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RESEARCH ARTICLE

ENHANCED CORROSION RESISTANCE OF *Tecoma stans* EXTRACT ON MILD STEEL IN 0.5M H_2SO_4 SOLUTION

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ABSTRACT

Inhibition of mild steel corrosion in 0.5M H_2SO_4 of *Tecoma stans* (leaves) has been studied using various investigation techniques such as weight loss, gasometric and polarization methods of monitoring corrosion. The influence of storage condition on inhibition efficiency of *Tecoma stans* extract was also studied. The result of the study revealed that the extract act as a potent inhibitor on mild steel in acid medium. The inhibition activity was confirmed by the different techniques and the inhibition efficiency of the extract increased with increasing concentration of the extract. The adsorption of the extract was found to be spontaneous and its adsorption characteristics were comparatively approximated by Langmuir, Temkin and Freundlich isotherms. Polarization studies showed that the extract is a mixed type inhibitor. The inhibition efficiency changes with storage period at lower concentration of the inhibitor.

INTRODUCTION

The use of inhibitors for the control of corrosion of metals and alloys that are in contact with an aggressive environment is an accepted practice. A large number of organic compounds (Popova *et al.,* 2007, Oguzie *et al.,* 2008) especially with nitrogen, sulphur and oxygen have been used as corrosion inhibitors (Bouklah *et al.,* 2006; Bhara and Singh, 2006). But, most of these compounds are not only expensive but also toxic. In order to overcome these problems 'green inhibitors' should be used. Several studies have been carried out on the inhibition of corrosion of metals using plant extract as green inhibitors (Okafor *et al.,* 2008; Sharma *et al.,* 2008, Okafor *et al.,* 2007a, Okafor *et al.,* 2007b, Kliski *et al.,* 2000, Loto, 2001, Oguzie, 2008a, Eddy *et al.,* 2008). Plant extracts have become important as a corrosion inhibitor as they are environmentally friendly, biodegradable, readily available, low cost and renewable source. They are the richest source of ingredients, which have very high inhibition efficiency. *Tecoma stans* (TS) plant is commonly known as Yellow bells belonging to Bignoniceae mainly used as an antioxidant. This plant has been evaluated as corrosion inhibitor in HCl aqueous solutions (Nagarajan *et al.,* 2006). To extend the research in this field, the present study aims to investigate the inhibition and adsorption properties of acid extract

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of *Tecoma stans* (leaves) for the corrosion of mild steel in 0.5M H_2SO_4 aqueous solution.

METERIALS AND METHODS

Rectangular samples of mild steel (C-0.049, Mn-0.046, P-0.038, Si-0.026, S-0.02, Cr-0.05, Mo-0.019, Ni-0.019 & remaining Fe) with surface area of 1x5cm^2 were used for weight loss and gasometric methods. The steel plates were mechanically polished, drilled a hole at one end and numbered by punching, finally degreased and stored in desiccators prior to use. The solution used for this experiments were prepared using commercial grade reagents with double distilled water.

Preparation of the inhibitor

The leaves of TS plant were collected, dried in shade and powdered. 100g of powdered dry leaves was refluxed in 0.5M H_2SO_4 aqueous solution for 3hrs and kept overnight. Then it was filtered and the volume of the filtrate was made upto 2000mL using the same acid. This solution was taken as stock solution, divided into two portions, one kept under room temperature (RT) and another under refrigerated conditions (RC). The stock solution was used in preparing different concentrations of the extract.

Weight loss method

Accurately weighed mild steel specimens in triplicate were immersed in 0.5M H_2SO_4 solution in absence and presence of various concentrations of the inhibitor. The immersion time for the weight loss method was 3 hours at room temperature. Test specimens were removed, then dipped in sodium bicarbonate solution to remove excess acid and then washed with distilled water, dried and reweighed. The loss in weight was determined in triplicate and the average results were recorded. Similar procedure was followed for the extract kept under RC after attaining the room temperature. From the weight loss, the corrosion rate (CR), the inhibition efficiency (%) and surface coverage (θ) were calculated using the following equations.

Corrosion rate (CR) =534xW/DAT (mpy) ------ (1)

where, mpy is Miles per year, W is weight loss in mg, D is density of specimen in g/cm^3 (7.9 g/cm^3), A is surface area of specimen in square inch, T is exposure time in hours.

I.E (%) = CR(b)-CR(inh)/ CR(b)*100 ------ (2)

where CR(b) and CR(inh) are corrosion rates in the absence and presence of the inhibitor respectively.

Surface coverage (θ) = W1-W2/W1 -------- (3)

where W1 and W2 are weight loss of mild steel in the absence and presence of the inhibitor respectively.

