



Corrosion Inhibition Studies of *Ecbolium Viride* Extracts on Mild Steel in HCl

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Abstract

The corrosion inhibition of *Ecbolium viride* plant extracts on the mild steel corrosion in 1 M HCl has been investigated by weight loss, Tafel polarization and electrochemical impedance spectroscopy (EIS). The corrosion inhibition efficiency increases on increasing the plant extract concentration. Adsorption of inhibitor was found to follow the Langmuir's adsorption isotherm. Thus, it can be classified as anionic inhibitor. Adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG_{ads}^0) were calculated and discussed. Surface analysis (SEM) was also carried out to establish the corrosion inhibitive property of *Ecbolium viride* in 1 M HCl solution.

Key words: *Ecbolium viride*, Mild steel, Tafel polarization, EIS, Langmuir's adsorption.

1. Introduction

Mild steel corrosion is one of the most widely studied phenomenon while it still contribute to gain its attention due to its importance in many of the industrial facilities. As an example, the refining of crude oil results in a variety of corrosive conditions. Refinery corrosion is generally caused by a strong acid attacking the equipment surface [1]. The other important fields of application are acid pickling, industrial cleaning, oil-well acid in oil recovery and the petrochemical processes [2]. Among the acid solutions, hydrochloric acid is one of the most widely used agents in the pickling, cleaning and descaling. Even after thorough cleaning the removal of acids are not always possible from small crevices and bents which can cause severe corrosion on a later stage. Hence there is always a pressing demand exists for more effective inhibitors. The recent trend is towards the usage of environment friendly inhibitors. As most of the natural products are nontoxic, biodegradable and readily available in plenty, various plant-seeds, fruits, leaves, flowers etc. have been studied for their corrosion inhibition [3]. The plant extract contains several organic compounds which are mostly heterocyclic aromatics and anti oxidants. It has been proposed that the presence of such compounds only makes the plant extract an effective inhibitor. The root extracts of *Ecbolium viride* contains a novel hetero furanoid compound 4-methoxy-5-[4-(4-methoxy-1,3-benzodioxol-5-yl)perhydro-1H,3H-furo[3,4-c]-furan-1-yl]-1,3-benzodioxole as shown in the Figure 1 [4] which paved the interest in the present study. *Ecbolium viride* belong to the Acanthaceae family and is a very commonly available plant in south India. They can be easily identified by their intense green leaves and greenish blue flowers. Traditionally the aqueous extracts of dried roots of the plant *Ecbolium viride* are used as a cure for menorrhagia, rheumatism and jaundice and has anti inflammatory activity [5].

Figure 1. 4-methoxy-5-[4-(4-methoxy-1,3-benzodioxol-5-yl)perhydro-1H,3H-furo[3,4-c]-furan-1-yl]-1,3-benzodioxole.

2. Experimental

2.1. Material and medium.

Mild steel specimens having a composition of 0.10 wt % C, 0.34 wt % Mn, 0.08 wt % P, and the remaining Fe with the dimensions 3 cm×2 cm×0.28 cm were used. The specimens were polished with different emery papers up to 4/0 grades, cleaned with acetone and doubly distilled water and finally dried. The electrochemical experiments were performed in three electrode cell assembly with mild steel as the working electrode, platinum as the counter electrode and saturated calomel electrode (SCE) as the reference electrode [6]. Analar grade hydrochloric acid (Merck) and doubly distilled water were used to prepare 1 M acid solutions for all experiments. Weight loss experiments were done with different inhibitor concentration range 100, 200, 300 and 400 ppm at 300 K, Tafel polarization potentiodynamic current–potential curves were recorded by changing the electrode potential automatically from -250 mV to +250 mV relative to open circuit potential with a scan rate of 20 mV/min. The corresponding corrosion current $I_{(corr)}$, were recorded. Tafel plots were constructed by plotting E versus log I; corrosion potential $E_{(corr)}$, corrosion current density $I_{(corr)}$, cathodic and anodic slopes (β_c and β_a) were calculated according to known procedures. Electrochemical impedance measurements were carried out in a frequency range from 0.1 to 10000 Hz using an amplitude of 10 mV peak to peak using an AC signal at the open circuit potential. The impedance diagrams were plotted in the Nyquist representation. Charge transfer resistance (R_{ct}) values were given by subtracting the high frequency impedance from the low frequency.

