MILD STEEL CORROSION INHIBITION BY AQUEOUS LEAVES EXTRACT OF SCOPARIA DULCIS IN ACID MEDIUM

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ABSTRACT

The inhibitive effect of *Scoparia dulcis* leaves extract on the corrosion of mild steel in acid medium was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The stability of the inhibition efficiency of *Scoparia dulcis* extract was examined by weight-loss method. The corrosion rates of steel and the inhibition efficiencies of the extract obtained from impedance and polarization measurements were in good agreement. Inhibition was found to increase with an increasing concentration of the plant extract. The results obtained show that the *Scoparia dulcis* could serve as an effective inhibitor for the corrosion of mild steel in acid medium.

KEYWORDS: Mild steel, Corrosion inhibition, *Scoparia dulcis* extract, HCl, potentiodynamic polarization, EIS.

INTRODUCTION

Corrosion is the deterioration of metal by chemical attack or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely. Prevention would be more practical and achievable than complete elimination. Acid solutions, widely used in industrial acid cleaning, acid descaling, acid pickling, and oil well acidizing, require the use of corrosion inhibitors in order to restrain their corrosion attack on metallic materials. Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origin in various corrosive media.[1–3] The role of inhibitors is to form a barrier of one or several molecular layers against acid attack. Several inhibitors in use are either synthesized from cheap raw material or chosen from compounds having hetero atoms in their

aromatic or long-chain carbon system. However, most of these inhibitors are toxic to the environment. This has prompted the search for green corrosion inhibitors.

Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment. Up till now, many plant extracts have been used as effective corrosion inhibitors for iron or steel in acidic media, such as: Matricaria recutita,[4] Moringa oleifera,[5] henna,[6] have a good inhibitive property. Ethanol extract of phyllanthus amarus green inhibitor has been used to prevent the corrosion of mild steel in H_2SO_4.[7] Terminalia catappa extract also exhibits excellent corrosion inhibitive properties.[8] The scale inhibition efficiencies of the aqueous extracts of plant materials, namely Cordia latifolia, Eucalyptus and Jasmine auriculatum have been evaluated.[8] Caffeine has been used as inhibitor in controlling corrosion of mild steel immersed in an aqueous solution containing 60ppm of Cl.[9] Rajendran et al. studied the aqueous extracts of rhizome powder,[10] beet root extract,[11] and Hibiscus rosa-sinensis as corrosion inhibitors. The inhibition performance of plant extract is normally ascribed to the presence of complex organic species, including tannins, alkaloids and nitrogen bases, carbohydrates and proteins as well as hydrolysis products in their composition.

The present work investigated the inhibition efficiency of an aqueous extract of plant material, *Scoparia dulcis* extract, in controlling corrosion of mild steel immersed in an 1.0 N HCl solution containing using a mass loss study, potentiodynamic polarization and impedance methods.

MATERIALS AND METHODS

Extract of *Scoparia dulcis* leaves is used as corrosion inhibitor in the present study. The leaves and flowers of *Scoparia dulcis* is shown in fig.1.

Fig 1: *Scoparia dulcis* plant.

The botanical details of *Scoparia dulcis* **are given below***: Scientific classification*

Kingdom: Plantae

(unranked): Angiosperms

(unranked): Eudicots

(unranked): Asterids

Order: Lamiales

Family: Plantaginaceae

Subfamily: Commelinoideae

Genus: Scoparia

Species: S. Dulcis

Binomial name: Scoparia dulcis

Therapeutic uses

In fresh or dried form *Scoparia dulcis* plants have been traditionally used as remedies for stomach troubles, hypertension, diabetes, bronchitis, analgesic and antipyretic as well as inhibition of herpes simplex virus replication, gastric H+,K+-ATPase activation and antitumor activity.