Gasometric method

A two-necked flask was connected *via* a delivery tube to a graduated gas collector (a reservoir of water). A volume of 100ml of the test solution was introduced into the flask. Then the initial volume of the air has been set to zero in the graduated gas collector. Thereafter one mild steel coupon was immersed into the test solution and the reaction vessel was immediately closed. The volume of the hydrogen gas evolved by the corrosion reaction was estimated from the volume change in the level of the water in the gas collector. The progress of the reaction was monitored by careful volumetric measurement of the evolved hydrogen gas at fixed time intervals. From the volume of gas collected in the absence and presence of the inhibitor, the I.E value was calculated.

$$\% IE = 1 - \frac{V'Ht}{V^{\circ}Ht} \times 100 \quad \text{----- (4)}$$

Where, V'Ht = Volume of hydrogen gas evolved at time t for inhibited solution

V°Ht = Volume of hydrogen gas evolved at time t for uninhibited solution

Polarization method

The mild steel specimens of 1cm^2 exposed area to aggressive solution were used for polarization studies. Polarization was carried out at room temperature using conventional three electrodes,

platinum foil as counter electrode, steel plate as working electrode and saturated calomel electrode (SCE) as reference electrode. Solartron electrochemical analyzer model 1280B and an IBM personal computer, which automatically controls low linear polarization and Tafel polarization, were used for the polarization studies. The potentiodynamic polarization curves were recorded at a scan rate of 2mV/sec after a steady corrosion potential was reached. The graph was plotted with potential E vs log(I) and from the plot, the Tafel slopes, corrosion potentials and corrosion currents were calculated using *corr.view* software. The IE% was calculated by using the following formula.

$$IE\% = [1 - \frac{i_{corr}}{i^0_{corr}}]x100$$

where i^0_{corr} and i_{corr} correspond to uninhibited and inhibited corrosion current densities. The corrosion currents were computed both from Tafel slopes (Stern-Geary equation) and from polarization resistance (LPR), determined from low polarization curves.

various concentrations of the inhibitor at 3hours immersion periods. The values of IE% of the extract at refrigerator and on table condition are listed in Table1. Inhibition efficiency changes with storage period at lower concentration of the inhibitor. However at higher concentrations above 1% (V/V) the change in inhibition efficiency is not significant. The inhibition efficiency is still greater than 90% and the plant extract has very good inhibiting effect even after a period of 60 days. Thus the extract would be used effectively upto 60 days of storage period. Comparing the data that is I.E obtained for the extract stored at room temperature with those obtained in refrigerated conditions it can be seen that inhibition efficiency shows no significant change with storage conditions.

Adsorption isotherm

The values of surface coverage (θ) for different concentrations of the inhibitor have been used to select the most appropriate isotherm to illustrate

Table 1. Values of Tecoma stans extract on mild steel in 0.5M H_2SO_4 at room temperature and refrigerated conditions during various storage periods of the extract solutions

Extract Conc.% (V/V)	Inhibition efficiency (%) Storage period of the extract (Days)									
	14		21		28		45		60	
	RT	RC	RT	RC	RT	RC	RT	RC	RT	RC
0.001	18.42	9.72	14.07	4.32	11.75	14.10	15.84	8.60	20.49	8.25
0.005	35.25	35.79	49.28	35.83	35.77	32.73	31.75	35.93	30.74	34.48
0.01	50.82	32.45	51.10	52.65	48.10	43.89	44.73	45.53	44.16	45.25
0.05	80.69	80.21	80.22	83.73	73.30	74.43	72.36	73.23	73.48	72.69
0.1	86.04	85.99	85.96	85.94	82.51	83.13	80.73	72.34	81.28	82.04
0.2	91.03	90.25	90.67	90.29	87.88	87.48	86.18	86.76	87.99	87.04
0.4	94.08	93.88	93.87	94.23	91.99	92.39	90.92	91.20	92.06	92.18
0.6	95.14	95.39	95.38	95.31	93.20	92.79	91.91	92.46	93.37	93.39
0.8	95.71	96.09	96.06	96.01	93.38	94.03	93.83	93.53	95.52	95.14
1.0	95.98	96.27	96.30	96.27	95.32	95.26	94.62	95.16	94.98	95.12
2.0	96.21	96.41	96.89	96.55	96.67	95.55	95.78	95.19	95.78	95.66

RESULTS AND DISCUSSION

Weight loss measurements

The weight loss measurements were carried out to calculate the CR and I.E for the mild steel in 0.5M H_2SO_4 solution in the absence and presence of the adsorption process. Attempts were made to fit θ values to various isotherms including, Langmuir, Temkin and Freundlich isotherms. The Figure1 shows a straight line indicating that Langmuir isotherm is approximately obeyed. The values of free energy of adsorption, ΔG_{ads}, are negative (Table 2) which reveal the spontaneity of the

adsorption process and the stability of the adsorbed layer on the mild steel surface. The negative ΔG_{ads} values are greater than -40 kJmol^{-1} indicating physical adsorption of the phytochemical constituents present in the extract on to the metal surface.