2.2. Preparation of extract

Ecbolium viride are collected in the month of December from Pattukkottai, Dindigul districts in Tamilnadu, India. Care is taken to select healthy plants. The plants were washed properly with water to remove the mud or dust if any; and were shade dried completely. The dried root and stems part were separated with reference to known procedure [7]. The dried stems were crushed and extracted in boiled hexane using soxhlet extractor. The extracts were filtered and then distilled. The solid extract was used to study the corrosion inhibition properties and to prepare the required concentration of *Ecbolium viride* stem extract. The dried root were crushed and extracted in methanol for using soxhlet extractor. The extracts were filtered and then the solvents were removed under vacuum. The solid extract was used for the further study. 1 M HCl solution were prepared by dilution of 37 % HCl (Merck) using distilled water. The concentration range of stem and root extract employed are varied from 0.1 to 0.4 g/L and the electrolyte used was 100 mL for each experiment.

2.3. Scanning electron microscope (SEM)

Immersion corrosion analysis of mild steel samples in the acid solution with and without the optimal concentration of the inhibitor was performed using SEM. Immediately after the corrosion tests, the samples were subjected to SEM studies to know the surface condition. Hitachi SU 6600 Scanning electron microscope was used for experiments.

3. Results and discussion

3.1. Weight loss measurements

Weight loss is obtained from the gravimetric measurements of the steel plate specimens before and after the immersion in the acid solution with and without the plant extracts. Different concentrations of stem extract and root extract (20 - 400 ppm) are added to the HCl and the specimen is immersed in the solution for 2 h at room temperature (300 K). The results are summarized in Table 1.

Table 1. Inhibition efficiency obtained by weight loss of mild steel in 1 M HCl containing various concentrations of *Ecbolium viride* plant extract of stem and root at 300 K

Ecbolium viride plant extract (ppm by weight)	Stem extract			Root extract		
	Weight loss ^a (mg cm ⁻²)	IE (%)	θ	Weight loss ^a (mg cm ⁻²)	IE (%)	θ
Blank	102			102		
20	77	24.51	0.2451	78	23.53	0.2353
40	62	39.22	0.3922	64	37.25	0.3725
60	52	49.02	0.4902	53	48.04	0.4804
80	44	56.86	0.5686	45	55.88	0.5588
100	39	61.8	0.618	42	58.8	0.588
200	32	68.6	0.686	34	66.7	0.667
300	21	79.4	0.794	23	77.5	0.775
400	17	83.3	0.833	19	81.4	0.814