Phyto-chemical screening of *Scoparia dulcis* **leaves extract is given in Table -1 [12]**

Constituent	Aqueous extract	Ethanol extract	Methanol extract	Chloroform extract	Hexane extract	Ether extract
Flavonoids	+	+	+	+	-	-
Steroids	-	-	-	-	+	+
Quinone	+	+	-	-	-	-
Starch	+	+	-	-	+	+
Anthocyanin	-	-	-	-	-	-
Cellulose	-	-	-	+	+	-
Terpenoids	+	+	-	-	+	-
Phenols	+	+	+	-	-	-
Carbohydrates	+	+	+	-	-	-
Fixed oil and Fat	+	-	-	+	-	-
Saponins	+	-	+	-	-	+

Preparation of Extract

Cold Percolation method

The leaves were collected, shade dried and powdered. About 1g of the powdered leaves was macerated with 1000 ml of double distilled water and tightly covered with aluminium foil and kept for 24 hrs. After 24 hrs, the macerated extract was filtered through Whatmann filter paper. From the extract, the various concentrations were prepared.

Materials and chemicals used

Composition of mild steel

Mild steel specimens (0.026%-S, 0.06%-P, 0.4%-Mn, 0.1%-C and the rest iron) of the dimensions $1\times5\times0.2$ cm were polished to mirror finish, degreased with acetone and used for the weight loss method.

For polarization, cylindrical mild steel rod embedded in Teflon with an exposed area of $1cm^2$ was used. The electrodes were polished with emery papers of 0/0, 2/0, 3/0, and 4/0 grades and degreased with acetone, dried and used.

Weight loss method

Weight loss measurements were performed in 1.0 N HCl with and without the presence of inhibitor. Concentrations in this acid was carried out by various concentrations using the formula

Inhibition efficiency (%) = W_0-W_i/$W_0\times100$

where, W_0 = Weight loss in blank

W_i = Weight loss in presence of inhibitor

Electrochemical studies

Polarisation study and AC impedance spectra were recorded in a potentiostate. The experiments were recorded in a three electrode cell assembly. Mild steel was used as working electrode. SCE was used as reference electrode. A platinum foil was used as counter electrode**.** The working electrode used was a mild steel rod of the same composition embedded in araldite and with an exposed area of 1 cm^2.

From potentiodynamic polarization study, corrosion current, corrosion potential and the Tafel slopes were derived. From AC impedance spectra, charge transfer resistance and double layer capacitance were calculated.

The area of the counter electrode is much larger compared to the area of the working electrode. This will exert a uniform potential field on the working electrode.

A solution quantity of 100 ml of the test solution was taken in a polarization cell. The working electrode was polished with 0/0, 1/0, 2/0, 3/0, and 4/0 emery papers successively and degreased with acetone. The working electrode, reference and auxiliary platinum electrodes were assembled and connections were made.

Stirring was provided to the test solutions to avoid for the system the concentrations polarization before start of experiment. A time interval of about 15 minutes was given for the system to attain state and open circuit potential was recorded.

RESULTS AND DISCUSSION

Weight loss studies

Table-2 gives the inhibition efficiency of different concentrations of *Scoparia dulcis* leaves extract in 1.0 N HCl. The inhibition depends upon the nature and mode of adsorption of metal surface. The adsorption is assumed to be a quasi-substitution process between the water molecules on the surface and any one of the natural components present in the inhibitor.

The interaction of inhibitor with the metal may occur through any of the component (anchoring group) present in the inhibitor and also to the interaction of π electrons present in the components with metal surface, thereby enabling the compound to get adsorbed on the metal surface.

Table 2: Inhibition effect of corrosion of mild steel in 1.0 N HCl using *Scoparia dulcis* leaves extract.

[Inhibitor], ppm	Rate of corrosion, g cm^{-2} hr^{-1}	Inhibition Efficiency (%)
Blank	0.002292	-
100	0.001958	14.55
200	0.001500	34.55
300	0.001042	54.55
400	0.000958	58.18
500	0.000792	65.45
600	0.000625	72.73
700	0.000458	80.00
800	0.000250	89.09
900	0.000083	96.36

Adsorption isotherms

Adsorption isotherms are usually used to describe the adsorption process. The most frequently used isotherms include: Langmuir, Temkin, Florry-Huggins, and the recently formulated thermodynamic/kinetic model of El-Awady et al. The establishment of adsorption isotherms that describe the adsorption of a corrosion inhibitor can provide important clue to the nature of the metal-inhibitor interaction. Adsorption of the organic molecules occurs as

the interaction energy between molecules and metal surface is higher than that between the H_2O molecules and the metal surface.

