

***Solanum Tuberosum* as an Inhibitor of Mild Steel Corrosion in Acid Media**

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ABSTRACT: Acid extract of *Solanum tuberosum* was tested as corrosion inhibitor for mild steel in 1 M HCl and H₂SO₄ media using different techniques: Weight loss (in different temperatures viz., 303, 313 and 323 K), Potentiodynamic polarization, Electrochemical Impedance Spectroscopy (EIS) and SEM techniques. The studies reveal that the plant extract act as good inhibitors in both the acid media and better in H₂SO₄ medium. Tafel polarization method indicated that the plant extract behaves as mixed mode inhibitor. Double layer capacitance and charge transfer resistance values derived from Nyquist plots obtained from AC impedance studies give supporting evidence for the anticorrosive effects of these plants. The inhibitive effect may be attributed to the adsorption of the inhibitor on the surface of MS following Temkin adsorption isotherm. Increase of inhibition efficiency with increase of temperature along with E_a values serve as proof for chemisorption. SEM studies provide the confirmatory evidence for the protection of MS by the green inhibitor. The study reveals the potential of the plant extract for combating corrosion which may be due to the adsorption of alkaloids and other phytoconstituents.

KEY WORDS: *Solanum tuberosum*, Corrosion inhibitor, Electrochemical studies, Chemisorption, SEM.

INTRODUCTION

Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Inhibitors are generally used in these processes to control the metal dissolution as well as acid consumption. Most of the well known acid inhibitors are organic compounds containing N, S and / or O atoms [1, 2]. These organic compounds can adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion rate. Most of investigated compounds are toxic and cause severe environmental hazards.

The toxic effects of most synthetic corrosion inhibitors have led to the use of natural products which are eco-friendly and harmless. The use of natural products as corrosion inhibitors is well documented [3]. In this present study authors have investigated the inhibition potential of *Solanum tuberosum* (*S. tuberosum*) extract in 1 M HCl and H₂SO₄ media through weight loss, electrochemical and SEM techniques. *S. tuberosum* belongs to Solanaceae family which is commonly known as potato and it contains glycoalkaloids [4].

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MATERIALS AND METHODS

Inhibitor preparation

Leaves of *S.tuberosum* were powdered well and 500 g was refluxed with 10 % HCl for 6 hours, with a view to extract the basic components present in the leaf portion to the acid layer. After this extraction the resultant acid solution contained the salts of basic component. Then the extract was filtered off and neutralized with 10 % NaOH up to pH 8 in order to liberate the base from the salt. The neutralized solution was then extracted with chloroform. The organic (chloroform) layer consisting of basic organic compounds was evaporated and the resultant gummy materials obtained were dried and powdered. Various concentrations of the plant extract were prepared by dissolving the known quantity of the resultant powder.

Specimen preparation

MS specimens containing C = 0.01 %, Mn = 0.34 %, P = 0.08 % and Fe = 99.51 % were used for the study. MS specimens of size 3×1×0.21 cm were used for weight loss study, specimens of exposed area 1×1 cm (square - the rest being covered with lacquer) with stem were used for electrochemical study and 1×1 cm were used for SEM analysis. The surface preparation of the mechanically polished specimens were carried out using different grades of emery paper and then degreased with acetone.

Weight loss method

The polished and pre weighed MS specimens of uniform size were suspended in 100 mL test solutions with and without the inhibitor at different concentrations for a period of 2 hours. Then the specimens were washed, dried and weighed. The weight loss was calculated. From this data, inhibition efficiency (IE) was calculated from the following equation [5]:

$$\text{Inhibition efficiency} = \frac{\text{Weight loss without inhibitor} - \text{Weight loss with inhibitor}}{\text{Weight loss without inhibitor}} \times 100 \quad (1)$$

In order to study the nature of adsorption activation energy was calculated using the following formula [6]:

$$E_a = \frac{RT_1T_2}{T_2 - T_1} \times \ln \left(\frac{r_2}{r_1} \right) \quad (2)$$

where, R is gas constant, T₁ and T₂ are temperatures 1 and 2, r₁ and r₂ are corrosion rates 1 and 2.

