Research Article

Mitigation of mild steel corrosion in 1M sulphuric acid medium by Croton Sparciflorus A green inhibitor

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Abstract

The influence of the addition of acid extract of Croton sparciflorus on the corrosion of mild steel in 1M Sulphuric acid medium was studied by weight loss and electrochemical methods. This study reveals that, the inhibition efficiency increases with increases of concentration of the plant extract, immersion period and temperature. The negative value of the free energy of adsorption indicates spontaneous adsorption. The impedance method reveals that charge-transfer process mainly controls the corrosion of mild steel. This inhibitor obeys Temkin adsorption isotherm. The SEM morphology of the adsorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the plant extract. The inhibition activity is due to the adsorption of active components which are found in the Croton sparciflorus extract.

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Introduction

The use of corrosion inhibitors has become an answer to the corrosion attack of mild steel which always lead to damage and total replacement of these mild steel. Most studies on corrosion inhibitors reported that a large number of inhibitors are organic compounds with O, N and S hetero atoms; they have higher basic properties with electron density, making them the reaction centers [1-5]. These compounds are adsorbed on the metallic surface and block the active corrosion sites; most of them are highly toxic to the human beings and the environment. Hence, sulphuric acid is the medium generally being used for pickling mild steel [6-7]. The recent and growing trend is using plant extracts as corrosion inhibitors [8-17] were reported to be effective acid corrosion inhibitors because of their low cost, easily available biodegradability and eco-friendliness.

In this study, the plant extract of Croton sparciflorus have been selected to study anticorrosion on mild steel in 1M sulphuric acid medium. It is an erect, small plant growing commonly in wastelands throughout the hotter parts of India. It belongs to the family Euphorbiaceae. Sulphuric acid extract was subjected to preliminary phyto- chemical testing for the detection of bioactive ingredients. Sparciflorine, crotsparine, N-ethylcrotsparine N, O-methyl crotsparine, β-sitosterol and hydrocarbons were isolated from this plant [11]. Hence, attempts are made to utilize the acid extracts of Croton sparciflorus as anticorrosion agent on mild steel in sulphuric acid medium.

Experimental Procedure
Materials
Preparation of Mild Steel Specimen

Mild steel strips were mechanically cut into strips of size 5 cm x1 cm x 0.2cm containing the composition of 0.03% C, 0.259 % Mn, 0.027 % Si, 0.004 % P and the remainder Fe and provided with a hole (2mm) of uniform diameter at one end of the coupons for easy hooking. For electro chemical studies, mild steel strips of the same composition were fabricated by fixing the mild steel of size 1 cm^2 to a mild steel rod of 1mm diameter using araldite. Each specimen was polished with different grades of emery paper, degreased with acetone and used. Accurate weight of the samples was taken using electronic balance.

Preparation of the Plant Extract

Reagent grade acid was used for preparation of acid extract of Croton sparciflorus. 5% of stock solution of the extract was prepared by refluxing 50 g of the dried and crushed leaves and twigs of Croton sparciflorus with 1000 ml of sulphuric acid for 3 hours and leaving it overnight. Next day the filtrate volume was made up to 1000 ml using the 1M H_2SO_4.Similar kind of preparation has been reported in studies using aqueous plant extracts in recent years [17-20].

Weight Loss Method

The pretreated specimen's initial weights were noted and were immersed in the experimental solution with the help of glass hooks at 298K temperature for the period of 0.5, 2, 4, 6, 8, 24 and 48 hours. The influence of temperature on the corrosion of mild steel has also been studied at five different temperatures ranging from 298K to 343K in absence and presence of the inhibitors at different concentrations (0.05, 0.1, 0.2, 0.3, 0.5, 0.7 and 0.9%) for 30 minutes. From the weight loss, the inhibition efficiency (IE %), surface coverage (θ) and corrosion rate (mmpy) of the plant extracts were calculated using the following formula.

$$\mathrm{IE}(\%) = \frac{W_U - W_I}{W_U} \times 100 \quad (1)$$

$$\text{Corrosion rate}\,(\text{mmpy}) = \frac{87.6 \text{ x weight loss}\,(\text{mg})}{\text{density}\,(\text{gm/cc}) \text{ x area}\,(\text{cm}^2) \text{ x time}\,(\text{hours})} \quad (2)$$

Where, W_U and W_I are the weight losses in absence and presence of inhibitor respectively.

