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Green *Capsicum annuum* Fruit Extract for Inhibition of Mild Steel Corrosion in Hydrochloric acid solution

Gopal ji[1], *Sudhish Kumar Shukla*[2], *Priyanka Dwivedi*[3], *Shanthi Sundaram*[3], *Eno E. Ebenso*[2], *Rajiv Prakash*[1,*]

[1] School of Materials Science and Technology, Indian Institute of Technology, Banaras Hindu University, Varanasi 221 005, India
[2] Department of Chemistry, School of Mathematical and Physical Sciences, North-West University (Mafikeng Campus), Mmabatho 2735, South Africa
[3] Centre of Biotechnology, Allahabad University, Allahabad, India
[*]E-mail: rajivprakash12@yahoo.com

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We are reporting green *capsicum annuum* fruit extract as inhibitor for mild steel corrosion in acid solution. Inhibition potential of this aqueous fruit extract has been determined with the help of weight loss method and electrochemical techniques. Results obtained by various techniques are close to each other and maximum efficiency of 85 % is acknowledged at the inhibitor concentration of 1400 mgl^{-1}. Langmuir isotherm model is found most suitable to explain adsorption behavior of inhibitor for mild steel surface. Molecular adsorption of inhibitor over mild steel surface is found responsible for corrosion inhibition of mild steel in acid which is also supported by OEM studies.

Keywords: *Capsicum annuum*, Fruit extract, Corrosion inhibition, Mild steel, Acid corrosion, Adsorption.

1. INTRODUCTION

Iron and alloys are most useful materials for engineering applications due to its high strength and reliability. Life of these materials are subjected to many factors like service condition, operating temperature etc. but corrosion is one of the most important factors which govern other parameters . In industries acids are extensively used in many applications like pickling, degreasing, cleaning, oil well acidization and descaling process [1].Due to acid exposure steel losses its functional properties and chance of failure is increased. To avoid such cases effort has been done in order to prevent the metals and alloys from corrosion using different methods but use of inhibitors [2-8] is widely accepted method for prevention of iron and steel especially in acidic solutions. Inhibitors became popular among scientists due to its high efficiency, easy application procedure and stability but toxicity and cost of synthesis forced scientists to develop another form of inhibitor which was introduced as green inhibitors [9-12]. In this regard plant extracts have been explored since many years due to its biodegradability, low cost and effectiveness in acidic medium [13-19].

In present work we report green *Capsicum annum* fruit extract to inhibit mild steel corrosion in 1 M hydrochloric acid. This fruit is very popular in India as 'Shimla mirch' and used as vegetable in many regions. Fruit of this plant contain many organic compounds as flavonoids, ascorbic acid, phenolic acids, polysaccharide and capsaicin [20-22]. This fruit is selected for the study due to simple extraction method, non toxic nature, low cast and presence of effective organic compounds which contain N,O heteroatoms,-OH group and π electrons in their strutcre. Although crude extract is used in this study for simplicity and effective cost but we are working on purification of the extract to enhance the inhibition efficiency at low concentration.

2. EXPERIMENTAL DETAILS

2.1Method of extraction

Fresh fruits were bought from the local market and washed with double distilled water. Fruits were cut and dried at 40˚C for two days. Powdered form of fruits was obtained using grinder and distilled water was added to make a solution. This solution was kept at room temperature for two days with constant stirring. Further extract was filtered and water was evaporated using rotatory evaporator. Solid residue obtained by this process was again dissolved in 100 mL distilled water and stock solution was prepared of concentration 100 mg mL^{-1}. Similar type of work is reported elsewhere[15] to obtain aqueous extract of the interested plant.

2.2 Test specimen

Mild steel test specimens of dimension $1\times5\times0.03$ cm^3 and $1\times1\times0.03$ cm^3 were used for weight loss and electrochemical study respectively. They were abraded using emery paper of grade 2/0 to 6/0 successively to ensure proper surface conditions. Cleaning and degreasing was done by AR grade acetone followed by rinsing with double distilled water. Constituents of Mild steel used were (wt%) C (0.15), Si (0.18), Mn (0.40), S (0.02), P (0.03) and rest Fe.