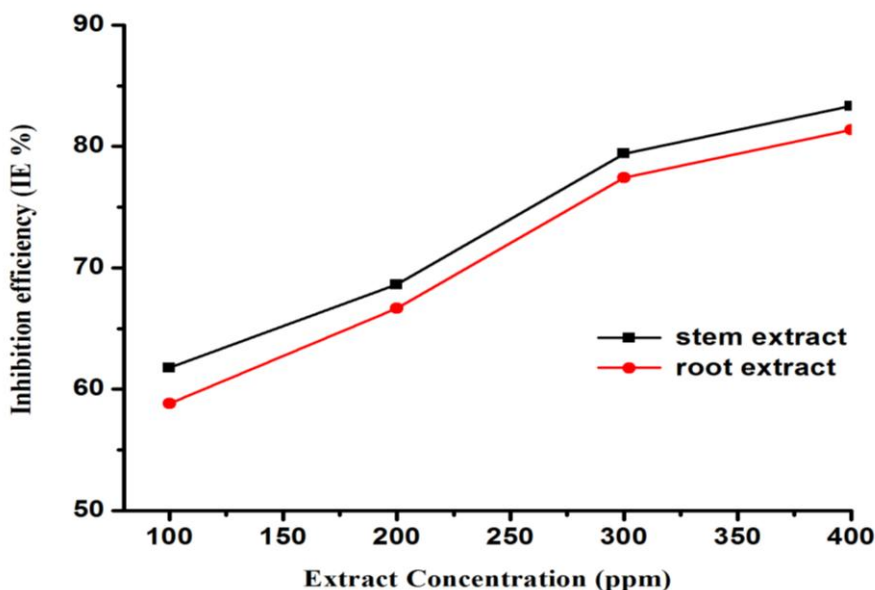


Figure 2. Variation in Inhibition efficiency with different inhibitor concentration *Ecbolium viride* plant extract of mild steel 1 M HCl at 300 K.

Inhibition efficiency increases with the increase of concentration of the extract. Maximum inhibition efficiency 83.3 % and 81.4 % respectively for stem extract and root extract were achieved at 400 ppm. A further increase in concentration of *Ecbolium viride* did not cause any appreciable change in the performance of the inhibition efficiency. This may be due to the reason that the total surface coverage is accomplished by the said concentration and beyond that any further addition will not yield any increase in the inhibition efficiency. At constant temperature the inhibition efficiency increases with the increase in concentration of the compound studied, explained on the basis of increased adsorption of the compound on the metal surface is shown in Figure 2.

3.2. Tafel polarization

The potentiodynamic polarization curves of mild steel in 1 M HCl solution in the presence and absence of different inhibitor concentration are shown in Figure 3. As can be inferred from the figure that after addition of inhibitor there is a decrease in both cathodic and anodic current. The electrochemical corrosion kinetic parameters, corrosion potential $E_{(corr)}$, cathodic and anodic Tafel slopes (β_c and β_a) and corrosion current density $I_{(corr)}$ obtained from the tafel polarization curves are listed in Table 2. Corrosion current rate decreases with increasing concentration of inhibitor for both stem and root. Maximum inhibition efficiency 92.4 % and 90.1 % respectively for stem extract and root extract were achieved at 400 ppm. It can be clearly seen that the inhibition efficiency increases with increasing concentration. The fact that the polarization curves show clear shift to more positive potential with increasing concentration of inhibitor indicate that inhibitor acts as the anodic inhibitor [8].

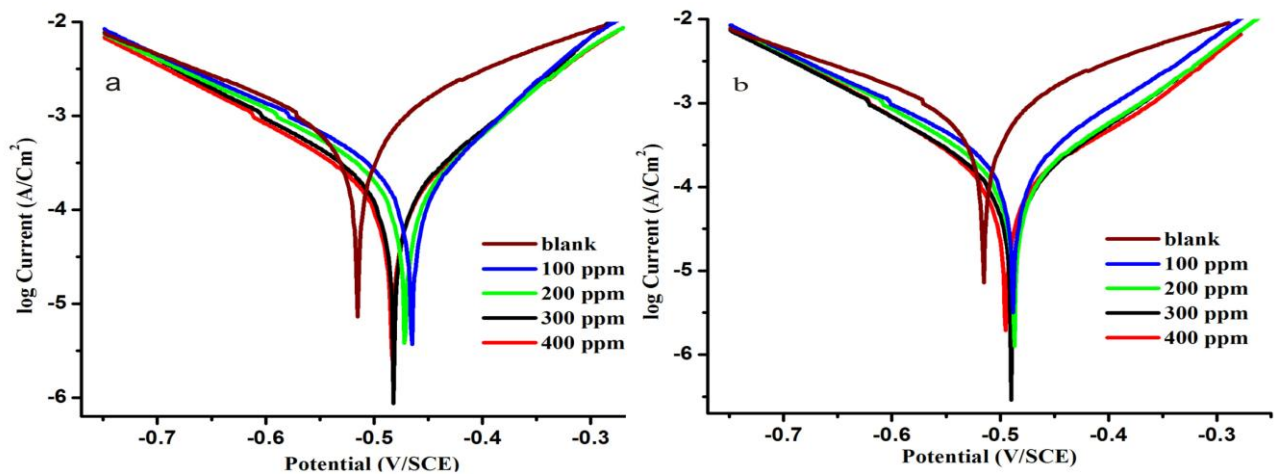


Figure 3. Tafel polarization curves of mild steel in 1 M HCl at 300 K in presence of different *Ecboium viride* concentration (a) Stem extract. (b)Root extract.

