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The Inhibition Effect of The Extract of Naturally Occurring Compounds On The Corrosion Of Copper And Brass In Acid Medium

P. Karuppasamy, M.Ganesan, T.Rajendran and V. K. Sivasubramanian*

*Post Graduate and Research Department of Chemistry, Vivekananda College,
Tiruvedakam West, Madurai -625 234, Tamil Nadu, **INDIA**

Email: pkaruppasamy23@gmail.com, vksiva1957@yahoo.com

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ABSTRACT

Corrosion of copper and brass was studied in 1M H_2SO_4 and the corrosion rate for these materials in the presence of two green inhibitors Phyllanthus amarus and Aegle marmelos was obtained by weight loss method. Very high inhibition efficiency is obtained using these green inhibitors. Formation of black film on the surface of the metal is mainly responsible for corrosion inhibition. A linear Langmuir plot supports the adsorption of the inhibitors on the surface of the metal. The decrease in inhibition efficiency with increase in exposure time clearly supports the formation of multilayer on the surface of the metal. Of the two inhibitors, Phyllanthus amarus and Aegle marmelos, the corrosion rate and inhibition efficiency are more favourable for the Aegle marmelos.

Keywords: Green inhibitors, Copper and Brass, Weight loss, Adsorption isotherm.

INTRODUCTION

The protection of metals against corrosion is a major industrial problem. Copper is a metal that has a wide range of applications due to its good properties. It is used in electronics, for production of wires, sheets, tubes, and also to form alloys [1]. Moreover, brasses are harder and a solid alloy (zinc and copper). However, their exhibition in acid media creates problems of corrosion [2]. When the brasses, containing more than 15% of zinc, are exposed in corrosive environments, they are affected not only by general corrosion damage, but also by dezincification process involving preferential dissolution of zinc, leaving a spongy mass of copper on the alloy surface [3]. 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 system. These organic compounds can adsorb on the metal surface, block the active sites and thereby reduce the corrosion rate considerably [4]. 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 [5]. The safety and environmental issues of corrosion inhibitors have always been a global concern to save human being and environment by using eco- friendly inhibitors. Some work has been studied by using the plant extracts has much importance as an environmentally benign, readily available, renewable and acceptable source for a wide range of inhibitors [6,7]. Several efforts have been made to use green corrosion inhibitors to prevent corrosion in practices

[8]. The plant extract are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as "Green Inhibitors" [9]. These inhibitors are biodegradable and do not contain heavy metals or other toxic compounds [10]. Some research groups has successfully studied the use of naturally occurring substances to inhibit the corrosion of metals in acid and alkaline medium [11 - 16]. In our present study, we have chosen two eco-friendly bio-inhibitor (*Phyllanthus amarus* and *Aegle marmelos*) a green approach to prevent the corrosion on copper and brass in hydrochloric acid medium (1M).

MATERIALS AND METHODS

In the present investigation effort has been taken to study the corrosion rate of different metals by means of weight loss method.

Selection of sample and Preparation of specimen, medium: Here we choose an alloy (brass). Brass is an alloy of copper and zinc, consisting of 70% Cu and 30% Zn. The corrosion rate of the above specimens studied in 1M H_2SO_4 condition using a weight loss method. Rectangular samples were cut from different metal plates. The samples are mechanically polished and numbered by punching before using. The specimens were polished by using emery papers with 80 grades and then the samples are degreased by acetone. Then a line is drawn with known area to have the same amount of corrosion possibilities. The area of the sample which we have taken is 1x1 cm^2. The two green inhibitors have been used in this study all are dissolved in deionized water. The solution of 5, 10, 15 and 20 % (v/v) were used in this present study.

Synthesis of green inhibitors: The leaves of *Phyllanthus amarus* (kellaneli) and *Aegle marmelos* (vilvam) were collected and dried for few days under controlled conditions. Then the leaves (10g) were extracted with 1M H_2SO_4 (50ml) for an hour by using an extraction apparatus. The resulting solution is filtered and the filtrate is used as a green inhibitors are given in Figures 1 &2.