2.3 Corrosive Medium

35 % GR grade hydrochloric acid was used as corrosive medium to explore inhibition potential of *Green capsicum annuum* fruit extract. Desired concentrations of HCl were obtained diluting with double distilled water.

2.4 Weight loss method

Weight loss of metal depends upon strength of the metal itself and reactivity of the corrosive medium. It can be considered as characteristics property of the material which is directly related with the corrosion rate. This method is very simple and widely accepted to determine the efficiency of inhibitors. For observation, mild steel specimens were immersed in 1 M HCl (100 mL) for 5 hours at room temperature with various concentrations of inhibitor. Three sets for each concentration were employed to achieve accurate results. Weight loss was recorded and inhibition efficiency was calculated using following equation:

$$\mu_{WL}(\%) = \frac{W_o - W_i}{W_o} \times 100 \qquad (1)$$

Surface coverage (θ) is an important parameter to know interaction of inhibitor with mild steel surface. It was determined using formula reported below:

$$\theta = \frac{W_o - W_i}{W_o} \qquad (2)$$

Where W_0 and W_i is weight loss of steel in blank and inhibited solution respectively.

Corrosion rate of steel is a measure of effectiveness of inhibitor and directly related with weight loss in corrosive medium for estimated period. It was computed from following stated formula:

$$Cr = \frac{87.6W}{td} \qquad (3)$$

Where Cr is corrosion rate in mmpy, W- weight loss per unit area of specimen, t - exposure time and d-density of metal used (Density of mild steel-7.85 g cm^{-3}).

2.5 Electrochemical Techniques

To know kinetics of corrosion process Tafel polarization and electrochemical impedance spectroscopy techniques were employed. A three electrode system was used to perform electrochemical tests which include mild steel specimen as working electrode, Ag-AgCl as reference electrode and platinum foil as counter electrode. Electrochemical Work Station, CHI 7041C (CH Instrument, USA) was used to monitor corrosion process using three electrode system.

Impedance spectroscopy was carried out in the frequency range of 100 kHz to 10 mHz using signal of amplitude 5 mV. For measurements system was left to obtain stable ocp and mild steel was allowed to corrode in HCl. Inhibition efficiency of inhibitor using this technique was calculated by formula given below:

$$\mu_{R_t}\,(\%) = \frac{R_t^i - R_t^o}{R_t^i} \times 100 \qquad (4)$$

Where R^i_t and R^o_t is charge transfer resistance in presence and absence of inhibitor.

Polarization measurements were obtained by applying potential from -0.25 V vs Ag-AgCl to + 0.25 V vs Ag-AgCl with respect to open circuit potential (ocp) at a scan rate of 0.5 mVs^{-1}. Efficiency of the inhibitor using data obtained by this test was obtained using following equation:

$$\mu_p\,(\%) = \frac{I^o_{corr} - I^i_{corr}}{I^o_{corr}} \times 100 \qquad (5)$$

Where I^o_{corr} and I^i_{corr} is corrosion current density in case of uninhibited and inhibited samples.

2.6 Surface Morphology

Optical microscope Leica DFC 295 was employed to record surface morphology of mild steel at different concentrations of inhibitor. To perform this test, mild steel specimens (1×1×0.03 cm^3) were immersed in 1 M HCl in presence and absence of inhibitor for 3 hours at room temperature. To observe the effect of inhibitor only one concentration (1400 mg L^{-1}), which gives maximum efficiency, was considered and surface morphology was compared with uninhibited samples.

3. RESULTS AND DISCUSSION

Results obtained by electrochemical and weight loss methods were in good agreement and discussed giving reason for enhanced resistance of mild steel in HCl in presence of inhibitor.

