

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

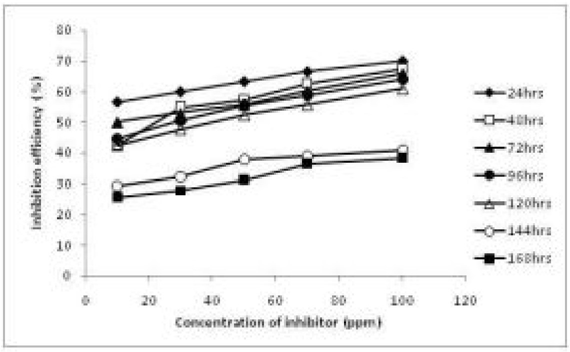
$$\theta = \frac{W_1 - W_2}{W_1} \longrightarrow (3)$$

Where W_1 and W_2 are the corrosion rate in the absence and presence of the bio-inhibitor respectively.

3. RESULTS AND DISCUSSION

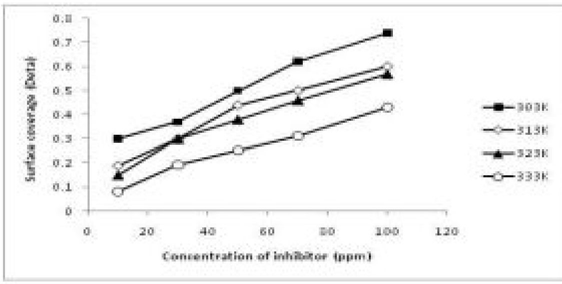
The dezincification and inhibition behaviour of brass in Natural sea water environment containing various concentration of ethanolic extract of Emblica officinalis seed (EOS) at different time (24hrs to168hrs) and temperature (303K to 333K) are investigated by mass loss methods. The percentage of inhibition efficiency versus various concentration of EOS extract on brass at different exposure time in Natural sea water is shown in Fig 1. It is clearly indicates that the percentage of inhibition efficiency increased with increase of EOS concentration and gradually decreased with increase of exposure time. The maximum of 70.00% inhibition efficiency is achieved initially and it is almost maintained above 60% even after 120hrs exposure time. The maximum inhibition efficiency may be the adsorption of the active plant constituent on the brass surface by the interaction of π- electrons or lone pair electron of hetero atom (Oxygen) with the metal. The maximum surface coverage is due the presence of big molecules can able to cover a large surface area on the metal.

Figure: 1. Inhibition efficiency of brass containing various concentration of EOS extract at different exposure time in Natural sea water environment.



The figure- 2 shows that the value of surface coverage versus different concentration of EOS extract on Brass at 303-333K. It can be seen from the figure, the value of surface coverage of EOS extract on brass is decreased with raise in temperature. The maximum of 74.99 and 43.75 percentage of inhibition efficiency is achieved at 303 and 333K respectively. The decrease of inhibition efficiency with rise in temperature is due to the rate of desorption on the metal surface is higher than the adsorption of active molecules present in the inhibitor. The decrease of surface coverage with rise in temperature is suggestive of physisorption process.

Figure: 2 Surface coverage of brass containing various concentration of EOS extract at different temperature in Natural sea water environment.



3.1. Activation energy

The Arrhenius equation was used to investigate the effect of temperature on the corrosion of Brass in the presence and absence of EOS inhibitor [12].

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

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

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-1. The activation energy increased from 25.96 to 42.06 kJ/mol with increase of inhibitor concentration. The average value of E_a obtained from the blank (19.36 kJ/mol) is lower than that of the values obtained for a system containing various concentrations of EOS extract. This result indicated that the inhibitor is adsorbed on the surface of Brass by physical adsorption.

Table -1: Calculated values of Activation energy (E_a) and heat of adsorption (Q_{ads}) of Brass containing different concentration of EOS extract in Natural Sea water.

