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Boswellia Serrata Gum : An Eco-Friendly Corrosion Inhibitor for Mild Steel in 1 M HCl Medium

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ABSTRACT

In present work, the corrosion behavior of mild steel induced by Boswellia Serrata Gum (BSG) was studied using different techniques such as weight loss, potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM) in 1 M HCl solution at different concentrations and temperatures (30-60º C). The result shows that BSG is good corrosion inhibitor for mild steel in 1 M HCl solution. The inhibition efficiency (%η) of mild steel in 1 M HCl increase with an increase in inhibitor concentrations. The highest percentage of inhibition efficiency was found to be 91.8% at 500 ppm concentration at the temperature 30°C. The adsorption of BSG on mild steel surface obeys Langmuir adsorption isotherm. Also, the electrochemical study exhibits that BSG acts as a mixed-type inhibitor in 1 M HCl medium. The AFM micrographs confirmed that inhibitor reduce the surface roughness in presence of 1 M HCl

Keywords: Boswellia serrata; Corrosion inhibition; Potentiodynamic polarization; EIS

INTRODUCTION

Mild steel corrosion in acid environment have been a subject of intensive research due to its relevance in several industrial applications such as acid pickling, industrial acid cleaning, acid descaling and oil well acidizing that consequently result in metallic loss. Corrosion inhibitors are generally introduced to the acid solution to minimize metal dissolution. Most of the well-known acid inhibitors are organic compounds having conjugate pie-electrons in their structure and contain heteroatoms such as nitrogen, sulphur and oxygen through which they are adsorbed on the metal surfaces and slow down the corrosion rate of metals [1]. However, majority of the synthetic corrosion inhibitors are expensive, non biodegradable and hazardous to environment and thus inspire to look for cheap, biodegradable and environmentally benign compounds with good inhibition efficiency [2]. Recently, plant extracts have gained attention as an environmentally acceptable, readily available and renewable source for a wide range of newly desired inhibitors. Plant extracts are an incredibly rich source of natural chemical compounds and their extraction procedure is quite simpler and economically feasible. Natural gum obtained from different plants have also been investigated as a green corrosion inhibitor. However, low to moderate inhibition efficiency associated with them have been a limiting factor in their application as an efficient corrosion inhibitors [3]. In a recent publication, Mobin et. al [4]. Xanthan gum alone exhibited a maximum inhibition efficiency of 74.24 % at comparatively higher concentration of 1000 ppm, which synergistically increased by adding surfactants. In the present study, we are for the first time reporting the inhibitory effect of *Boswellia serrata* gum (BSG) for mild steel corrosion in 1 M HCl solution. The plant *Boswellia serrata* belongs to Burseraceae family and is a native tree of India which widely grows on dry hills of northwest India. The exudate obtained from *Boswellia serrata* is an oleo gum-resin, which chiefly contains an acid resin, essential oil and water soluble gum. In present investigation we are using gum portion of plant *Boswellia serrata*, which contains various polysaccharides such as arabinose, galactose, xylose and D-glucuronic acid [5]. Since the BSG contains a mixture of polysaccharides it is expected to act as better corrosion inhibitor at comparatively lower concentration.

EXPERIMENTAL PROCEDURE

PREPARATION OF MILD STEEL SAMPLE AND TEST SOLUTION

Rectangular coupons of mild steel of size 2.5 x 2.0 x 0.1 cm were press cut and used for weight loss measurements. Circular coupons of diameter 1 cm^2 were used in electrochemical measurements. Composition of mild steel used in weight loss and electrochemical measurements is as follows: 0.06841 C, 0.039397 Mn, 0.00080 S, 0.02197 P, 0.04561 Cr, 0.06743 Mo, 0.01539 Al, 0.03347 V and remaining Fe. The mild steel coupons were polished successively using different grades of SiC papers (grade 320-1200). Polished coupons were then degreased with acetone, washed with double distilled water and finally dried in warm air. HCl of analytical grade 37% was used to prepare solution of 1 M HCl. 500 ppm stock solution of BSG was prepared in 1 M HCl and different concentrations were obtained by diluting the 500 ppm stock solution.