Potentiodynamic Polarization Method

Potentiodynamic polarization measurements were carried out using electrochemical analyzer. The polarization measurements were made to evaluate the corrosion current, corrosion potential and Tafel slopes. Experiments were carried out in a conventional three electrode cell assembly with working electrode as mild steel specimen with exposed area of 1 cm^2 and the rest being covered with insulation tape, a rectangular Pt foil was used as the counter electrode and the reference electrodes as SCE. A time interval of 10-30 minutes was given for each experiment to attain the steady state open circuit potential. The polarization was carried from a cathodic potential of -700mV (vs. SCE) to an anodic potential of -200mV (vs. SCE) at a sweep rate of 10mV per second. From the polarization curves Tafel slopes, corrosion potential and corrosion rate were calculated. The inhibitor efficiency was calculated using the formula.

$$\text{Inhibition efficiency} = \frac{I_{corr} - I_{corr\,(i)}}{I_{corr}} \text{ x } 100 \quad (3)$$

Where I_{corr} is the corrosion current in the absence of inhibitor and $I_{corr\ (i)}$ is the corrosion current in presence of inhibitor.

Electrochemical Impedance Methods

For the measurements of impendence, the cell used was same as that used for potentio dynamic polarization. An AC potential of 50 mV was super imposed on the steady open circuit potential. The real part (Z') and the imaginary part (Z") were measured at various frequencies in the range of 10 kHz to 10MHz. The real and imaginary parts of the impendence were plotted in Nyquist plots. The value of (R_t + R_s) corresponds to the point where the plot cuts z' and at higher frequency the difference between R_t and R_s gives the charge transfer resistance R_{ct} values and obtained from the plots of Z' vs. Z". The double layer capacitance C_{dl} values were obtained from the equation (4),

$$C_{d1} = \frac{1}{2\pi f_{max} R_{ct}} \qquad (4)$$

Where, C_{dl} **-** double layer capacitance, R_{ct} **-** charge transfer resistance and f_{max} **-**frequency at Z" value maximum
Besides, the above method, the inhibition efficiencies were obtained from R_p and R_{ct} values as follows

$$\text{Inhibition efficiency} = \frac{R_{p\ (i)} - R_p}{R_{p\ (i)}} \text{ x } 100 \qquad (5)$$

Where, $R_{p(i)}$ and R_p are the charge transfer resistance in the presence and absence of inhibitor.

Surface Examination Studies

Mild steel specimens immersed in optimum concentration (0.7%) of the test solution with and without inhibitor for 6 hours were examined under SEM Hitachi model S-3000 N at magnification from 500 to 3000 operated at an accelerating voltage of 25 kV.

Result and Discussion

Weight Loss Studies

Using the weight loss data, corrosion rate (CR), inhibition efficiency (IE) and surface coverage (θ) and the optimum concentration of the extract have been calculated. Corrosion parameters obtained from weight loss measurements are listed in **Table 1**.It indicates inhibition efficiency had increased with an increase in the extract concentration from 0.05% to 0.7%. **Figure 1** illustrated that, the variation of inhibition efficiency of Cs extract, at different concentrations, on mild steel in 1M H_2SO_4, at different temperatures. The maximum efficiency was found to be 94.02% at 323K for 0.7% concentration of the extract. This result indicated that the plant extract could acts as effective corrosion inhibitor for mild steel in 1M H_2SO_4.

Thermodynamic Consideration

The calculated values of activation energy (E_a), free energy of adsorption (ΔG_{ads}), the enthalpy of adsorption (ΔH) and the entropy of adsorption (ΔS) for mild steel in 1M H_2SO_4 with and without Cs extract showed in **Table 2**.The negative value of free energy of adsorption (ΔG_{ads}) indicates the spontaneous adsorption and the positive values of entropy and enthalpy indicate an endothermic reaction suggesting that a high temperature favours the complexation process and it is in good agreement with the increase in stability with the temperature. Temkin adsorption isotherm is used to explain the nature of the adsorption of the inhibitor. **Figure 2** shows that the Cs inhibitor follows the Temkin adsorption isotherm for the chemisorption of species to form a monolayer on the surface [15].This also support the assumption of chemical adsorption.

