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REGULAR ARTICLE

INHIBITIVE AND ADSORPTION PROPERTIES OF *PUNICA GRANATUM* EXTRACT ON BRASS IN ACID MEDIA

P. Deepa Rani[1*] and S. Selvaraj[2]
[1]*Post graduate and Research Department of chemistry, Sri Paramakalyani College, Alwarkurichi-627412, Tamil Nadu, India*
[2]*Post graduate and Research Department of chemistry, Sri Paramakalyani College, Alwarkurichi-627412, Tamil Nadu, India*

SUMMARY

The inhibition efficacy of *Punica granatum* extract on the corrosion of Brass in 1N HCl has been studied by mass loss measurments at various time and temperature. The inhibition efficiency is markedly higher in HCl environment with addition of *Punica granatum* 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. Based on the values of activation energy, free energy of adsorption and variation of inhibition efficiency with temperature, a physical adsorption mechanism is proposed for the adsorption of *Punica granatum* on the surface of Brass. It is found to follows Langmuir and Fremkin adsorption isotherms. The alcoholic extract of bio-inhibitor and the corrosion product (with inhibitor) is analysed by UV, IR and XRD studies leads to the bio-inhibitor as an adsorption inhibitor.

Key words: Corrosion inhibition, Brass, *Punica granatum*, Isotherm

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*Corresponding Author, Email: rani.Deeps@yahoo.in, Cell no: 9489303051; drselvaraj.paramakalyani@gmail.com, Ph no: 04634-283226, Cell no: 9442064252, Fax no: 04634-283530

1. Introduction

Copper and its alloy are widely used in industries because of their good resistance to corrosion in cooling water systems, for shipboard condensers, power plant condensers and petrochemical heat exchanger tubes etc. Copper and its alloy are very interesting because of its great industrial importance. Most of the scientists are attempted for their research work in this intrusting field. The heavy loss of metal whenever it contact with acids can be minimized to a great extent by the use of corrosion inhibitors [1]. Most of the well known acid inhibitors are organic compounds containing hetero atoms such as nitrogen, sulphur, oxygen [2]. The organic compounds present in the inhibitor can adsorb on the metal surface, block the active sites and thereby reduce the corrosion rate considerably [3]. Most of the synthetic organic compounds show good anti-corrosive activity, which are highly toxic to cause severe hazards to both human beings and the environment during its application [4]. 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 investigators studied the plant extract and the derived organic species become more important as an environmentally benign, readily available, renewable and acceptable source for a wide range of inhibitors [5,6]. Several efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors [7]. The plant extract are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as "Green Inhibitors" [8]**.** These inhibitors are biodegradable and do not contain heavy metals or other toxic compounds [9] 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 [10 to 16]. 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 *Punica granatum* (pomegranate) extract on Brass in 1N HCl using mass loss measurements with different time and temperature has been studied. The characterization of corrosion product on Brass in the presence of bio-inhibitor is also reported by UV, IR, and XRD studies.

2. Materials and Methods

Stock solution of *Punica granatum* peel extract

Wastage of *Punica granatum* fruit peel about 1 Kg collected from the fresh fruit stall 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 48 hrs and boiled with activated charcoal (about 1g) to remove hung and the pure fruit peel extract was collected.

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, rinsed and dried then stored in desiccators for present study.

Mass Loss method

In the mass loss measurements, Brass coupon in triplicate was completely immersed in 50ml of the test solution of 1N HCl in the presence and absence of the bio-inhibitor. The metal specimens were withdrawn from the test solutions after an hour at 303K and 333K and also measured 24, 48, 72, 96, 120 and 144hrs 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.

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

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.

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

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

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

3. Results

The values of corrosion rate and the percentage of inhibition efficiency derived from mass loss measurements on Brass (63/37) in the presence and absence of *Punica granatum* peel (PGP) extract in 1N HCl acid at different time (24 to 144 hrs) are shown in Fig:1 and 2 respectively. The Fig:1 is clearly indicate that the corrosion rate increased (0.6227 to 1.4501mmpy) with increase of exposure time and the dissolution rate is decreased with increase of bio-inhibitor concentration from 0 to 1000ppm. The Fig: 2 shows that the inhibition efficiency increased with increase of bio-inhibitor concentration. The maximum 94.52 percentage of inhibition efficiency is achieved at 1000ppm of bio-inhibitor concentration.

