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Citrus sinensis peels as a Green Corrosion Inhibitor for Mild Steel in 5.0 M Hydrochloric Acid Solution

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Abstract

Corrosion characteristics of dried peels of Citrus sinensis (sweet orange) on mild steel (MS) in 5.0 M HCl solution was studied by Weight loss, Gasometric, Electrochemical Polarization and Impedance Spectroscopic techniques. The percentage corrosion inhibition efficiency (PCIE) increases with increase in concentration of the Citrus sinensis from 0.1 to 4.0 g/l. Polarization measurement indicates that Citrus sinensis acts as mixed-type corrosion inhibitor. The corrosion protection to metal surface was provided via adsorption of green corrosion inhibitor. SEM and Metallurgical Research Microscopy study proves adsorption of green corrosion inhibitor (CI) molecules on MS surface. More than 93.0 PCIE was observed for MS at 4.0 g/l of Citrus sinensis in 5.0 M HCl solution.

Keywords: Acid corrosion, EIS, SEM, Corrosion inhibition, Mild Steel, *Citrus sinensis*.

Introduction

Protection of different metals and their alloys from corrosion in acidic solution is the most demanding work in present research due to the large number of applications in the field like acid handling and cleaning industry, descaling industry, oil recovery industry and petrochemical related industry[1-5]. Most of the chemical based corrosion inhibitors used nowadays are organic compounds based which possess hetero atoms like N, O, S and some unsaturation[6]. Although organic compounds based corrosion inhibitors (CI) shows high PCIE but they are very poisonous to life as well as environment[7]. The current research is focused on the development of cost effective, safe and green corrosion inhibitors like plants or their products. The plant parts or their products are extensively researched for their anticorrosive properties as these are low in cost, bio-degradable and are eco-friendly in nature[8]. The purpose of using plants parts or their products like leaves, flowers, seeds, roots and fruits is that they are cheap, easily available and biodegradable in nature[9]. Sethuraman and his co-workers[10] investigated the anticorrosive properties of black pepper in 1.0 M acid solution for MS. Anticorrosive properties of leaves, seeds and their combinations of *Phyllanthus amarus* on mild steel in HCl and H_2SO_4 solutions was investigated by P.C. Okafor[11]. Abdel-Gaber and his co-workers investigated the corrosion inhibitive properties of *lupinous albus L.* on the MS in 1.0 M H_2SO_4 and 1.0 M HCl[12]. Orubite and his co-workers studied the anticorrosive properties of mild steel in hydrochloric acid medium by the use of leaves of *Nypa fruticans wurmb*[13]. Eddy and his team mates investigated the corrosion inhibition and surface adsorption characteristics of alcoholic extract of *Verninia amygdalina* on MS[14].

Present study is focused on corrosion characteristics of *Citrus sinensis* as a green CI for MS in 5.0 HCl. The dried peels of fruit of *Citrus sinensis* plant in 5.0 M hydrochloric acid was experienced by weight loss, Gasometric technique, electrochemical polarization and impedance spectroscopic techniques. Scanning Electron Microscopy and Metallurgical research microscopy techniques were used to study the surface characteristics and types of corrosion taking place at the surface of mild steel.

The citrus fruit *orange* popularly known as sweet *orange,* belongs to species *Citrus sinensis* in family of Rutaceae. The orange is extensively cultivated throughout the world. The fruit peels of *Citrus sinensis* have been reported to be used in the treatment of different ailments[15]. However, literature survey shows that no experiments have been carried out on the inhibitive effects of peels of *Citrus sinensis* on mild steel in acidic environment.

Materials and Methods

Preparation of Citrus Sinensis: Double distilled water and analytical reagents-grade HCl (Sigma Aldrich, percentage purity 99.999%, 37.0 wt % in water) were used for preparing solutions. The dried fruit peels of *Citrus sinensis* were cut fresh direct from the plant and washed with supply water and then with double distilled water. Then peels of the fruits were separated out and dried first in sun and then in oven maintained at a fix temperature of 80.0^0C for 24.0 hrs. Then dried orange peels were crushed and grinded to make very fine powder which was used as such in different amount in 5.0 M HCl.