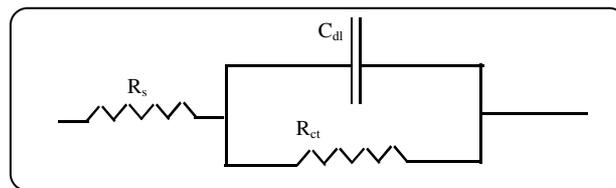


Fig. 1: The electrical equivalent circuit for a.c. impedance measurement.

Electrochemical studies

CH electrochemical analyzer model 650 B was used to record Tafel polarization curve and Nyquist impedance curve. A conventional three electrode system was used for this purpose. MS specimen of exposed area of 1cm² with stem was used as a working electrode. Pt electrode and calomel electrode served as auxiliary and reference electrodes respectively. The working electrode was polished with 1/0, 2/0, 3/0 and 4/0 grade emery papers and washed with distilled water before usage. The polarization measurements were recorded at the end of 30 min; the electrode potential was prearranged by changing automatically from -300 mV to -700 mV with the scan rate of 100 mVsec⁻¹. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities. IE values were calculated from the I_{corr} values from the following formula [5].

$$IE = \frac{I_{\text{corr}(b)} - I_{\text{corr}(i)}}{I_{\text{corr}(b)}} \quad (3)$$

where, I_{corr(b)} and I_{corr(i)} were the uninhibited and inhibited corrosion current density values respectively. AC impedance measurements were carried out at E_{corr} immersion on standing in the atmosphere of air at the range from 0.1 Hz to 1000 Hz at an amplitude of 10 mv. The impedance diagrams are given in Nyquist representation. The electrical equivalent circuit for the system is shown in Fig. 1 and its corresponding equation is given below:

$$Z = R_s + \frac{R_{ct}}{1 + (j\omega R_{ct})^\alpha} \quad (4)$$

In the electrical equivalent circuit (Fig. 1) R_s is the solution resistance, R_{ct} the charge transfer resistance and C_{dl} is the double layer capacitance. IE was calculated from the charge transfer resistance (R_{ct}) values from following equation [5].

Table 1: Effect of *S. tuberosum* extract on MS corrosion in acid media.

S. No.	Concentration of Inhibitor (ppm)	% of IE (in HCl)			% of IE (in H ₂ SO ₄)		
		303 K	313 K	323 K	303 K	313 K	323 K
1	4	60.47	73.01	82.13	68.56	72.95	76.94
2	8	64.71	76.82	83.35	71.78	76.86	79.17
3	12	68.47	80.64	85.99	73.29	79.16	83.81
4	16	74.59	85.82	88.43	76.89	81.38	87.05
5	20	78.35	87.05	91.37	80.11	82.99	93.28

Table 2: Activation Energy (E_a) values of MS corrosion in acid media in presence and absence of green inhibitor.

S. No.	Corrosive medium	E_a (kJmol ⁻¹)	
		HCl	H ₂ SO ₄
1	Blank	89.88	129.39
2	<i>Solanum tuberosum</i>	49.45	69.80

$$IE = \frac{R_{ct(i)} - R_{ct(b)}}{R_{ct(i)}} \quad (5)$$

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

SEM analysis

The specimens used for surface morphological examination were immersed in acid containing optimum concentration of inhibitor and blank for 2h. Then, they were removed, rinsed quickly with rectified spirit and dried. The analysis was performed on HITACHI - model S-3000 H Scanning Electron Microscope.

RESULTS AND DISCUSSION

Weight loss studies

The values of inhibition efficiency obtained from weight loss measurements for MS in acid solution containing different concentrations of extract of *S. tuberosum* at different temperatures viz., 303 K, 313 K and 323 K are listed in table 1. From the table it is clear that *S. tuberosum* extract inhibited the corrosion of MS in both the acid media. The inhibition efficiency increases with increase of concentration of the green inhibitors reaching a maximum at a higher concentration (20 ppm). This suggests that increase in the inhibitor concentration increases the number of molecules adsorbed over the MS

surface, blocks the active sites in which direct acid attack proceed and protects the metal from corrosion. Further the inhibition efficiency increases with increase of temperature also. This suggests that phytoconstituents of the green inhibitors adsorb chemically on the MS surface; form a protective layer and shield the metal from corrosion [7].

Table 2 represents the average E_a values for MS corrosion in acid media in the presence and absence of green inhibitor at different temperatures. From the table it is clear that E_a values decrease in the presence of inhibitors which clearly support the chemisorption process [8]. This observation also correlated well with the weight loss results wherein IE increased with the increase of temperature thus confirming the chemisorption mode of adsorption involved in the corrosion inhibition process.

