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*Azardirachtaindica*as Environment FriendlyCorrosion Inhibitor for Mild Steel in 5.0 M HCl Solution

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ABSTRACT

The dried powder of Azardirachtaindicaleaveson corrosion inhibition of mild steel in 5.0 M hydrochloric acid solution was investigated by Weight loss method, Potentiodynamic polarization, Gasometeric and Electrochemical Impedance Spectroscopy (EIS)techniques. The corrosion inhibition efficiency was found to increase with increase in concentration of the Azardirachtaindicafrom 0.1 to 4.0 g/l. Polarization measurement indicates that Azardirachtaindicaacts as a mixed-typecorrosion inhibitor. The inhibition is assumed to occur via adsorption of inhibitor molecules on metal surface. SEM and Metallurgical research microscopy studies confirmed the adsorption of inhibitor molecules on mild steel surface. More than 89.25 % corrosion inhibition efficiency was observed for mild steel in presence of 4.0 g/l of Azardirachtaindicain 5.0 M HCl solution.

Keywords: **Acid corrosion, EIS, SEM,Green corrosion inhibition, Mild Steel,*Azardirachta Indica*.**

I.INTRODUCTION

Corrosion is defined as loss in useful properties of material due to attack of atmospheric gases and moisture. Protection of materials from corrosion is very essential. Use of corrosion inhibitors is one of the methods to protect metal and their alloys from corrosion [1-5]. Majority of corrosion inhibitors are organic compounds containing heteroatoms, such as O, N, S and multiple bonds [6]. Many synthetic compounds show good anticorrosive properties, but most of them are highly toxic to both human beings and environments [7]. The natural product extracts such as plants and their products are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost, and are biodegradable in nature [8, 9]. The use of these natural products, such as extracted compounds from the leaves, flowers, seeds, roots and fruits as corrosion inhibitors have been recently reported by different authors. M.G. Sethuraman et al. [10] studied the anti-corrosiveproperties of the extract of black pepper on mild steel in 1.0 M acid media. P.C. Okafor [11] studied the inhibitive action of leaves, seeds and a combination of leaves and seeds extracts of phyllanthusamarus on mild steel corrosion in HCl and H_2SO_4solutions. A.M.Abdel-Gaber et al. [12] studied the anti-corrosive properties of lupine (lupinousalbus L.) extract on the corrosion of steel in aqueous solution of 1.0 M H_2SO_4 and 1.0 M HCl solution.

This study aims to gain some insight into the corrosion of mild steel in 5.0HCl in the presence of *Azardirachtaindica*as a green corrosion inhibitor. The dried powder of *Azardirachtaindica*leaves in 5.0 M HCl solution was tested by Weight loss, Gasometric technique, Potentiodynamic polarization and Electrochemical impedance techniques. SEM and metallurgical research microscopy studies were also carried out to study the surface morphology of corroded and non-corroded specimens.

II.MATERIAL AND METHODS

Preparation of Azardirachtaindica:

Double distilled water and analytical reagents-grade HCl(Sigma Aldrich, percentage purity 99.999%, 37.0wt % in water) were used for preparing solutions. The green leavesof *Azardirachtaindica*plantwere takenfrom the CDLU, campus. The leaves were first cleaned (Hand picked method)then dried first in sun and then in oven maintained at a constant temperature of 50.0 ^{0}C for 24.0 hours.Then dried leaves were crushed and grinded with help of mortar and pestle to make very fine powder which was used as such in different amount in 5.0 M HCl.

Weight loss method

Mild steel specimens having %age composition of C (0.17), Si (0.18), Mn (0.53), P (0.044), S (0.057), Cr (0.14), Ni (0.09), Mo (0.02), Cu (0.06), V (less than 0.01) and remaining Fe (chemical analysis: % by weight by equipment, IS:228) were used. Rectangular specimens with dimension 1.5×3.0×0.1 cm were used in weight loss experiments. The specimens were polished successively using emery papers of 100, 200, 320, 400, 600 and 1000 µ grade. The polished surface were degreased with acetone and washed with distilled water before the experiment. Weight loss of mild steel coupons immersed in 200.0 ml of the electrolyte with and without the green corrosion inhibitor was determined after 3.0 hours at 298.0 K. The corrosion rate and percentage corrosion inhibition efficiency (PCIE%) were calculated from the following equation[13]:

Corrosion rate (mpy) = $\frac{534 \times W}{DAT}$ …(1) Where, W = Weight loss (mg), D = Density of mild steel (gm/cm^3), A = Area of specimen (sq. inch), T = Exposure time (hours).