Langmuir isotherm

In order to obtain the adsorption isotherm, the degree of surface coverage (Θ) for various concentrations of the inhibitor has been calculated according to its equation. Langmuir isotherm was tested for its fit to the experimental data. Langmuir isotherm is given by

$$C/\Theta = 1/K_{ads} + C$$

Where Θ is the degree of surface coverage, C the molar inhibitor in the bulk solution and K_{ads} is the equilibrium constant of the process of adsorption. Langmuir isotherm assumes that:

The metal surface contains a fixed number of adsorption sites and each site holds one adsorbate;

ΔG^0_{ads} is the same for all sites and it is independent of Θ;

The adsorbates do not interact with one another, ie, there is no effect of lateral interaction of the adsorbates on ΔG^0_{ads}

Table-3 shows the obtained values were fitted to Langmuir isotherm and the best fit to the experimental data was obtained.

The plot of log ($\Theta/1-\Theta$) vs. log C is a straight line shown in fig. 2. Thus the Langmuir isotherm is valid for the inhibitor.

Table 3: Langmuir adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 N HCl using *Scoparia dulcis* leaves extract.

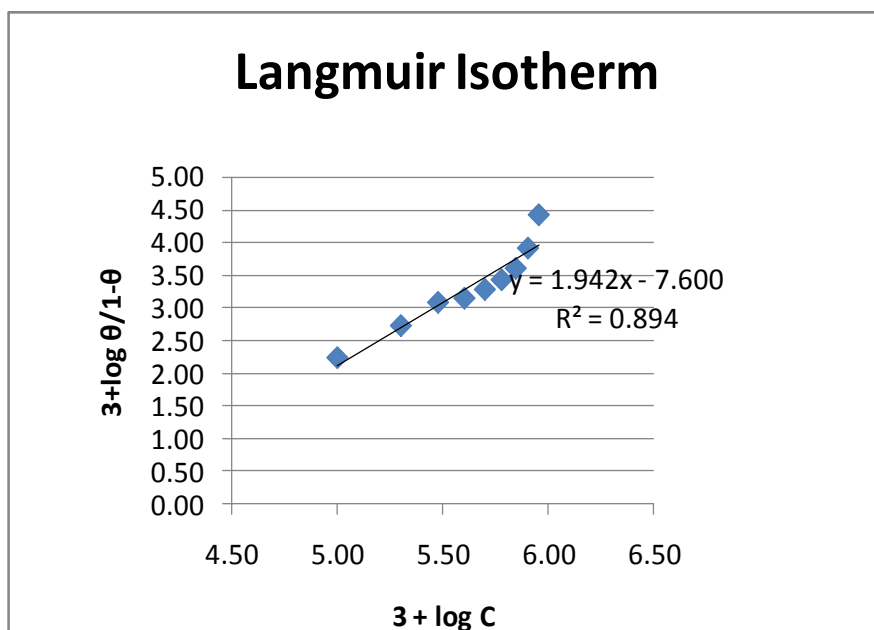| [Inhibitor], ppm	$\Theta/(1-\Theta)$	$3+\log\Theta/(1-\Theta)$	$3+\log C$
Blank	-	-	-
100	0.1702	2.2310	5.0000
200	0.5278	2.7225	5.3010
300	1.2000	3.0792	5.4771
400	1.3913	3.1434	5.6021
500	1.8947	3.2775	5.6990
600	2.6667	3.4260	5.7782
700	4.0000	3.6021	5.8451
800	8.1667	3.9120	5.9031
900	26.5000	4.4232	5.9542

Fig. 2: Langmuir adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 N HCl using *Scoparia dulcis* leaves extract

Temkin adsorption isotherm

It is given by the expression:

θ = -2.303 log K/2a – 2.303 log C/2a

Where 'K' is the adsorption equilibrium constant, 'a' is the lateral interaction parameter. **Table-4** shows the values of Temkin isotherm and the plots of (2+log C) against θ is shown in **fig. 3.** The linear plot indicates that Temkin adsorption isotherm was obeyed.