Table 1 Inhibition efficiency (IE) and surface coverage (θ) parameters of Cs extract on mild steel in 1M H_2SO_4 for different concentrations at different temperatures using weight loss method.

Conc. (%)		Inhibition efficiency (%) 298 K	313 K	323 K	333 K	343 K
	IE (%)	34.59	67.39	70.31	59.43	42.57
0.05	θ	0.3459	0.6789	0.7031	0.5943	0.4257
	IE (%)	44.03	71.47	74.12	68.78	55.11
0.10	θ	0.4403	0.7147	0.7412	0.6878	0.5511
	IE (%)	61.01	80.58	82.57	81.80	73.03
0.20	θ	0.6101	0.8058	0.8257	0.8180	0.7303
	IE (%)	72.96	85.27	87.84	83.97	80.56
0.30	θ	0.7296	0.8527	0.8784	0.8397	0.8056
	IE (%)	80.50	88.71	91.24	87.95	85.85
0.50	θ	0.8050	0.8871	0.9124	0.8795	0.8585
	IE (%)	85.53	92.16	94.02	89.87	88.57
0.70	θ	0.8553	0.9216	0.9402	0.8987	0.8857

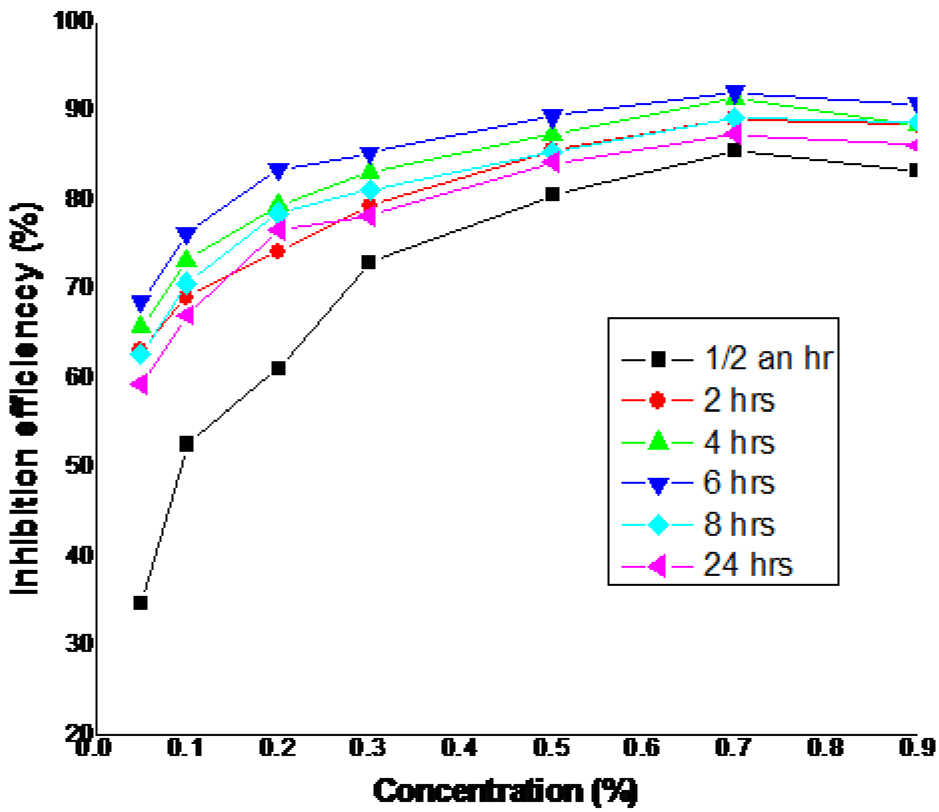

Figure1 Variation of inhibition efficiency of Cs extract, at different concentrations, on mild steel in 1M H_2SO_4, at different temperatures.

