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ORIGINAL ARTICLE

Spirulina platensis – A novel green inhibitor for acid corrosion of mild steel

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Abstract The inhibition of the corrosion of mild steel in 1 M HCl and 1 M H_2SO_4 by *Spirulina platensis* has been studied at different temperatures viz., 303 K, 313 K and 323 K by weight loss method, potentiodynamic polarization method, electrochemical impedance spectroscopy measurements and SEM analysis. The inhibition efficiency increased with increasing concentration of the inhibitor in both HCl and H_2SO_4 media. The results of weight loss studies correlated well with those of impedance and polarization studies. From the results of weight loss studies at various temperatures, the mode of adsorption is confirmed to be physisorption. Further the adsorption has been found to follow Temkin isotherm. From this isotherm, the free energy of adsorption (ΔG) and entropy (ΔS) are calculated. The study reveals the corrosion inhibition potential of *S. platensis* in both the acid media, thus bringing to light another facet of this microalga as it has so far been used only to produce antioxidant principles, finding extensive use in medicine especially as neutraceutical.

1. Introduction

Acids such as HCl and H_2SO_4 are widely used as pickling, descaling and cleaning agents in several industries for the removal of undesirable oxide films and corrosion products (Bothi Raja and Sethuraman, 2009a). In many industries, mild steel (MS) is the material of choice in the fabrication of reaction vessels, storage tanks etc., which get corroded easily in the presence of acids (Bothi Raja and Sethuraman, 2009b).

Among the methods of corrosion control, use of inhibitors is very popular due to the ease of application. Mostly, the heterocyclic compounds containing O, S and N as heteroatoms serve as good inhibitors for corrosion (Senthil Kumar et al., 2009). In view of the disadvantages of the compounds of synthetic origin, there has been an upsurge in screening of compounds of natural origin for their corrosion inhibition effect (Bothi Raja and Sethuraman, 2008). In the present study, a marine alga viz., *Spirulina platensis* is examined for its potential to control corrosion of MS in acid media.

S. platensis belongs to the family, Oscillatoriaceae which has several therapeutic properties such as hypocholesterolemic,

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immunological, antiviral and antimutagenic (Herrero et al., 2004; Aleisa, 2008; Belay et al., 1993). This alga is reported to contain amino acids such as methionine, γ-linolenic acid, peptides, proteins, carbohydrates and phycocyanins (Chamorro-Cevallosa et al., 2008). *S. platensis* finds use as an antioxidant especially for the production of nutraceuticals (Wang and Zhao, 2005). Further, it is widely used in food industries due to its rich protein content (Diraman et al., 2009; Rahman et al., 2006; Pelizer et al., 2003; http://www.nbent.com/spirulina.htm).

In the present study, the corrosion inhibitive property of *S. platensis* has been investigated in both HCl and H_2SO_4 media by weight loss method, electrochemical method as well as SEM analysis.

2. Experimental

2.1. Preparation of *S. platensis* sample

Powdered form of *S. platensis* (100 g) supplied by Ms. Sanat Food Products Pvt. Ltd., Kodai Road, Dindigul Dist., India was extracted with absolute ethanol using Soxhlet apparatus. The ethanolic extract was distilled to obtain a solid residue, which was used as the inhibitor. Then, the inhibitor was dissolved in 1 M HCl and 1 M H_2SO_4 separately and appropriately diluted to get solutions of desired concentrations.

2.2. Specimen preparation

MS specimens of the composition C = 0.07%, Mn = 0.34%, P = 0.08% and the remaining % of Fe were chosen for the present study. Mild steel specimens of the size $1.5 \times 5.0 \times 0.2$ cm were used for weight loss studies, while coupons of size 1 cm^2 were used for electrochemical studies and SEM analysis. The specimens were well cleaned and then degreased with acetone, prior to use.

2.3. Weight loss study

The mechanically polished and preweighed mild steel specimens of uniform size were suspended in 100 ml test solutions with and without *S. platensis* at different concentrations for a period of 2 h at three different temperatures viz., 303 K, 313 K and 323 K. Then the specimens were washed, dried and weighed. From the weight loss data, the inhibition efficiency (IE) was calculated as follows (Bothi Raja and Sethuraman, 2009a),

$$IE\ (\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 and W_2 are the weights of the MS coupons in presence and absence of inhibitor, respectively.

