Plant Archives Vol. 20, Supplement 2, 2020 pp. 668-672 **e-ISSN:2581-6063 (online), ISSN:0972-5210**

USE OF *ALBIZIA LEBBECK* PLANT EXTRACT AS A CORROSION INHIBITOR FOR REINFORCEMENT STEEL IN A SALINE MEDIUM

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Abstract

In this research, the extract of *Albizia lebbeck* pods and seeds has been used as a corrosion inhibitor for carbon steel in a saline medium. The processes conducted were drying, grinding and soaking in distilled water of the pods with their seeds and then steaming the volume in half. A small concentration of 0.004%, 0.006% and 0.01% of the aqueous extract was used with the saline solution NaCl where the inhibition of corrosion was 1.04 μAcm^{-2}, 31.48 and 27 $nAcm^{-2}$ respectively. The tests were carried out using potentiodynamic static polarization. In addition to, antioxidant activity of the extract *Albizia lebbeck* pods and seeds were determined by free radical 2, 2-diphenyl-1-picrylhydrazyl (DPPH) method. The result displayed the highest antioxidant activities in Albizia pods extract in comparison to Ascorbic acid as green antioxidant for corrosion inhibition of carbon steel in (500ml) of the saline medium due to presence of organic compounds containing N, S and/or O atoms as mentioned by previous researches. These compounds can be adsorbed on the metal surface, block the active sites and thereby reduce the corrosion rate.

Keywords: Corrosion Inhibitions, *Albizia lebbeck*, Carbon Steel, Antioxidant Activity.

Introduction

Pure metals and alloys react with chemicals or electrochemically with corrosive medium to make a stable compound, within which the loss of metal happens. The compound therefore shaped is termed corrosion product and metal surface becomes corroded. Corrosion involves the movement of metal ions into the solution at active areas (anode), passage of electrons from the metal to an acceptor at less active areas (cathode), introduce an ionic current in the solution and an electronic current in the metal. The cathodic procedure requires the presence of an electron acceptor such as oxygen or oxidizing agents or hydrogen ions (Bentiss *et al.*, 2000; Hukovic-Metikos *et al.*, 2002; Lagrenee *et al.*, 2001). Corrosion of metals is a major problem that must be faced with safety, environment and economic reasons. It can be minimized by suitable strategies which in turn stifle, retard or completely stop the anodic or cathodic reactions or both (Raja and Sethuraman, 2009). The indirect costs resulting from actual or possible corrosion are more difficult to evaluate but are probably even greater. It is estimated realistically to be around 300 billion dollars in United States of America (USA), while in developing countries like Nigeria it is assumed to be around 10 billion dollars and it is estimated to be around Rs 2.0 lakh crores per annum in India (Natarajan, 2013).

Recently, plant extracts are being important as a readily available, environmentally acceptable and renewable source for a wide range of needed inhibitors. Plant extracts are showed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple technique with low cost. However, synergistic (and antagonistic) effects are often expected with these mixtures of inhibitors that may affect their inhibition efficiency. Economic plant extracts proved by several investigations (Hosary *et al.*, 1972). Continuing the work on development of green corrosion inhibitors (Quraishi *et al.*, 2010; Singh *et al.*, 2010; *Singh *et al.*, 2010). Generally, the potential and ability of plants extracts to be used as corrosion inhibitors depend on their phytochemical constituents, the types of bonds presence in the hydrocarbon molecules constituting the plants extracts, the length of the hydrocarbon molecule and the presence of N, S, O and P bearing molecules. Over the years, plant extracts have been reported as good corrosion inhibitors. However, the characteristics of the constituents that provide the inhibitions are still subject of debate and an important research focus (Ameer *et al.*, 2010).