Table 2. Free energy of adsorption (ΔG_{ads}) for mild steel in 0.5M H_2SO_4 solution in presence of the Tecoma stans extract under room temperature conditions

Conc % (V/V)	-ΔG_{ads} KJmol^{-1} Storage period of the extract (Days)						
	1	7	14	21	28	45	60
0.001	23.36	22.06	23.77	22.96	22.44	23.31	24.10
0.005	22.18	21.73	21.93	23.39	21.99	21.54	21.42
0.01	22.18	21.56	21.80	21.83	21.53	21.18	21.13
0.05	21.76	20.67	21.27	21.19	20.21	20.09	20.23
0.1	21.20	20.07	20.50	20.48	19.84	19.53	19.62
0.2	20.56	19.25	20.01	19.91	19.16	18.78	19.19
0.4	20.01	18.79	19.39	19.90	18.57	18.23	18.60
0.6	19.40	18.20	18.90	19.03	18.00	17.52	18.07
0.8	19.13	17.68	18.50	18.72	17.34	17.53	18.39
1.0	18.65	17.69	18 .11	18.33	17.71	17.34	17.52
2.0	17.27	16.75	16.52	17.03	16.85	16.23	16.23

Table 3. Inhibition efficiency of Tecoma stans extract for the corrosion of mild steel in 0.5M H_2SO_4 solution using gasometric technique

Extract Conc. % (V/V)	IE (%)
Blank	-
0.005	46
0.05	52
1.0	70

Gasometric technique

The hydrogen evolved displaces the water in the gasometric setup, the hydrogen volume being read directly (cm^3). The calculated I.E is given in theTable 3. Table shows the decrease in volume of hydrogen gas evolved and increase in inhibition

Polarization technique

The cathodic and anodic polarization curves of mild steel in 0.5M H_2SO_4 solution in the absence and presence of different concentration of the inhibitor at room temperature are shown in Figure 2. The values of corrosion kinetic parameters such as Tafel slopes (b_c and b_a), corrosion current density (I_{corr}) and corrosion potential (E_{corr}) obtained from potentiodynamic polarization studies on mild steel in the absence and presence of different concentrations of TS are given in the Table 4. Values of E_{corr} for mild steel become less negative with increase in the concentration of the extract. Values of both b_c and b_a increase with increase in concentration of the extract. For all concentration of the inhibitor b_c is greater than b_a suggesting that though the inhibition was under mixed control, the effect of the inhibitor on the

Table 4. Electrochemical parameters for corrosion of mild steel in 0.5M H_2SO_4 solution in Presence of Tecoma stans Extract

Extract conc %(V/V)	- E_{corr} mV	I_{corr} μA/cm^2	b_a mV/dec	b_c mV/dec	R_P Ohmcm^2	IE (%)	
						Tafel method	Polarization method
Blank	502	2.34	365.17	429.91	3.7198	-	-
0.005	500	1.92	337.28	435.75	4.3339	17.76	14.16
0.05	485	0.829	223.07	306.53	6.6239	64.57	43.84
1.0	457	0.233	136.22	203.24	13.621	90.05	72.69

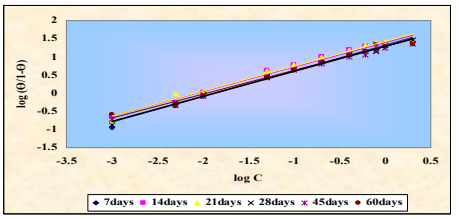

Fig. 1. Langmuir adsorption isotherm of TS extract on mild steel surface in H_2SO_4 solution at room temperature

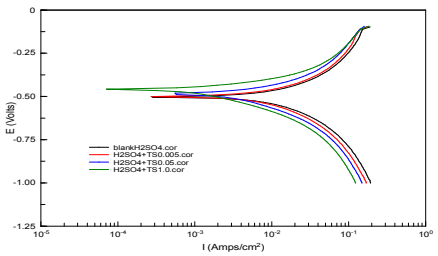

Fig. 2. Potentiodynamic polarization curves for mild steel electrode ($1cm^2$) in 0.5M H_2SO_4 solution in the presence of different concentrations (%V/V) of TS extract

cathodic polarization was more pronounced than on the anodic polarization. Values of I_{corr} decreased as the concentration of inhibitor increased, providing the inhibitive nature of the plant extract. Inhibition increases with increase in the TS extract concentration in the acid medium. Maxima of 90.05% and 72.69% of inhibition efficiency were obtained for maximum concentration of 1% (V/V) by Tafel and LPR methods.

Conclusions: All methods for investigation show that orrosion inhibition increases with increase in the concentration of the Tecoma stans extract. The extract could be used effectively upto 60 days of storage period and the extract could be stored at room temperature (no need to store under refrigerated condition). By comparing the adsorption of the constituents present in the acid extract on the mild steel surface obey Temkin and Freundlich adsorption isotherms. Isotherms show linearity with more accuracy for Langmuir isotherm. Negative values of change in free energy adsorption show the spontaneity of the adsorption process. Polarization studies revealed that the extract under study behaves as a mixed type inhibitor.,The corrosion inhibition efficiencies of the inhibitor evaluated by various techniques is in good agreement. The inhibition of corrosion of mild steel immersed in sulphuric acid medium may be due to the adsorption of each molecule of the phytochemical constituents present in the extract to more than one active site on the metal surface.

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