2.4. Electrochemical studies

The CHI electrochemical analyzer Model No. 650B was used to record Tafel polarization curve and impedance curve. MS plates served as working electrode while platinum and calomel electrodes were used as counter electrode and the reference electrode, respectively. The electrodes were immersed for 30 min to obtain steady state open circuit potential. Impedance measurements were carried out at E_{corr} potential at the range from 0.1 to 1000 Hz at an amplitude of 10 mV. The impedance diagrams are given in Nyquist representation (Bothi Raja and Sethuraman, 2009b). The impedance and polarization parameters such as double layer capacitance (C_{dl}), charge transfer resistance (R_{ct}), corrosion current (i_{corr}), corrosion potential (E_{corr}), anodic Tafel slope (b_a) and cathodic Tafel slope (b_c) were computed from the polarization curves and Nyquist plots (Bothi Raja and Sethuraman, 2009a).

The IE values were calculated from potentiodynamic polarization measurements using the Eq. (2),

$$\text{IE}\ (\%) = \frac{I_{corr} - I_{corr(1)}}{I_{corr}} \times 100 \quad (2)$$

where I_{corr} is the corrosion current without inhibitor and $I_{corr(1)}$ is the corrosion current with inhibitor.

To obtain the double layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum, ($-Z_{\max}$), is found and C_{dl} values are obtained from the equation:

$$f(-Z''\max) = \frac{1}{2\pi C_{dl} R_{ct}} \quad (3)$$

From a.c. impedance measurements, the IE values were calculated from the following relation,

$$\text{IE} = \frac{R_{ct(i)} - R_{ct(b)}}{R_{ct(i)}} \times 100 \quad (4)$$

where $R_{ct(i)}$ and $R_{ct(b)}$ were the inhibited and uninhibited charge transfer values, respectively.

2.5. SEM images

For taking SEM images, the MS specimens were immersed in the solution without inhibitor as well as in the solution containing optimum concentration of inhibitor (500 ppm) separately for 2 h. Then, the specimens were removed and rinsed with rectified spirit quickly. The images were taken using HITACHI – Model S – 3000 H Scanning Electron Microscope.

3. Results and discussion

3.1. Weight loss study

The inhibition efficiency was obtained from weight loss measurements at different concentrations of inhibitor at various temperatures viz., 303 K, 313 K and 323 K in the usual way (Senthil Kumar et al., 2009). The variation in inhibition efficiency with concentration of the green inhibitor is shown in Table 1. From the values of Table 1, it is clear that the *S. platensis* effectively inhibits the corrosion rate of MS in both HCl and H_2SO_4 media with higher IE in H_2SO_4 medium. This is due to the availability of more sites on metal surface for adsorption in H_2SO_4 medium because of lesser adsorption of the sulphate ions on the metal surface (Ahamad and Quraishi, 2009).

Inhibition efficiency was found to increase with the concentration of inhibitor (Table 1), with maximum IE at a concentration of 500 ppm. The increase in inhibition efficiency is due to the increase in the number of constituent molecules of *S. platensis* adsorbed on the metal surface at higher concentrations (Zhang and Hua, 2009), so that the active sites of the metal are protected by the inhibitor molecules.

Table 1 Effect of *S. platensis* on MS in acid media (weight loss studies).

S. No.	Concentration of inhibitor (ppm)	% of IE (in H_2SO_4)			% of IE (in HCl)		
		303 K	313 K	323 K	303 K	313 K	323 K
1	100	54.62	48.98	41.42	50.56	48.88	37.41
2	200	60.32	52.72	44.88	56.81	51.68	41.98
3	300	70.04	62.99	53.64	66.29	56.17	52.29
4	400	76.39	68.89	59.52	68.38	65.16	57.63
5	500	82.65	73.54	64.57	74.15	70.79	61.45

In both HCl and H_2SO_4 media, the inhibition efficiency decreased as the temperature increased. This may be due to the fact that constituents of inhibitor are adsorbed physically on the surface of the mild steel. The increase of the temperature might cause the desorption of the inhibitor constituents from the surface of the metal, due to the decrease in the strength of adsorption process at higher temperatures (Abboud et al., 2009).