This research used *Albizia lebbeck*, that it is (L.) Benth. (Mimosaceae), known in India as shirish, where it is an unarmed deciduous woody tree, 12–21 m in height, having pale bark with glabrous young shoots. It is cultivated in many parts of Pakistan in farmlands, along roadsides, on irrigated plantations, along rivers and as an ornamental plant in gardens due to its pleasant appearance (Ali, 1973; Burkil, 2000). This plant is found throughout India, Bangladesh, tropical and subtropical Asia and Africa (Kirtikar and Basu, 1980). *A. lebbeck* contains macrocyclic alkaloids, saponins, anthraxquinone glycosides, flavonols and tannins (Rahul *et al.*, 2010). The saponin constituents of Albizia where described are echinocystic acid glycosides (Carpani *et al.*, 1989; Orsini *et al.*, 1999). Phytochemical investigations of A. lebbeck pod stated that they contains N-Benzoyl L phenyl alaninol and 3, 5 Dihydroxy 4, 7 dimethoxy flavone (Rashid *et al.*, 2003). The plant extract is concerning in have anti-nootropic, ovulatory, anti-dysenteric, antiseptic, antimicrobial activity, anti-inflammatory and anti-tubercular activities (Chintawar *et al.*, 2002; Pratibha *et al.*, 2004; Kapoor *et al.*, 2007 and Rahul *et al.*, 2010).

It reports the effect of aqueous extracts of Albizia▪ s L. pods and seeds, as corrosion inhibitors for reinforcement steel (carbon steel) in saline medium (3.5% NaCl), it is tested using potentiostatic polarization before and after addition of aqueous extracts to the saline solution and polarization curves were determined.

Materials and Methods

It includes: preparation of plant and specimen, polarization cell and preparation of electrodes, anti-oxidant activity.

Preparation of Albizia extracts

The pods and their seeds of *Albizia* (Fig. 1) were collected (from the garden in the ministry of the Science and Technology, identified, authenticated by Dr. Sukaina Abbas Elaiwye by the University Herbarium, Collage of Science, University of Baghdad) and air-dried in shadow, laboratory conditions, ground and sieved (Ø = 250 µm) to powder using an electric miller. The powder (50 g) was soaked in 700 ml of distilled water for 72h. The soaked was dried to 300 ml using hot plate 50-60 ˚C with stirring. The extracts filtered to prepare for testing.

Preparation of specimens

Carbon steel specimen with dimensions (Ø =20mm and thick. 4mm) were cut, grinded and polished to mirror then finished with different grade of emery sand papers 800, 1000, 2000. It degreased with alcohol. The alloy used after X-ray verified contains the flowing components (wt %), (C =0.3), (Mn =1.5), (Si =0.5), (S =0.045), (P =0.035) and reminder Fe =97.62.

Polarization cell

Three neck polarization cells Winking M Lab-Germany/ Potentiostatic of corning glass of 0.5 L capacity (Fig.2) located in Industrial Application Center, Corrosion Department were used in this research. The middle neck was used to accommodate working electrode (WE) of carbon steel and the remaining two for the reference electrode, and the auxiliary electrode of platinum (99.5% pure).

Preparation of electrodes

In this research, three types of electrodes were used as mentioned above. Working electrode (WE) rod (Fig.3) was prepared by molding Carbon steel specimen with polymeric material (epoxy). These three electrodes represent cell measurement for Potentiostatic. When the device is turned on and then open-circuit potentials of carbon steel surface in the saline medium (500 ml) with inhibitor (0.02, 0.03 and 0.05ml), respectively from aqueous extracts or without after 30 min of immersion are determined and the effort required for the measurement. EIC (Electron Ion Collider) measurements were performed at corrosion potentials Ecorr, over a frequency range of 100 kHz to 10 mHz with an AC signal amplitude perturbation of 10mV peak to peak.

The data that are shown in Table 1 are recorded by the device on the word program. The corrosion potential is determined, and then corrosion current (Icorr) by diagram (Fig. 4, 5, 6 and 7) appears in program. When Identify Icorr before and after addition can compress the results that refer to increase in Icorr to efficiency of inhibitor performance that its addition. All experiments were performed at 25 ˚C.