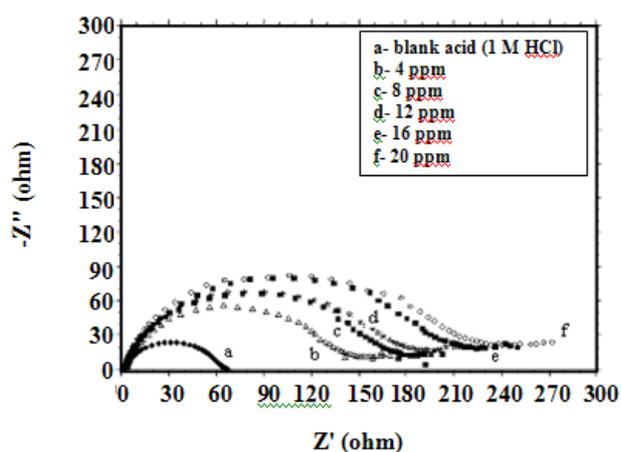
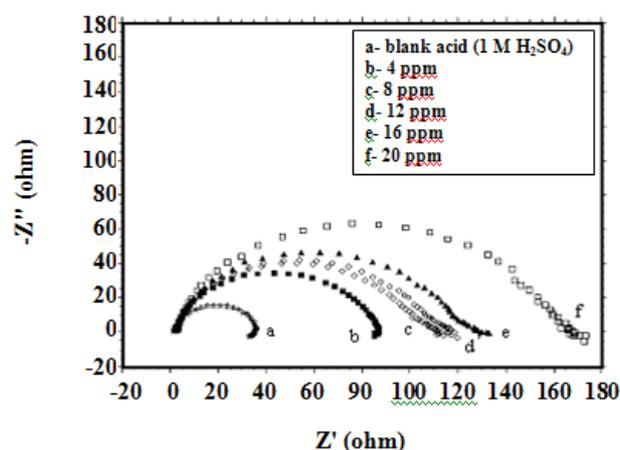
Electrochemical studies

Impedance studies

The Nyquist plots of the impedance behavior of MS in 1 M HCl and 1 M H₂SO₄ in the presence of various concentrations of green inhibitor is shown in Figs. 2 and 3. The existence of a single semicircle shows the presence of single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecule. The slightly depressed nature of semicircle is the characteristic for solid electrodes and such frequency dispersion has been attributed to roughness and other inhomogenities of the solid electrode [9]. The charge transfer resistance (R_{ct}) and the interfacial double layer (C_{dl}) values derived from these curves are listed in table 3. From the table it is obvious that R_{ct} values increase with increase in the inhibitor concentration while C_{dl} values decrease. *S. tuberosum* shows maximum inhibition efficiency at the maximum concentration (20 ppm).

Table 3: Effect of *S. tuberosum* on MS in 1 M HCl & 1 M H₂SO₄ media (a.c. impedance studies).

S. No.	Acid medium	Concentration of Inhibitor (ppm)	R _{ct} (Ω cm ²)	C _{dl} (μFcm ⁻²)	% of IE
1	HCl	0	64.41	35.44	-
		4	165.68	15.82	61.12
		8	199.45	15.71	67.70
		12	216.40	13.87	70.23
		16	246.77	12.15	73.89
		20	269.80	10.33	76.12
2	H ₂ SO ₄	0	32.20	232.93	-
		4	84.27	19.34	61.78
		8	110.97	17.63	70.98
		12	116.41	17.31	72.34
		16	131.81	16.80	75.57
		20	169.41	16.36	80.99

Fig. 2: Nyquist plot of *S. tuberosum* on MS in HCl medium.Fig. 3: Nyquist plot of *S. tuberosum* on MS in H₂SO₄ medium.

Tafel polarization method

The potentiodynamic polarization behaviour of MS in 1 M HCl and H₂SO₄ with the addition of various concentrations of *S. tuberosum* is shown in Figs. 4 and 5. The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic and cathodic Tafel slopes (b_a and b_c) derived from these curves are given in table 4. From the table it is found that the addition of green inhibitor decreases the dissolution rate of MS in acid media. The corrosion current density values decreased considerably for green inhibitor in both the acid media.

