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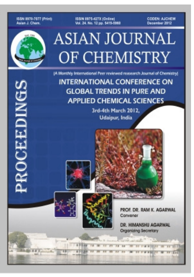

Green Corrosion Inhibitor of Mild Steel in Hydrochloric Acid by the Extract of Native Plant *Stevia rebaudiana* Leaves†

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The inhibition of the corrosion of mild steel in hydrochloric acid solution by the extract of *Stevia rebaudiana* leaves has been studied using weight loss, electrochemical impedance spectroscopy and potentiodynamic polarization techniques. Inhibition was found to increase with increasing concentration of the leaves extract. The effect of temperature, immersion time and acid concentration on the corrosion behaviour of mild steel in 1M HCl with addition of extract was also studied. The inhibition was assumed to occur *via* adsorption of the inhibitor molecules on the metal surface. The adsorption of the extract on the mild steel surface obeys the Temkin adsorption isotherm. The activation energy as well as other thermodynamic parameters (E_a, ΔH and ΔS) for the inhibition process was calculated. These thermodynamic parameters show strong interaction between inhibitor and mild steel surface. The results obtained show that the extract of the leaves of *Stevia rebaudiana* could serve as an effective inhibitor of the corrosion of mild steel in hydrochloric acid media.

Key Words: *Stevia rebaudiana*, Corrosion, Green, Inhibitor, Acidic solutions.

INTRODUCTION

Inhibitors are required to protect metals against acid attack. The need is growing in corrosion inhibitors more and more necessity to stop or delay the process of corrosion[1]. A number of organic compounds have been reported as effective corrosion inhibitors[2-4]. But, most of them are highly toxic to both human being and environment. The known hazard effects of most synthetic corrosion inhibitors are the motivation for the use of some nature products as safe (green) inhibitors.

Recently, plant extracts have again become important as an environmentally acceptable, readily available and renewable source for a wide range of needed inhibitors. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost[5].

Stevia rebaudiana (S. rebaudiana) is a species of composite, in which glucosides, sterols, amino acids and flavonoids are the main components. The aim of this study is to investigate the ability of *S. rebaudiana* as friendly and environmentally safe inhibitors to protect the steel against corrosion in 1 M HCl.

EXPERIMENTAL

Dried *S. rebaudiana* (5 g) plant leaves were soaked in 1 mol L^{-1} HCl (50 mL) solution for 24 h. This concentrated solution (0.1 g mL^{-1}) was used to prepare solutions of different concentrations by dilution method. The steel specimen was embedded in Teflon holder using epoxy resin with an exposed area of 0.29 cm^2. Before each experiment, the electrode was first mechanically polished with various grades of sandpaper (up to 1200 grit) and then ultrasonically cleaned in acetone for 2 min, followed by a rinse in double-distilled water.

Electrochemical experiments were carried out using a CHI660B electrochemical workstation. A classical three-electrode cell, which used with a platinum counter electrode and a saturated calomel electrode (SCE) as reference electrode, was used for electrochemical measurements. Potentiodynamic polarization curves were recorded at a sweep rate of 1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were carried out at open-circuit potential over a frequency range of 0.1 Hz-100 kHz. The sinusoidal perturbation was 5 mV in amplitude.

RESULTS AND DISCUSSION

Weight loss studies: The effect of inhibitor concentration, temperature, immersion time and acid concentration on the corrosion behaviour of mild steel in 1 M HCl with addition of extract was studied by the weight loss experiments (Table-1). Fig. 1 presents the results obtained from the experiments.