Weight loss method: Coupons of Mild steel were taken for corrosion study having percentage composition of different elements like Carbon (0.17), Silicon (0.18), Manganese (0.53), Phosphorous (0.044), Sulphur (0.057), Chromium (0.14), Nickel (0.09), Molybdenum (0.02), Copper (0.06), Vanadium (less than 0.01) and rest is Iron (percentage by weight). Metal coupons of dimension 1.5 × 3.0 × 0.1 cm were used for weight loss experiments. The mild steel coupons were mechanically polished by the use of emery papers of different grades like 100, 200, 320, 400, 600 and 1000 µ. The mechanically polished surface of coupons were first treated with acetone in order to degreased and then washed with plenty of double distilled water before storing in a desiccators having silica gel. Mild steel coupons were then treated with 200.0 ml of 5.0 M HCl solution as corroding medium in presence and in absence of the green corrosion inhibitor. Change in weight was determined after 3.0 hours of exposure at 298.0 K. The corrosion rate (mpy) and inhibition efficiency (IE) were determined by the use of following equations[16]:

$$\text{Corrosion rate (mpy)} = \frac{534 \times W}{DAT} \quad (1)$$

Where, W is the weight loss in mg, D is the density of MS in gm/cm^3, A is the area of MS in sq. inch and T is the time in hours.

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

Where, CRo and CR is the weight loss in absence and in presence of inhibitor.

Electrochemical Polarization Measurements: A three electrodes based electrochemical cell assembly was used for electrochemical polarization experiments. Mechanically polished mild steel coupons itself act as working electrode. Ag/AgCl electrode was used as a reference electrode and a platinum electrode was used as a auxiliary counter electrode. Mechanical polishing of the mild steel coupons was successively done with 100, 200, 400, 600, 1000 µ grade emery papers. The mechanically polished surfaces of metal coupons were treated with acetone in order to remove grease or oil from MS surface and then washed with plenty of double distilled water before performing the corrosion experiments. The surface area of exposure of working electrode was 1.0 cm^2 for the corrosion study and rest of area was coated with epoxy resin. The electrochemical polarization experiments were performed on electrochemical workstation PGSTAT 128N Metrohm Autolab. Ltd., Netherland. Before starting the electrochemical polarization experiments, the working electrode i.e. MS was kept into the acidic solution as a corrosion medium for 2.0 hrs to gain the constant value of equilibrium potential. Electrochemical polarization experiments were carried out under constant temperature of 298.0 K constantly flowing water from thermostat maintained at a constant temperature. Electrochemical polarization experiments were performed from -1.2 to 2.0 V at a scan rate of 0.01(V/s). The corrosion rate (CR) and PCIE was found out by the use of following equations[17]:
The corrosion rate was observed by the Stern-Gerry equation given in equation (3) as below:

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

Where, *Eq. Wt.* is the gram eq. wt. of MS, D is the density of MS in gm/cm^3 and i_{corr} is the corrosion current density in µA/cm^2.

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

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

Electrochemical Impedance Measurements: Impedance measurements were performed with the help of electrochemical workstation at 298.0 K temperature and the behavior of the MS to alternating current (ac) was observed in a frequency range 10,000 to 1.0 Hz and ac amplitude of 0.05 V. The PCIE was calculated by making use of Charge Transfer Resistance, R_{CT} in the form of equation-5 given below[18].

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

Where, $Rct_{(Inhibitor)}$ and $Rct_{(Blank)}$ are the Charge Transfer Resistance (R_{CT}) with and without green corrosion inhibitor.

Gasometric Technique: The rate of evolution of gas during cathodic reactions was determined from gasometric technique from the slope of graph 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 corrosion 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 washed initially under tap water and then with double distilled water and then with acetone. Finally metal coupons were inspected for the surface study by SEM model JEOL JSM 6150 and inverted trinocular metallurgical research microscopy techniques.

Results and Discussion

Weight loss method: PCIE of *Citrus Sinensis* at 4.0 to 0.1 g/l concentration at 298.0 K temperature are shown in the Table-1. It is observed that the PCIE of the *Citrus Sinensis* move up to high value with increase in concentration of green inhibitor i.e. 0.1 to 4.0 g/l. It shows a maximum of 93.38 % when the concentration of the inhibitor was 4.0 g/l. *Citrus Sinensis* acts as very good green corrosion inhibitor even at very low concentration i.e. 0.1 g/l and provides more than 60.0 % protection to mild steel surface at room temperature.

