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Green Inhibitors: Inhibitory Effect Of Acacia Auriculiformis And Ixora Coccinea Extracts Against Corrosion Of AA5083 In Acidic Medium

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Abstract

The corrosion behavior of AA5083 in Hydrochloric acid and Sulphuric acid in presence of a cathodic material, at 0.4N and 0.5N concentration was studied by gravimetric method. The results showed that the rate of corrosion is influenced by concentration of acid and presence of chloride ions. The corrosion of AA5083 was found to be many folds greater in acid chloride medium compared to that of neutral chloride medium. The ethanolic extract of Acacia auriculiformis leaf exhibited appreciable inhibition against AA5083 in 0.5N HCl. The flower extract of Acacia auriculiformis was found to possess better efficacy than the flower extract of Ixora coccinea. The results revealed that inhibition is dependent on concentration of the inhibitor and is due to adsorption of poly phenols on to the surface of the alloy resulting in the formation of Al- poly phenol complexes.

***Keywords**: Green inhibitors, AA5083, Acacia auriculiformis, Ixora coccinea, Acid corrosion, Aluminium alloys, FSW.*

1. Introduction

In marine, air craft and cryogenic applications Al-Mg alloys are widely used structural material due to their high ductility, appreciable corrosion resistance, weldability and moderate strength [1, 2]. Increase in corrosion resistance decreases maintenance cost and increases the life of metallic components. Various chemicals have been used to prevent different forms of metallic corrosion [3]. Most of the synthetic anti corrosive agents degrade environment and are hazardous to human health. With the growing concern about the environment, the research for eco friendly green inhibitors has attained priority.

The use of plant products as corrosion inhibitors has been well documented [4]. Green inhibitors are preferred as they are eco friendly, easily available and economic. Various parts of plants contain different amount of tannins. The effectiveness of tannins in retarding metallic corrosion in acid medium is discussed by Semra [5].

Ixora coccinea is a common flowering shrub native to Asia. It is found to possess various biological activities. Latha and Panikar have reported the chemo protective effect of Ixora coccinea against toxicity induced by cyclophosphamide and cis-platin [6]. However, Ixora has gained importance due to its antimicrobial [7], anti oxidant [8], anti inflammatory and anti mitotic [9] properties.

Acacia auriculiformis has gained commercial importance due its use as fire wood and timber [10].Acacia ariculiformis is also used as analgesic [11]. Saponins, isolated from Acacia auriculiformis is reported to be active against certain microbes and helminthes [12].Its flowers are a source of bee forage for honey production [13].

The present study aims to evaluate the corrosion behavior of AA5083 in acidic medium and also to study the inhibitory effects of Ixora coccinea and Acacia auriculiformis against the corrosion of AA5083 in acidic medium containing chloride ions.

2. Materials and Methods

2.1 Material: Test Coupon Composition (%wt)

Mg - 4.15 , Mn - 0.73 , Fe- 0.31 ,Si- 0.13 , Cu <0.025 , Cr <0.01 , Ti < 0.01 and rest Al.

Dimension: Length – 50mm, Breadth – 15mm and thickness- 6mm

2.2 Preparation of Ethanolic extract

The spindle like leaves and flowers from Acacia auriculiformis and the flowers from Ixora coccinea were collected early morning, washed with distilled water .The moisture was removed by straining through sieve and air dried. The dry leaves and flowers were cut into small pieces. About 20 grams each and 100 ml of ethyl alcohol were taken in different Soxhlet apparatus. Extraction was carried out at $60^{O}C$ for an hour. The extract was cooled to room temperature and poured into evaporation trays. The solid left behind weighed about 3-4 grams. This was preserved in air tight amber containers.

2.3 Reagents

All chemicals used are Analar Grade. NaCl, HCl and H_2SO_4 were diluted with double distilled water to obtain the required concentration. The strength of these solutions was established by carrying out conductometric titration [14].

2.4 Methods

Weight Loss measurement

AA 5083 base alloys **(BA)** and Friction Stir Weld alloys **(FSW- cathodic material)** were cut as per the given dimension. 7 coupons of each were used for various methods of measurement. Weight loss measurements were carried out according to the procedure stated in ASTM G31 [15].

The test coupons were mechanically polished using emery paper. It was then rinsed with double distilled water and washed with acetone. The dry coupons were preserved in desiccator cabinet.

Both base alloy and friction stir weld samples were weighed using an analytical and digital balance with a precision of 0.0001g. The weighed samples were suspended using inert glass hooks and immersed in the electrolyte.