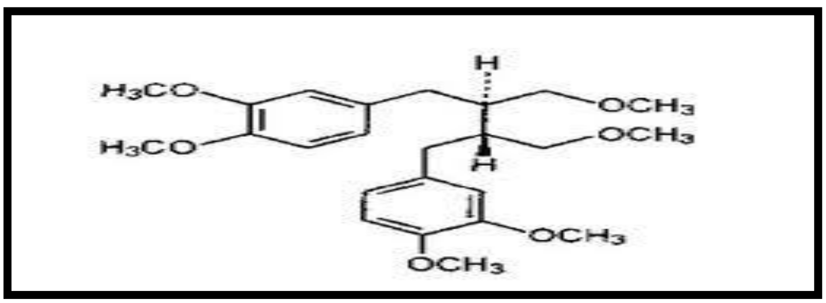

Figure 1. Chemical component in *Phyllanthus amarus*: Phyllanthin

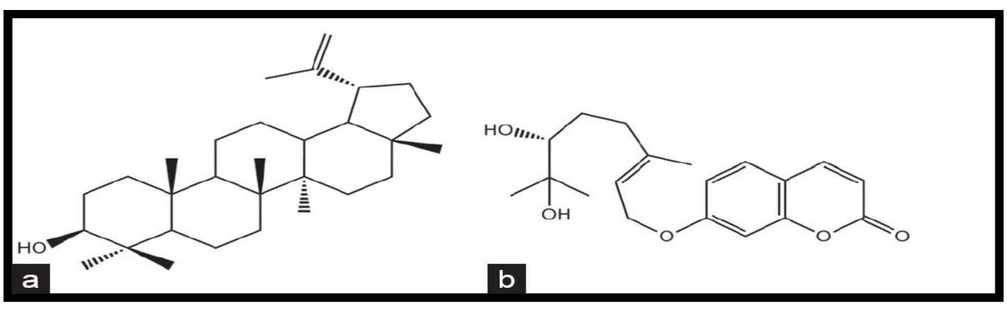

Figure 2. Chemical components in *Aegle marmelos* (a) Lupeol (b) Marmin

Weight loss method: These weight loss values are used to calculate the corrosion rate and inhibition efficiency. The corrosion rate was calculated from the weight loss using the relationship.

$$\text{Corrosion rate (mmpy)} = \frac{87.6 \times W\,(mg)}{A\,(cm^2) \times T\,(hrs) \times D\,(g/cc)}$$

Where -W is the weight loss in mg, D is the density in g cc^{-1}, A is the area of exposure in cm^2, T is the exposure time in hour, mmpy is millimeter per year.

Inhibitor efficiency has been determined by using the following relationship.

$$\text{Inhibition efficiency (\%)} = \frac{W_{free} - W_{add}}{W_{free}} \times 100$$

$$\text{Inhibition efficiency (\%)} = \frac{CR_{free} - CR_{add}}{CR_{free}} \times 100$$

RESULTS AND DISCUSSION

The present work describes our investigations to study the effectiveness of the acid extract of two green inhibitors *Phyllanthus amarus* and *Aegle marmelos* leaves on the corrosion of copper and brass in 1M H_2SO_4. Weight loss is a non electrochemical technique for the determination of corrosion rates and inhibitor efficiency which provides more reliable results than electrochemical techniques because the experimental conditions are approached in a more realistic manner. Table 1 represents the weight loss of copper in 1M H_2SO_4 devoid and in the presence of the inhibitor *Phyllanthus amarus* with increasing concentrations. Among the whole exposure period, the loss of weight of copper in the free acid medium was always higher than that in the solutions containing the inhibitor indicating the inhibitive effect of the added inhibitor on the copper corrosion in acid medium. The highest inhibition efficiency of 95% is achieved by adding *Phyllanthus amarus* (20% v/v). Variation of corrosion rate with the increasing concentration of the inhibitors is shown in Figure 3. In the same way the increase in the inhibition efficiency with the increasing concentration of inhibitor is shown in Figure 2. Corrosion of copper devoid and in the presence of another inhibitor *Aegle marmelos* is studied. Here also there is increase in the inhibition efficiency, with the increase in concentration of the inhibitor (Table. 1). However the inhibition efficiency is higher in almost all the concentrations in compare with the inhibitor *Phyllanthus amarus.* At 20% v/v concentration of the inhibitor *Aegle marmelos* highest inhibition efficiency of 92.59% is achieved. Variation of corrosion rate and inhibition efficiency of copper by using *Aegle marmelos* is explained in Figure. 3 and Figure. 4 respectively.