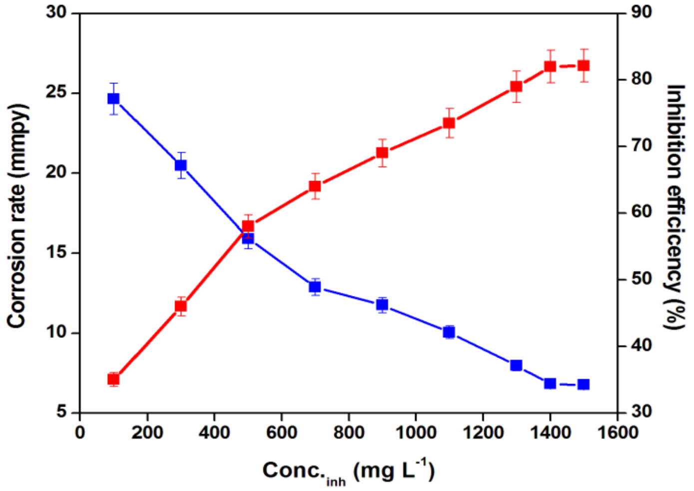


Figure 1. Corrosion rates and inhibition efficiencies obtained at different concentrations of inhibitor in 1 M HCl at 26±1° C for 5h.

3.1 Weight loss measurements

Initially mild steel corroded at higher rate in acid but presence of inhibitor retarded the corrosion rate and remarkable improvement in inhibition efficiency was achieved (Figure1).It was observed from Figure 1 that corrosion rate was decreasing with increasing inhibitor concentration whereas inhibition efficiency was increased with increasing amount of inhibitor. Maximum inhibition efficiency of 82 % was found at 1400 mg L^{-1} inhibitor concentration. From data listed in Table 1 decreased value of weight loss was noticed with increasing concentration of inhibitor due to increased surface coverage which can be accounted for inhibitive action of inhibitor.

Table 1. Corrosion parameters for mild steel in 1 M HCl in absence and presence of different concentrations of *Green capsicum annuum fruit* extract obtained from weight loss measurements at 26±1° C for 5h.

Concentration of Inhibitor (mg L^{-1})	Weight loss (mg/cm ^{2})	Inhibition efficiency μ_{WL} (%)	Corrosion rate (C_r) *(mm/y)*	Surface Coverage (θ)
Blank	17.00	-	37.91	-
100	11.05	35.00	24.64	0.3500
300	9.18	46.00	20.47	0.4600
500	7.14	58.00	15.92	0.5800
700	5.78	64.00	12.89	0.6400
900	5.27	69.00	11.75	0.6900
1100	4.51	73.50	10.05	0.7350
1300	3.57	79.00	7.96	0.7900
1400	3.06	82.00	6.82	0.8200
1500	3.04	82.15	6.76	0.8215

3.2 Adsorption Isotherm

Adsorption of inhibitor over iron and steel surface occurs through one of the ways stated below:

1. Physical adsorption through electrostatic reaction between negatively charged metal surface and positively charged organic species.
2. Chemical adsorption caused by interaction of π electrons and /or lone pair electrons (from organic moieties) with vacant d orbit electrons of iron forming chemical bond.
3. Combined mode of above stated interactions.

There are many isotherm models which are being used for describing adsorption phenomenon but Langmuir, Frumkin, Temkin, Freundlich and Flory-huggins are frequently used isotherms for explaining adsorption characteristics of inhibitor. We fitted data for the Langmuir and Temkin isotherm and Langmuir isotherm was found most appropriate (higher regression coefficient) to describe adsorption of inhibitor over mild steel surface. Fitting of data is shown in Figure 2 and Figure 3.

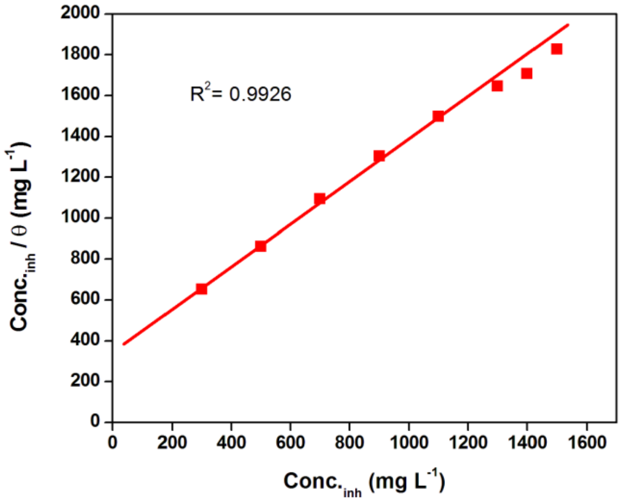


Figure 2. Langmuir adsorption isotherm for mild steel in 1 M HCl containing different concentrations of *Green capsicum annuum* fruit extract.