Table-1
Weight loss, Corrosion rate and Percentage Corrosion Inhibition Efficiency (PCIE) of *Citrus sinensis* at different concentrations by weight loss technique at 298.0 K temperature in 5.0 M HCl solution

Concentration (g/l)	Weight loss (mg)	Corrosion rate (mpy)	PCIE
Blank	0.05075	664.231	-
4.0	0.0034	43.972	93.38
2.0	0.00679	88.861	86.62
1.0	0.0075	98.218	85.21
0.5	0.0132	172.094	74.09
0.1	0.0203	265.404	60.04

Electrochemical Polarization Experiment: Table-2 shows electrochemical polarization data for MS in 5.0 M HCl solutions in presence and absence of *Citrus Sinensis* at 298.0 K temperature. The values of i_{corr}, E_{corr}, β_a and β_c and PCIE are tabulated in Table-2.

It is observed that the addition of dry powder of peels of fruit *Citrus sinensis* to the acid solution as a corroding medium increases both i.e. anodic and cathodic over-potentials and but corrosion current density ($i_{Corr.}$) decreases. The behavior of anodic and cathodic Tafel slopes (βa and βc) confirms the adsorption of *Citrus sinensis* on the surface of MS. It is clear from the Table-2 that cathodic hydrogen evolution and anodic metal dissolution reactions are inhibited to the same extent and the magnitude of corrosion inhibition of MS increases as the concentration of green corrosion inhibitor increases in corrosive acid media. No definite trend was observed in $E_{corr.}$ values in presence of different concentrations of *Citrus sinensis* in 5.0 M HCl solution. This result indicates that *Citrus sinensis* may be regarded as mixed type of green corrosion inhibitor in presence of 5.0 M HCl solutions.

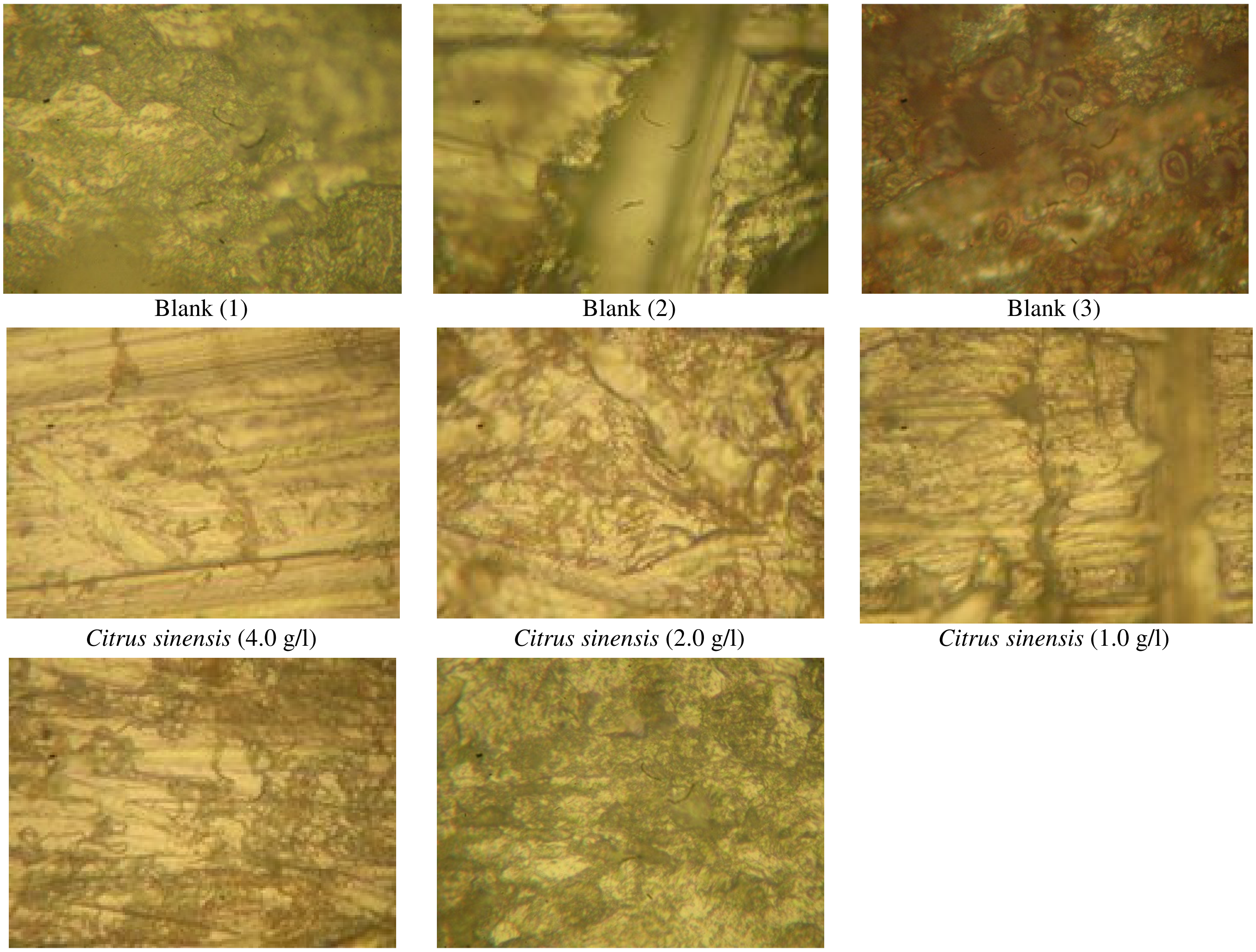
Gasometric measurements: Amount of gas evolved (ml), surface coverage (θ) and PCIE of *Citrus sinensis* at five concentrations by Gasometric method at 298.0 K temperature in 5.0 M HCl solution are shown in Table-3. It is observed from Table-3 that the value of RVh decreases with increase in concentration of inhibitor i.e. 0.1 to 4.0 g/l. The PCIE increases with increase in concentration of green corrosion inhibitor.