Table 2. Thermodynamic parameters for mild steel in 1M H_2SO_4 in the presence and absence of acid extract of Croton sparciflorus at 298 K to 343 K

Conc. (%)	Ea kJ/mol	- (ΔG) (kJ/mol) 298 K	313 K	323 K	333 K	343 K	Average	(ΔH) kJ/mol	(ΔS) kJ/mol
Blank	70.09	-	-	-	-	-	-	67.41	-
0.05	68.46	23.55	25.35	29.12	29.34	29.62	27.30	45.78	0.227
0.1	59.59	23.01	24.18	27.88	27.92	28.23	26.18	46.91	0.227
0.2	55.33	22.38	23.16	26.52	26.70	26.93	25.06	47.65	0.226
0.3	52.27	21.83	22.57	26.45	25.85	26.36	24.63	49.60	0.231
0.5	48.51	21.02	21.96	25.89	25.30	25.50	24.01	45.83	0.217
0.7	48.23	22.06	21.51	26.19	24.64	25.26	24.12	40.86	0.264

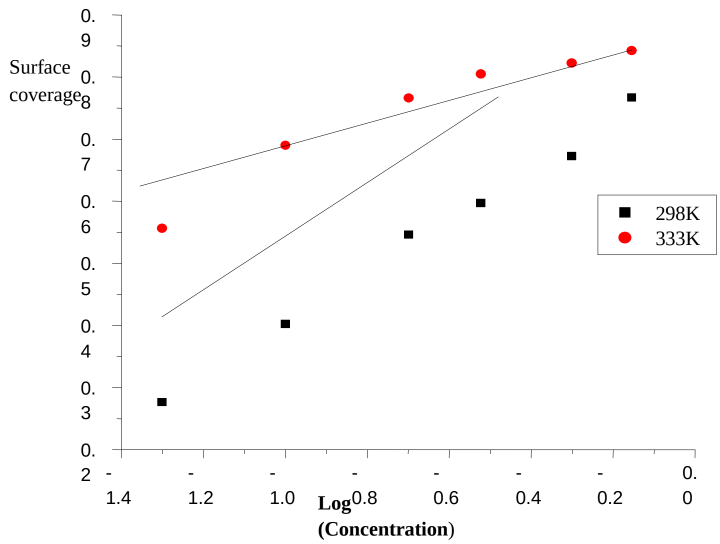

Figure 2 Temkin adsorption isotherm plot for the different concentrations of Cs extract on the mild steel in 1M H_2SO_4 at 298K and 333K.

Tafel Polarization Studies

The electrochemical parameter obtained from the Tafel polarization studies observed that the i_{corr} values decreased from 1.170mA/cm^2 to 0.182mA/cm^2 with increased concentration of Cs extract. The inhibition value is also found to increase from 32.62% to 88.46%.

The calculated polarization resistance (R_p) had increased from 14.00Ωcm^2 to 112.2Ωcm^2 with increase of inhibition efficiency from 32.07% to 87.51% for the concentration of 0.05% to 0.7%. **Figure 3** shows the Tafel polarization behavior of mild steel in 1M H_2SO_4 in the presence of Cs extract. From the graph it is observed that Cs extract behaved like a mixed type of inhibitor (Kann et al 2006).

Electrochemical Impedance Measurement

The impedance parameters for mild steel in 1M H_2SO_4 with and without Cs extract are given in **Table 3**.It was observed that the charge transfer resistance (R_{ct}) values had increased from 4.70 to 30.46Ωcm^2 and in double layer capacitance (C_{dl}) the values had decreased from 990 to 154μF/Cm^2 with increase in Cs extract concentrations.

The decrease in C_{dl} values indicates the adsorption of phytochemical constituents in the acid extracts of Cs on the mild steel surface and also the metal-solution interface. The maximum inhibition efficiency obtained for Cs extract is. 84.47 % at 0.7% concentration.