It is assumed in Langmuir isotherm that all sites have equal possibility for adsorption and it is not affected by activity (partially and/or fully filled or vacant) at nearby sites [23]. According to this isotherm surface coverage θ is related with concentration C of inhibitor through following formula:

$$\frac{C}{\theta} = \frac{1}{K} + c \qquad (6)$$

Where K is adsorption coefficient for metal-inhibitor interaction.

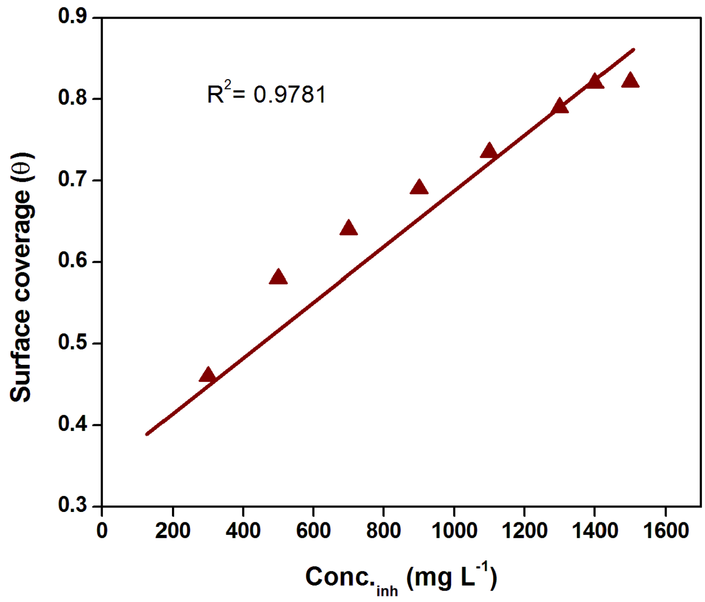


Figure 3. Temkin adsorption isotherm for mild steel in 1 M HCl containing different concentrations of *Green capsicum annuum* fruit extract.

3.3 Tafel polarization Curves

Figure 4 shows Tafel polarization plot obtained for mild steel in 1 M HCl at various concentrations of inhibitor. It can be observed from Figure 4 that in presence of inhibitor corrosion potential become more positive showing retarded mid steel corrosion. Various parameters like E_{corr}, I_{corr}, cathodic (b_c) and anodic (b_a) slope were calculated by extrapolation of polarization curves and listed in Table 2.

From inspection of Table 2 it was found that corrosion current density decreased (from 1082 to 154 μA cm^{-2}) with increasing concentration of inhibitor and attained minimum value for highest concentration used in study. It is also evident from Table 2 that addition of inhibitor shifted corrosion potential E_{corr} in anodic direction which indicated that adsorption of inhibitor was more successful at anodic sites than cathodic sites. Maximum shift in potential was found as 41 mV which informed that inhibitor retarded corrosion rate showing mixed type property [24,25]. Further influence of inhibitor on cathodic and anodic reactions can be seen from changing value of b_a and b_c (Table 2). Influence on anodic slope b_a can be attributed to adsorption of positively charged organic species and/or chroride ions at anodic sites whereas b_c is related with hydrogen evolution at cathodic sites which also alters with amount of inhibitor. Inhibition efficiency obtained from polarization curves followed same trend as in case of weight loss method and it was found maximum (86 %) at 1400 mg L^{-1} inhibitor concentration.