Table 4: Temkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 N HCl using *Scoparia dulcis* leaves extract.

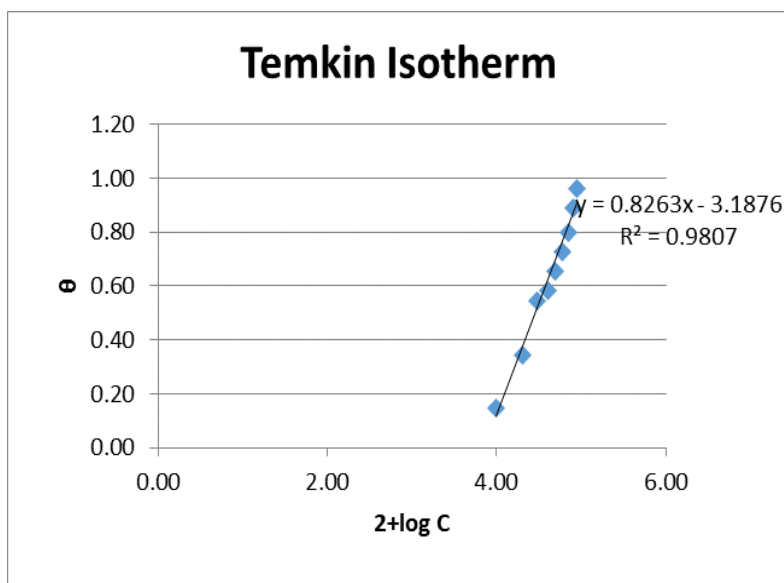| [Inhibitor], ppm	2+log C	θ
100	4.00	0.15
200	4.30	0.35
300	4.48	0.55
400	4.60	0.58
500	4.70	0.65
600	4.78	0.73
700	4.85	0.80
800	4.90	0.89
900	4.95	0.96

Fig. 3: Temkin adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 N HCl using *Scoparia dulcis* leaves extract.

Florry-Huggins adsorption isotherm

It is given by the expression,

$\log \theta/c = \log K + x \log (1-\theta)$

Where 'x' is the size parameter and it is a measure of the number of adsorbed water molecules substituted by an inhibitor molecule. Table-5 shows the values of Florry-Huggins adsorption isotherm and the plot of 3+log Θ/C against 3+log (1-Θ) is linear as shown in fig. 4 indicating Florry-Huggins isotherm was obeyed.

Table 5: Florry-Huggins adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 N HCl using *Scoparia dulcis* leaves extract

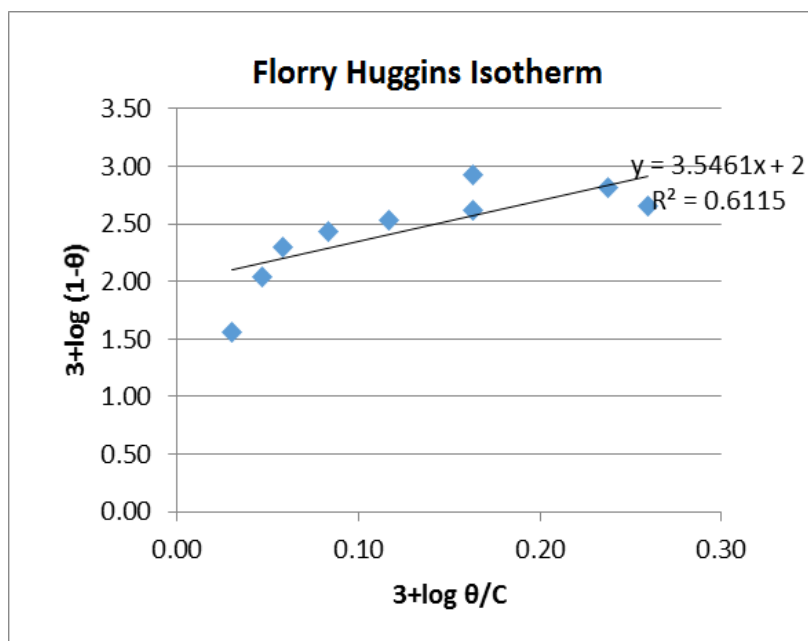| Θ	[C], ppm	Θ/C	3+logΘ/C	1- Θ	3+log(1-Θ)
0.1455	100	0.0015	0.1627	0.8545	2.9317
0.3455	200	0.0017	0.2374	0.6545	2.8159
0.5455	300	0.0018	0.2596	0.4545	2.6576
0.5818	400	0.0015	0.1627	0.4182	2.6214
0.6545	500	0.0013	0.1170	0.3455	2.5384
0.7273	600	0.0012	0.0835	0.2727	2.4357
0.8000	700	0.0011	0.0580	0.2000	2.3010
0.8909	800	0.0011	0.0467	0.1091	2.0378
0.9636	900	0.0011	0.0297	0.0364	1.5607