Table-2
OCP, Corrosion Current Density (Icorr), anodic Tafel slope (βa), cathodic Tafel slope (βc), resistance polarization (Rp), corrosion rate and PCIE of *Citrus sinensis* at different concentrations by electrochemical polarization method at 298.0 K temperature in 5.0 M HCl solution

Conc.(g/l)	OCP	I_{corr} (μA/cm^2)	β_a	β_c	Rp	CR (mpy)	PCIE
Blank	-0.528	4.48	5.935	7.637	3.66×10^5	1.7279	-
4.0	-0.680	0.78	0.508	1.380	7.75×10^4	0.3008	82.59
2.0	-0.572	1.55	0.916	4.442	8.09×10^4	0.5978	65.40
1.0	-0.650	1.88	23.078	2.665	1.67×10^5	0.7251	58.03
0.5	-0.611	2.15	7.730	3.787	1.66×10^5	0.8292	52.01
0.1	-0.439	2.39	6.266	7.384	2.09×10^5	0.9218	46.65

Table-3
Amount of gas evolved (ml), Surface coverage (θ) and Percentage Corrosion Inhibition Efficiency (PCIE) of *Citrus sinensis* at different concentrations by Gasometric method at 298.0 K temperature in 5.0 M HCl solution

Concentration (g/l)	RVh	Surface coverage (θ)	PCIE
Blank	1.0787	-	-
4.0	0.1443	0.8662	86.62
2.0	0.1551	0.8561	85.61
1.0	0.1674	0.8447	84.47
0.5	0.1851	0.8283	82.83
0.1	0.2737	0.7462	74.62



Blank (1) Blank (2) Blank (3)
Citrus sinensis (4.0 g/l) *Citrus sinensis* (2.0 g/l) *Citrus sinensis* (1.0 g/l)
Citrus sinensis (0.5 g/l) *Citrus sinensis* (0.1 g/l)