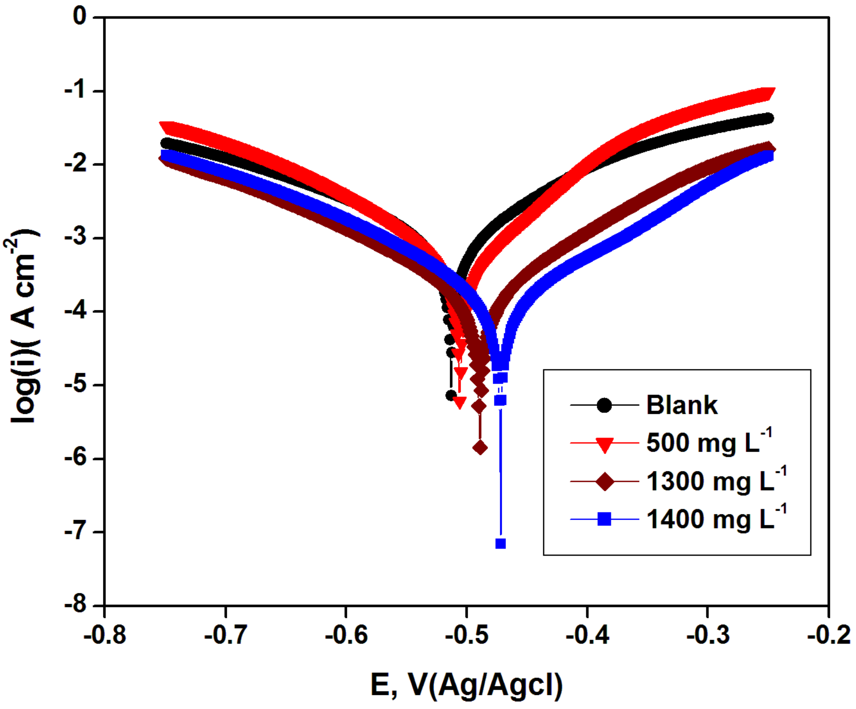


Figure 4. Polarization curve plot for mild steel in 1 M HCl with different concentrations of *Green capsicum annuum* extract .

Table 2. Parameters obtained from polarization curves at different concentration of inhibitor for 1 M HCl.

Concentration (mg L^{-1})	-Ecorr (mV , Ag-AgCl)	I corr (µA cm^{-2})	b_a (mV dec^{-1})	b_c (mV dec^{-1})	μ_p %
Blank	513	1082	79.69	62.41	-
500	506	412	85.30	69.51	61.92
1300	489	177	97.07	79.07	83.64
1400	472	154	96.19	79.83	85.76

3.4 Impedance Spectroscopy

Results obtained by impedance spectroscopy are shown in Figure 5 which demonstrates influence of inhibitor concentration on charge transfer resistance. It can be noticed from Figure 5 that charge transfer resistance is increasing with inhibitor concentration and maximum for highest concentration used in study. Further depressed capacitive loops can be seen in Figure 5 which reflects surface conditions and often observed due to surface roughness, irregularity, dislocations, or adsorption of inhibitor molecules at active sites [26-28].

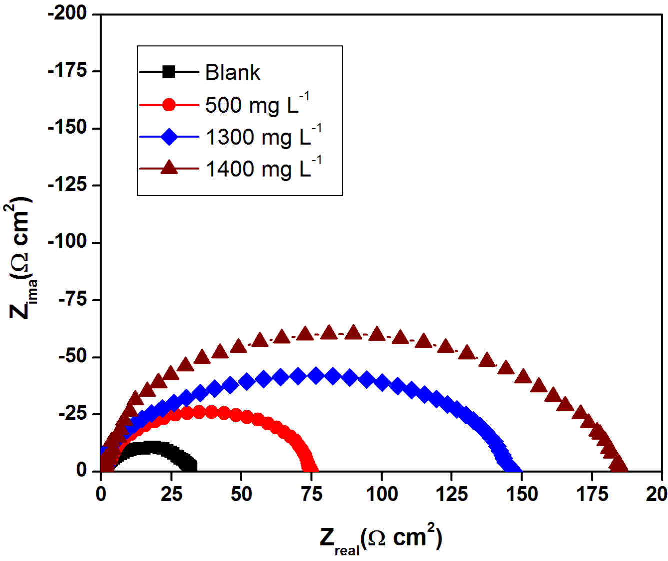


Figure 5. Impedance spectra obtained at various concentration of *Green capsicum annuum* fruit extract.