Fig.1: *Albizia lebbeck* pod and their seeds

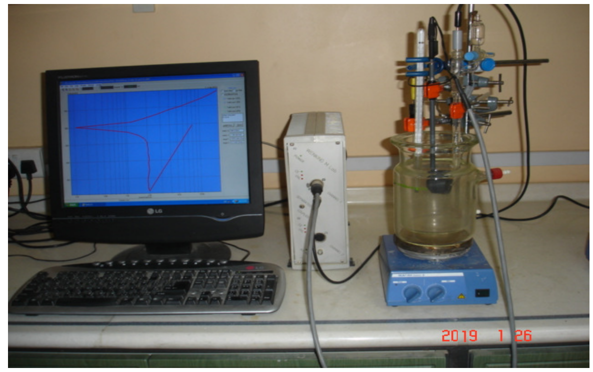

Fig. 2: Potentiostatic polarization

Table 1: Potentiostatic polarization parameters of carbon steel without and with different volume of Albizia' aqueous extract in the saline medium

Sample No.	Inhibitor, ml	Ecorr	Icorr
1	0	-682.50(mV/SCE)	28.64 (**ìAcm**$^{-2}$)
2	0.02	-408.06 (mV/SCE)	1.04 (**ìAcm**$^{-2}$)
3	0.03	-730.20(mV/SCE)	31.48 (**nAcm**$^{-2}$)
4	0.05	-741.0(mV/SCE)	27.89 (**nAcm**$^{-2}$)

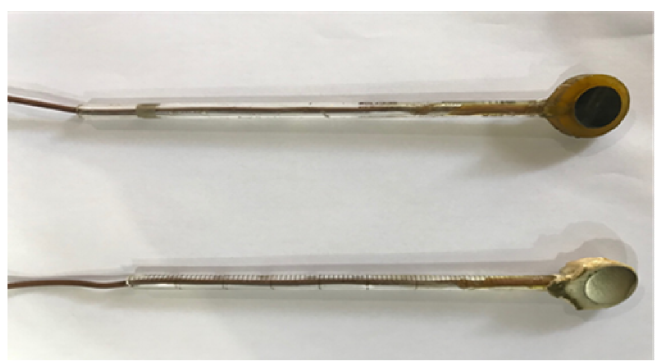

Fig. 3 : Working Electrode (WE)

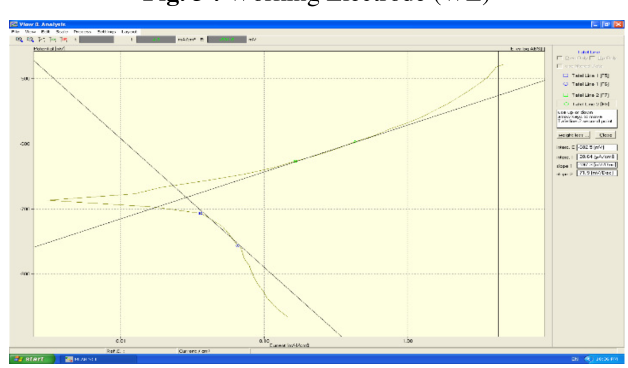

Fig. 4 : Polarization curves for Carbon steel without addition

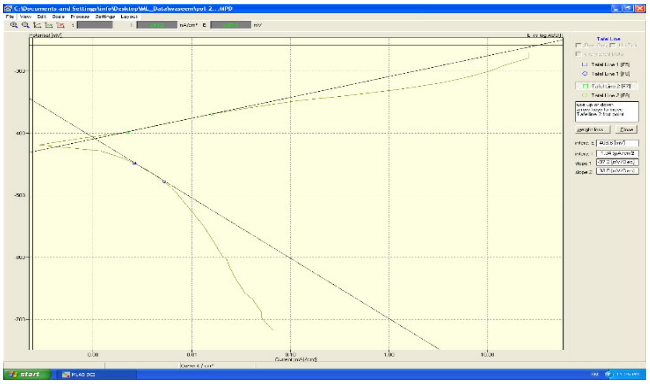

Fig. 5 : Polarization curves for carbon steel in 0.004% of aqueous extract solution

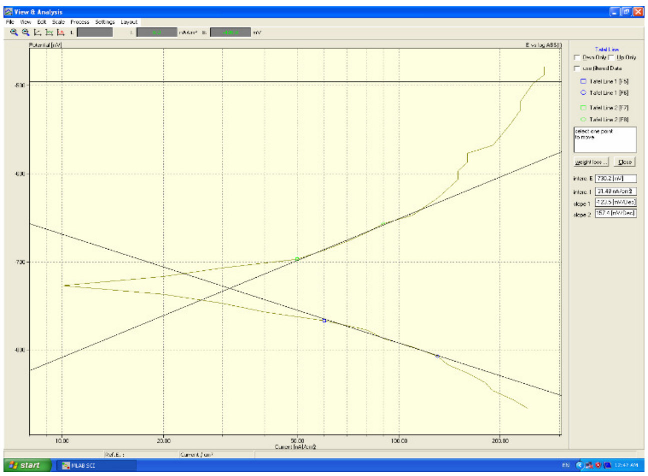

Fig. 6 : polarization curves for carbon steel in 0.006% of aqueous extract solution.