Table 2. Inhibition efficiency obtained by Tafel polarisation of mild steel in 1 M HCl containing various concentrations of *Ecboium viride* plant extract of stem and root at 300 K.

3.3. Electrochemical impedance spectroscopy (EIS)

Inhibitor concentration (ppm by weight)	$I_{(corr)}$ ($\mu\text{A cm}^{-2}$)	$E_{(corr)}$ (mV vs SCE)	β_c (mV/dec ¹)	β_a (mV/dec ¹)	IE (%)	θ
Stem (Scan rate 20 mV/min)						
Blank	794	510	190	250		
100	125	480	210	210	84.3	0.843
200	100	482	228	226	87.4	0.874
300	83	475	261	269	89.5	0.895
400	63	460	170	220	92.4	0.924
Root (Scan rate 20 mV/min)						
100	144	451	171	179	81.9	0.819
200	128	452	192	188	83.8	0.839
300	97	453	183	207	87.9	0.878
400	79	453	183	197	90.1	0.901

The effect of inhibitor concentration on the impedance behaviour of mild steel in 1 M HCl solution at 300 K is presented in Figure 4. The curves show a similar type of Nyquist plot in the presence of various concentrations of inhibitor. The Nyquist plots contain a depressed semi-circle, which size is increased by increasing the inhibitor concentration. Electrochemical corrosion kinetic parameters, charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) calculated from Nyquist plot is listen in Table 3. Maximum Inhibition efficiency (IE %) for the stem (92.6 %) and root (90.8 %) was achieved at 400 ppm. The corrosion is mainly a charge transfer resistance (R_{ct}) process. The charge transfer resistance (R_{ct}) value increasing with increasing inhibitor concentration. On the other hand, the values of C_{dl} are decreased with increase in inhibitor concentration which is most probably due to the decrease in local dielectric constant and/or increase in thickness of the electrical double layer, suggests that the inhibitor act via adsorption at the metal/solution interface [9, 10]. It could be assumed that the decrease of C_{dl} values is caused by the gradual replacement of water molecules by adsorption of organic molecules on the electrode surface, which decreases the extent of the metal dissolution.