WEIGHT LOSS MEASUREMENTS

Mild steel coupons were accurately weighed and triplicate set of coupons were immersed in 100 ml of each test solution to ensure accuracy in results at temperature of 30, 40, 50 and 60ºC in thermostated water bath. The coupons were taken out after 6 hours of immersion, corrosion product removed mechanically, washed with double distilled water, dried in warm air and weighed again to measure weight loss. Average of triplicate set was calculated to record the average weight loss. The corrosion rate (CR) in mg cm^{-2} h^{-1} was calculated as:

$$CR = \frac{\Delta W}{St} \tag{1}$$

Where, ΔW is average weight loss in mg, S is the total area of the sample, t is the immersion time of sample in h. The surface coverage (θ) was calculated by equation (2) and % η can be calculated by multiplying equation (2) by 100.

$$\theta = \frac{CRo - CRi}{CRo} \tag{2}$$

Where, CRo and CRi are the corrosion rates of mild steel coupons in the absence and presence of inhibitor, respectively.

POTENTIODYNAMIC POLARIZATION AND AC IMPEDANCE MEASUREMENTS

Electrochemical measurements were carried out by Autolab Potentiostat/galvanostat, model 128N with inbuilt impedance analyzer FRA 2. The instrument consists of three electrode cell assembly in which working electrode (WE) was mild steel, counter electrode was platinum (Pt) wire and reference electrode was Ag/AgCl (saturated KCl). Working electrode was allowed to stabilize in the test solution for 60 min to attain steady open circuit potential (OCP). Each observation was taken at room temperature and repeated at least three times to check the consistency of results. During potentiodynamic polarization, Tafel slopes were recorded by sweeping the potential between -250 to 250 mV at a scan rate of 0.001 v/s with respect to steady state potential. Linear segment of tafel cathodic and anodic curves was used to calculate corrosion current densities (I_{corr}) and corrosion potential (E_{corr}). The %η was calculated by using following equation:

$$\%\eta = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} \times 100 \tag{3}$$

Where, I^o_{corr} and I_{corr} are corrosion current densities in the absence and presence of inhibitor, respectively.

Electrochemical impedance measurements were carried out at open circuit potential within the frequency range of 10^{-2} Hz to 10^5 Hz with 10 mV perturbation. The charge transfer resistance were calculated from Nyquist plots. % η was calculated by using following equation:

$$\%\eta = \frac{Rct - Rct^{o}}{Rct} \times 100 \qquad (4)$$

Where, Rct and Rct^0 are charge transfer resistances in presence and absence of inhibitor, respectively.

ATOMIC FORCE MICROSCOPY (AFM)

For AFM analysis coupons of mild steel were immersed in 1 M HCl solution with and without inhibitor for the duration of 6 h at room temperature. Then the specimens were washed with double distilled water, dried and subjected to AFM analysis. The AFM analysis were conducted in tapping mode using AFM (Model: Dimension icon ScanAsyst equipped with Nanoscope V) instrument.

RESULTS

TAFEL POLARIZATION STUDY

The anodic and cathodic potentiodynamic polarization plots for mild steel in absence and presence of different concentrations of inhibitor are shown in Figure 1. The appropriate electrochemical polarization parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), cathodic branch slope (βc) and anodic branch slope (βa) and inhibition efficiency (%) were calculated by Tafel extrapolation method and are listed in Table 1. As observed from the results, the value of I_{corr} decreases as the concentration of inhibitor increases from 10 ppm to 500 ppm, which indicates retardation of corrosion process in presence of BSG. Also %η increases as the concentration of BSG increases, which shows inverse relationship between corrosion current density and %η. The change in the slope of anodic (βa) and cathodic (βc) tafel plots indicate that the kinetics of anodic and cathodic processes are affected by the presence of inhibitor. Slight variation is observed in the anodic and cathodic Tafel slopes (βa and βc) with respect to the blank, suggesting that BSG acts as mixed type of inhibitor. Furthermore, the values of βa were comparatively more affected than the values of βc in presence of BSG, which suggests that BSG predominantly shows anodic effect. Displacement in E_{corr} value <85 mV, shows mixed type of inhibition. In current study, maximum displacement in E_{corr} value is <85 mV which indicates that the BSG acts as mixed type of inhibitor i.e., BSG firstly get adsorbed on metal's surface by merely blocking the active metal surface without affecting the anodic and cathodic reaction mechanisms [6].