3.2. Adsorption isotherms

The adsorption isotherms provide the basic information on the interaction between the green inhibitor and the mild steel surface (Senthil Kumar et al., 2009). The areas of surface coverage (θ) computed from the weight loss data were plotted against concentration to fit into Temkin isotherm (Figs. 1a and 1b).

From the slope of the Temkin isotherm, ΔG was calculated by the following relation (Bothi Raja and Sethuraman, 2009b),

$$\Delta = -RT\ \ln(55.5\ K) \tag{5}$$

where R is universal gas constant in kJ mol^{-1}, 55.5 is a concentration of water in mol/L (Bouklah et al., 2006), T is the temperature and K is the equilibrium constant.

The negative values of ΔG (Table 2) in both the acids reflect a spontaneous adsorption of phytoconstituents of *S. platensis* on the surface of the MS (Bentiss et al., 2009). The ΔG values are less than −40 kJ mol^{-1}, which indicated that the molecules are physisorbed (De Souza and Spinelli, 2009) in the following ways.

(i) Green inhibitor may be adsorbed through the donor (inhibitor)–acceptor (metal) interaction between the π-electrons and the unshared electron pairs of the hetero-atoms of the constituents of *S. platensis* to make a bond with vacant *d* orbitals of the metal surface (Bothi Raja and Sethuraman, 2008) and
(ii) –NH_2 groups of amino acids present in *S. platensis* may be readily protonated in acid media by which, it might be adsorbed over the metal surface through negatively charged acid anions (Cl^-, SO_4^{2-}) (Bothi Raja and Sethuraman, 2008).

Further, the entropy (ΔS) is calculated by the following equation,

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{6}$$

where ΔG and ΔH are the free energy of adsorption and enthalpy, respectively, and T is the temperature.

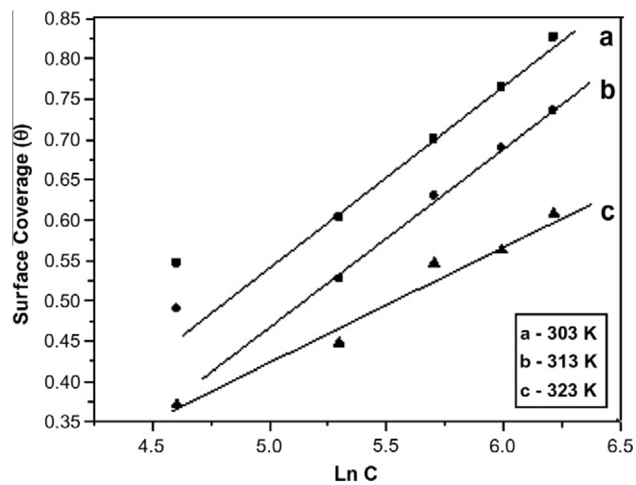

Figure 1a Temkin isotherm of *S. platensis* on MS in 1 M H_2SO_4.

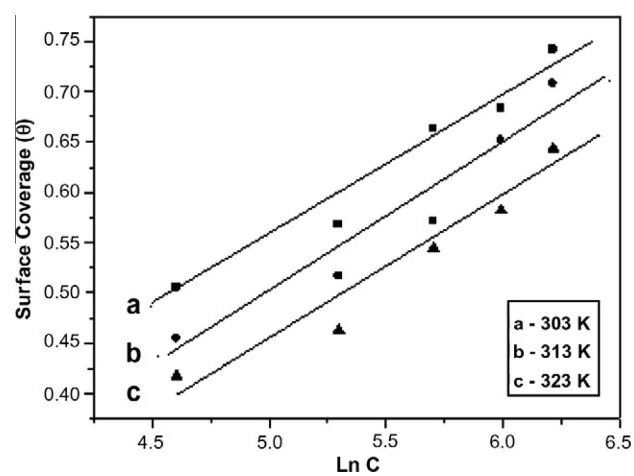

Figure 1b Temkin isotherm of *S. platensis* on MS in 1 M HCl.

Table 2 Thermodynamic parameters for of *S. platensis* on MS in acid media.