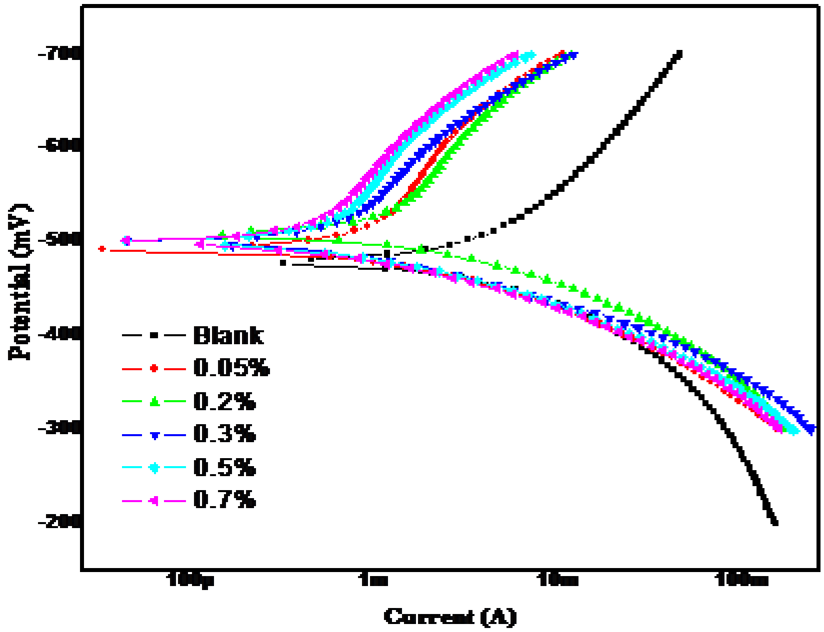

Figure 3 Potentiodynamic polarization curves for mild steel in 1M H_2SO_4 in the absence and presence of different concentrations of Cs extract

Table 3 Electrochemical impedance parameters for mild steel in 1M H_2SO_4 containing different concentrations of Cs extract at room temperature.

Conc. (%)	**R_{ct} (Ωcm^2)**	**C_{dl} $\mu F/cm^2$**	**IE (%)**
Blank	4.70	990	-
0.05	7.06	659	33.43
0.20	12.14	384	61.13
0.30	16.10	272	70.81
0.50	23.35	199	79.87
0.70	30.46	154	84.47

The Nyquist plots **Figure 4** are semi circle in shape corresponding to a charge transfer controlled process. These results support the results of polarization measurements. Bode plots for effect of Cs extract on the corrosion of mild steel in 1M H_2SO_4 solution is shown in **Figure 5** & **6.** These reveal that there is a marked shift in the phase angle with concentration. Initially the shift around 50^o on the blank gradually increases to 75^o at 0.7%.

The presence of one phase maximum at intermediate frequencies indicates the presence of one time constant corresponding to the impedance of the formed protective film. The phase angle obtained indicates the uniform adsorption of inhibitor on the mild steel surface.

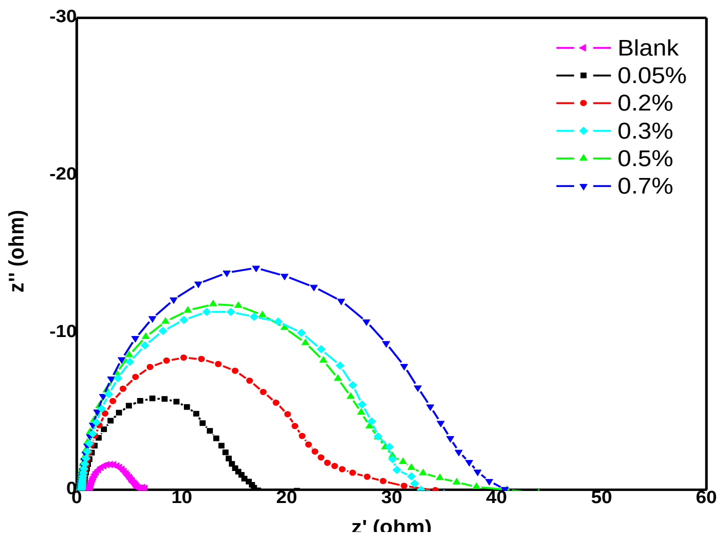

Figure 4 Impedance diagram for mild steel in 1M H_2SO_4 in the presence and absence of different concentrations of Cs extract