Percentage Corrosion Inhibition Efficiency = $\frac{CRo - CR}{CRo} \; X \; 100$ ... (2)

Where, CRo = weight loss in absence of inhibitor and CR = Weight loss in presence of inhibitor.

III.ELECTROCHEMICAL POLARIZATION MEASUREMENTS

An electrochemical cell assembly of three electrodes was used for potentiodynamic polarization and electrochemical impedance measurements. The working electrode (Mild steel) was coated thoroughly with epoxy resin keeping exposed surface area of 1.0 cm^2 for the study. The surface of the mild steel was abraded into uniform surface with 100, 200, 400, 600 µ grade emery papers and finally polished by 1000 grade emery papers.

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The polished surfaces were degreased with acetone and washed with distilled water before the experiment. The measurements were done by using computer controlled electrochemical workstation of PGSTAT 128N model of MetrohmAutolab. Ltd., Netherland. Before each polarization and EIS measurement, the working electrode was introduced into the test solution and kept for 2.0 hours to attain the open circuit potential (OCP). Polarization measurements were made under thermostatic conditions at 298 K, and the measurements were carried out in the range of potential from -1.2 to 2.0 V with scan rate of 0.01(V/s). The corrosion rate and percentage corrosion inhibition efficiency (PCIE) from the polarization measurement was calculated using the following equations [14]:

The corrosion current density i_{Corr}, is related to the corrosion rate by the equation,

Corrosion rate (C.R.) (mpy) = $\frac{0.1288 \times I_{Corr.} \times Eq.Wt.}{D}$ ….(3)

Where, Eq. Wt. = Gram equivalent weight of metal/alloy, D = Density of metal (g/cm^3), i_{Corr} = Corrosion current density (μA/cm^2).

PCIE = $\frac{CR_{(Blank)} - CR_{(Inhibitor)}}{CR_{(Blank)}} \times 100$ … (4)

Where, $CR_{(Blank)}$ is the corrosion rate in blank and $CR_{(Inhibitor)}$ is the corrosion rate in presence of inhibitor.

IV.ELECTROCHEMICAL IMPEDANCE MEASUREMENTS

Electrochemical Impedance measurements were carried out at 298.0 K temperature and the measurement of the response of the electrochemical system to a.c. excitation, with a frequency ranging from 10 000 to 1.0 Hz and peak to peak a.c. amplitude of 0.05 V with quiet time of 2.0 seconds, was done. The percentage corrosion inhibition efficiency (PCIE%) from the electrochemical impedance measurement was calculated using the following equation [15].

PCIE = $\frac{Rct_{(Inhibitor)} - Rct_{(Blank)}}{Rct_{(Inhibitor)}} \times 100$ …(5)

Where, $Rct_{(Inhibitor)}$ and $Rct_{(Blank)}$ are the values of charge transfer resistance in presence and in absence of inhibitor.

Gasometric Technique:

Gasometric technique is based upon the principle that corrosion reactions in aqueous media is characterized by the evolution of gas resulting from the cathodic reaction of the corrosion process, which is proportional to the rate of corrosion. The rate of evolution of gas is determined from the slope of volume of gas evolved versus time. Inhibition surface coverage and efficiencies will be determined with the help of rate of evolution of gas in the presence and absence of inhibitor molecule.

Surface analysis

The test coupons of mild steel after weight loss experiments in absence and presence of the plant extracts in 5.0 M HCl solutions at 298.0 K temperature were washedinitially under tap water and then with double distilled water and then with acetone. After drying the specimens,they were examined by SEM and inverted trinocular metallurgical research microscopy techniques for the surface study of corroded specimens.

V.RESULTS AND DISCUSSIONS

Weight loss method

The percentage corrosion inhibition efficiency (PCIE) at different concentrations of *Azardirachtaindica*at 298.0 K temperature are summarized in the Table 1. From the Table 1, it isclear that the percentage corrosion inhibition efficiency of the *Azardirachtaindica*increases with increase in concentration i.e. 0.1 to 4.0 g/l. It increases up to 85.25% when theconcentration of the inhibitor increases up to 4.0 g/l.*Azardirachtaindica*acts as very good green corrosion inhibitor even at very low concentration i.e. 0.1 g/l and provides more than 50.64% protection to mild steel surface at room temperature.