Table.1 Corrosion rate and Inhibition efficiency of copper in H_2SO_4 (1M) with **Inhibitor 1** and **Inhibitor 2** as a function of variation of concentration of Inhibitor.

Time in (hours)	[Inhibitor 1] % (v/v)	W_1 gm	W_2 gm	W gm	Corrosion rate $\times 10^{-3}$ mmpy	IE%	θ
3	0	2.3739	2.3712	0.0027	0.8183	-	-
3	5	2.5097	2.5079	0.0018	0.5455	33.33	0.3333
3	10	2.2291	2.2279	0.0012	0.3637	55.55	0.5555
3	15	2.6072	2.6064	0.0008	0.2424	70.37	0.7037
3	20	2.3388	2.3384	0.0004	0.1212	85.18	0.8518
Time in (hours)	**[Inhibitor 2] M**	**W_1 gm**	**W_2 gm**	**W gm**	**Corrosion rate $\times 10^{-3}$ mmpy**	**IE%**	**θ**
3	0	2.3739	2.3712	0.0027	0.8183	-	-
3	5	2.5236	2.5227	0.0009	0.2727	66.66	0.6666
3	10	2.6501	2.6496	0.0005	0.1515	81.48	0.8148
3	15	2.1418	2.1416	0.0002	0.0606	92.59	0.9259
3	20	2.3540	2.3540	0.0001	0.0424	95.71	0.9571

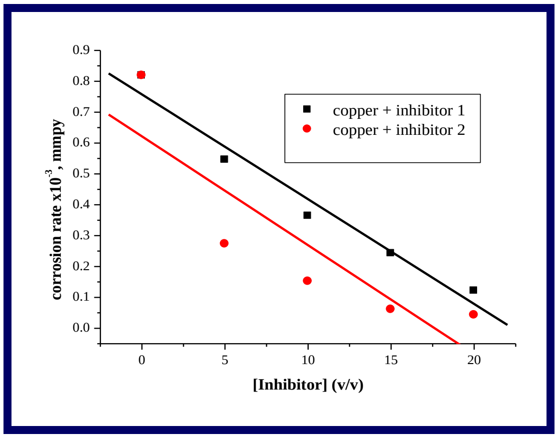

Figure. 3 Corrosion rate of copper in H_2SO_4 (1M) with Inhibitor 1 and Inhibitor 2

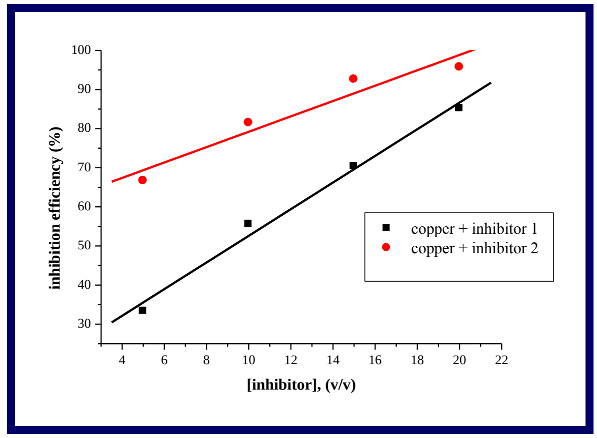

Figure. 4 Inhibition efficiency of copper in H_2SO_4 (1M) with Inhibitor 1 and Inhibitor 2