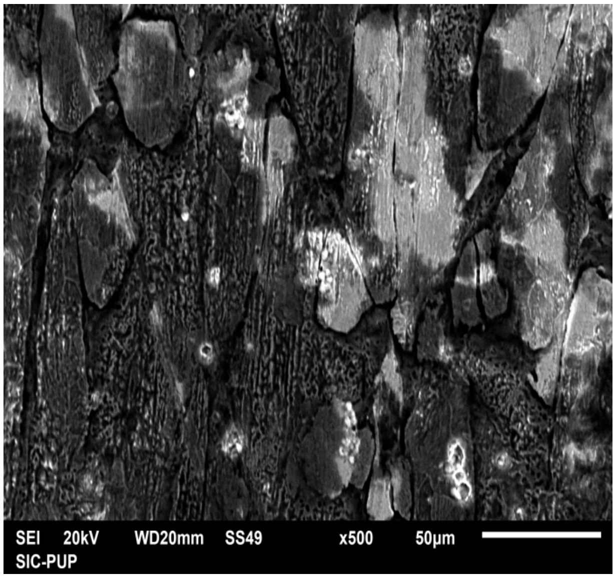
Figure-1
Trinocular Inverted Metullurgical Research Micrographs of different mild steel samples with and without *Citrus sinensis* as green corrosion inhibitor at different concentrations

EIS Experiments: Impedance spectroscopy technique was used to study the electrode/electrolyte interface behavior of the electrode and corrosion processes taking place on the surface of mild steel in presence and absence of *Citrus sinensis* peels. For understanding the phenomenon, electronic structure of electrified interface formed at the surface of working electrode and surface processes, EIS experiments were carried out at equilibrium potential in frequency range i.e. 10,000 to 0.1 Hz at 298.0 K. Figure 3 shows EIS plots for MS coupons dipped in 5.0 M HCl medium at 298.0 K with and without green corrosion inhibitor at the OCP. It is also observed from Nyquest plots that the diameter of the semicircle augment with the augment in concentration of *Citrus sinensis* peels in the corroding medium, which indicates an increase in resistance to corrosion.

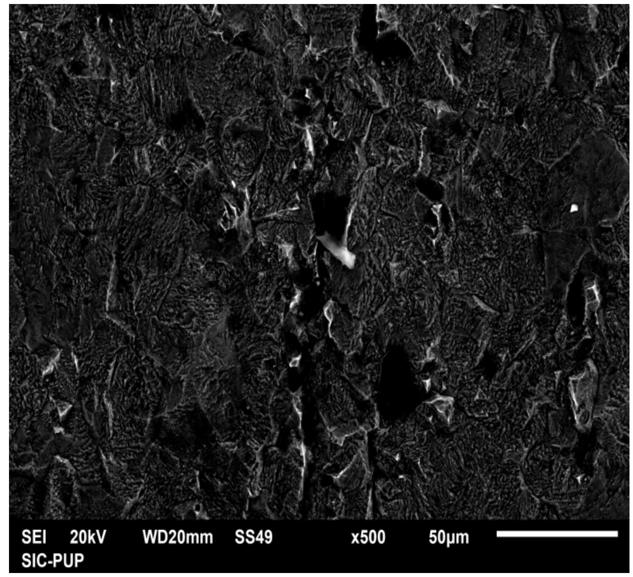
The electrochemical double layer capacitance (C_{dl}) was calculated at the frequency at which the imaginary component of the impedance is maximum, f_{max} using the equation-6 given below:

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

It is observed from electrochemical impedance data presented in the Table-5. Table file point out that both R_{CT} and PCIE were found to increase with increase in the concentration of green corrosion inhibitor and the values of double layer capacitance (C_{dl}) was found to be decrease with increase in concentration of green CI. The present behavior can be accredited due to either decrease in the dielectric constant value or may be due to increase in the width of the electrical double layer of the electrified interface, representing that the green CI molecules get adsorbed on the MS interface.