Fourteen BA coupons and Fourteen FSW coupons were immersed in each electrolyte (0.4N HCl, 0.5N HCl, 0.4N H_2SO_4 and 0.5N H_2SO_4). After 24 hours, seven coupons each (7BA and 7 FSW) were removed and washed with doubled distilled water. It was then rinsed with acetone and air dried. The dry samples were weighed as before.

The remaining 14 samples (7 each) were removed after 72 hours and treated in the same way.

Experiment 1: Weight loss of BA in presence and in absence of FSW was studied without stirring the electrolytes.

Experiment 2: Weight loss of BA in presence and in absence of FSW was studied by stirring the electrolyte using a mechanical stirrer (75 rpm).

Experiment 3: Seven BA and 7 FSW coupons were immersed in 3.5% NaCl for 360 hours with and without stirring and the extent of corrosion is calculated from the loss in weight.

Experiment 4: Weight loss of BA in presence of FSW, after 72 hours in 0.5N HCl and varying amounts of different inhibitors was studied without stirring the electrolyte. The efficacy of inhibitor is calculated from the loss in weight

3. Results and Discussion

Both, the coupons and the electrolyte were analysed to understand the mechanism of corrosion and inhibition.

Qualitative analysis of the electrolyte (0-inhibitor concentration, 72 hours immersion with FSW) after removing the control samples was carried out as per the procedure given in Vogel [14].The spot test results showed the presence of Aluminium and Magnesium, indicating that both Al and Mg are leached out from the base metal alloy during corrosion, even though aluminium is cathodic with respect to magnesium (standard reduction potentials of Magnesium and aluminium are -2.37V and -1.66V respectively).

This shows that the film has undergone dissolution exposing the fresh surface of alloy resulting in the leaching of magnesium.

Metals and alloys corrode at a faster rate and to a greater extent in acidic medium than in alkaline or neutral medium. It has also been proved that the presence of chloride ions is detrimental to metals [16]. Table 1 shows the loss in weight of AA5083 in presence of HCl and H_2SO_4. The AA5083 test coupons were found to undergo corrosion in HCl medium at much faster rate than in H_2SO_4 as the acidic chloride is more detrimental and the rate of corrosion was found to be dependent on the concentration of the acid.

Table 1:

Weight Loss of AA 5083 in acidic medium

Acid/Immersion	Hydrochloric acid		Sulphuric Acid	
Time in Hours	0.4N	0.5N	0.4N	0.5N
24without FSW	0.052 ± 0.008	0.25 ± 0.018	0.024 ± 0.002	0.058 ± 0.013
24 with FSW	0.099 ± 0.006	0.455 ± 0.07	0.04 ± 0.002	0.099 ± 0.005
72without FSW	0.596 ± 0.039	0.675 ± 0.044	0.174 ± 0.019	0.262 ± 0.063
72 with FSW	1.074 ± 0.035	1.276 ± 0.08	0.297 ± 0.011	0.44 ± 0.07

The corrosion of base alloy AA5083 in both Hydrochloric acid medium and Sulphuric acid medium is more prevalent in presence of Friction Stir Welded sample (Fig 1), than in absence of FSW samples. This suggests that the unweld AA5083 samples behave anodically on coupling with FSW coupons. F.Zucchi et al have observed the Cathodic behaviour of FSW AA5083 in salt solution [17].

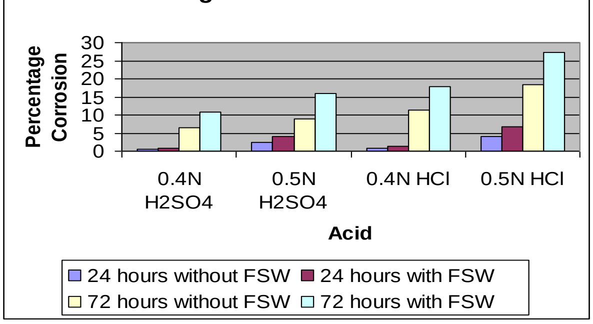


Fig.1 : Effect of Acid

This indicates that an unweld part lying near a Friction stir welded part becomes susceptible to corrosion

Table 2 shows the loss in weight of the base alloys on agitating the electrolytes containing chloride ions, (0.5N HCl and 3.5 % NaCl) continuously using a mechanical stirrer, at a rate of 75 rpm.