Fig 4: Florry-Huggins adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 N HCl using *Scoparia dulcis* leaves extract.

El-awady isotherm

It is given by the expression:

log (θ/1-θ) = log K + y log C.

Here K_{ads} is the equilibrium constant of adsorption process is calculated by the relationship, $K_{ads} = 1/k$. Table-6 and a plot of 2+log (θ/1-θ) against 2+log C is linear as in fig. 5 showing that El-awady isotherm was obeyed.

Table 6: El-awady adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 N HCl using *Scoparia dulcis* leaves extract.

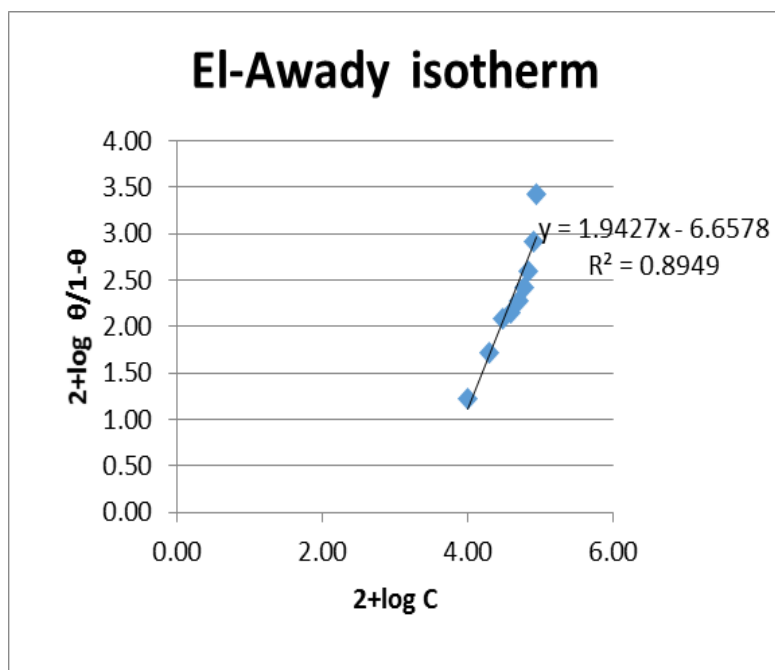| [C], ppm	2+log C	θ	1- θ	θ/1- θ	2+log (θ/1-θ)
100	4.0000	0.1455	0.8545	0.1702	1.2310
200	4.3010	0.3455	0.6545	0.5278	1.7225
300	4.4771	0.5455	0.4545	1.2000	2.0792
400	4.6021	0.5818	0.4182	1.3913	2.1434
500	4.6990	0.6545	0.3455	1.8947	2.2775
600	4.7782	0.7273	0.2727	2.6667	2.4260
700	4.8451	0.8000	0.2000	4.0000	2.6021
800	4.9031	0.8909	0.1091	8.1667	2.9120
900	4.9542	0.9636	0.0364	26.5000	3.4232

Fig. 5: El-awady adsorption isotherm for the inhibition of corrosion of mild steel in 1.0 N HCl using *Scoparia dulcis* leaves extract.