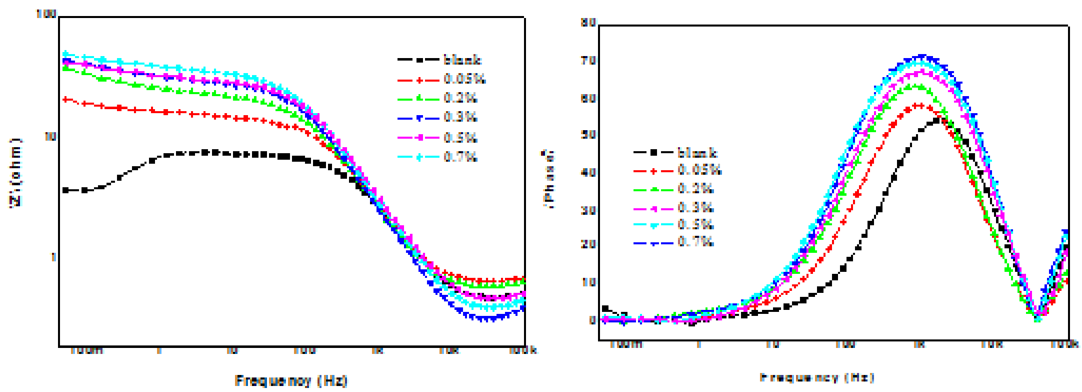

Figure 5 Bode diagram for mild steel in 1M H_2SO_4 in the presence and absence of different concentrations of Cs extract

Morphology Examination of Mild Steel with Cs Extract

The photograph for iron in 1M H_2SO_4 containing with and without Cs extract is given in **Figures 7** and **8**. The SEM morphology of the adsorbed protective film on the mild steel surface has confirmed performance of inhibitive effect of plant extract

Mechanism of Inhibition

The results of the preliminary phytochemical screening are given in the **Table 4**. The extract was found to contain alkaloids, terpenoids and saponins compound. FTIR spectrum of Eh extract in 1M H_2SO_4 **Figure 9** shows the presence of NH, OH and π electrons of aromatic ring.This indicates that the phytochemical compound is involved in complex formation with the metal through its functional groups and π electrons of aromatic ring.

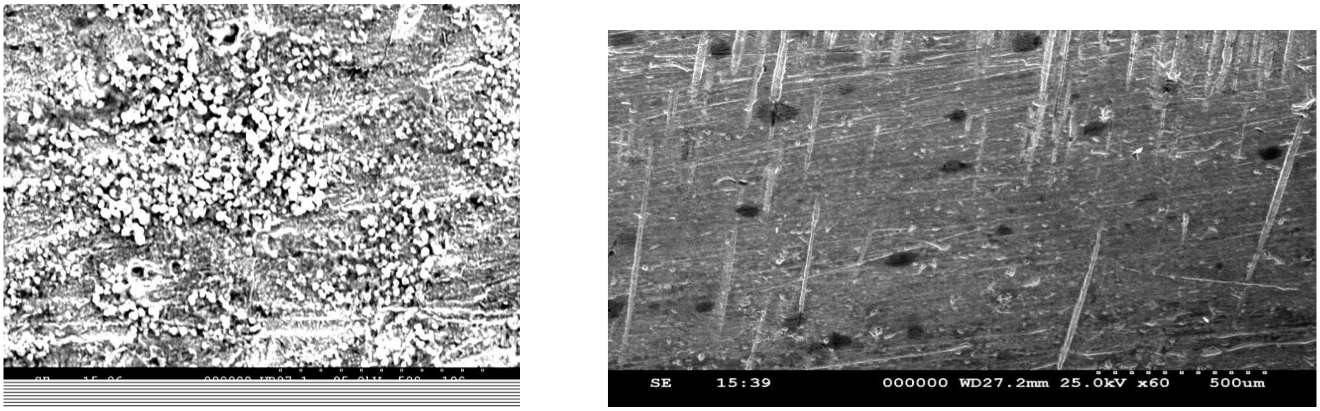

Figure 6 SEM photograph of mild steel immersed in 1M H_2SO_4 (left), and mild steel immersed in 1M H_2SO_4 containing 0.7% of Cs extract (right).