Blank 100 magnification (5.0 M HCl)



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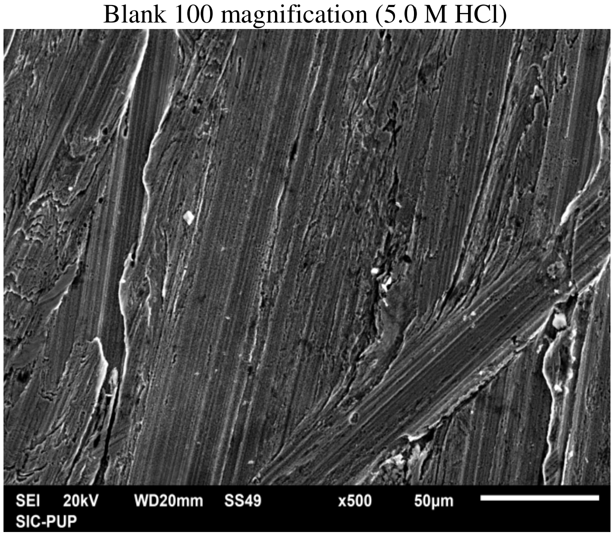
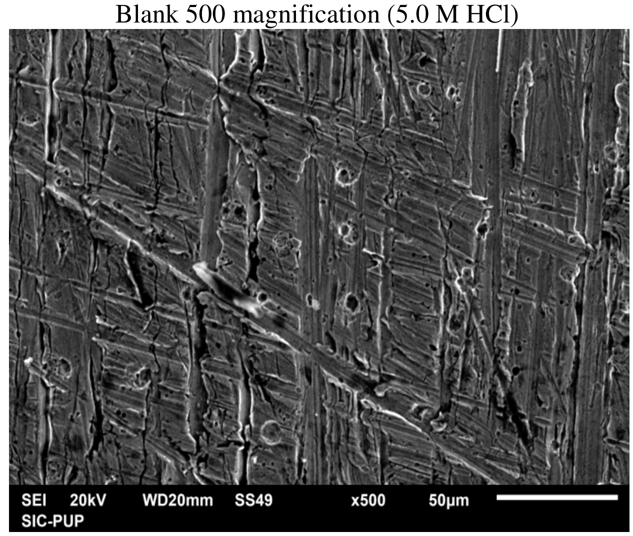
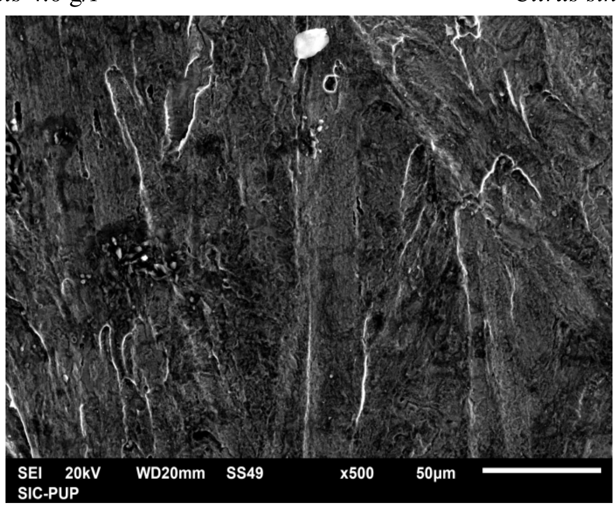


