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PHYLLANTHUS NIRURI LEAVES EXTRACTS AS A GREEN CORROSION INHIBITOR

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ABSTRACT

The anti-corrosion behavior of Phyllanthus Niruri leaves extracts in Well water solution on mild steel were studied using gravimetric method (weight loss method), FTIR spectroscopy and scanning electron microscope(SEM) techniques. The extracts were shown to have good inhibition efficiencies for the gravimetric method. Synergistic effect exists between the Phyllanthus Niruri - Ni²⁺ system in controlling the corrosion of mild steel immersed in Well water in the absence and presence of Ni²⁺. The formulation consisting of 250

ppm Phyllanthus Niruri, 20 ppm of Ni²⁺ have 90% inhibition efficiency. A more stable and compact protective film formed on the metal surface. The FT-IR and SEM analysis reveal that the protective film is formed on the metal surface.

KEY WORDS:

Phyllanthus Niruri, Corrosion Inhibition, Mild Steel, FT-IR and SEM.

1. INTRODUCTION:

Corrosion of metals and alloys particularly in acidic media is an important industrial problem. Hydrochloric acid which is widely used for pickling, cleaning, descaling and etching of metals, on the other hand also contributes to the corrosion of metal surface. A huge amount of money is wasted each year as a result of metallic corrosion, an estimated loss of 276 USD or equivalent to 3.1 percent of the United States GDP [1]. It is estimated that with proper corrosion prevention technologies, about 25 to 30 % of this loss could be avoided [1]. One of the best methods to reduce the rate of metallic corrosion is by the addition of inhibitors; even small concentrations can result in the decrease of the corrosion rate of the metal surface [2-8]. Several conditions must be fulfilled for the selection of a suitable inhibitor; (a) the cost and amount of the inhibitors, (b) long term toxicological effects on the environment and living species, (c) the inhibitor's availability and stability in the environment.

It has been found that different organic compounds could be used as effective corrosion inhibitors





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during acid pickling process [9-11]. Literature review reveals that organic compounds containing heteroatoms with high electron density such as phosphorus, nitrogen, sulfur, oxygen, with double or triple bonds in their structures are effective corrosion inhibitors due to their high tendency for adsorption [12-15]. It has been confirmed that the compounds having both nitrogen and sulfur in their molecular structure have excellent corrosion inhibition ability compared to those containing only nitrogen or sulphur, moreover sulfur containing compounds have generally stronger corrosion inhibition ability compared to nitrogen containing compounds [16–21]. Also the quantum chemical calculation analysis proves that enhancement of electron donor ability causes higher corrosion inhibition efficiency as a result of the presence of sulfur compounds [21]. It has been reported that the adsorption properties of organic inhibitors mainly depend on some physicochemical properties of the molecules; the functional groups, possible steric effects, electronic density of donor atoms and the possible interaction of p-orbitals of the inhibitor with d-orbitals of the surface atoms, establish a degree of adsorption of organic inhibitor molecules on the solid surface and results a barrier film for corrosion protection [22]. Literature study reveals a significant relationship between adsorption of organic compounds and corrosion inhibition process, as corrosion inhibition is a well-known surface phenomenon and adsorption is a function of degree of protection of the metal surface [23-26].

Phyllanthus niruri is a widespread tropical plant commonly found in coastal areas, known by the common names gale of the wind, stonebreaker or seed-under-leaf. It is a relative of the spurges, belonging to the Phyllanthus genus of Family Phyllanthaceae.

The major compounds in ethanol extract of P. amarus are benzene, 1, 2 – dimethoxy – 4 - [[(4-methylphenyl) sulfonyl] methyl] - (53.78%), Phenethylamine, 2-methoxy-alpha-methyl-4,5- (methylenedioxy) (28.57%) and phenanthylamine, 2-methoxy (8.40). The remaining compound in this extract are cyclopentane, phentyl (3.36%), 3-(3-(1-Axirdinyl) propoxy)- 2,5-dimethylpyrazine (2.52%) and 3- (Cycloprophylamino) propioitrile (1.68%) [27].

2. EXPERIMENTAL

2.1. Preparation of Specimen

Mild steel specimen [0.0267 % S, 0.06 % P, 0.4% Mn, 0.1 % C and the rest iron] of dimensions 1.0 cm × 4.0 cm × 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

2.2. Preparation of Extract

The Phyllanthus Niruri (PN) plant is shown in fig.1. An aqueous extract of Phyllanthus Niruri was prepared by grinding 25 g of Phyllanthus Niruri with double distilled water, filtering and suspending impurities, and making up to 250 ml. The extract was used as corrosion inhibitor in the present study.



Fig 1. Phyllanthus Niruri plant



2.3. Weight-Loss Method

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Mild steel specimens in triplicate were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the presence and absence of Ni²⁺ for one day. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleaned with Clarke's solution. The inhibition efficiency (IE) was then calculated using the equation:

IE = 100 [1- (W2/W1)] %

where W1 is the weight loss value in the absence of inhibitor and W2 is the weight loss value in the presence of inhibitor.