Potentiodynamic polarization measurement

Potentiodynamic polarization curves for mild steel in 5.0 M HCl solutions inabsence and presence of different concentration of *Azardirachtaindica*at298.0 K temperature are shown in Table 2. The values of icorr, corrosion potential (Ecorr), cathodic and anodic Tafel slopes (βc and βa) and percentage corrosion inhibition efficiency (PCIE) are given in the Table 2.

At a given temperature, the addition of *Azardirachtaindica*to theacid solution increases both the anodic and cathodic over-potentials and decreases the corrosion current density ($i_{Corr.}$). The change in cathodic and anodic Tafel slopes (βc and βa) shown in Table 2 indicates that adsorption of *Azardirachtaindica*modifies the mechanism of the anodic dissolution as well ascathodic hydrogen evolution. It is clear that both cathodic andanodic reactions are inhibited and the inhibition increases as the green corrosion inhibitorconcentration increases in acid media. From Table 2, it is clear that $E_{Corr.}$ values increases in presence of different concentrations of*Azardirachtaindica*in 5.0 M HCl solution. This result indicates that*Azardirachtaindica*can be classified as a mixed type of inhibitor in 5.0 MHCl solutions.

Gasometric measurements

Amount of gas evolved (ml), Surface coverage (θ) and Percentage corrosion inhibition efficiency (PCIE) of *Azardirachtaindica*at different concentrations by Gasometric method at 25^0C temperature in 5.0 M HCl solution are shown in Table 3. It is observed from Table 3 that the value of RVh decreases with increase in concentration of inhibitor i.e. 0.1 to 4.0 g/l. The PCIE increases with increase in concentration of inhibitor.

EIS measurements

EIS technique was applied to investigate the electrode/electrolyte interface andcorrosion processes that occur on mild steel surface in presence and absence of*Azardirachtaindica*. To ensure complete characterization of the interfaceand surface processes, EIS measurements were made at OCP in a wide frequency range at 298 K. Figure 3 shows Nyquist plots for mild steel electrode immersed in5.0 M HCl solution at 298 K in absence and presence of various concentrationsof the green corrosion inhibitor at the respective open circuit potential. It is clear from Figure 3 thatthe diameter of the semicircle increases with the increase in inhibitorconcentration in the electrolyte, indicating an increase in corrosion resistance ofthe material.

The value of electrochemical double layer capacitance (C_{dl}) was calculated at the

frequency, $f_{max.}$ using the following equation.

$$C_{dl} = \frac{1}{2\pi f_{max.} R_{CT}} \qquad \ldots(6)$$

Where, $f_{max.}$ is the frequency at which the imaginary component of the impedanceis maximum.

The impedance data listed in the Table 6 indicate that the values of both R_{CT} andPCIE % are found to increase with increase in green corrosion inhibitor concentration, while thevalues of C_{dl} are found to decrease. This behavior can be attributed to a decrease in the dielectric constant and/ or an increase in the thickness of the electric double layer, suggesting that the inhibitor molecules act by adsorptionmechanism at mild steel/acid interface

VI.METALLURGICAL RESEARCH MICROSCOPY TECHNIQUE

Trinocular Inverted metallurgical research micrographs of different mild steels samples with and without *Azardirachtaindica*as green corrosion inhibitorat different concentrations are shown in Figure 2. It is observed from the Figure 2 that surface of sample becomes more clear and clean with increase in concentration of *Azardirachtaindica*. Cracks and pits are clearly visible in blank specimens but there are no cracks or pits in the samples treated with 4.0, 2.0, 1.0 and 0.5 g/l of *Azardirachtaindica*. However, there is slight uniform type of corrosion in the samples treated with 0.1 g/l of *Azardirachtaindica*.

Coating thickness, percentage porosity and pits pore length of mild steel coupons with and without corrosion inhibitor are shown in Table 5. It is observed from the Table 5 that coating thickness increases with increase in concentration of inhibitor. Percentage porosity decreases with increase in concentration of *Azardirachtaindica*i.e. 0.1 to 4.0 g/l.