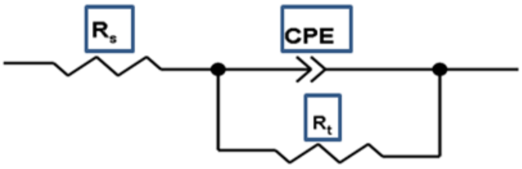


Figure 6. Equivalent c electrical circuit used to fit impedance data

To fit the data obtained by impedance spectroscopy an equivalent electrical circuit is used and shown in Figure 6. In this circuit R_s stands for solution resistance, R_t for charge transfer resistance and CPE for constant phase element which is generally used to describe iron/acid interface model [29] and considered to compensate ideal capacitive behavior. Impedance of CPE can be calculated by following equation:

$$Z_{CPE} = Y^{-1}(j\omega)^{-n} \qquad (7)$$

where Y is used for magnitude of CPE, ω for angular frequency and n for surface factor showing deviation from ideal capacitive behavior . From equation 7 three cases can be considered for variation in the value of n. If (a) n=0, CPE will correspond to resistance with Y= 1/R, (b) n=1, capacitance with Y=C, and (c) n=-1, an inductance with Y= 1/L [30]. In iron/acid interface system generally ideal capacitor characteristics are not observed due to non uniform adsorption of inhibitor over electrode surface which results frequency dispersion and uneven current distribution [27, 31, 32].

Corrosion parameters (R_s, R_t, Y_0, n) obtained from fitting data according to circuit shown in Figure 6 are listed in Table 3. Further value of Double layer capacitance of the film formed at interface was calculated from following formula [33]:

$$C_{dl} = [\![(Y]\!]_o \, . \, R_t^{1-n})^{\frac{1}{n}} \qquad (8)$$

Table 3. Impedance parameters for mild steel in 1 M HCl in absence and presence of different concentrations of *Green capsicum annuum* fruit extract.

Concentration (mg L^{-1})	R_s (Ω cm^2)	R_t (Ω cm^2)	n	Y_0 ($10^{-6}\Omega^{-1}cm^{-2}$)	C_{dl} (μF cm^{-2})	μ_{Rt} %
Blank	1.02	31	0.810	154	44.0	-
500	0.76	75	0.770	140	35.90	58.67
1300	1.10	147	0.730	80	15.47	79.00
1400	1.24	188	0.720	68	12.48	83.50

Value of C_{dl} can also be calculated from Helmholtz model and written as [34]:

$$\mathbf{C_{dl} = \varepsilon^0 \, \varepsilon \, \frac{A}{t}} \qquad (9)$$

where ε^0 is the permittivity of free space, ε is local dielectric constant, A is surface area of the electrode and t is thickness of the layer formed due to adsorption of organic species over mild steel surface.

From analysis of data listed in Table 3 it was noticed that charge transfer resistance increased remarkably (from 31 to 188 Ω cm^2) with increase in concentration of inhibitor due to adsorption of organic species at active sites available on mild steel surface [35]. Further value of n was found decreased with addition of inhibitor which can be attributed to the non ideal capacitive behavior of the system due to changing surface property of electrode with amount of inhibitor. It is evident from Table 3 that value of C_{dl} decreased with inhibitor concentration which corresponds to decreased value of dielectric constant ε and/or increasing layer thickness formed at acid/metal interface (from equation 9) with increased adsorption of inhibitor over steel surface.

Inhibition efficiency obtained by impedance spectroscopy was in good agreement with inhibition efficiency found by weight loss method and polarization curves and maximum efficiency of 83.50% was acknowledged for 1400 mg L^{-1} inhibitor concentration. Increase in charge transfer resistance and inhibition efficiency can be attributed to decrease in capacitance with addition of inhibitor and formation of protective layer at steel/acid interface.