The shift in the values of corrosion potential (E_{corr}) for

S. tuberosum extract is not significant. However from the variations seen in both anodic and cathodic Tafel slopes it can be concluded that the green inhibitor exert through mixed mode inhibition.

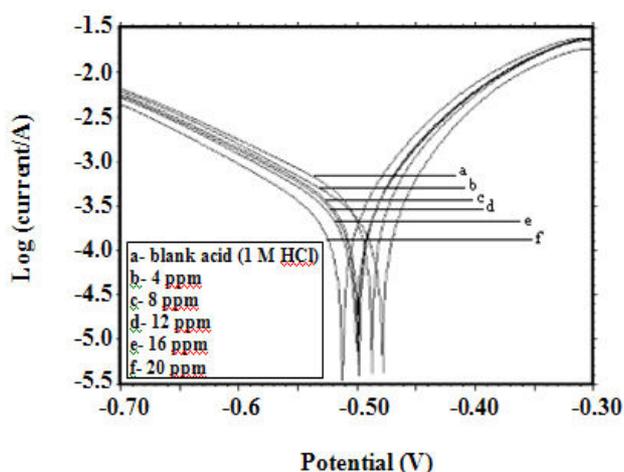
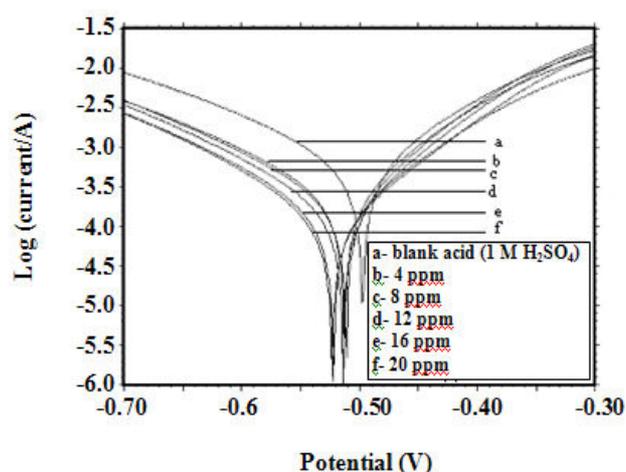
The results of electrochemical studies agreed well with those of weight loss studies with the slight deviation in the values. Variation in the immersion period of MS in corrosion medium is the reason for the observed deviation [10].

SEM analysis

Scanning Electron Microscope (SEM) images were taken in order to study the changes that occur during the

Table 4: Effect of *S. tuberosum* on MS in 1 M HCl & 1 M H₂SO₄ media (Polarization studies).

S. No.	Acid medium	Concentration of Inhibitor (ppm)	b_c (mVdec ⁻¹)	b_a (mVdec ⁻¹)	E_{corr} (mV)	I_{corr} (μ Acm ⁻²)	% of IE
1	HCl	Blank	95	110	480	398.10	-
		4	95	80	488	251.18	36.90
		8	88	162	500	199.52	49.88
		12	70	150	500	158.48	60.19
		16	70	150	500	125.89	68.37
		20	65	140	512	100	74.88
2	H ₂ SO ₄	Blank	95	110	495	1000.00	-
		4	88	162	515	446.68	55.33
		8	70	150	488	398.10	60.19
		12	70	150	500	316.22	68.37
		16	65	140	500	251.18	74.89
		20	62	123	500	199.52	80.04

Fig. 4: Tafel plot of *S. tuberosum* on MS in HCl medium.Fig. 5: Tafel plot of *S. tuberosum* on MS in H₂SO₄ medium.

corrosion of MS in the presence of and absence of green inhibitor (Figs. 6-10). Parallel features on the polished steel surface before exposure to the corrosive solution, which are associated with polishing scratches, were observed (Fig. 6). Examination of Figs. 7 and 8 revealed that the specimen immersed was highly damaged in the presence of 1 M HCl and H₂SO₄ respectively due to the direct attack of aggressive acids. But, Figs. 9 and 10 clearly showed that the metal surface was highly covered with the protective layer formed by the green inhibitor which prevents the metal from further attack of acid media thus inhibiting corrosion.

Mechanism of corrosion inhibition

To understand the mechanism of corrosion inhibition, the adsorption behavior of the organic adsorbates on the metal surface must be known. The surface coverage (θ) $\{\theta = IE/100\}$ values were evaluated using weight loss values.