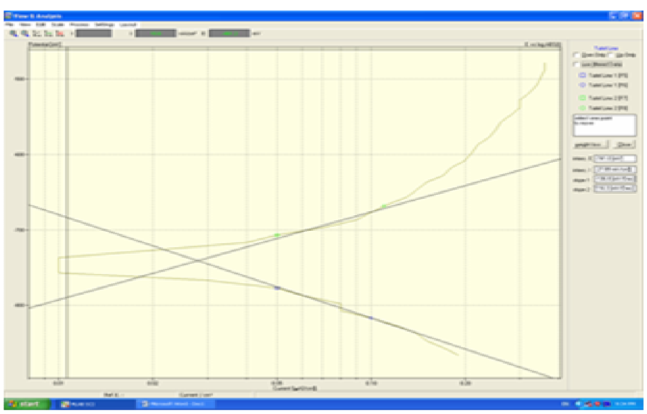

Fig.7: polarization curves for carbon steel in 0.01% of aqueous extract solution.

Anti-oxidant activity

The antioxidant activity in vitro was evaluated by measuring the trapping power of radical DPPH (1, 1-Diphenyl-2-picryhydrazyl) as described by Burits and Bucar (Burits and Bucar, 2000). The free radical scavenging activities and the Albizia's aqueous extract was measured with DPPH assay. The DPPH radical has deep scavenging violet color due to its unpaired electron and radical capability can be followed spectrophotometrically by absorbance at loss 518 nm when the pale yellow non-radical from is produced. Based on this assay, equal volumes (0.1 ml) of DPPH (0.1 μM) and 1 ml of each concentration (6.5, 12.5, 25, 50, 100, and 200 μg/ml) from 0.05 g of dried aqueous extract in 50 ml of methanol and Ascorbic acid as positive control were mixed and allowed to stand for 30 min. (at 25°C). Then, the absorbance was read at 518 nm in a UV/VIS shimadzu spectrophotometer and converted into percentage radical scavenging activity as follows:

$$\text{Scavenging activity}(100\%) = \frac{\text{A518control} - \text{A518sample}}{\text{A518control}} \times 100$$

Where A518 control is the absorbance of DPPH radical+ methanol; A518 sample is the absorbance of DPPH radical or compound. Ascorbic acid was used as a standard reference. The antioxidant effect was done in department of early detection of cancer diseases.

Results and Discussion

Potentiostatic polarization study

A polarization study was used to detect the formation of protective film on the metal surface. Electrochemical kinetics parameters, i.e., the corrosion potential (Ecorr) corrosion current density (Icorr); anodic and cathodic Tafel slopes, obtained from extrapolation of the polarization curves are listed in Table 1. When carbon steel is immersed in the saline water, the corrosion potential (Ecorr) is -682.5 mV/SCE and the corrosion (Icorr) is 28.64 (μA/cm^{-2}). When 0.02 ml of *Albizia lebbeck* aqueous extract was added to the saline water (3.5% of NaCl) medium, the corrosion potential (Ecorr) was -408.06 mV/SCE and corrosion current (Icorr) was 1.04μA/cm^{-2}. The corrosion current decreased from 1.04μA/cm^{-2} to 31.48nA/cm^{-2} when inhibitor increased to 0.03 ml. The corrosion current density (Icorr) decreases with increasing the dose of Inhibitor. The values of Icorr were found to decrease in the presence of inhibitors. The decrease in Icorr values can be due to the adsorption of *Albizia lebbeck* aqueous extract on the carbon steel surface, which indicates that the extract acts as a good corrosion inhibitor. This shows that the formation of functions as anodic inhibitor controlling both anodic and cathodic processes but more predominantly anodic process. This indicates that protective film is formed on the surface (Chauhan and Gunasekaran, 2007). Organic inhibitors react by adsorption on metallic surface. Cationic inhibitors, like amines, or anionic inhibitors, sulphates are preferentially adsorbed upon the charge of the metal surface. The formation of a bond between the metal substrate and the organic inhibitor hinders the anodic and cathodic technique and protects the metal surface through film formation. The formed film provides a barrier that keeps water away and thus prevents corrosion. The hydrocarbon chain attracts the organic molecules and forms an oily layer that prevents corrosion acts as a barrier against fluids. The main features of corrosion inhibitions by organic inhibitors. *Albizia lebbeck* contains macrocyclic alkaloids, saponins, tannins, anthraquinone glycosides and flavonols. The mechanism of inhibition is resulted from the physical adsorption of extract molecules on the carbon steel surface.