The percentage of inhibition efficiency against various concentration of bio-inhibitor for Brass in 1N HCl at different temperature (303K and 333K) is investigated and results are reflected in Fig: 3. It shows that the inhibition efficiency increased with increase of bio-inhibitor concentration and decreased with raise in temperature. The maximum of

90% and 60% inhibition efficiency is attained at 303K and 333K respectively.

Fig. 1: Variation of corrosion rate with concentration of PGP extract on Brass in 1N HCl acid environment

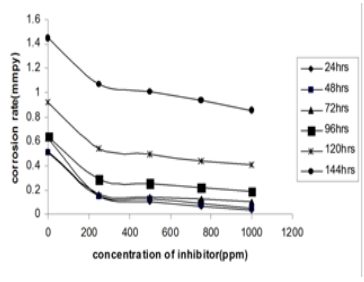


Fig. 2: Variation of inhibition efficiency with concentration of PGP extract on Brass in 1N HCl acid environment

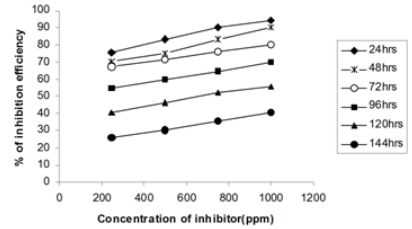
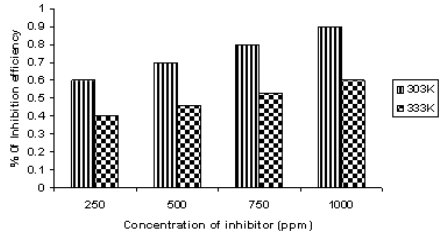


Fig. 3: Inhibition efficiencies of Brass in different concentrations of PGP extract in 1N HCl acid at 303K and 333K



4. Discussion

From the above observed results clearly indicate that the percentage of inhibition efficiency and the degree of surface coverage (θ) increased with increase of bio- inhibitor concentration. 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 phytoconstituents (tannic acid (19%) phenolic punicalagins, gallic acid, catechin, pectins, quercetin, rutin, flavonols, anthocyanidins (17)) 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. Thus, the inhibition efficiency increases as the metal surface area covered by the adsorbed molecules is increased. The adsorbed molecule is increased by increase of bio-inhibitor concentration. To determine the mode of adsorption ,the relation between bio-inhibitor concentration and the fraction of metal surface covered (θ) by the adsorbed molecules due to the direct relation between surface coverage (θ) and the percentage of inhibition efficiency. From the results, it can be noticed that the inhibition efficiency increased with increase of PGP extract concentration. The inhibitive property of PGP may be a synergetic manner. It is revealed that the PGP extract retards the dealloying process of Brass in 1N HCl acid. The gradual decrease of inhibition efficiency with rise in temperature is suggestive of physical adsorption mechanism.

Activation energy

The Arrhenius equation was used to investigate the effect of temperature on the corrosion of Brass in the presence and absence of PGP bio-inhibitor [18].

$CR = A\exp(-E_a/RT)$ ----------(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 (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 22.66 to 50.10 KJ/mol with increase of bio-inhibitor concentration. The average value of E_a obtained from the blank (11.00KJ/mol) is lower than that of the values obtained for a system containing various concentrations of PGP extract. This result indicated that the PGP bio- inhibitor is adsorbed on the surface of Brass by physical adsorption.

Table:1 Calculated values of Activation energy and Heat of adsorption of PGP extract in 1N HCl media at 303K and 333 K

S.no	Concentration of inhibitor (ppm)	E_a (KJmol^{-1})	Q_{ads} (KJmol^{-1})
1.	Blank	11.00	----
2.	250	22.66	-22.96
3.	500	27.42	-28.20
4.	750	35.02	-35.42
5.	1000	50.10	-50.11

Adsorption consideration

The heat of adsorption on Brass in the presence of bio-inhibitor is calculated by the following Equation -6 [19].