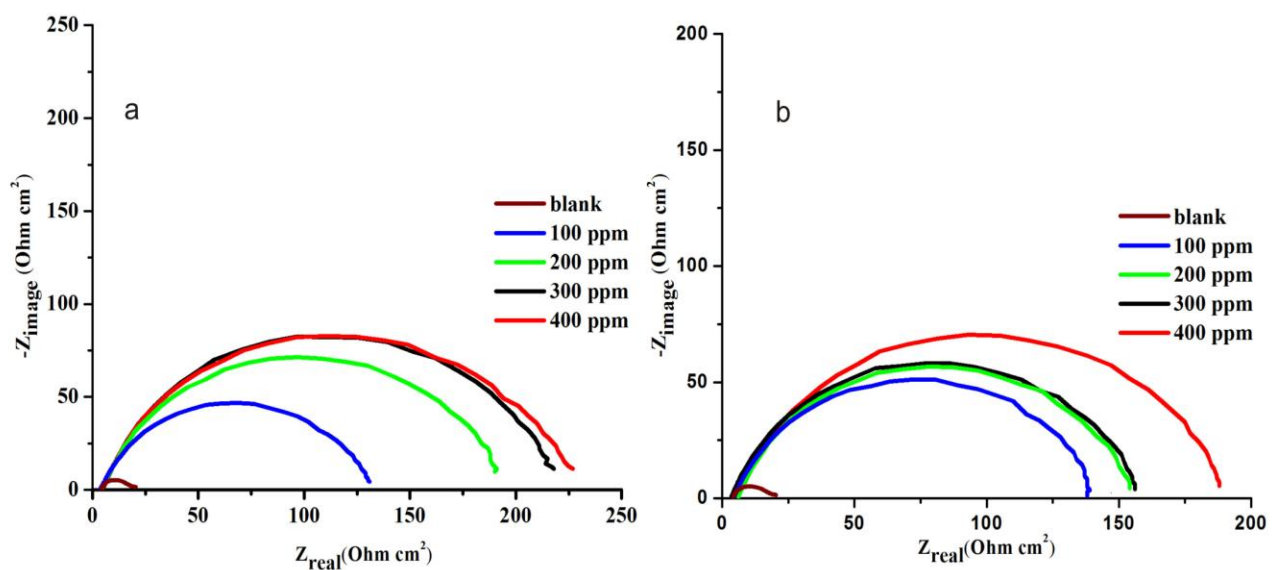


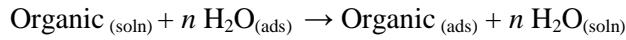
Figure 4. Nyquist plots of EIS measurements of mild steel in 1 M HCl at 300 K in presence of different concentration of *Ecbolium viride*. (a) Stem extract (b) Root extract.

Table 3. Inhibition efficiency obtained by EIS measurements mild steel in 1 M HCl containing various concentrations of *Ecbolium viride* plant extract of stem and root at 300 K

Inhibitor concentration (ppm by weight)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} (μF)	IE (%)	θ
Stem (Amplitude 10 mV)				
Blank	16.84	52.2		
100	128.06	6.86	86.9	0.869
200	190.74	4.60	91.2	0.912
300	214.69	4.09	92.2	0.922
400	228.45	3.84	92.6	0.926
Root (Amplitude 10 mV)				
100	130.52	6.73	87.6	0.876
200	149.64	5.87	88.8	0.888
300	154.74	5.60	89.1	0.891
400	183.89	4.70	90.8	0.908

3.4. Adsorption Isotherm behaviour

The adsorption of organic substance (surfactant in this case) at the metal/solution interface may be written according to the following displacement reaction



Where n is the number of water molecules removed from the metal surface for each molecule of inhibitor adsorbed. Clearly, the value of n depends on how the molecule arrange on the surface due to the surface roughness, and the interaction among the molecules. Basic information on the interaction between the inhibitor molecules and the surface of mild steel can be provided by adsorption isotherm. A correlation between surface coverage (θ) defined and the concentration of inhibitor (C_{inh}) in electrolyte can be represented by the Langmuir adsorption isotherm,

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K} + C_{\text{inh}}$$

Where, K is the adsorption constant.

Surface coverage values (θ) for the inhibitor were obtained from the weight loss measurements for various concentrations at 300 K as shown in Table 1. The best fitted straight line is obtained for the plot of C_{inh}/θ versus C_{inh} with slopes around unity. The correlation coefficient (r^2) was used to choose the isotherm that best fit experimental data. This suggests that the adsorption of *Ecbolium viride* extracts on metal surface follows the Langmuir adsorption isotherm (Figure 5). From the intercepts of the straight lines C_{inh}/θ -axis, K values were calculated and are given in Table 4. The most important thermodynamic adsorption parameters are the free energy of adsorption (ΔG^0_{ads}). The adsorption constant, K , is related to the standard free energy of adsorption, ΔG^0_{ads} with the following equation [11]:

$$\Delta G^0_{\text{ads}} = -RT \ln (55.5 K_{\text{ads}})$$

Where 55.5 is the water concentration of solution in mol/L

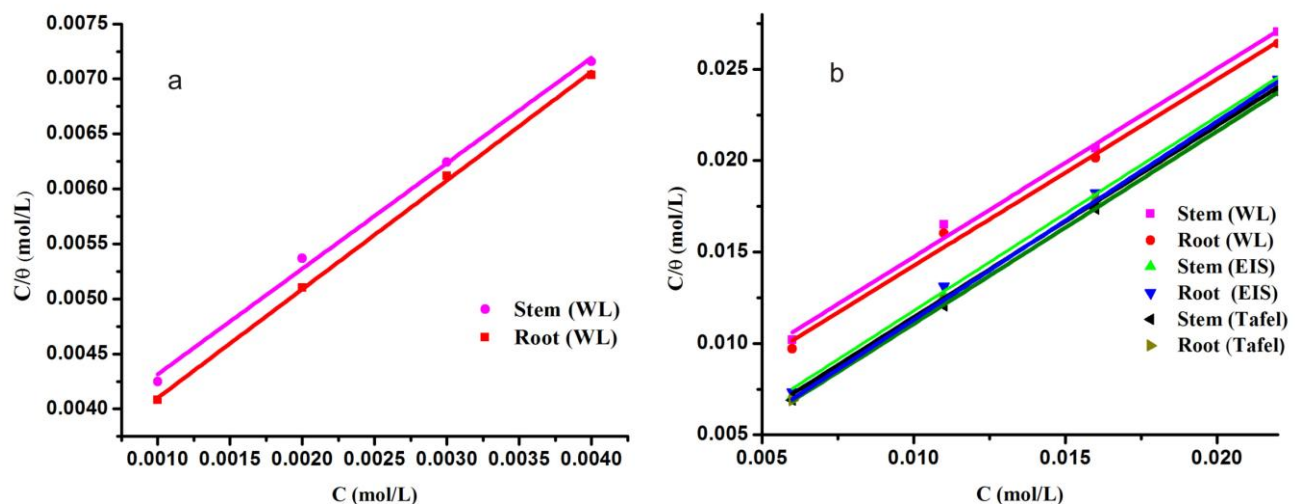


Figure 5. (a) Langmuir adsorption plots for *Ecbolium viride* on mild steel in 1 M HCl weight loss for lower concentration (b) Langmuir adsorption plots for *Ecbolium viride* on mild steel in 1 M HCl weight loss , EIS and Tafel Polarization at 300 K

The negative values of ΔG^0_{ads} indicate the stability of the adsorbed layer on the steel surface and spontaneity of the adsorption process. The dependence of ΔG^0_{ads} on temperature can be explained by two cases as follows [12] (a) ΔG^0_{ads} may increase (becomes less negative) with the increase of temperature which

indicates the occurrence of exothermic process (b) ΔG_{ads}^0 may decrease (becomes more negative) with increasing temperature indicating the occurrence of endothermic process.

Generally, the magnitude of ΔG_{ads}^0 around -20 kJ/mol or less negative is assumed for electrostatic interactions exist between inhibitor and the charged metal surface (i.e., Physisorption). Those around -40 kJ/mol or more negative are indicating of charge sharing or transferring to the metal surface to form a coordinate type of metal bond (i.e., chemisorptions).

The relationship between C_{inh}/θ and C presents linear behaviour at all temperatures studied (Figure 5) with slopes equal to unity (1.00). The correlation factor is 0.99. This suggests that the adsorption of *Ecbolium viride* extracts on metal surface followed the Langmuir adsorption isotherm. From the intercepts of the straight lines C_{inh}/θ -axis, K value calculated. The standard free energy of adsorption ΔG_{ads}^0 calculated shown in Table 4. The negative values of ΔG_{ads}^0 indicate the stability of the adsorbed layer on the steel surface and spontaneity of the adsorption process [13].

Regarding the present work, the calculation ΔG_{ads}^0 values for stem and root extract show that an electrostatic interaction between the inhibitors and charged metal surface. In physisorption process, it can be assumed that acid anion such as Cl^- ions are specifically adsorbed on the the metal surface, donating an excess negative charge to the metal surface.

Table 4. Estimation of the equilibrium adsorption constant (K_{ads}) and the free energy of adsorption (ΔG_{ads}^0) of the *Ecbolium viride* plant extract of stem and root at 300 K on mild steel surface immersed in 1 M HCl.