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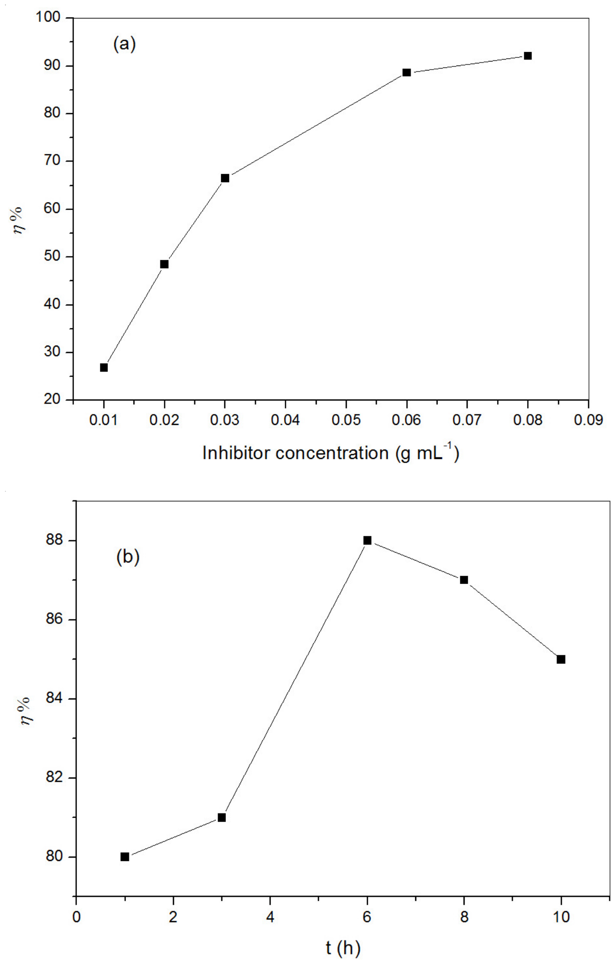
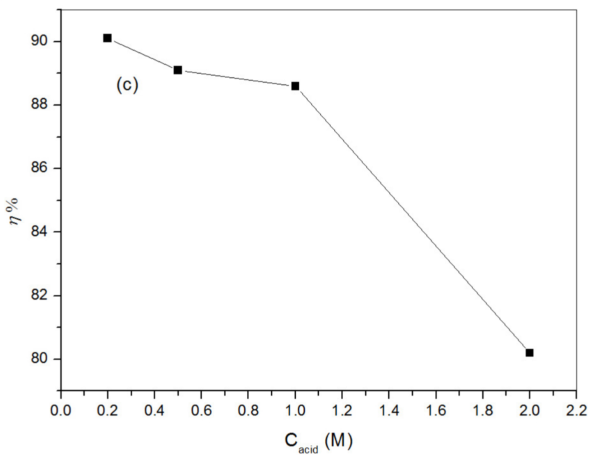
Fig. 1a shows the effect of inhibitor concentration on inhibition efficiency in HCl. The variation of inhibition efficiency with immersion time in HCl is shown in Fig. 1b. It is found that inhibition efficiency increases first and then decreases with time in HCl. The inhibition efficiency at different acid concentration is given in Fig. 1c. It is seen that inhibition efficiency of extract in 1 M HCl decreases from 90.1 to 80.2 %. To evaluate the adsorption of *S. rebaudiana* and activation parameters of the corrosion process of steel in acid media, weight loss measurements are investigated in the range of temperature 303-333 K, as shown in Fig. 1d, in the absence and presence of extract at optimum concentration during 1 h immersion time. The inhibition efficiency (η, %) decreases with increasing temperature. This is due to increased rate of dissolution process of mild steel and partial desorption of the inhibitor from the metal surface[6].

TABLE-1
CORROSION PARAMETERS FOR MILD STEEL IN 1 M HCl WITHOUT AND WITH DIFFERENT CONCENTRATIONS OF *S. rebaudiana* EXTRACT FROM WEIGHT LOSS MEASUREMENTS AT 303 K FOR 6 h

C_{inh} (g mL^{-1})	Weight loss (mg cm^{-2})	η (%)	C_R (mm $year^{-1}$)
Blank	21.40	-	38.87
0.01	15.66	26.79	29.12
0.02	11.03	48.44	20.51
0.03	7.17	66.45	13.33
0.06	2.43	88.60	4.51
0.08	1.69	92.08	3.14





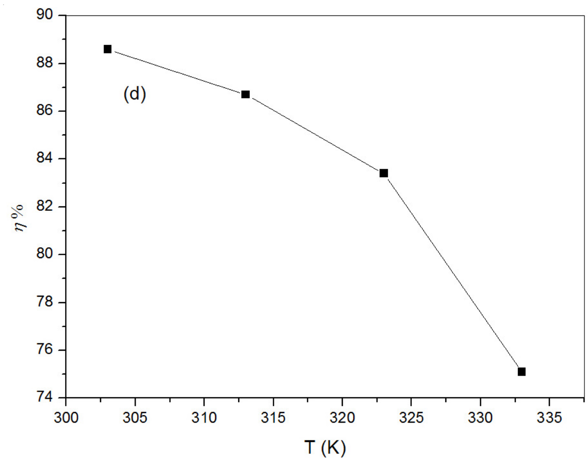


Fig. 1. Variation of inhibition efficiency with (a) inhibitor concentration, (b) immersion period, (c) acid concentration and (d) temperature of solution