Table 1: Potentiodynamic polarization parameters for mild steel in 1 M HCl without and with different concentrations of the BSG at 30ºC.

Inhibitor concentration (ppm)	E_{corr} (mv)	I_{corr} (A/cm^2)	βa/ (mV/dec)	βc/ m(V/dec)	CR (mmpy)	%
Blank	- 487.66	1.07×10^{-3}	117.1	73.9	12.43	-
10	- 431.38	3.37×10^{-4}	186.4	111.9	3.92	68.47
50	- 435.86	1.31×10^{-4}	131.6	127.9	1.52	87.73
150	- 440.66	1.14×10^{-4}	138.9	117.6	1.32	89.36

250	- 460.01	8.96×10^{-5}	125.8	98.1	1.04	91.62
350	- 464.99	7.93×10^{-5}	111.1	106.1	0.92	92.59
500	- 443.88	4.83×10^{-5}	102.8	74.4	0.56	95.49

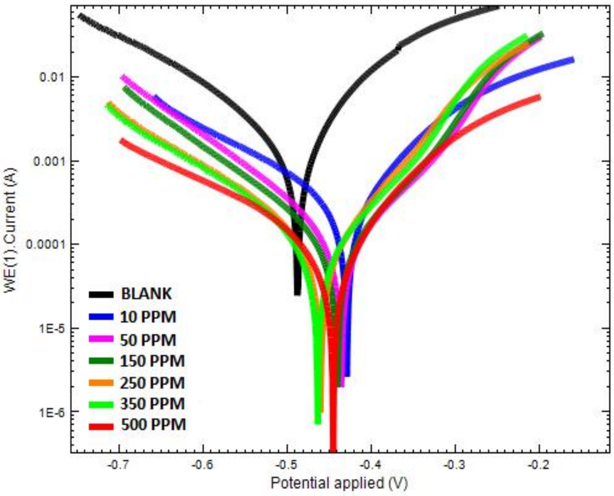

Figure 1: Potentiodynamic polarization curves obtained for mild steel in 1 M HCl solution without and with different concentrations of BSG at 30º C

EIS MEASUREMENTS

The EIS measurement was carried out to know the kinetics of the electrochemical process occurring on surface of metal as well as at interface of mild steel/solution in inhibited medium. The Nyquist plot obtained for mild steel immersed in 1 M HCl without and with different concentration of BSG are shown in Figure 2 and related parameters are mentioned in Table 2. It is evident from Nyquist plots that impedance spectra of mild steel coupons appeared as single capacitive loop, but it must be noted that these loops are not perfect semicircles they are somewhat depressed at centers under the real axis. This kind of deviation is attributed due to frequency dispersion effect and due to surface irregularities and heterogeneities. The diameter of capacitive loops increases with increasing concentration of BSG, which indicates that the charge transfer process occurring at interface was retarded by BSG extract [7].To obtain more accurate and desired fit a constant phase element (Z_{CPE}) is introduced in place of double layer capacitance (Cdl).

$$Z_{CPE} = \frac{1}{Y_0 (j\omega)^n} \tag{5}$$

where Y_0 is a proportional factor, j is the imaginary unit and its value is equal to the square root of -1, ω is the angular frequency in rad s^{-1} (ω=2Πfmax) and n corresponds to the phase shift and it tells the extent of deviation from ideal behavior. The Cdl can be calculated by following equation:

$$Cdl = Y_0 (\omega_{max})^{n-1} \tag{6}$$

where ω_{max} = 2Πfmax (fmax= maximum frequency of imaginary component of impedance).The higher diameter of the semi-circle is obtained when monolayer of inhibitor is densely packed which tends to increase the Rct and decrease the Cdl values, respectively. These condition provides better protection by the inhibitor. It is observed that the value of Rct increases with increasing concentration of BSG, which is due to increase in the surface coverage by the BSG. Also, the value of Cdl decreases as the concentration of inhibitor increases which is due to the substitution to water molecules with inhibitor molecule at metal/solution interface leading to reduction in local dielectric constant which in turn increases the thickness of electrical double layer [8].