These molecules may inhibit the corrosion because of formation of complex compounds via chelating with Fe^{+2} cations which adsorbed on carbon steel surface, thus prohibiting the adsorption aggressive ions such as Cl^{-} (from the medium), or the adsorption of the extract molecules on the carbon steel surface because of the donor-acceptor interaction between π electrons of donor atoms of aromatic rings of the molecules and the vacant d orbital of iron surface atoms and/or the *Albizia lebbeck* extract molecules can also be adsorbed on the metal surface in the form of negatively charged species which can interact electrostatically with positively charged species metal surface, which led to increase the surface coverage and to increase the IE.

Antioxidant activity study

The aqueous extracts of *Albizia lebbeck* pods and their seeds were used as antioxidant and determined by scavenging action way against 1, 1-Diphenyl-2-picryhydrazyl which is considered as free radical and convert it into 1,1-Diphenyl-2-picryhydrazine.

Free radical scavenging assays is one of the simple and widely used. The scavenging of DPPH radicals by antioxidants because of their hydrogen or electron is donating ability. In alcoholic solution, DPPH appears a strong absorption band at 517 nm. When the odd electron becomes paired off in the presence of a scavenger, the absorption reduces and the DPPH solution is decolorized as the color changes from deep violet to light yellow. The degree of reduction is indicative of the radical scavenging (antioxidant) power of the substances (Sudharshan *et al.*, 2010; Naik *et al.*, 2015). The statistical results displayed in Table 2 show that the extract from Albizia Lebbeck pods and their seeds had a higher antioxidant effect by 100%, in (25, 50, 100, 200 and 300 µg/ml), 50.5% in 12.5 µg/ml, and 33.6% in 6.5 µg/ml from 0.05g of dried aqueous extract in 50ml of methanol compared with the standard control of Ascorbic acid. The results showed that the aqua extract of *Albizia lebbeck* is a high antioxidant from the standard controller. The extract had a higher antioxidant effect because of containing many types of active compounds, which proved that the plant posses antioxidant proprieties. The presence of phenolic compounds causes the antioxidant activity in the extract (Braca *et al.*, 2002; Rakesh *et al.*, 2013). Higher content of phenolic–OH is indeed beneficial for later applications especially antioxidant activity and corrosion inhibition.

In addition, the pure antioxidant molecules of the extract also show an inhibition of the anodic reaction of iron oxidation. The anodic inhibiting mechanism can be seen as chemisorptions of the organic molecules on steel with the formation of conversion products between $Fe+^2$ and the organic antioxidant compounds. The organic depositions on steel surface after lengthy time immersion in the solution involved the pure inhibiting molecules corroborate. Actually, the same functional groups of the pure molecules are involved in their ability to chelate metallic cations (especially $Fe+^2$) as in their radical scavenging activity (Van Acker *et al.* 1996).

Table 2: DPPH radical scavenging activity of aqueous extract of *Albizia L.* pods and seeds

No	concentration µg/ml	Antioxidant Activity	
		Extract	Ascorbic acid
1	300	100%	93%
2	200	100%	95%
3	100	100%	85%
4	50	100%	81%
5	25	100%	73%
6	12.5	50.5%	87%
7	6.5	33.6%	83%

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