Table 2: Weight Loss of AA 5083 on agitation

Condition	3.5 % NaCl (360 hrs immersion) (neutral chloride)		0.5N HCl (24 hrs immersion) (acidic chloride)	
	Without FSW	With FSW	Without FSW	With FSW
With stirring	0.008 ± 0.0025	0.011 ± 0.0028	0.24 ± 0.018	0.459 ± 0.05
Without stirring	0.009 ± 0.003	0.01 ± 0.003	0.25 ± 0.018	0.455 ± 0.07

The results indicated that, stirring does not have any profound effect on the corrosion behavior of base alloys both in presence and in absence of FSW. The results also indicated that the rate of corrosion in neutral chloride medium is very less, even after prolonged exposure compared to that of acidic chloride medium. Aluminium and its alloys possess natural Al_2O_3 film at the surface which is less soluble in neutral chloride medium than in acidic chloride medium.. This explains the significant difference in the rate of corrosion in neutral chloride and acidic chloride solutions.

As this investigation was designed to study the inhibitory efficiency of plant products, the most offensive medium had been chosen and it was decided to conduct further investigation without stirring the electrolyte as agitation did not have profound effect on the corrosion behaviour.

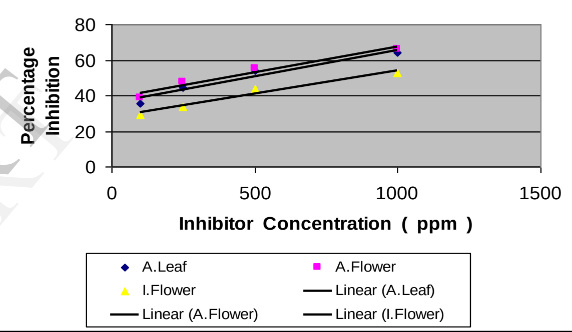
The loss in weight of the test coupons in 0.5N HCl containing varying amounts of ethanol extract of Acacia auriculiformis and Ixora coccinea is given in Table 3.

Table 3: Loss in weight in presence of inhibitor (0.5N HCl, after 72 hours)

Concentration (ppm)	Acacia auriculiformis		Ixora coccinea
	Leaf extract	Flower extract	Flower extract
0	1.276 ± 0.08		
100	0.82 ± 0.054	0.78 ± 0.072	0.906 ± 0.022
250	0.71 ± 0.051	0.67 ± 0.046	0.846 ± 0.047
500	0.59 ± 0.012	0.57 ± 0.026	0.72 ± 0.024
1000	0.46 ± 0.03	0.43 ± 0.1	0.606 ± 0.04

The inhibition efficacy of the leaf and flower extract of Acacia and the flower extract of Ixora can be understood from Fig .2.

Fig.2 : Inhibition Efficiency



Both leaf and flower extract of Acacia offered more protection against corrosion induced by 0.5N HCl on AA5083 , than the Ixora flower extract .The inhibition of ethanolic extract of Acacia may be due to the high concentration of poly phenolic compounds present in various parts of the plant [18] .

Poly phenols, due to their characteristic structure, have a tendency to form complexes with Fe, Cu, Zn and Al [19, 20]. Formation of Al- flavanoid complex in biological systems had been reported by Z. Deng et al [21]. Poly phenols are capable of forming stable complex even at room temperature. The inhibitory action of the flower and leaf extracts under test indicates the formation of Al-poly phenol complexes at the surface of the test coupons, which is stable even in presence of dilute acids.

The result clearly shows that the inhibition efficiency of Acacia flower extract is greater than that of the Acacia leaf extract. It was also found to increase with increase in concentration. Poly phenols are usually concentrated in flowers, fruits, seeds and bark than in leaves [22]. This explains the greater inhibition of the flower extract on comparison to leaf extract .Of the two flower extracts under test, Acacia auriculiformis extract was found to offer 12.3 % more inhibition than that of Ixora coccinea.

The results followed Langmuir adsorption isotherm and the plot of log C /θ Vs log C (Fig.3) gave a straight line whose slope is given in Table 4. The slope for the line obtained for all the plant products were near unity suggesting that the inhibitory action is due to consistent adsorption of the poly phenols at the surface of the alloy resulting in the probable formation of an adhering Al-poly phenol complex. As the Langumir adsorption isotherm is obeyed, it can also be concluded that there is no lateral interaction between the adsorbed molecules [23].