Table 4 Preliminary phytochemical screening of extract of Croton sparciflorus

Plant	Croton sparciflorus
Tannins	-
Alkaloids	+
Terpenoids	+
Glycosides	-
Flavanoids	-
Saponins	+
Anthraquinones	-
Steroids	-

Note
(+)= Presence **(-) = Absence**

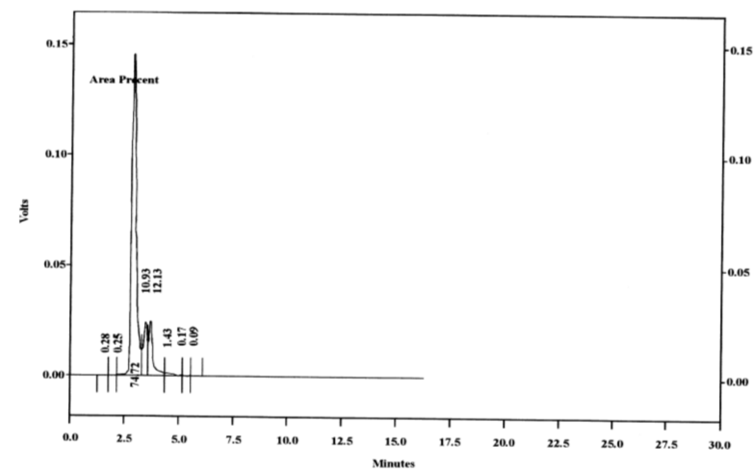

Figure 9 HPLC spectrum of Cs residue in 1M H_2SO_4

Evaluation of Inhibition Efficiency of Cs Extract Obtained from Different Techniques

The inhibition efficiency obtained by the Weight loss measurements, polarization and electrochemical impedance techniques are given in the **Table 5**. The inhibition efficiency of the Cs extract studied by various techniques is almost similar. Hence the Cs extract can be effectively used as an anti corrosion agent for static and dynamic conditions.

Conclusion

The extract of Croton sparciflorus leaves acts as good and efficient inhibitor for the corrosion of mild steel in1 M sulphuric acid medium. The maximum inhibition efficiency was found to increase with concentration, immersion period and temperatures studied. The effect of immersion time of the plant extract at the optimum concentration showed maximum efficiency in 6h immersion time at 323K and found sufficient for pickling. A Potentiodynamic polarization study reveals that the extract acts through mixed mode of inhibition.

The impedance method revealed that charge transfer process mainly controls the corrosion mild steel. The adsorption of the extract of Croton sparciflorus on mild steel obeys Temkin adsorption isotherm. The thermodynamic parameters such as activation energy (Ea) and free energy of adsorption (Gads) obtained from this study indicated spontaneous adsorption of inhibitor on the surface of the metal. The inhibitive action of the plant extract may be due to strong chemisorptions of the active ingredients of the acid extract. The SEM morphology of the adsorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the plant extract. Results obtained in weight loss method were very much in good agreement with the electrochemical methods.

Table 5 Inhibition efficiency of Cs extract for mild steel in 1M H_2SO_4 from weight loss, polarization and impedance techniques.

Conc. (%)	Inhibition efficiency (%)			
	Weight loss	Polarization I_{corr}	Polarization R_p	Impedance
0.05	34.59	32.62	32.07	33.43
0.20	61.01	63.25	62.17	61.13
0.30	72.96	71.62	72.95	72.51
0.50	80.50	79.23	78.75	79.87
0.70	85.53	88.46	87.51	84.47

Reference

[1] Peter N S,Jauhari S, Mehta G N (2009)"Mild steel corrosion inhibition by Bauhinia Purpureal leaves extract in1N sulphuric acid"Arb J Sci & Engg 34(2) 1-13