VII.CONCLUSIONS

The corrosion inhibition efficiency of dried powder of *Azardirachtaindica*on mildsteel in 5.0 M HCl solution increases with increase in concentration of thegreen corrosion inhibitor. tentiodynamicpolarizationmeasurement shows that *Azardirachtaindica*act as a mixed type inhibitor.EIS measurement reveals that charge transfer resistance increases withincrease in concentration of the *Azardirachtaindica,* indicating that the inhibition increaseswith increase in concentrations.Surfacestudies confirm that corrosion inhibition of mild steel in 5.0 MHCl is due to adsorption of the *Azardirachtaindica*on it. Metallurgical research microscopy images reveal that coating thickness increases and percentage porosity decreases with increase in concentration of *Azardirachtaindica*. More than 89.25 % corrosion inhibition efficiency was shown to the mild steel by 4.0 g/l of dried powder of *Azardirachtaindica*in 5.0 M HCl solution at room temperature.

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Table 1. Weight loss, Corrosion rate and Percentage Corrosion Inhibition Efficiency (PCIE) of Neem Leaves (*Azardirachtaindica*) at different concentrations by Weight Loss technique at 25.0^{0}C in 5.0 M HCl solution.

S. No.	Concentration (g/l)	Weight loss (g)	Corrosion rate (mpy)	PCIE
1.	Blank	0.05075	664.231	-
2.	4.0	0.00545	71.3896	89.25
3.	2.0	0.00902	117.9793	82.23
4.	1.0	0.0108	141.2088	78.74
5.	0.5	0.0129	168.4952	74.63
6.	0.1	0.0251	327.8949	50.64

Table 2. Open Circuit Potential (OCP), Corrosion Current Density (I_{corr}), anodic Tafel slope (β_a), cathodicTafel slope (β_c), Resistance polarization (R_p), Corrosion Rate (CR) and
PCIEof Neem Leaves (*Azardirachtaindica*) at different concentrations for mild steel by electrochemical polarization method at 25.0 ^{0}C in 5.0 M HCl solution.

S. No.	Conc. (g/l)	OCP	I_{corr}(μA/cm^2)	βa	βc	Rp	CR (mpy)	PCIE
1.	Blank	-0.528	4.48	5.935	7.637	3.66 ×10^{5}	1.7279	-
2.	4.0	-0.676	0.92	0.286	0.549	2.65×10^{4}	0.3548	79.46
3.	2.0	-0.298	1.10	4.215	2.501	1.38×10^{5}	0.4242	75.44
4.	1.0	-0.467	1.78	8.164	15.659	3.85×10^{5}	0.6865	60.26
5.	0.5	-0.603	2.01	15.493	0.990	6.29×10^{4}	0.7752	55.13
6.	0.1	-0.618	2.27	3.811	2.828	1.03×10^{5}	0.8755	49.33

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Table 3. Amount of gas evolved (ml), Surface coverage (θ) and Percentage corrosion inhibition efficiency (PCIE) in presence of *Azardirachtaindica*(Neem leaves) as green corrosion inhibitor at different concentrations by Gasometric method at25^{0}C temperature in 5.0 M HCl solution.

S. No.	**Concentration (g/l)**	**RVh**	**Surface coverage (θ)**	**PCIE**
1.	Blank	1.0787	-	-
2.	4.0	0.2106	0.8047	80.47
3.	2.0	0.2146	0.8010	80.10
4.	1.0	0.2146	0.8010	80.10
5.	0.5	0.2681	0.7515	75.15
6.	0.1	0.3363	0.6882	68.82

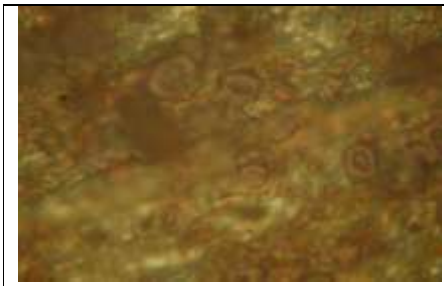
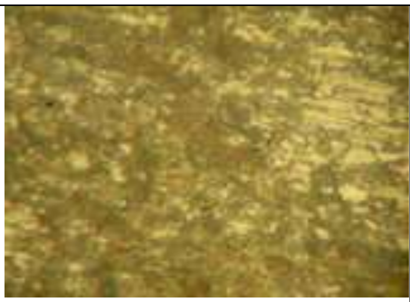
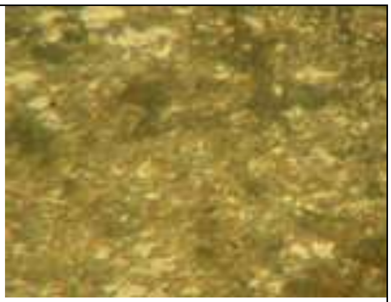
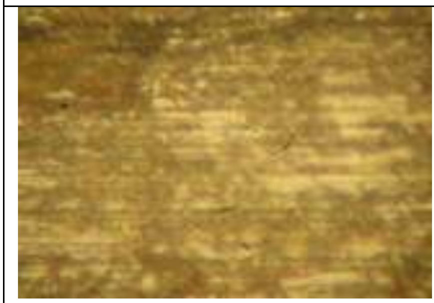
		