Fig.3 : Langmuir Adsorption Isotherm

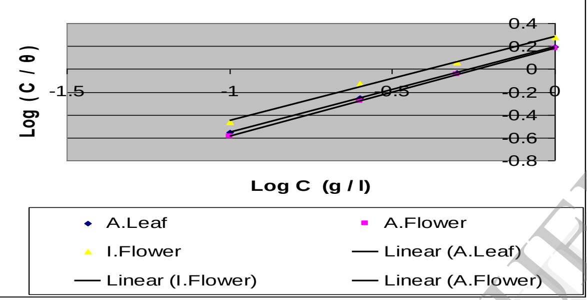


Table 4: Adsorption Characteristics

log c (g/l)	log (C / θ)		
	A.Leaf	A. Flower	I. Flower
-1	-0.553	-0.589	-0.461
-0.6	-0.249	-0.279	-0.128
-0.3	-0.032	-0.044	0.059
0	0.194	0.178	0.279
Slope obtained	0.7452	0.7689	0.7322

4. Conclusions

AA 5083 Friction stir welded alloy behaves cathodically with respect to base alloy in acidic medium .

Ethanolic extract of Acacia auriculiformis leaves, flowers and Ixora coccinea flowers exhibited appreciable inhibition against corrosion of AA5083 in 0.5NHCl.

Acacia auriculiformis leaf extract is more effective than Ixora coccinea flower extract

Acacia auriculiformis flower extract shows better inhibition than its leaf extract

Acacia auriculiformis flower extract is more effective than Ixora coccinea flower extract

The inhibition efficacy increased with increase in inhibitor concentration.

The inhibition may be due to the formation of Al-poly phenol complex after the adsorption of poly phenol on the alloy surface.

The adsorption follows Langmuir adsorption isotherm.

5. Acknowledgement

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6. References

[1] I.J.Polmear, Light Alloys – Metallurgy Of The Light Metals, 3rd Edition: Arnold , a division of Hodder Headline PLC,1995

[2] ASM metals Handbook, Properties and selection of non ferrous alloys and special purpose materials. 2, 10th edt., Ohio, USA, ASM International: 1990.

[3] M. A. Migahed and A. M. Al-Sabagh, Chemical Engineering Communications, 196 (9), (2009)1054-1075.

[4]E.E. Ebenso, N.O.Eddy and A.O. Odiongenyi, African Journal of Pure and Applied Chemistry, 2(11), (2008)107-115.

[5] Semra BILGIC , KOROZYON,13(1), (2005) 3-11.

[6] P.G.Latha and K.R.Panikar, Phytother .Res., 13(6),(1999),517-520.

[7] J.Annapoorna, P.V.S.Amarnath, D.Amar Kumar, S.V.Ramakrishna and K.V.Raghavan, Fitoterapia, 74(3), (2003), 291-293.

[8] S.Moni Rani, Md.Ashraful Alam, A.Raushnara and J.Rumana, Bangladesh J. Pharmacol. 3, (2008), 90-96.

[9] R.Zachariah, C.R.S.Nair and P.P.Velayudha, Indian Journal Of Pharmaceutical Sciences, 56 (4),(1994),129-132.

[10] M.A.Abdul Razak, C.K.Low and A.Abu Said, Malaysian Forester,44, (1981), 87-92.

[11] The Australian New Crops News Letter, 10, July 1998.

[12] P.Mandal, S.P.Sinha Babu and N.C.Mandal, Fitoterapia, 76(5), (2005), 462-465.

[13] M.W.Moncur, G.Kleinschimdt and D.Somerville, Advances in Tropical Acacia Research, (1991), 123-127.

[14] A.I.Vogel, Text Book of Quantitative Inorg.Anal, 4th edition, Longman, NY, 1978

[15] Practice for Lab Immersion Corro. Testing of Metals, ASTM Standard G31, 1995.

[16] V.P.Kassyura and E.M.Zaretskii, Chem. and Petrol. Eng., 4(11), (1968)915-917.

[17] F.Zucchi, G.Trabanelli, V.Grassi, Materials and Corrosion, 52(11), (2001), 853-859.

[18] Abdul Razak MA, LowCK and Abu Said A, Malaysian Forester, 44, (1981), 87-92.

[19] G. Weber, Journal: Chromatography, 26 (1), (1988), 133- 138.

[20] Dušan Malešev and Vesna Kunti, J. Serb. Chem. Soc. 72 (10), 921–939 (2007)

[21] Z. Deng, C. Coudray, L. Gouzoux, A. Mazur, Y. Rayssiguier, D. Pepin, Biol. Trace Elem. Res.76(2000) 245

[22] E. Middleton, C. Kandaswami, in: The Flavonoids: Advances in Research since 1986, J. B. Harborne, Ed., Chapman & Hall, London, 1994

[23]H.Ashassi–Sorkhabi, M.R.Majidi and K.Seyyedi, Appl.Surf.Sci.225, (2004)176- 185.