[2] Umeoren S A,Obobe O, Igwe I O,Ebenso E E (2007)"Polyethylene glycol and polyvinyl alcohol as corrosion inhibitor for aluminum in acidic medium".J app.poly sci 105 3363-3370

[3] Umeoren S A,Obobe O, Igwe I O,Ebenso E E (2008)"Inhibition of mild steel corrosion in acid medium using synthetic and natural occurring polymers and synergistic halide additives". Corr sci 50 1998-2006

[4] Umeoren S A, Eduok U M, Oguzie E E (2008)" Corrosion Inhibition of mild steel in 1M H2SO4 by polyvinyl pyrrolidone and synthetic and synergistic iodide additives". Port Electrochemical acta 26(6) 533-546

[5] Arora P,Kumar S, Sharma M K,Mathur S P (2007)" Corrosion Inhibition of aluminium by capparis deciduous in acidic medium". E.J of Chem 4(4) 450-456

[6] Ajmal M, Mideen A S,Quarshi M A (1994) "2-hydrazino-6-methyl-benzothiazole as an effective inhibitor for the corrosion of mild steel in acidic solution". Corro sci 36 79-84

[7] Hoasry A A, Saleh R M,Eldin A M S (1972) "corrosion inhibition by naturally occurring substances-1 The effect of Hibiscus subdariffa (Karkade) extract on the dissolution of Al and Zn". Corro sci 12(1) 897-904

[8] Chandrasekarn V, Muralisankar M (2006)"Adhatoda vasika alkaloids as inhibitor for Al corrosion in acids", J. Met. Matet Sc., 48(2) 93-102

[9] Ebenso E.E (2004) "Effect of halide ions on the corrosion inhibition of mild steel in H2SO4 using methyl red - Part 1. Bull". Electro Chem 19(5) 209-216

[10] El-Etre A Y, Abdallah M, El-Tantawy Z.E(2005) "Corrosion inhibition of some metals using Lawsonia extract". Corr sci 47 385-389

[11] Fraz Mojab, Mohammad Kamalinejad, Nayasaneh Ghaderi , Hamid Reza, Vahidipour (2003)" Phytochemical screening of some species of Iranian plants", Iran J of Pharm Rese 77-82

[12] Kalpana M, Mehta G.N (2003)" Evalution of Enicostemma axillare as Biodegradable less toxic inhibitor for acid corro- sion of mild steel". Bull. Electrochem 19(8) 381-384

[13] Kasthuri P K, Arulanantham A, Natesan M (2006) "The effects of Acalypha indica extract as corrosion inhibitor on the mild steel in 1M sulphuric acid", J.Metallurgy and Mat. Sci 48(2) 109-116

[14] Orubite-OkorosayeK, Oforka N.C (2004)"Corrosion inhibition of zinc on HCl using Nypa fructicans Wurmb extract and 1,5-diphenyl carbazone" J Appl. Sci., Environ. Manag 9(2) 56-61

[15] Sankarapapavinasam S, PushpnadevA A, Ahmed M F(1989) "Piperidine, piperidones and tetrahydrothiopyrones as inhibitiors for the corrosion of copper in 1N H2SO4", Corr Sci 32 193-203

[16] Shand SH,Ismail A A,El-Miligi A A (1995) " The effect of temperature on the corrosion and corrosion inhibition of steel alloys in hydrochloric acid solution",Bull, Electrochem 11(10) 462-469
[17] El-Etre AY (2007) "inhibition of acid Corrosion of carbon steel using aqueous extract of olive leaves", J of coll & intf sci 314(2) 578-583Corr sci 47 385-389
[18] Anand B, BalasubramanianV(2011)"Corrosion behavior of mild steel in acidic medium in presence of aqueous extract of Allamanda blanchetti",E-J Chem 8(1) 226-230
[19] Abdel kabir A M,Abd-El Nabey B A,Saadawy M (2009)"The role of acid anion on the inhibition of the acidic corrosion of steel by lupine extract",Corr Sci51(5) 1038- 1042
[20] Husaain M H,Kassim M J (2010) "Electrochemical studies of mild steel corrosion Inhibition in aqueous solution by Uncaria gambir extract",J Phy Sci21 1-13

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