Blank (1)	*Azardirachtaindica* (0.1 g/l)	*Azardirachtaindica* (0.5 g/l)
		
Azardirachtaindica(1.0 g/l)	*Azardirachtaindica*(2.0 g/l)	*Azardirachtaindica*(4.0 g/l)

Figure 1. Trinocular Inverted MetullurgicalResearch Micrographs of different mild steel samples with and without *Azardirachtaindica*as green corrosion inhibitor at differentconcentrations.

Table 4. Coating thickness, percentage porosity and pore length of mild steel coupons with andwithout green corrosion inhibitor.

Name of Sample	**Coating Thickness (**Micron)	**Percentage porosity**	**Pore Length (**Micron)
Blank	48.764	77.27	577.397 645.23
Neem leaves 4.0 g/l	233.652	18.8	94.842 93.487
Neem leaves 2.0 g/l	215.907	24.66	113.706 116.044
Neem leaves 1.0 g/l	185.233	36.51	142.235 148.870
Neem leaves 0.5 g/l	140.338	48.37	157.865 157.982
Neem leaves 0.2 g/l	83.325	59.28	188.407 181.640
Neem leaves 0.1 g/l	56.816	61.35	194.883 194.334

Table 5. Electrochemical impedance parameters for mild steel samples in 5.0 MHClsolution in absence and presence of different concentrations of *Azardirachtaindica*at room temperature.

(Conc.) g/L	**Cdl($\times 10^{-3}$ F cm^2)**	**Rct(Ω cm^2)**	**PCIE %**
0.0	208	8.76	-
4.0	48.42	37.62	76.71
2.0	53.08	34.32	74.47
1.0	61.86	29.45	70.25
0.5	71.95	25.32	65.40
0.1	85.77	21.24	58.75

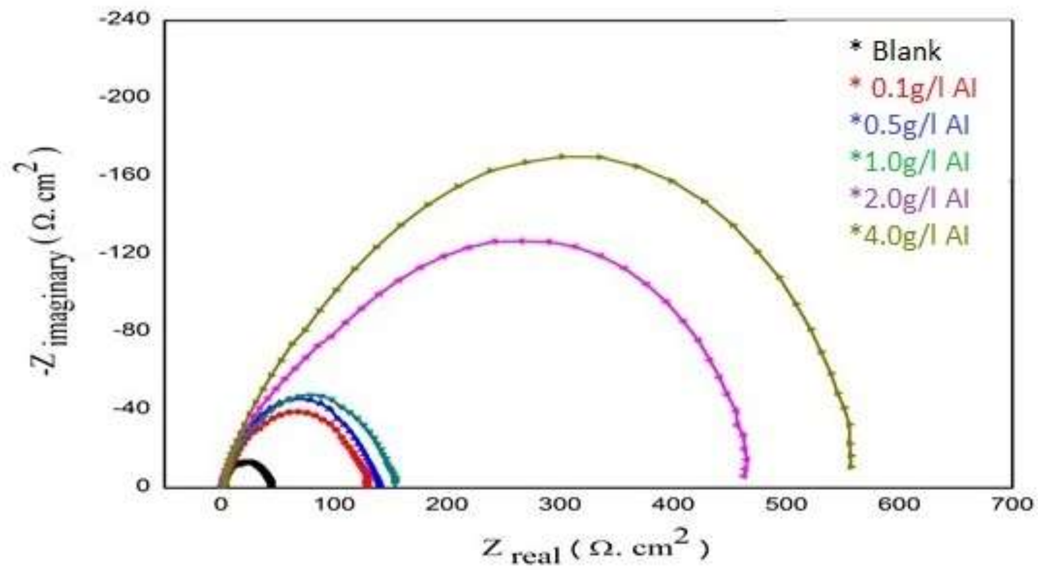


Figure 2.Nyquist plots (EIS) of mild steel immersed in 5.0 M HCl in absence andpresence of different concentrations of *Azardirachtaindica*(AI) at 298.0 K temperature.