The log of corrosion rate is a liner function with 1/T (Arrhenius equation):

$$\log C_R = \frac{-E_a}{2.303RT} + \lambda$$

where, E_a is the activation energy of the corrosion process, R the general gas constant and λ is the Arrhenius pre-exponential factor. A plot of log of corrosion rate obtained by weight loss measurement *vs.* 1/T gave a straight line as shown in Fig. 2, with a slope of - E_a/2.303 R. The values of activation energy are listed in Table-2.

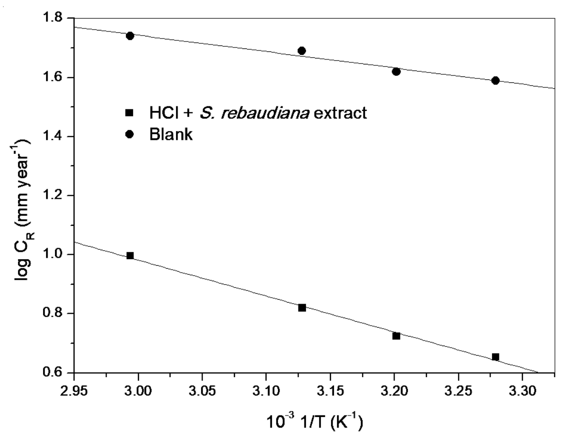


Fig. 2. Arrhenius plot for log CR *vs.* 1/T in HCl with and without 0.06 g mL^{-1} extract

TABLE-2
ACTIVATION PARAMETERS FOR THE CORROSION OF MILD STEEL IN HCl WITH AND WITHOUT 0.06 g mL^{-1} EXTRACT

Systems	E_a (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	ΔQ (kJ mol^{-1})
0.5 M HCl	29.53	23.36	-119.90	-
0.5 M HCl + 0.06 g mL^{-1} extract	52.54	54.75	11.38	341.4

An alternative formulation of Arrhenius equation is[7]:

$$i_{corr} = \frac{RT}{Nh}\exp(\frac{\Delta S}{R})\exp(\frac{-\Delta H}{RT})$$

where, h is the plank's constant, N is Avogadro's number, ΔS is the entropy of activation and ΔH is the enthalpy of activation. A plot of $\ln(i_{corr}/T)$ *vs.* 1/T gave a straight line with the slope of -ΔH/R and the intercept of ln(R/Nh) + ΔS/R, from which the values of ΔS and ΔH were calculated and given in Table-2. The positive signs of enthalpy (ΔH) reflect the endothermic nature of dissolution process. The shift towards positive value of entropy (ΔS) imply that the activated complex in the rate determining step represents dissociation rather than association, meaning that disordering increases on going from reactants to the activated complex[8,9].

Potentiodynamic polarization: Polarization curves for mild steel at various concentration of *S. rebaudiana* leaves extract are shown in Fig. 3. The extrapolation of Tafel straight line allows the calculation of the corrosion current density (i_{corr}). The values of icorr, the corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_c and b_a) and inhibition efficiency (η, %) are given in Table-3. The η (%) is defined as:

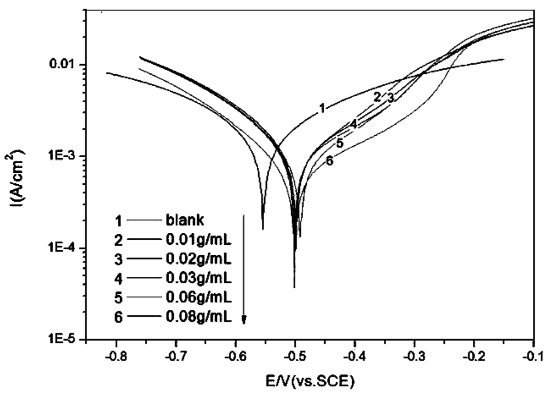


Fig. 3. Polarization curves in absence and presence of different concentrations of the extract

$$\eta\ (\%) = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100$$

where, i^0_{corr} and i_{corr} are the corrosion current density values without and with inhibitor, respectively. It is very clear from Fig. 3 that both anodic and cathodic reactions of mild steel corrosion were suppressed in the presence of *S. rebaudiana* extract and the suppression effect increases with the increasing concentration of the extract. No distinct change is observed in the slopes of the cathodic Tafel lines in the presence of various concentrations of extract, while the slopes of the anodic Tafel lines have an increasing trend with the increase of the concentration of extract. This result suggests that *S. rebaudiana* extract dose not change the mechanism of the hydrogen evolution, whereas modify the anodic metal dissolution reaction.