The θ values for different concentrations of inhibitors were tested graphically by fitting to Temkin isotherm. A plot of θ against $\log C$ for different concentrations shows a straight line indicating that all the green inhibitors follow the Temkin adsorption isotherm (Figs. 11 and 12).

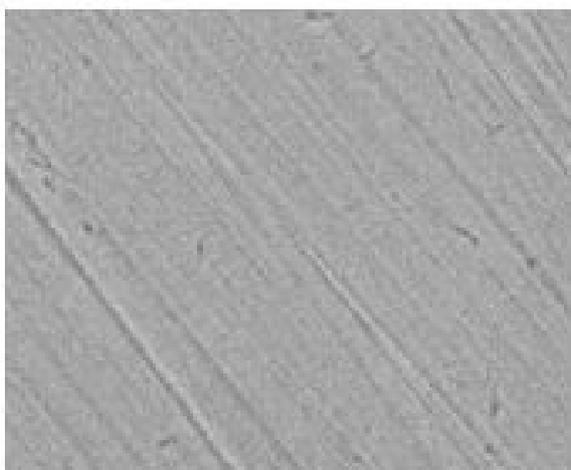


Fig. 6: SEM image of polished MS surface.

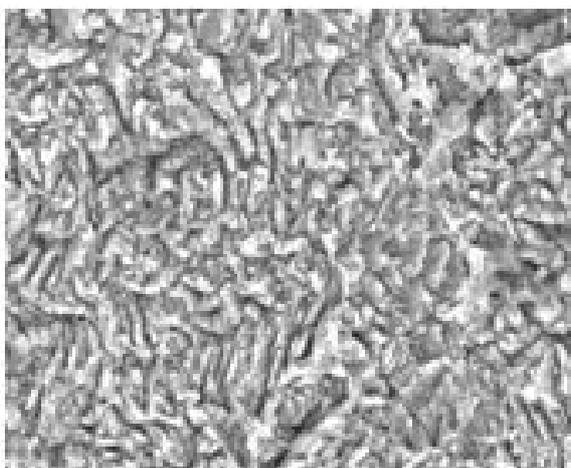


Fig. 7: SEM image of MS in 1M HCl medium.

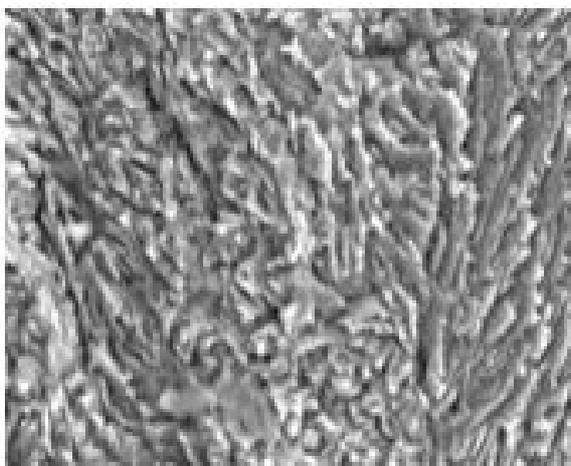


Fig. 8: SEM image of MS in 1M H₂SO₄ medium.

As far as the inhibition process is concerned, it is generally assumed that the adsorption of the inhibitor at the metal-solution interface is the first step in the mechanism of action of inhibitor in aggressive media. Four types of adsorption may take place involving organic molecules at the metal - solution interface.

i- Electrostatic between charged molecules and the charged metal.

ii- Interaction of unshared electron pairs in the molecule with the metal.

iii- Interaction of π - electrons with the metal and.

iv- a combination of the above [11].

The data obtained from the temperature dependence of the inhibition process suggest a chemical adsorption. To further elucidate the mechanism of inhibitor adsorption, it is necessary to establish the adsorption modes of the inhibiting species. The predominant adsorption mode depends upon factors such as the extract composition, type of acid anion as well as chemical changes to the extract. Since, the isolated inhibitor from chloroform layer is basic in nature; protonation occurs easily in HCl and H₂SO₄ media. The protonated species can get adsorbed on cathodic sites of the MS surface and reduce H₂ gas evolution.