Corrosion rate and inhibition efficiency of copper corrosion in the presence of acid and with the addition of inhibitor of definite concentration (20% v/v) was studied with the variation in the exposure time 3h to 48 h (Table. 2). It is interesting to note that with increase in the time of exposure the corrosion rate increases sharely and there is corresponding a sharp decrease in the inhibition efficiency. At 3 h duration the inhibition efficiency is 92.59% whereas at the exposure time of 48 h the inhibition efficiency is only 16.66% shown in fig. 5 (Table 3). The same procedure is followed in corrosion studies of brass in 1M H_2SO_4. In this system also with the increasing in the concentration of inhibitor the inhibition efficiency increases as shown in Figure. 6. The inhibition efficiency also follows the same trend as with copper. the above results show the two green inhibitors are acting as very good inhibitors in the corrosion of copper and brass in 1M H_2SO_4. It is also interesting to note that with increase in the time of exposure the corrosion rate increases and there is corresponding a sharp decrease in the inhibition efficiency. At 3 h duration the inhibition efficiency is 80.94% whereas at the exposure time of 48 hours the inhibition efficiency is only 22.24% shown in fig. 6 (Table 4).

Table.2 Corrosion rate and Inhibition efficiency of brass in H_2SO_4 (1M) with **Inhibitor 1** and **Inhibitor 2** as a function of variation of concentration of Inhibitor.

Time in (hours)	**[Inhibitor 1] %**	**W_1 gm**	**W_2 gm**	**W gm**	**Corrosion rate x10^{-3} mmpy**	**IE%**	**θ**
3	0	3.6400	3.6379	0.0021	0.6759	-	-
3	5	3.6195	3.6185	0.0010	0.3218	52.38	0.5238
3	10	3.9216	3.9208	0.0008	0.2574	61.90	0.6190
3	15	3.6903	3.6896	0.0007	0.2253	66.00	0.6600
3	20	3.6116	3.6111	0.0005	0.1609	76.19	0.7619

Time in (hours)	**[Inhibitor 2] M**	**W_1 gm**	**W_2 gm**	**W gm**	**Corrosion rate x10^{-3} mmpy**	**IE%**	**θ**
3	0	3.6400	3.6379	0.0021	0.6759	-	-
3	5	3.6545	3.6538	0.0011	0.3540	47.61	0.4761
3	10	3.7325	3.7317	0.0008	0.2574	61.90	0.6190
3	15	3.4989	3.4983	0.0006	0.1931	71.42	0.7142
3	20	3.6824	3.6820	0.0004	0.1287	80.95	0.8095

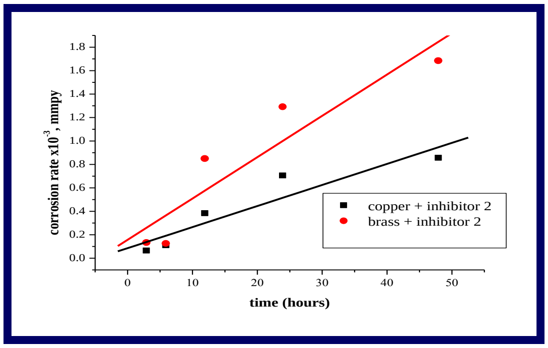

Figure. 5 Corrosion rate of copper and brass in H_2SO_4 (1M) with Inhibitor 2 for the variation of immersion time (hours)