3.5 Surface Morphology

Figure 7 shows surface morphology of mild steel in HCl with and without inhibitor.

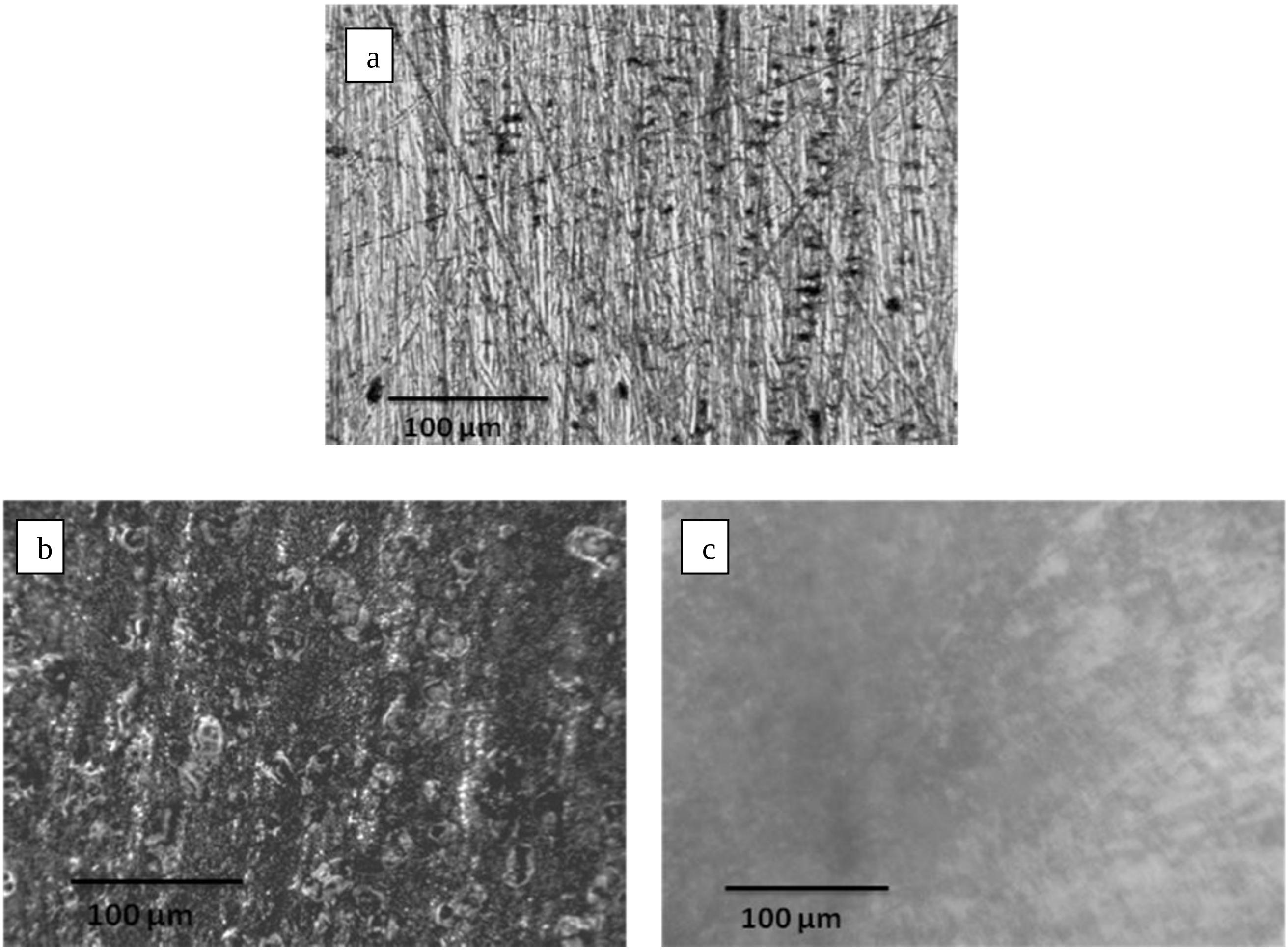
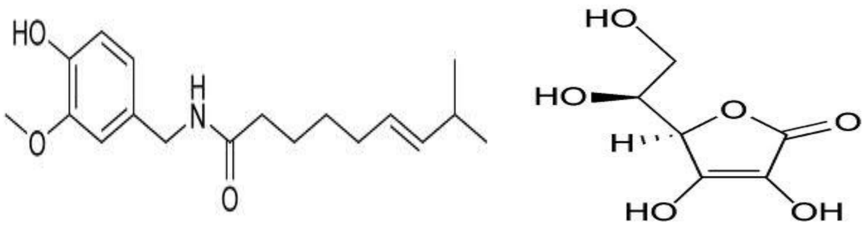