Citrus sinensis 4.0 g/l



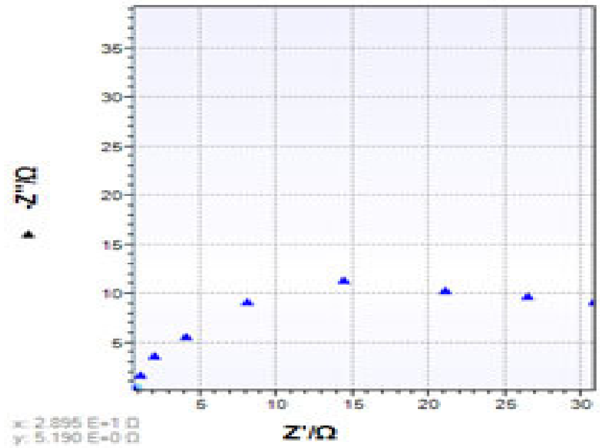
Citrus sinensis 1.0 g/l



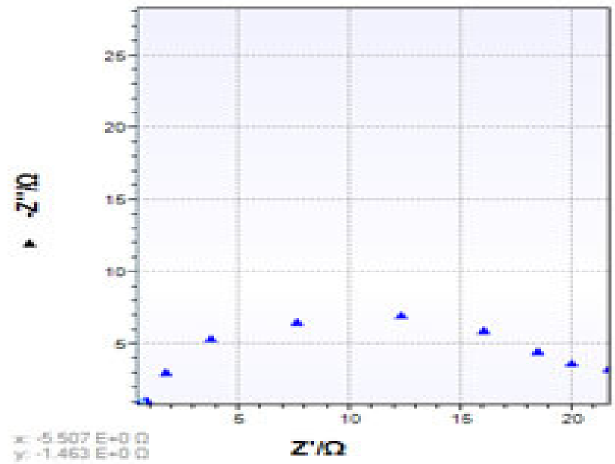
Citrus sinensis 0.1 g/l

Figure-2

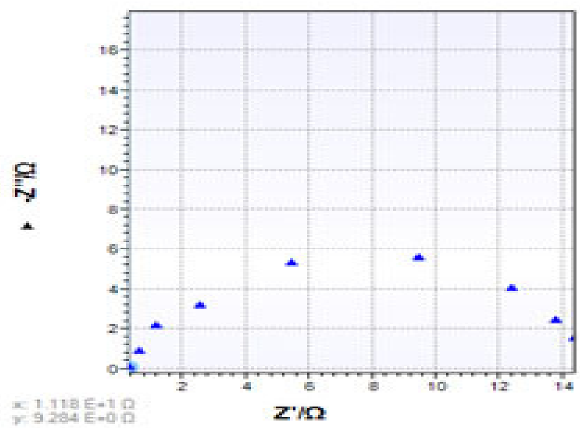
SEM images of mild steel samples with and without green corrosion inhibitors at different concentrations



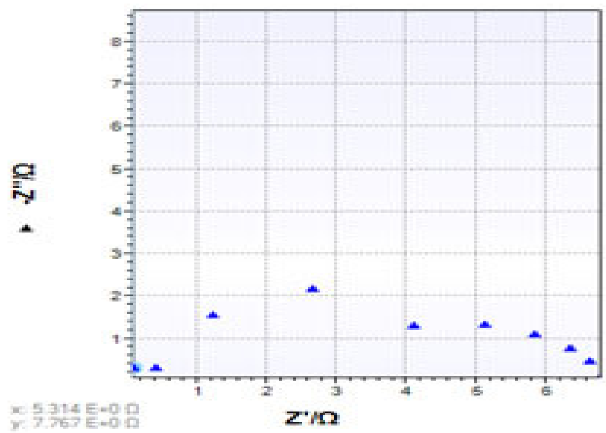
Nyquest plot of *Citrus sinensis* 4.0 %.



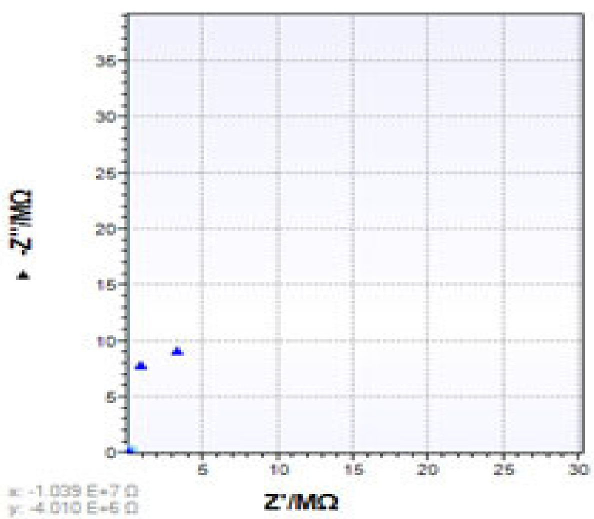
Nyquest plot of *Citrus sinensis* 2.0 %.



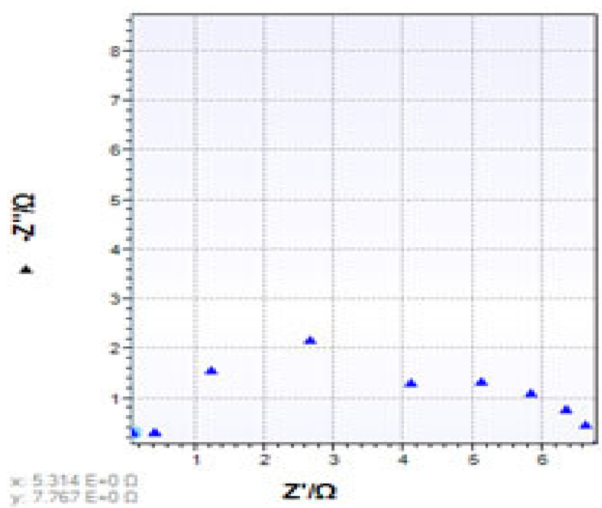
Nyquest plot of *Citrus sinensis* 1.0 %.