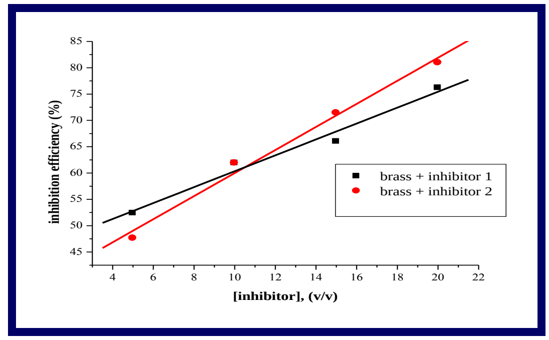

Figure. 6 Inhibition efficiency of brass in H_2SO_4 (1M) with Inhibitor 1 and 2

Table.3 Corrosion rate and Inhibition efficiency of copper in H_2SO_4 (1M) with **Inhibitor 2** as a function of variation of exposure time (hours)

Time in (hours)	**[Inhibitor 2] %**	**W_1 gm**	**W_2 gm**	**W gm**	**Corrosion rate x10^{-3} mmpy**	**IE%**	**θ**
3	20	2.3541	2.3539	0.0002	0.0606	92.59	0.9259
6	20	2.5026	2.5019	0.0007	0.1060	87.27	0.8727
12	20	2.4854	2.4804	0.0050	0.3788	56.10	0.5610
24	20	2.1192	2.1007	0.0185	0.7009	29.11	0.2911
48	20	2.6243	2.5793	0.0450	0.8524	16.66	0.1666

Table.4 Corrosion rate and Inhibition efficiency of brass in H_2SO_4 (1M) with **Inhibitor 2** as a function of variation of exposure time (hours)

Time duration (hours)	**[Inhibitor 2] %**	**W1 gm**	**W2 gm**	**W gm**	**Corrosion rate x10^{-3} mmpy**	**IE%**	**θ**
3	20	3.6824	3.6820	0.0004	0.1287	80.95	0.8095
6	20	3.5872	3.5856	0.0016	0.1212	73.33	0.7333
12	20	3.7019	3.6914	0.0105	0.8449	58.00	0.5800
24	20	3.7019	3.4386	0.0320	1.2870	37.62	0.3762
48	20	3.6597	3.5672	0.0835	1.6797	22.25	0.2225

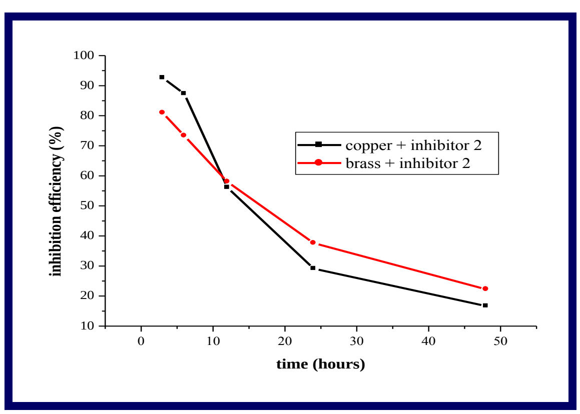

Figure. 7 Inhibition efficiency of copper and brass in H_2SO_4 (1M) with **Inhibitor 2** for the variation of immersion time (hours).

Langmuir adsorption isotherm: The inhibitive action of the two green inhibitors used in the present study is attributed to the adsorption of their molecules on the metal surface leading to a decrease in the corrosion rate. The values of surface coverage (θ) were calculated for different concentrations of inhibitors. In order to find out the mode of adsorption of the inhibitors on the metal surface, the relationship between the inhibitor concentration (C) and the surface coverage (θ) is obtained. Graphic representations of the relationships between log C and (log θ/1-θ) for the inhibitors are given in Figure. 8 and Figure. 9. The Figures 8 & 9 shows that there is a straight line relationship. This result suggests that the adsorption of inhibitors on the copper and brass surface following the Langmuir adsorption isotherm.