Concentration of inhibitor (ppm)	% of I.E		E_a (kJmol^{-1})	Q_{ads} (kJmol^{-1})
	30°	60°		
Blank	--	--	19.365	---
10	30.84	08.57	25.962	-44.63
30	37.50	18.75	26.723	-27.52
50	50.00	25.00	30.725	-30.75
70	62.50	31.25	36.338	-29.53
100	74.99	43.75	42.064	-37.13

3.2. Adsorption consideration

The heat of adsorption on Brass in the presence of inhibitor is calculated by the following Equation -6 [13].

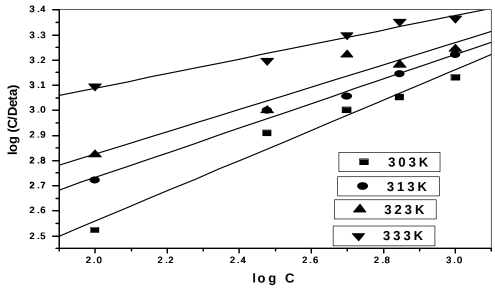
$$Q_{ads}=2.303\ R\ [\log(\theta_2/1-\theta_2)-\log(\theta_1/1-\theta_1)] \times (T_2T_1/T_2-T_1) \longrightarrow (6)$$

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-1. These values are ranged from -44.62 to -37.13 kJ/mol. The negative values are indicated that the adsorption of inhibitor on Brass surfaces is exothermic [14].

The adsorption isotherms are used to investigate the mode of adsorption and the characteristic of adsorption of inhibitor on the metal surface. In our present study the langmuir isotherm are investigated.

Langmuir adsorption isotherm is the ideal adsorption isotherm for physical and chemical adsorption on a smooth surface. Langmuir adsorption isotherm of EOS extract on Brass surface proceeded according to the Equation- 7.

Figure: **3** Langmuir adsorption isotherm for the adsorption of EOS extract on brass in Natural sea water environment.



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

From Equation-7, by plotting the values of log(C/ θ) versus log C, linear plots are generated (fig-3). Inspection of this figure reveals that the experimental data fitted the Langmuir adsorption isotherm of EOS extract on Brass surface, meaning that there is no interaction between the adsorbed species.

The equilibrium constant of adsorption of EOS extract on the surface of Brass is related to the free energy of adsorption ΔG_{ads} by Equation-8.

Table -2: Langmuir and Frumkin adsorption parameters for the adsorption of Brass containing different concentration of EOS in Natural Sea water.

Adsorption Isotherms	Temperature (Kelvin)	Slope	logK	R^2	ΔG_{ads} KJ/mol
Langmuir	303	0.7048	0.0281	0.9739	10.282
	313	0.4905	0.2434	0.9944	11.912
	323	0.4269	0.2927	0.9977	12.597
	333	0.2844	0.4027	0.9936	13.688

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

Where R is the gas constant, T is the temperature and K is the equilibrium constant of adsorption. The values of K obtained from Langmuir and Frumkin adsorption isotherm were substituted in Equation-8 and the calculated values of ΔG_{ads} are recorded in Table-2. The negative values of ΔG_{ads} suggested that the adsorption of PGP extract onto Brass 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) [15].

3.3. UV ANALYSIS

Figures 4 and 5 shows that the UV spectrum of alcoholic crystals of inhibitor and the corrosion product on the surface of Brass in the presence of EOS extract in Natural sea water environment. On comparing both spectra, three absorption band around 247.50nm, 263.50nm, 314.00 nm and three band around 212nm, 240nm, 277nm are noticed in figures 4 and 5 respectively. In the presence of inhibitor (Figure 5) all the three bands are shifted to shorter wavelength region i.e.; Hypsochromic shift (or) Blue shift. This results reveal that the formation of thin film between the active group present in the inhibitor and the metal surface.

Figure: 4. UV spectrum of ethanolic recrystals of *Emblica officinalis* seed extract.