Figure 7. Micro photograph obtained by optical microscope for Surface morphology of mild steel (a) abraded by emery paper (b) corroded in 1 M HCl and (c) in 1 M HCl with 1400 mg L^{-1} inhibitor concentration.

Before immersing in acid mild steel sample was prepared using emery paper which created scratches on the surface and can be observed in Figure 7 a. When sample was immersed in HCl, corrosion pits were created on the surface due to aggressive attack of acid. A rough surface with dark shade can be seen in Figure 7 b which indicates deposition of corrosion products and/or chloride ions on the surface. Presence of inhibitor retarded the corrosion rate and smooth layer was recognized due to adsorption of organic species present in the extract at most active sites (Figure 7 c). Brightness of the image indicates good interaction of inhibitor with mild steel. On the basis of information provided by the optical microscope it can be concluded that inhibitor protected mild steel in acid forming a insulating film over mild steel surface.

3.6 Inhibition Mechanism

Corrosion of mild steel in HCl was found inhibited in presence of inhibitor. From analysis of the results obtained by various techniques it was recognized that changing surface property of steel with concentration of inhibitor was responsible for retarded corrosion rate which corresponds to molecular adsorption of inhibitor over mild steel surface. It is well known fact that most of the inhibitors falls under the category of adsorption type inhibitors and inhibit the corrosion by getting absorbed on the surface [36].



A B

Figure 8. Organic compounds present in extract (a) Capsaicin (b) Ascorbic acid

There are plenty of organic compounds present in the extract and few of them are shown in figure 8. These organic species probably became protonated in acid solution which favored adsorption of these molecules over surface of negatively charged mild steel (electrostatic bonding) [37]. Adsorption of Cl^- over mild steel surface produced unbalanced negative charge which promoted adsorption of inhibitor molecules at most active sites and inhibition efficiency was enhanced due to synergistic effect. Also these organic compounds contain N,O heteroatoms, fused benzene rings and OH molecules in their chemical structure which contributed electrons for sharing with vacant d orbit electrons of iron (chemi adsorption).

On the basis of facts discussed above it can be said that corrosion inhibition greatly depends upon adsorption of inhibitor molecules over surface of mild steel. In our case adsorbed inhibitor molecules accumulated at the metal/acid interface and constructed a layer surrounding mild steel. This layer prevented mild steel from further being corroded and can be visualized in surface images obtained for mild steel in HCl with inhibitor.

4. CONCLUSIONS

Mild steel corrosion in acid was found considerably retarded in presence of green capsicum annuum fruit extract. Results obtained by various techniques were in good connection and maximum efficiency of 86 % was acknowledged for highest inhibitor concentration used in the study. From investigation of polarization curves it was found that extract performed as mixed type inhibitor. Further Impedance spectroscopy showed increase in charge transfer resistance accompanying decreased capacitance with increase in inhibitor concentration. Molecular adsorption of organic species over metal surface was found responsible for inhibitive performance of green capsicum annuum fruit extract and confirmed by surface images obtained for mild steel in acid with inhibitor. Langmuir and Temkin model was used to know adsorption characteristics of inhibitor and Langmuir model was found most appropriate to describe adsorption isotherm.

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