S. tuberosum inhibits the dissolution reaction by adsorption at the metal surface in two different ways [12]. First, the inhibitor may compete with Cl⁻ or SO₄²⁻ ions for sites at the water covered anodic surface. In doing so, the protonated inhibitor loses its associated protons in entering the double layer and chemisorbs by donating electrons to the metal. In addition, the protonated inhibitor electrostatically adsorbs onto the anion covered surface, through its cationic form. Both the modes are depicted in Fig. 13. But, since chemisorption plays a main role, competitive adsorption of the green inhibitor which involves the donation of electron pair to the metal surface appears predominant.

Moreover, the green inhibitor shows good inhibition efficiency in H₂SO₄ medium than in HCl medium. This may be due to the availability of more sites on the metal surface in H₂SO₄ medium because of lesser adsorption of the sulphate ions on the steel surface.

Phytochemical analysis

For isolating the inhibitor from plant species; the procedure for crude alkaloid isolation was carried out.

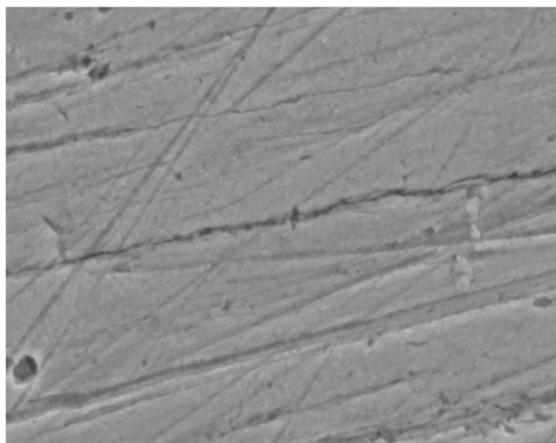


Fig. 9: SEM image of MS in 1 M HCl medium in presence of *S. tuberosum* extract at concentration of 20 ppm.

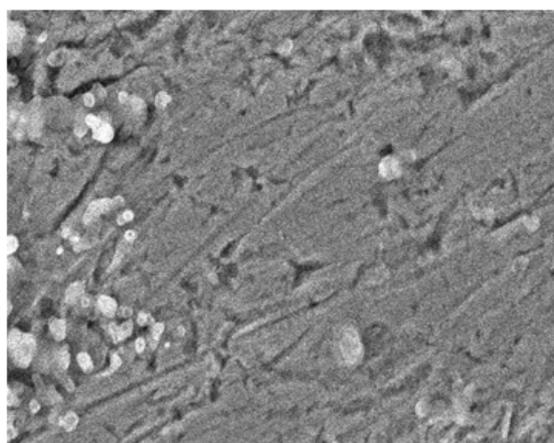


Fig. 10: SEM image of MS in 1 M H₂SO₄ medium in presence of *S. tuberosum* extract at concentration of 20 ppm.

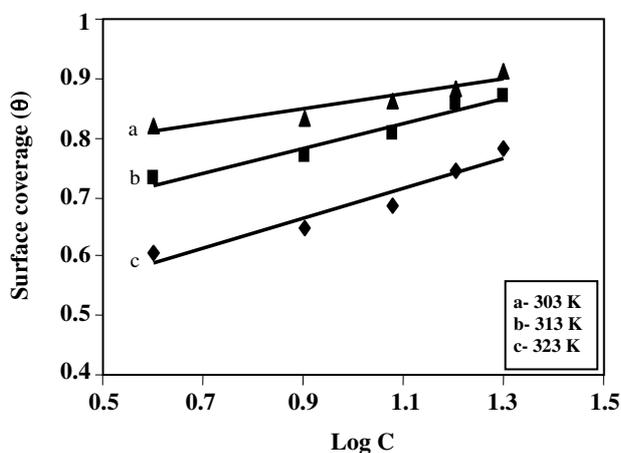


Fig. 11: Temkin plot of *S. tuberosum* in HCl medium.