Table 2: Electrochemical impedance parameters for mild steel in 1 M HCl solution in the absence and presence of different concentrations of BSG at 30ºC.

Inhibitor concentration (ppm)	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	C_{dl} x 10^{-4} (Fcm^{-2})	%
Blank	0.85908	14.66	6.36	-
10	0.99044	41.67	5.86	64.80
50	1.9483	120.36	3.03	87.81
150	1.8421	213.78	1.01	93.14
250	4.0569	301.31	0.92	95.13
350	1.6486	367.54	0.81	96.01
500	4.8673	443.68	0.72	96.69

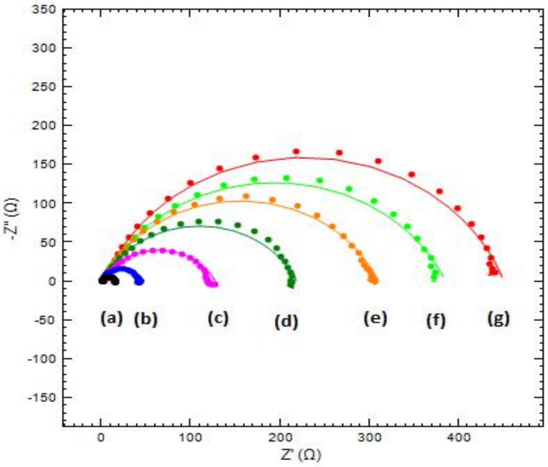

Figure 2: Nyquist plots for mild steel in 1 M HCl in absence and presence of (a) blank (b) 10 ppm (c) 50 ppm (d) 150 ppm (e) 250 ppm (f) 350 ppm and (g) 500 ppm of BSG at 30º C.

WEIGHT LOSS MEASUREMENTS

The values of corrosion rate, %η and θ obtained from weight loss measurements at different concentration of BSG in 1 M HCl at 30ºC, 40ºC, 50ºC and 60ºC are summarized in Table 3. It is clearly shown from Table 3 that on increasing the inhibitor concentration large number of molecules of inhibitor get adsorbed on the mild steel surface, which suggest that inhibitor cover more active sites of mild steel for direct acid attack and hence retards the dissolution of mild steel by protecting it against corrosion. No remarkable increase in % η was observed beyond 500ppm. This can be attributed due to withdrawal of inhibitor back into the solution when concentration reaches close to or beyond critical concentration resulting decrease in inhibition efficiency due to replacement of inhibitor molecule by water or chloride present in solution. %η decreases as we increase the temperature which was probably due to decrease in strength of adsorption to the mild steel surface i.e., desorption of inhibitor molecules occurred and also due to roughening of electrode surface which in turn enhances the corrosion process [9].

Table 3:Corrosion parameters for mild steel in 1 M HCl in absence and presence of the BSG from weight loss measurements at different temperatures.

	Temperature											
	30ºC.			**40ºC.**			**50ºC.**			**60ºC.**		
Inhibitor concentration (ppm)	CR (mgcm $^{-2}$h^{-1})	θ	%	CR (mgcm $^{-2}$h^{-1})	θ	%	CR (mgcm $^{-2}$h^{-1})	θ	%	CR (mgcm $^{-2}$h^{-1})	θ	%
Blank	0.157			0.444			2.933			6.838		
10	0.067	0.57	57.1	0.243	0.45	45.4	1.963	0.33	33.0	5.262	0.23	23.0
50	0.038	0.75	75.9	0.178	0.59	59.9	1.420	0.51	51.5	4.076	0.40	40.3
150	0.029	0.81	81.4	0.144	0.67	67.6	1.241	0.57	57.6	3.543	0.48	48.1
250	0.023	0.85	85.0	0.116	0.73	73.8	0.976	0.66	66.7	2.956	0.56	56.7
350	0.017	0.88	88.9	0.097	0.78	78.0	0.846	0.71	71.1	2.671	0.60	60.9
500	0.013	0.91	91.8	0.075	0.83	83.0	0.671	0.77	77.1	2.264	0.66	66.8

Adsorption Studies

Various adsorption isotherms were studied to know the adsorption of inhibitor molecules on the mild steel surface. Best fit was obtained for Langmuir adsorption isotherm.