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

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. The calculated values of Q_{ads} are reported in Table-1. These values are ranged from -22.96 to -50.11 KJ/mol. The negative values are indicated that the adsorption of bio-inhibitor on Brass surfaces is exothermic [20].

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 and frumkin isotherm are investigated.

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

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

From Equation-7, by plotting the values of $\log(C/\theta)$ versus log C, linear plots are generated (fig-4). Inspection of this figure reveals that the experimental data fitted the Langmuir adsorption isotherm of PGP extract on Brass surface, meaning that there is no interaction between the adsorbed species.

Fig. 4: Langmuir isotherm for the adsorption of PGP extract on Brass in 1N HCl acid at 303K and 333K

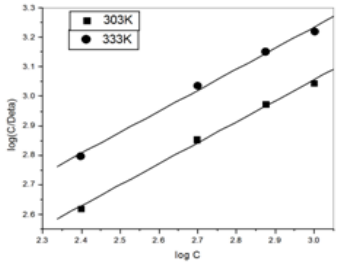
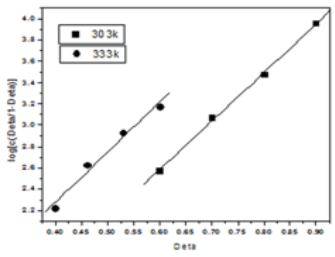


Fig. 5: Frumkin isotherm for the adsorption of PGP extract on Brass in 1N HCl acid at 303K and 333K



Frumkin adsorption isotherm can be expressed according to Equation-8

$\text{Log}\ \{[C](\theta/1-\theta)\} = 2.303 \log K + 2\ \alpha\ \theta$ ----------(8)

Where K is the adsorption-desorption equilibrium constant and α is the lateral interaction term describing the molecular interaction in adsorbed layer. Figure: 5 shows that the adsorption plots of PGP extract on Brass surface. From the observed results, the values of α are found to be positive indicating that the attractive behaviour of inhibitor on the surface of the metal [21].

The equilibrium constant of adsorption of PGP extract on the surface of Brass is related to the free energy of adsorption ΔG_{ads} by Equation-9.

ΔG_{ads} = -2.303 RT log (55.5 K) ----------(9)

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 (ΔG_{ads} < 40 KJ/mol)[22].

Table:2 Langmuir and frumkin adsorption parameters for the adsorption of PGP extract on the surface of Brass

Adsorption Isotherms	Temperature (Kelvin)	Slope	logK	R^2	ΔG_{ads} ($KJmol^{-1}$)
Langmuir	303	0.7124	0.91868	0.99839	-9.271
	333	0.7128	1.09596	0.99739	-10.216
Frumkin	303	4.5514	4.55143	0.9994	-13.937
	333	4.6939	4.69397	0.9888	-15.403

Morphology examination of Brass

UV Analysis

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The Fig: 6 and 7 shows that the UV spectrum of ethanolic crystals of PGP extract and the corrosion product on the surface of Brass in the presence of inhibitor. The absorption band is shifted from 261.00nm to 243.50nm i.e, λ_{max} value shifted from bathochromic to hypsochromic shift. The results revealed that the formation of complex between the Zinc present in the alloy and the active molecules present in the bio- inhibitor.

Fig. 6: UV spectrum of ethanolic crystals of PGP

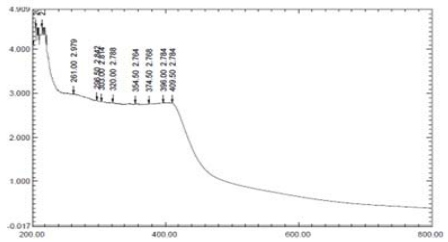
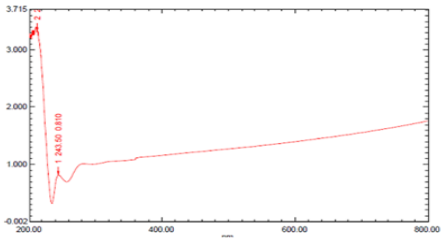


Fig. 7: UV absorption spectrum of the corrosion product of Brass in the presence of PGP extract 1N HCl acid



IR Analysis

The Fig:8 and 9 shows that the IR spectrum of ethanolic crystals of PGP extract and the corrosion product on the surface of Brass in the presence of inhibitor. On comparing Fig: 8 and 9 clearly shows that the certain peaks have been disappeared completely and some have shifted to higher frequency region, providing that some interaction/ adsorption has been taking place over the metal surface. The –OH stretching shifted from 3380 to 3460 cm^{-1} may suggest that there is an interaction between PGP extract and the metal surface.