Free energy change

The free energy change of adsorption (ΔG^0_{ads}) of inhibitor on mild steel surfaces related to the constant of the adsorption according to equation.

$$\Delta G^0_{ads} = -2.303 \ RT \log (K_{ads} \times 55.5)$$

From the results, showed in table-7 values of ΔG^0_{ads} were found to be negative and were above and below the threshold value of -40kJ/mol indicating that the adsorption of *Scoparia dulcis* on mild steel surface is spontaneous and that mechanism of both physical adsorption and chemical adsorption is applicable.

Table 7: Adsorption isotherms parameter for inhibition of corrosion of mild steel in 1.0 N HCl using *Scoparia dulcis* leaves extract.

System	Isotherm	ΔG^0_{ads}	Slope	R^2	A	1/y
	Langmuir Isotherm	-1481.35	-7.600	0.8949	-	0.5147
Scoparia dulcis leaves extract	Temkin Isotherm	-3087.50	-3.1876	0.9807	-0.3612	1.2102
	Florry-Huggins Isotherm	-5362.50	2.0000	0.6115	-	0.2819
	El-awady Isothern	-1645.50	-6.6578	0.8949	-	0.5147

The R^2 value shows that Temkin is the best fit isotherm.

Potentiodynamic polarization studies

Table-8 and figs. 6-8 gives the values of potentiodynamic parameters such as corrosion current (I_{corr}), corrosion potential (E_{corr}) and the cathodic Tafel slopes (b_c and b_a) for the different concentrations shown in the green inhibitor understudy. It can be seen that the any one of the compound present in the inhibitor adsorbed on metal surface.[13-17]

Table 8: Corrosion parameters obtained from polarization curves for mild steel in 1.0 N HCl in the presence and absence of inhibitor.

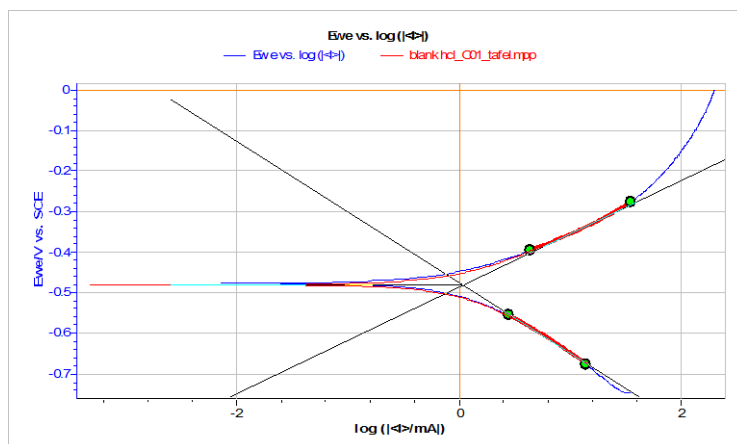| System	[Inhibitor], ppm	I_{corr}., mV	$-E_{corr}$., mV	b_a., mV dec^{-1}	b_c., mV dec^{-1}	Inhibition Efficiency, (%)
Blank	-	1092.015	480.818	131.1	165.4	-
Scoparia dulcis leaves extract	100	936.794	496.140	135.3	174.2	14.21
	900	42.582	533.461	184.4	211.6	96.10

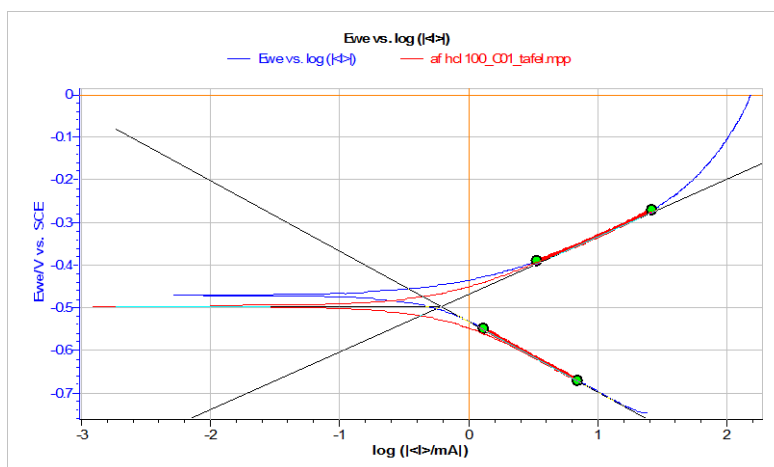**Fig. 6: Potentiometric polarization curve for mild steel in 1.0 N HCl.**