TABLE-3
POTENTIODYNAMIC POLARIZATION PARAMETERS FOR THE CORROSION OF MILD STEEL IN 1 M HCl WITHOUT AND WITH DIFFERENT CONCENTRATIONS OF THE EXTRACT

C_{inh} (g mL^{-1})	E_{corr} (vs. SCE/ V)	i_{corr} (mA cm^{-2})	b_a (mV dec^{-1})	b_c (mV dec^{-1})	η (%)
Blank	-0.489	1.72	113.76	115.38	-
0.01	-0.493	1.23	128.63	120.88	25.77
0.02	-0.492	0.94	148.04	119.69	44.23
0.03	-0.491	0.62	149.05	112.13	69.52
0.06	-0.485	0.36	161.46	115.00	87.22
0.08	-0.483	0.27	181.50	108.21	90.06

Electrochemical impedance spectroscope: The corrosion of mild steel in 1 M HCl in the presence of *S. rebaudiana* extract was investigated by electrochemical impedance at open circuit potential. Impedance spectra for mild steel in absence and presence of different concentrations of the extract are shown in the form of Nyquist plot (Fig. 4). These diagrams show a "depressed" semicircle with single capacitive loop, which is attributed to charge transfer of the corrosion process and the diameters of the loops increase with the increase of the extract concentration. The impedance data were analyzed by fitting to the equivalent circuit (Fig. 5), in which R_s represents the electrolyte resistance, R_{ct} is the charge transfer resistance and CPE is a constant phase element. Excellent fit with this model was obtained for all experimental data.

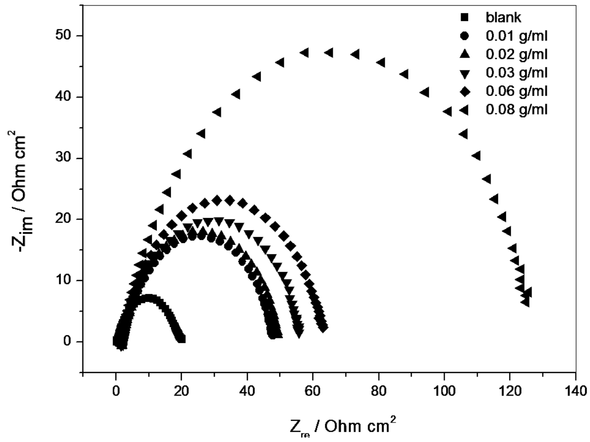


Fig. 4. Nyquist plots in absence and presence of different concentration of the extract in 1 M HCl at 303 K

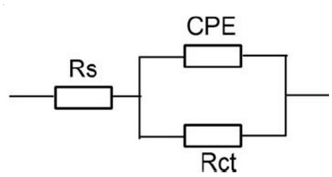


Fig. 5. Equivalent circuit model used to fit the impedance spectra

The impedance parameters such as solution resistance (R_s), charge transfer resistance (R_{ct}), Y_0, n, double-layer capacitance (C_{dl}) and inhibition efficiency (η, %) are listed in Table-4. The values of η are calculated by the charge transfer resistance as follows:

$$\eta(\%) = \frac{R_{ct} - R^0_{ct}}{R_{ct}} \times 100$$

where, R_{ct} and R^0_{ct} are the charge transfer resistance in presence and absence of inhibitor, respectively. It is clear from Table-4 that by increasing the inhibitor concentration, the double-layer capacitance (C_{dl}) values trend to decrease and the inhibition efficiency increases.