	Slope	r^2	$K_{ads} \text{ L mol}^{-1}$	$\Delta G_{ads}^0 \text{ kJ mol}^{-1}$
Stem (WL)*	0.99	0.99	3.22×10^2	-24.44
Root (WL)*	0.98	0.99	2.98×10^2	-24.22
Stem (WL)	1.02	0.99	2.48×10^2	-23.77
Root (WL)	1.03	0.99	2.26×10^2	-23.54
Stem (Tafel)	1.04	0.99	1.05×10^3	-27.36
Root (Tafel)	1.06	0.99	1.15×10^3	-26.89
Stem (EIS)	1.05	0.99	1.87×10^3	-28.80
Root (EIS)	1.08	0.99	2.25×10^3	-29.26

*lower concentration

3.5. SEM Analysis

SEM micrographs of the surface of the mild steel specimens were taken in order to see the changes that occur during the corrosion of mild steel in the presence and absence of the inhibitor. Figure 6(a) shows that the mild steel specimen immersed in 1 M HCl is highly damaged, it can be concluded that the mild steel surface is highly corroded in aggressive acid media. This type of corrosion is typical in aggressive acid solutions. Figure 6(b) shows a smooth surface with deposited inhibitor on the surface of mild steel after the addition of 400 ppm of inhibitor to the 1 M HCl solution. It is clearly seen from SEM images that the irregularities in the surface due to corrosion is absent in the inhibited surface and the surface is now almost free from corrosion.

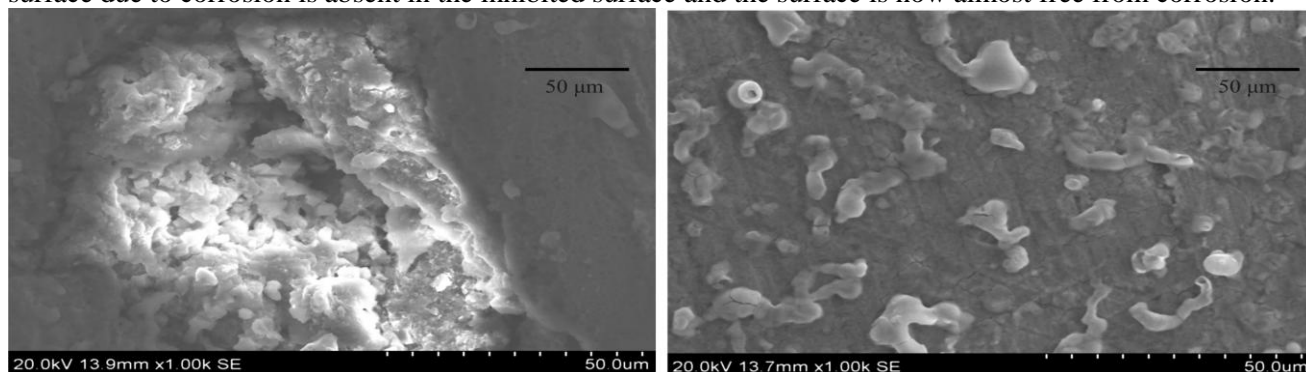


Figure 6. SEM micrographs of the surface of the mild steel specimens after 2 h immersion in 1 M HCl (a) without *Ecbolium viride* plant stem extract showing the damaged surface in acid solution (b) with *Ecbolium viride* plant stem extract showing the inhibited smooth surface.

Conclusion

Ecbolium viride can act as an effective corrosion inhibitor for mild steel in 1 M hydrochloric acids. The inhibition efficiency measured through weight loss method, potentiodynamic and EIS were reach stem and root concentration at 400 ppm. The potentiodynamic measurement result indicated anodic processes are suppressed. The inhibition is due to the adsorption of the inhibitor molecules on mild steel surface and blocking is active sites. Beside protective effect of by means of adsorbing on metal surface according to the Langmuir isotherm mode, the result demonstrated that the *Ecbolium viride* under investigation acts as physisorption.

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