Fig. 7: Potentiometric polarization curve for 1.0 N HCl medium in the presence of 100ppm concentration of *Scoparia dulcis* leaves extract.
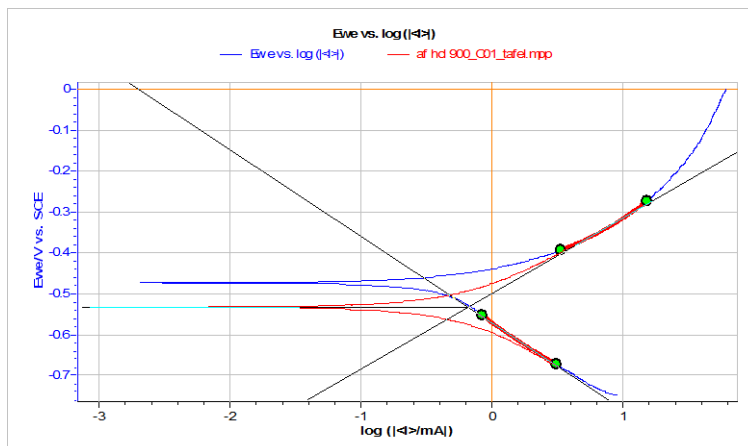
Fig. 8: Potentiometric polarization curve for 1.0 N HCl medium in the presence of 900ppm concentration of *Scoparia dulcis* leaves extract.

AC impedance study

Table-9 and figs. 9-11 indicates that AC impedance curves and values for inhibitor concentration. The R_t value increases and C_{dl} value decreases with inhibitor concentration. This implies the formation of protective film on the metal surface. It can be also seen from table-10 that there is a close agreement between the values of inhibition efficiencies obtained from weight loss measurements, polarization and impedance studies.[18-23]

Table 9: Corrosion parameters obtained from impedance study for mild steel in 1.0 N HCl in the presence and absence *of Scoparia dulcis* leaves extract.

[Inhibitor], ppm	R_t, Ohm cm²	C_{dl}, F/cm²	Inhibition Efficiency (%)
Blank	23.08	0.210	-
100	27.29	0.179	14.76
900	40.48	0.008	96.19

Table 10: Comparison of inhibition efficiency measured by weight loss, polarization and impedance studies for 1.0 N HCl.

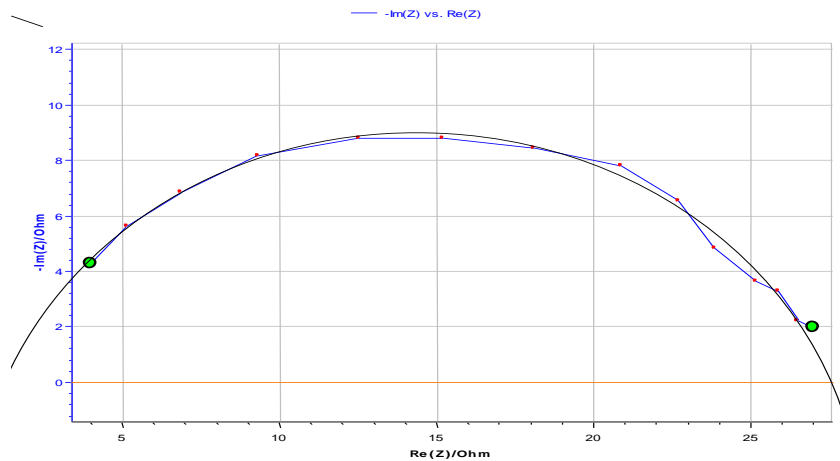| [Inhibitor], ppm	Inhibition Efficiency (%)		
	Weight loss study	Polarization study	Impedance study
100	14.55	14.21	14.76
900	96.36	96.10	96.19