TABLE-4
FITTING THE EIS FOR MILD STEEL IN HCL CONTAINING DIFFERENT CONCENTRATION OF THE EXTRACT

C_{inh} (g mL^{-1})	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	Y_0 (μF cm^{-2})	n	C_{dl} (μF cm^{-2})	η (%)
Blank	1.75	9.81	276.90	0.82	106.88	-
0.01	1.24	144.51	177.14	0.83	94.84	24.42
0.02	1.34	159.68	156.95	0.81	91.16	36.71
0.03	1.19	261.48	144.58	0.81	85.02	66.07
0.06	1.77	277.65	117.75	0.82	80.79	80.76
0.08	1.78	317.34	98.43	0.83	76.72	86.67

It is apparent from Nyquist plots that the impedance response of mild steel has significantly changed after the addition of *S. rebaudiana* in acid solutions and that the impedance of inhibited substrate increases with increasing concentration of inhibitor. From Table-4, it is clear that the greatest effect was observed at 0.06 g mL^{-1} of *S. rebaudiana* extract which gives R_{ct} values of 317.34 Ω cm^2, inhibition efficiency is found to increase with inhibitor concentration in HCl solution. The data obtained from EIS are in good agreement with those obtained from weight loss and potentiodynamic polarization methods.

Adsorption isotherm: The type of the adsorption isotherm can provide additional information about the properties of the tested compounds. For this purpose, the values of surface coverage (θ) corresponding to different concentrations of *S. rebaudiana* extract have been used to determine the adsorption isotherm.

Attempts were made to fit the θ values to various isotherm including Langmuir, Temkim and Frumkin isotherms. The plot of C_{inh}/θ against C_{inh} give straight lines with the slope of 1.172 and the value of correlation coefficient is 0.993 (Fig. 6). The results indicate that obeys the Langmuir adsorption isotherm on the mild steel surface in the sulphuric acid:

$$\theta = \frac{KC_{inh}}{1 + KC_{inh}}$$

where, K is the equilibrium constant of the adsorption process. The value of K in the case of 1 M HCl indicates that *S. rebaudiana* extract is strongly adsorbed on the steel surface. This is good agreement with the results obtained from impedance spectroscopy and polarization measurements.

Microstructure study of steel surface by SEM: SEM examination of steel surface in 1 M HCl without and with 0.06 g mL^{-1} *S. rebaudiana* extract was carried out after immerse the steel in acid solution with 6 h at room temperature. It is very clear from Fig. 7a that deep cracks and irregular pits were produced after the immersion. This indicates that the mild steel become corroded in 1 M HCl. Fig. 7b shows that the deep cracks and pits disappeared in the HCl solution with the *S. rebaudiana* extract, which indicates that the extract prevented the corrosion of steel in the acid solution. From the micrograph as shown in Fig. 7, the mechanism of the *S. rebaudiana* extract inhibitor may be the formation of the film adsorbed on the metal surface. These observations were in good agreement with those obtained from chemical and electrochemical measurements.

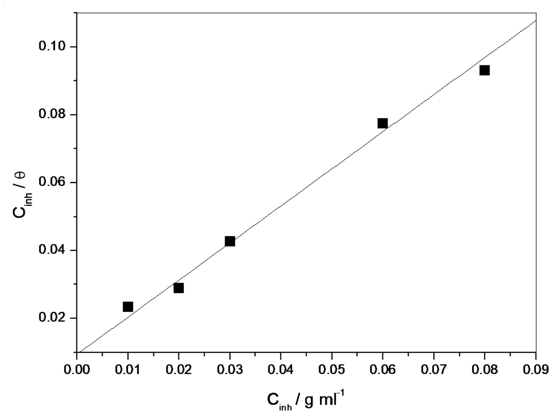


Fig. 6. Langmuir adsorption isotherm plot for the adsorption of the extract in 1 M HCl

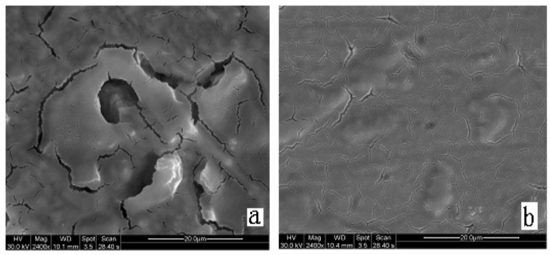


Fig. 7. SEM of mild steel surface after 6 h of immersion in 1 M HCl (a) without and (b) with 0.06 g mL^{-1} *S. rebaudiana* extract at room temperature

Conclusion

The examined extract of *S. rebaudiana* leaves inhibits the corrosion of mild steel in 1 M HCl and found to be good efficiency. Polarization curves indicated that *S. rebaudiana* extract acts as anodic type inhibitor in HCl solution. The inhibition is accomplished by adsorption of the extract components on the iron surface and the adsorption is spontaneous and obeys the Langmuir isotherm.

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