S. No.	Medium	Temperature (K)	ΔG (kJ mol^{-1})	ΔS (kJ mol^{-1})
1	H_2SO_4	303	−12.02	8.2764
		313	−12.04	8.3521
		323	−12.06	8.3574
2	HCl	303	−11.99	8.2741
		313	−12.01	8.3512
		323	−12.05	8.3523

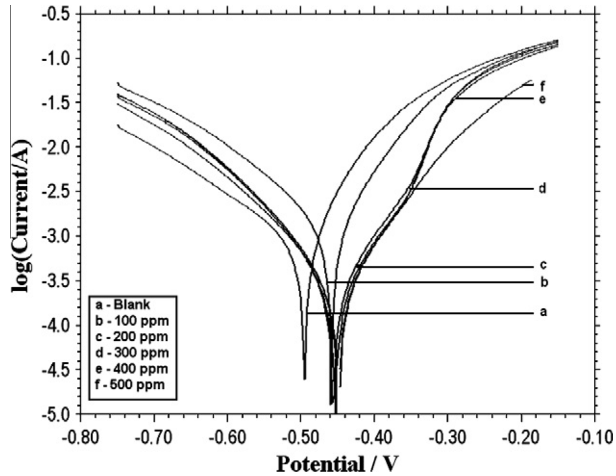

Figure 2a Tafel plots of *S. platensis* on MS in 1 M H_2SO_4.

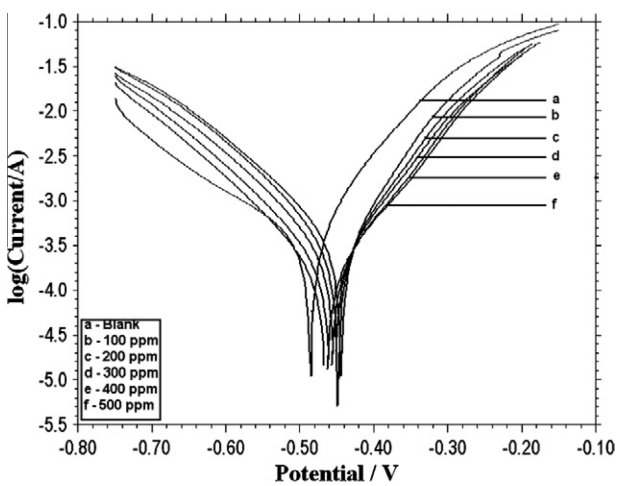

Figure 2b Tafel plots of *S. platensis* on MS in 1 M HCl.

3.3. Electrochemical studies

3.3.1. Potentiodynamic polarization

From the anodic and cathodic polarization curves (Figs. 2a and 2b) for *S. platensis* in 1 M HCl and H_2SO_4 media at different concentrations, various electrochemical parameters were computed and listed (Tables 3 and 4). From the i_{corr} values, the inhibition efficiency was calculated as in Eq. (2) (Senthil Kumar et al., 2009).

From Figs. 2a and 2b, it can be seen that, the inhibitor begins to desorb at a potential closer to −350 mV/SCE, which can be called as desorption potential. The similar behaviour has been obtained with other organic compounds (Lorenz and Mansfeld, 1981; Aksut et al., 1982; El Azar et al., 2002).

From the Tables 3 and 4, it is observed that the E_{corr} values were shifted slightly to the anodic region. Both the anodic and cathodic Tafel slope values decreased with the increase in the concentration of the inhibitor, thus indicating the mixed mode of inhibition with predominantly anodic type of inhibition (El-Etre et al., 2004).

This reveals that the green inhibitor reduces anodic dissolution along with the reduction of cathodic hydrogen evolution.

3.3.2. Impedance studies

The Nyquist plots for MS in both acid media as shown in Figs. 3a and 3b are not perfect semicircles, which is attributed to non-homogeneity of the surface and roughness of the metal (Bentiss et al., 2009). From the plots, it could be seen that impedance response of mild steel is increased by the addition of green inhibitor (Ahamad and Quraishi, 2009). For a corrosion system, the formation of double layer at metal/solution interface can be represented by the electronic equivalent circuit (Fig. 3c).

The C_{dl} and R_{ct} values calculated from the Nyquist plots are listed in Tables 5 and 6.