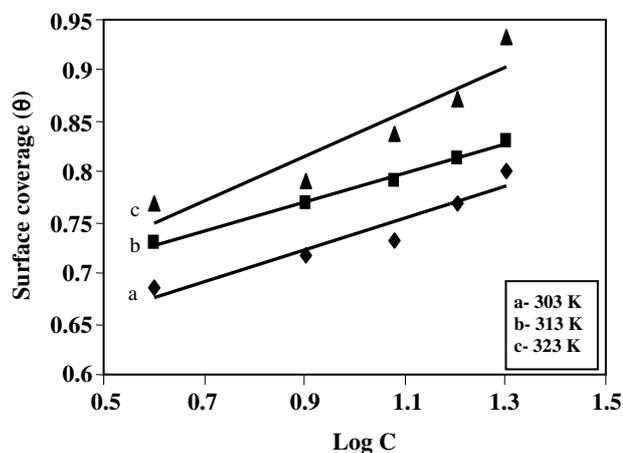


Fig. 12: Temkin plot of *S. tuberosum* in H₂SO₄ medium.

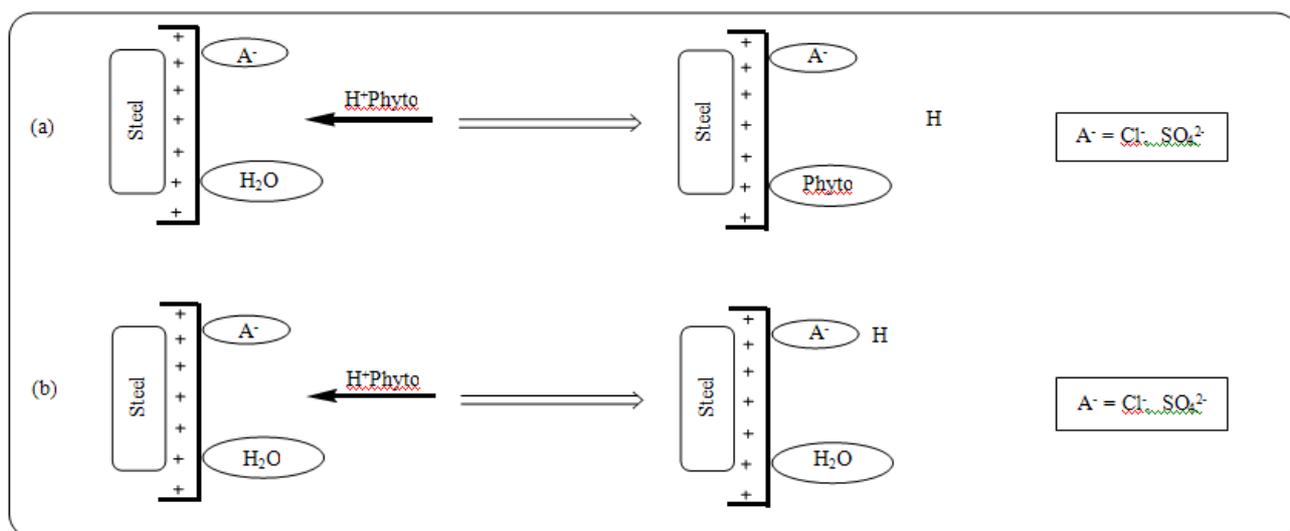


Fig. 13: a) competitive and b) cooperative adsorption of green inhibitor in acid solutions.

After isolation, the powdered compound was analyzed chemically for characterizing the corrosion inhibitory constituent. *S. tuberosum* tested positive for alkaloids [13] and the alkaloids present may be the responsible for anticorrosion effect. Solasodine the glyco alkaloid is the main alkaloidal constituent present in *S. tuberosum* and which has N and O atom in their skeletons which are required for corrosion inhibition effects. Moreover it is likely that protein, cellulose and other ingredients of the plant extract synergistically increase the strength of the layer formed by the solasodine. Thus the formation of strong chemisorbed layer between the metal surface and the phytoconstituents of plant extract could be the cause for the inhibitive effect.

CONCLUSIONS

Following conclusions can be drawn from the present study. The extract of *S. tuberosum* shows significant corrosion inhibition activity in a dose dependent manner. *S. tuberosum* showed a better performance in H₂SO₄ medium than in HCl medium. *S. tuberosum* produces corrosion inhibition following Temkin adsorption isotherm and the temperature studies and Ea values revealed the chemisorption of plant constituents over MS surface.

The green inhibitor affects both cathodic and anodic Tafel slopes in both HCl and H₂SO₄ media and act through mixed mode. SEM images offer a perfect proof for the formation of protective layer of green inhibitor over MS surface thus preventing corrosion. Solasodine the alkaloidal *S. tuberosum* constituent present may be responsible for the corrosion inhibitive effect.

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