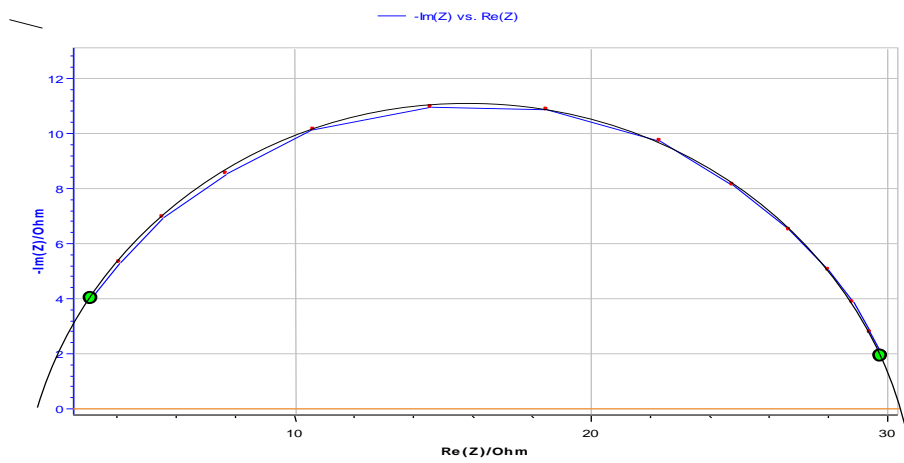**Fig. 9: Impedance diagram for mild steel in 1.0 N HCl.**

Fig. 10: Impedance diagram for mild steel in 1.0 N HCl medium in the presence of 100ppm concentration of *Scoparia dulcis* leaves extract.
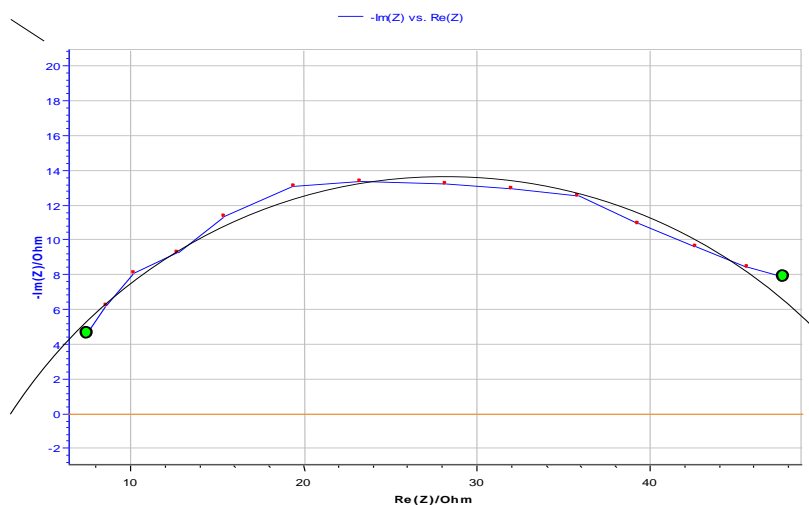

Fig. 11: Impedance diagram for mild steel in 1.0 N HCl medium in the presence of 900ppm concentration of *Scoparia dulcis* leaves extract.

CONCLUSIONS

1. Leaves extract of *Scoparia dulcis* inhibited mild steel in acid solution.

2. The percentage of inhibition efficiency increases with increases of the inhibitor concentration.

3. The mass loss measurements are in good agreement with electrochemical method.

4. From the results obtained we can conclude the following. *Scoparia dulcis perfectly inhibits the corrosion of mild steel in* 1.0 N HCl solution.

5. The free energy values for the adsorption processes indicates that both physisorption and chemisorptions (comprehensive adsorption) of the *Scoparia dulcis* leaves extract studied on the mild steel surface.

6. The values obtained from the weight loss technique for the studied inhibitor fit into the Temkin adsorption isotherm.

7. The inhibition efficiency is attributed to the strong adsorption of *Scoparia dulcis* leaves extract onto the mild steel surface.

8. The results suggest *Scoparia dulcis* leaves extract is a best eco-friendly inhibitor.

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