The R_{ct} values increased with the increase of the concentration of inhibitor, which shows protection of MS surface by the inhibitor while the values of C_{dl} decreased with the increase in the concentration of inhibitor, which is due to the increase in

Table 3 Effect of *S. platensis* on MS in 1 M H_2SO_4 (polarization studies).

S. No.	Concentration of inhibitor (ppm)	b_a (mV dec^{-1})	b_c (mV dec^{-1})	E_{corr} (mV)	I_{corr} (μA cm^{-2})	% of IE
1	0	116.26	179.46	−0.4961	1192	–
2	100	105.21	154.51	−0.4593	678.22	43.01
3	200	66.35	122.98	−0.4572	315.24	73.55
4	300	64.97	119.11	−0.4561	256.57	78.48
5	400	60.64	116.25	−0.4536	218.96	81.63
6	500	59.41	116.13	−0.4502	214.61	81.99

Table 4 Effect of *S. platensis* on MS in 1 M HCl (polarization studies).

S. No.	Concentration of inhibitor (ppm)	b_a (mV dec^{-1})	b_c (mV dec^{-1})	E_{corr} (mV)	I_{corr} (μA cm^{-2})	% of IE
1	0	106.55	201.32	−0.4857	488.2	–
2	100	93.37	133.28	−0.4651	367.8	24.66
3	200	92.67	127.35	−0.4593	290.9	40.41
4	300	92.42	126.93	−0.4531	241.9	50.45
5	400	92.33	125.18	−0.4514	185.8	61.94
6	500	90.99	125.03	−0.4502	163.2	66.57

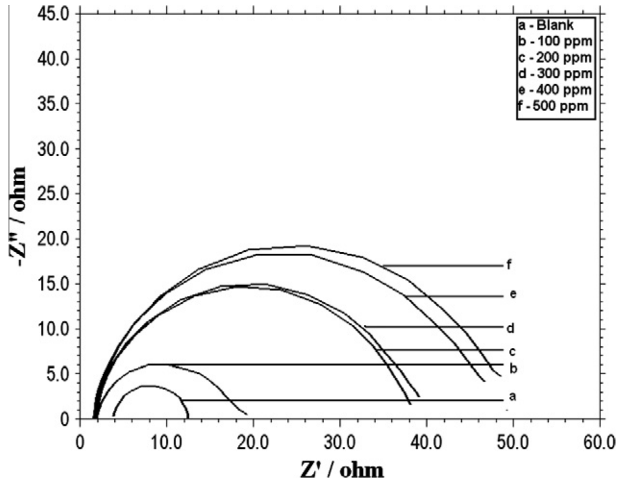

Figure 3a Nyquist plots of *S. platensis* on MS in 1 M H_2SO_4.

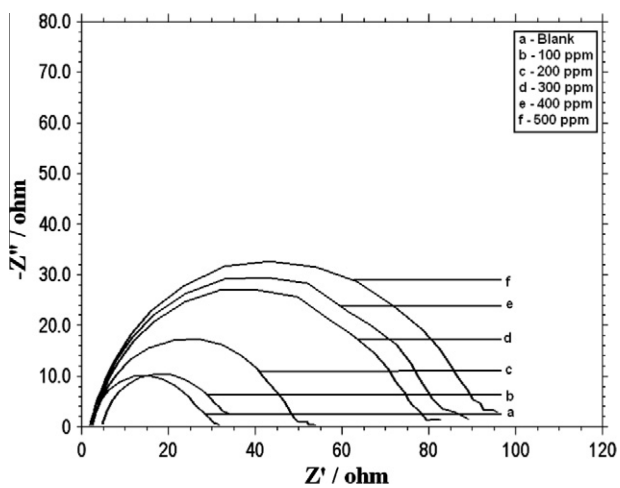

Figure 3b Nyquist plots of *S. platensis* on MS in 1 M HCl.

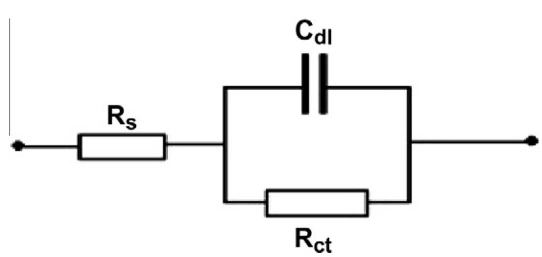

Figure 3c Equivalent circuit model for Nyquist plots.