Fig. 8: IR spectrum of ethanolic crystals of PGP

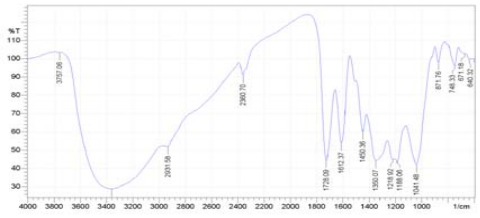
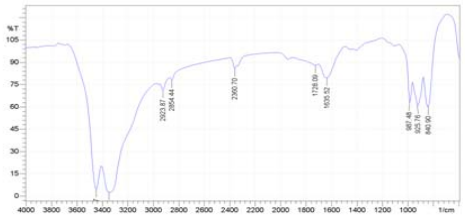


Fig. 9: IR spectrum of Brass in the presence of PGP extract 1N HCl acid



XRD analysis

The ethanolic crystals of PGP extract and the Corrosion product released from the Brass surface is examined by XRD studies are shown in Fig: 10 and 11. Most of the peaks of Fig: 11 match with the standard peaks for $ZnCl_2$ crystal structure taken from the JCPDS file no. PDF 740519. From the XRD spectrum it is confirmed that the sample is crystalline nature and tetragonal structure with lattice parameter values a = b = 5.410 AU and c = 10.300 AU and α=β=γ=90°. Hence the present XRD pattern is indeed a $ZnCl_2$ compound. It is due to the preferential dissolution mechanism of Zinc followed by Copper. It reflect that the film may be mainly combine with a rich amount of $ZnCl_2$, and also containing $Zn(OH)_2$, $CuCl_2$, etc with the bio-inhibitor.

Fig. 10: XRD spectrum of ethanolic crystals of PGP

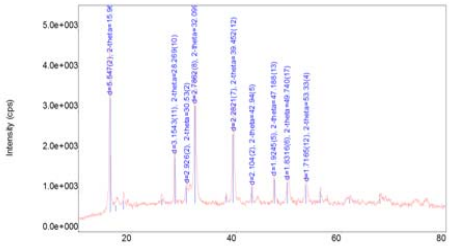
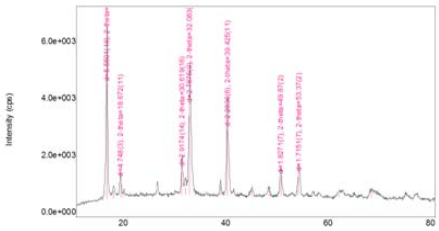


Fig. 11: XRD spectrum of Brass in the presence of PGP extract 1N HCl acid



5. Conclusion

The following conclusions can be drawn from our present study:

The PGP inhibitor acts as an effective and efficient inhibitor for the dealloying process of Brass in 1N HCl.

The inhibition efficiency increased with increase of inhibitor concentration to reach maximum of 94.52 %, but it is gradually decreased with raise in temperature and period of contact.

The adsorption of the inhibitor on the Brass surface is exothermic, spontaneous process and is consistent with the mechanism of physical adsorption. Langmuir and Frumkin isotherms are best described the adsorption characteristics of the inhibitor.

The corrosion product over the surface of Brass in the presence of PGP extract is characterized by UV, IR, and XRD studies and may conform the complex film formed with a rich amount of $ZnCl_2$, $Zn(OH)_2$ and $CuCl_2$ on the surface of Brass. The observed results may also suggested that the mechanism of preferential dissolution of Zinc followed by Copper present in the alloy.

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