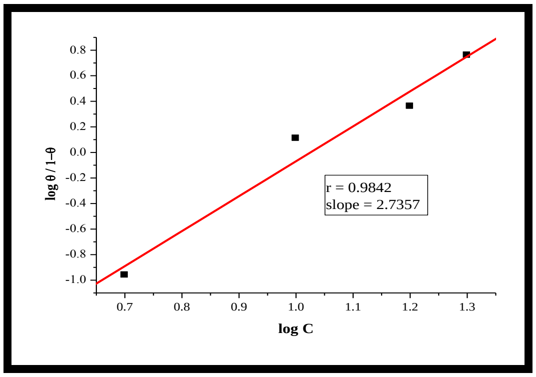

Figure. 8 Langmuir adsorption isotherm of copper in H_2SO_4 (1M) with Inhibitor 1

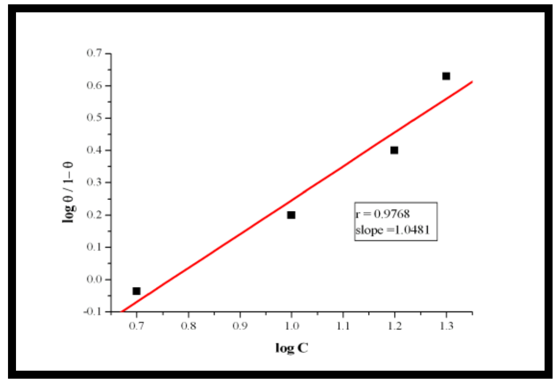

Figure. 9 Langmuir adsorption isotherm of brass in H_2SO_4 (1M with Inhibitor 1

APPLICATIONS

The different parts of Aegle marmelos and Phyllanthus amarus are used for various therapeutic purposes, such as for treatment of Asthma, Anemia, Fractures, Healing of Wounds, Swollen Joints, High Blood Pressure, Jaundice, Diarrhoea Healthy Mind and Brain Typhoid Troubles during Pregnancy [17]. Aegle marmelos has been used as a herbal medicine for the management of diabetes mellitus in Ayurvedic, Unani and Siddha systems of medicine in India [18], Bangladesh [19] and SriLanka [20]. The main usage of the parts of this tree is for medicinal purposes. The unripe dried fruit is astringent, digestive, stomachic and used to cure diarrhea and dysentery [21]. Sweet drink prepared from the pulp of fruits produce a soothing effect on the patients who have just recovered from bacillary dysentery [22]. Aegle Marmelos has variety of applications such as anti diabetic activity [23], Analgesic anti-inflammatory, & antipyretic Activity [24] Antimicrobial Activity [25], Anticancer Activity [26], Radio protective Activity [27], Antispermatogenic Activity [28] Toxicity Studies [29] Medicinal Studies [30]. Phyllanthus amarus belongs to the family Euphorbiaceae is a small herb well known for its medicinal properties and widely used worldwide. P. amarus is an important plant of Indian Ayurvedic system of medicine which is used in the problems of stomach, genitourinary system, liver, kidney and spleen. It is bitter, astringent, stomachic, diuretic, febrifuge and antiseptic. The whole plant is used in gonorrhea, menorrhagia and other genital affections. It is useful in gastropathy, diarrhoea, dysentery, intermittent fevers, ophthalmopathy, scabies, ulcers and wounds [31].

CONCLUSIONS

Corrosion of copper and brass was studied in 1M H_2SO_4 and the corrosion rate for these materials in the presence of two green inhibitors *Phyllanthus amarus* and *Aegle marmelos* was obtained by weight loss method. Weight loss measurements show that the two green inhibitors have been reducing the corrosion rate and with increasing of concentration of inhibitors the inhibition efficiency increases. Formation of black film on the surface of the copper and brass is mainly responsible for corrosion inhibition. When compared the two inhibitors, *Phyllanthus amarus* and *Aegle marmelos*, the corrosion rate and inhibition efficiency are more favourable for the *Aegle marmelos*. A linear Langmuir plot supports the adsorption of the inhibitors on the surface of the metal. The decrease in inhibition efficiency with increase in exposure time clearly supports the formation of multilayer on the surface of the metal.

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