Table 5 Effect of *S. platensis* on MS in 1 M H_2SO_4 (impedance studies).

S. No.	Concentration of inhibitor (ppm)	R_{ct} (Ω cm^{-2})	C_{dl} (μF cm^{-2})	% of IE
1	0	9.12	1765.22	–
2	100	17.18	436.58	46.91
3	200	36.09	252.99	74.72
4	300	37.2	246.17	75.41
5	400	45.11	245.93	79.77
6	500	46.93	240.53	80.21

Table 6 Effect of *S. platensis* on MS in 1 M HCl (impedance studies).

S. No.	Concentration of inhibitor (ppm)	R_{ct} (Ω cm^{-2})	C_{dl} (μF cm^{-2})	% of IE
1	0	24.48	93.26	–
2	100	31.43	88.23	22.11
3	200	49.72	85.28	50.76
4	300	80.32	83.58	69.52
5	400	87.53	81.97	72.03
6	500	101.25	80.42	75.82

the thickness of protective layer at higher concentrations (Xu et al., 2008; Elayyachy et al., 2006).

Inhibition efficiency, calculated from the values of R_{ct} (Eq. (3)) El-Etre et al., 2004, was found to be maximum at a concentration of 500 ppm of the inhibitor. The results of electrochemical studies were in good agreement with the results of gravimetric studies with slight deviations. This is due to the difference in immersion period of MS in the aggressive media (El-Etre et al., 2004).

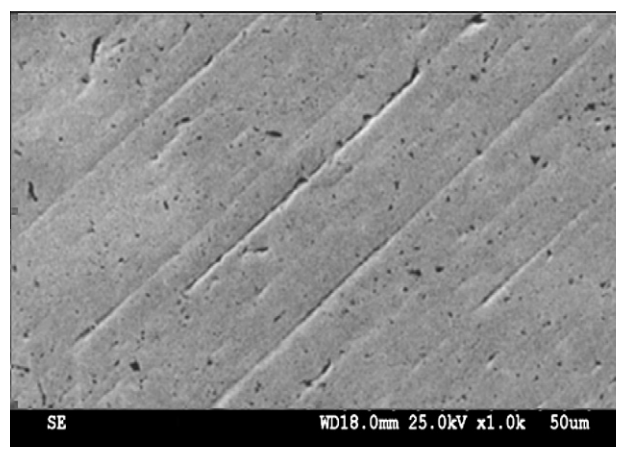

Figure 4 SEM micrograph of the polished MS specimen.

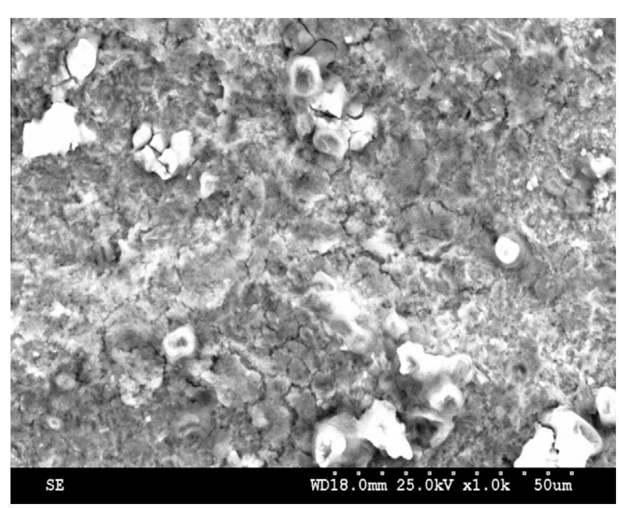

Figure 5a SEM micrograph of MS in 1 M H_2SO_4.