Nyquest plot of *Citrus sinensis* 0.5 %.



Nyquest plot of *Citrus sinensis* 0.1 %.



Nyquest plot (Blank)

Figure-3

Nyquist plots (EIS) of mild steel immersed in 5.0 M HCl in absence and presence of different concentrations of *Citrus sinensis* at 298.0 K temperature

Table-4
Coating thickness, percentage porosity and pore length of mild steel coupons with and without green corrosion inhibitor

Name of Sample	**Coating Thickness** (Micron)	**Percentage porosity**	**Pore Length** (Micron)
Blank	48.764	77.27	577.397 645.23
Orange peels 4.0 g/l	215.67	17.28	45.29 51.45
Orange peels 2.0 g/l	187.45	18.19	57.68 55.13
Orange a peels 1.0 g/l	146.94	28.29	67.19 65.41
Orangepeels 0.5 g/l	86.69	49.53	80.35 87.25
Orange peels 0.2 g/l	52.47	51.37	95.45 99.67
Orange peels 0.1 g/l	28.57	67.88	98.34 91.40

Table-5
Electrochemical impedance parameters for mild steel samples in 5.0 M HCl solution in absence and presence of different concentrations of *Citrus sinensis* at room temperature

(Conc.) g/L	**Cdl ($\times 10^{-3}$ F cm^2)**	**Rct (Ω cm^2)**	**PCIE %**
Blank	208	8.76	-
4.0	53.07	34.33	74.48
2.0	61.50	29.62	70.42
1.0	68.44	21.31	58.89
0.5	85.56	17.43	49.74
0.1	98.23	14.14	38.04

Metallurgical Research Microscopy technique: Trinocular Inverted Metallurgical research micrographs of different mild steels samples with and without *Citrus sinensis* as green CI at different concentrations are presented in Figure-2. It is observed from the Figure-2 that surface of sample becomes more clear and clean with increase in concentration of *Citrus sinensis*. 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 *Citrus sinensis*. However, there is slight uniform type of corrosion in the samples treated with 0.1 g/l of *Citrus sinensis*.

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 augment with raise in concentration of inhibitor. Percentage porosity decreases with increase in concentration of *Citrus sinensis* i.e. 0.1 to 4.0 g/l.

SEM studies: Figure-2 shows SEM image of MS coupons dipped in 5.0 M HCl solutions for 3.0 hours with and without five investigated concentrations i.e. 4.0, 2.0 and 0.1 g/l of *Citrus sinensis* peels. On comparing SEM images, it is observed that there was a coarse (uneven) surface of MS in absence of green corrosion inhibitor and a very smooth and clear surface in presence of the green corrosion inhibitor. SEM study shows that the *Citrus sinensis* acts as very good green corrosion inhibitor and inhibition occurs by the adsorption of the *Citrus sinensis* molecules on mild steel surface.

Conclusion

The percentage corrosion inhibition efficiency of fruit peels of *Citrus sinensis* on mild steel in 5.0 M HCl solution increases with rise in concentration of the green corrosion inhibitor. Potentiodynamic polarization experiment shows that *Citrus sinensis* act as a mixed type green corrosion inhibitor. Impedance spectroscopy experiments show that magnitude of charge transfer resistance increases with rise in concentration of the *Citrus sinensis.* SEM study confirms that protection from corrosion of MS in 5.0 M HCl was due to adsorption of the *Citrus sinensis* on the surface of MS. Metallurgical research microscopy images reveal that coating thickness increases and percentage porosity decreases with increase in concentration of *Citrus sinensis*. More than 93.0 PCIE was shown to the MS by 4.0 g/l of dried peels of fruit of *Citrus sinensis* in 5.0 M HCl medium at 298.0 K temperature.

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