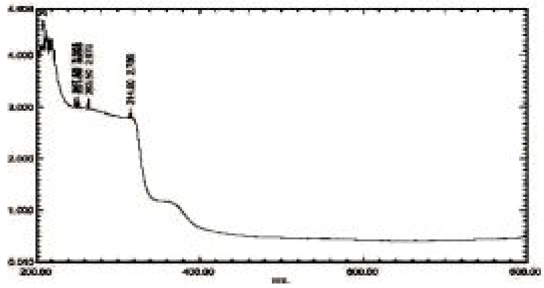
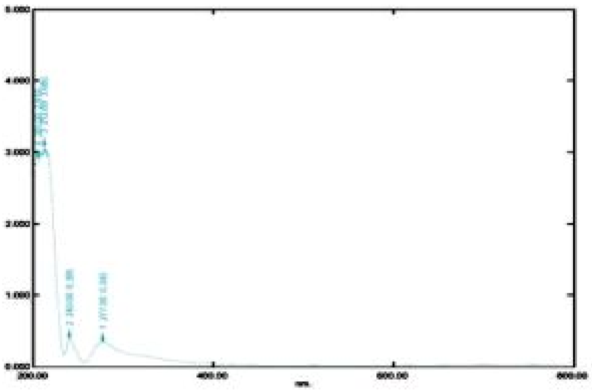


Figure: 5. UV spectrum of corrosion product on brass containing in the presence of EOS extract in sea water environment.



3.4. FT-IR STUDIES

Figure 6 and 7 found out that the alcoholic crystals of EOS extract and the corrosion product on the brass surface in the presence of EOS inhibitor. On comparing these spectra, the –OH stretch at 3240 Cm^{-1} is shifted to 3390 Cm^{-1}, the carbonyl –C=O stretch at 1728.09 Cm^{-1} is shifted to 1743.52 Cm^{-1}, the acidic –C-O stretch at 1234.35 Cm^{-1} is shifted to 1280.64 Cm^{-1} and the =CH stretch at 694.32 Cm^{-1} is shifted to 725.47 Cm^{-1}, clearly indicating that there is a interaction between the inhibitor and the surface of the metal. In figure 7, appearance of few peaks and also the disappearance of some peaks are concluded 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. The alcoholic recrystals of *Emblica officinalis* seed extract.

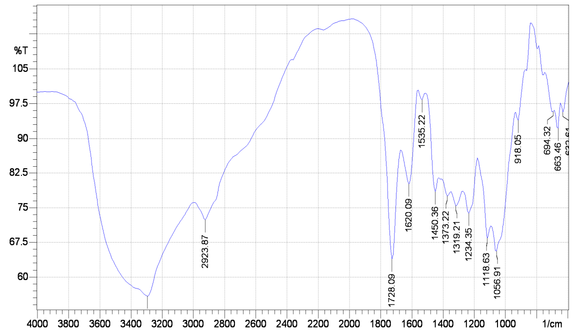
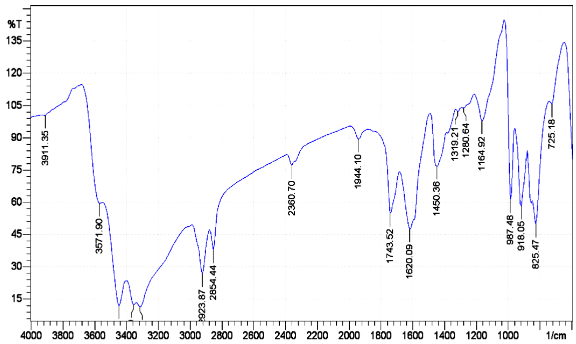


Figure: 7 The corrosion product of Brass in the presence of EOS extract in Natural sea water environment.



4. CONCLUSION

From our present investigation the following conclusions can be drawn.

The *Emblica officinalis* seed extract is used as a good corrosion inhibitor for Brass in Natural Sea water environment. The dezincification behaviour of Brass in Natural sea water environment is depending upon the exposure time, temperature and zinc content present in the alloy. The value of surface coverage increased with increase of inhibitor concentration is due to the active phytochemical constituent present in the inhibitor can able to cover the large surface area by adsoption process. The value of E_a, Q_{ads} and ΔG_{ads} also confirm the spontaneous physical adsorption of inhibitor on the metal surface. The inhibitor obeys langmuir adsorption isotherm. The UV and FT-IR spectral studies clearly indicates that the co-ordination between the active molecules present in the inhibitor and the metal surface.

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