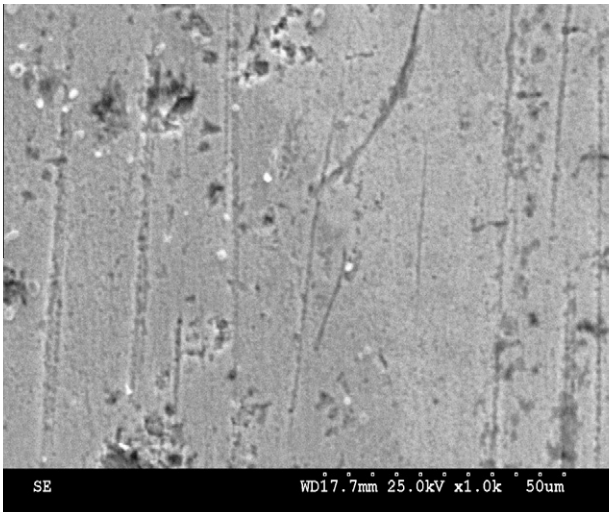

Figure 5b SEM micrograph of MS in 1 M H_2SO_4 with green inhibitor (500 ppm).

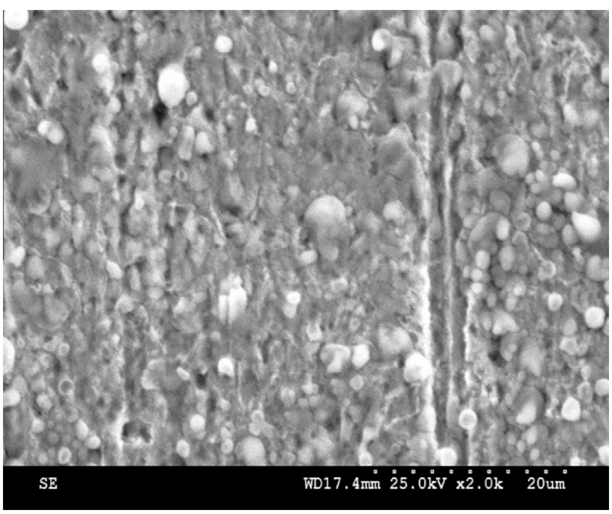

Figure 6a SEM micrograph of MS in 1 M HCl.

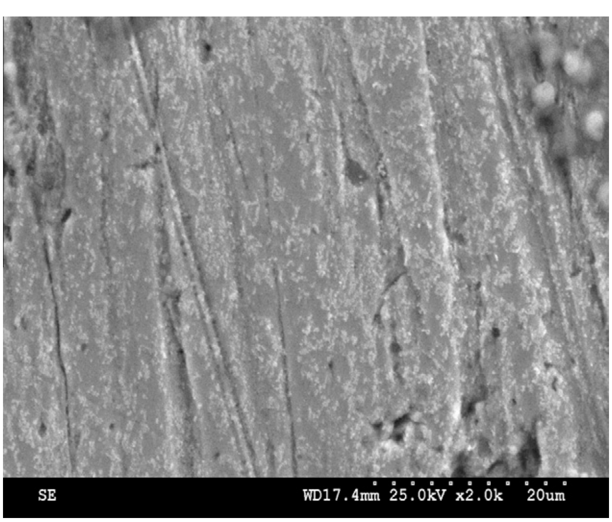

Figure 6b SEM micrograph of MS in 1 M HCl with green inhibitor (500 ppm).

3.4. SEM images

Scanning Electron Microscope (SEM) images were indicative of the changes that accompany the corrosion and protection on the MS surface of the mild steel (Figs. 4–6b). Figs. 5a and 6a showed the damage caused to the surface by the acids, while Figs. 5b and 6b revealed the formation of a protective layer by the constituents of *S. platensis*.

4. Conclusions

The following conclusions are drawn from the present study:

i. *S. platensis* inhibits the corrosion of mild steel in both HCl and H_2SO_4 media in a concentration dependent manner.
ii. The inhibition efficiency is better in H_2SO_4 medium than in HCl medium.
iii. *S. platensis* inhibits the corrosion through adsorption following Temkin isotherm. The values of ΔG were indicative of the physisorption.
iv. The inhibitor altered both anodic and cathodic Tafel slopes, which showed the mixed mode of action of the inhibitor molecules.
v. The increase in R_{ct} values and decrease in C_{dl} values confirm the formation of an insulated protective layer over the mild steel surface, which was supported by SEM images.
vi. The corrosion inhibitive effect shown by *S. platensis* can be correlated to the presence of phytoconstituents such as amino acids (methionine), fatty acids (γ-linolenic acid), peptides and proteins.

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