2.4. Surface Examination Study

The mild steel specimens were immersed in various test solutions for a period of three days. After three days, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analysed by various surface analysis techniques.

2.4.1. Scanning Electron Microscopic studies (SEM)

The mild steel specimen immersed in blank and in the inhibitor solution for a period of three days was removed, rinsed with double distilled water, dried and observed in a Scanning Electron Microscope to examine the surface morphology. The surface morphology measurements of the mild steel were examined using Hitachi S-3000 H computer controlled scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1. Weight-Loss Method

The corrosion inhibition efficiencies (IE) and corrosion rates of PN in controlling the corrosion of carbon steel immersed in Well water for a period of three days in the absence and presence of Ni²⁺ obtained by weight-loss method are given in table 1.

The inhibition efficiency increases with the increase of inhibitor concentration. This behavior could be attributed to the increase of the surface area covered by the adsorbed molecules of PN with the increase of its concentration. It is observed that PN alone has some IE and high rate of corrosion. Also, Ni²⁺ alone is found to have some IE. However, by increasing the concentration of PN as well as Ni²⁺, the maximum inhibition is achieved and the corrosion rate is decreased to a great extent. The formulation consisting of 250 ppm of PN and 20 ppm of Ni²⁺ has 90% IE. Therefore, the mixture of inhibitors shows better IE than the individual inhibitors. Thus, a synergistic effect is obtained.

Table 1. Inhibition efficiency (IE) of PN-Ni²⁺ system in controlling the corrosion of carbon steel immersed in Well water for a period of one day

Inhibition system: PN-Ni ²⁺			Immersion period: 3 days			
PN	Ni ²⁺ (0 ppm)		Ni ²⁺ (10 ppm)		Ni ²⁺ (20 ppm)	
(ppm)	IE %	CR (mmpy)	IE %	CR (mmpy)	IE %	CR (mmpy)
0	-	0.1493	12	0.1314	17	0.1239
50	24	0.1135	33	0.1000	61	0.0582
100	31	0.1030	41	0.0881	73	0.0403
150	39	0.0911	50	0.0747	84	0.0239
200	42	0.0866	58	0.0627	88	0.0179
250	46	0.0806	66	0.0508	90	0.0149



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3.2. Scanning electron microscopy (SEM)

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The scanning electron micrographs of mild steel are shown in Fig 2. The SEM micrograph of polished mild steel surface (control) is shown in Fig 2a. This shows the smoothness of the metal surface. This implies the absence of any corrosion product formed on the metal surface. The SEM micrograph of mild steel immersed in Well water is shown in Fig 2b. This shows the roughness of the metal surface by the corrosive environment and the porous layer of corrosion product is present. Pits are observed on the metal surface. Fig 4c shows that the presence of 250 ppm of PN and 20 ppm of Ni²⁺in Well water gives the formation of thick films on the mild steel surface. This may be interpreted as due to the adsorption of the inhibitor on the metal surface [28].



Fig.2. SEM images of mild steel surface (a) Polished metal (b) Well water (c) Well water+ 20 ppm of Ni^{2+} + 250 ppm PN

3.3. Mechanism of corrosion inhibition

In order to explain the above results, the following mechanism of corrosion inhibition is proposed: When mild steel is immersed in Well water, the anodic reaction is,

Fe $Fe^{2+} + 2e^{-}$

The corresponding cathodic reaction is reduction of oxygen to hydroxyl ions,

 $O_2 + 2H_2O + 4e^{-1}$ 4OH-

When the formulation consists of 250 ppm of PN and 20 ppm Ni^{2+} in Well water, there is formation of PN – Ni^{2+} complex in solution.

When mild steel is immersed in this environment, the $PN - Ni^{2+}$ complex diffuses from the bulk of the solution to the metal surface. The $PN - Ni^{2+}$ complex is converted into $PN - Fe^{2+}$ complex on the anodic sites of the metal surface, the stability of $Fe^{2+} - PN$ complex is higher than the corresponding Nickel complex. Ni^{2+} - PN + Fe^{2+} Fe^{2+} - PN + Ni^{2+}

The released Ni2+ combines with OH- to form Ni(OH)2 on the cathodic sites of the metal surface. Ni $^{2^+}$ + 2OH- Ni(OH)₂

The protective nature of the film is due to the presence of metal inhibitor complex and Nickel hydroxide. Formation of the metal inhibitor complex fills the pores of the otherwise porous film and makes it a protective film.

Thus, the protective film consists of Fe^{2+} – PN complex and Ni(OH)₂.

4. CONCLUSION

Synergistic effect exists between the Phyllanthus Niruri - Ni²⁺ system in controlling the corrosion of mild steel immersed in Well water in the absence and presence of Ni²⁺. The formulation consisting of 250



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