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{9}$$

C_{inh} is the concentration of inhibitor in ppm, θ is the surface coverage by inhibitor and K_{ads} is the equilibrium constant. Figure 3 shows a linear plot between C_{inh}/θ vs C_{inh} (A) for different concentration of inhibitor at 30º C using weight loss (WL), potentiodynamic polarization (PDP) and electrochemical impedance (EIS) techniques and (B) for different concentration of inhibitor at various temperature using WL technique. Value of correlation coefficient R^2 was close to unity, which indicates best fitting of Langmuir isotherm . From the intercept of graph C_{inh}/θ vs C_{inh} value of K_{ads} were calculated. ΔG_{ads} were calculated by using the value of K_{ads} as follows:

$$\Delta G_{ads} = -RT\ln(1 \times 10^{6} K_{ads}) \tag{10}$$

where, 1x10^6 is the concentration of water molecules expressed in ppm, T is the temperature expressed in Kelvin and R is the universal gas constant [10]. All parameters of adsorption are mentioned in Table 4. Generally value of ΔG_{ads} helps in predicting the physisorption and chemisorptions process [11]. Here, it is clear from the table that value of ΔG_{ads} are negative which shows the feasibility of the process and values are more than 20 kJ/mol and less than 40 kJ/mol which signifies mixed type of inhibition process.

Table 4: Calculated adsorption parameters for mild steel corrosion in 1 M HCl solution containing different concentrations of BSG.

Temperature(ºC)	Method	R^2	K_{ads} (Lmg^{-1})	$-\Delta G_{ads}$(kJ/mol)
30	WL	0.998	0.066	-27.95
	EIS	0.999	0.131	-29.68
	PDP	1	0.162	-30.21
40	WL	0.995	0.036	-27.27
50	WL	0.991	0.024	-27.03
60	WL	0.989	0.016	-26.86

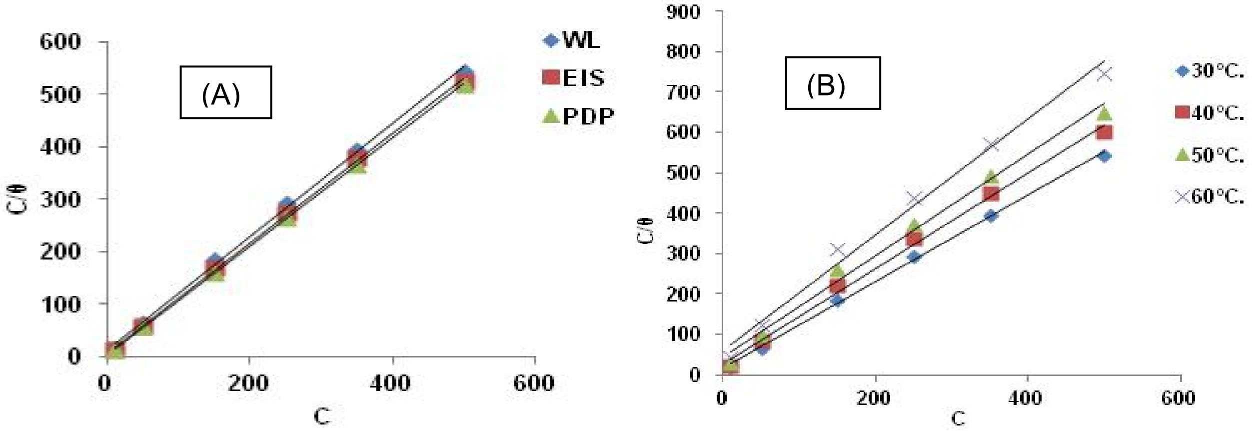

Figure 3. Langmuir plots of C/θ versus C from (A) WL, EIS, and PDP data at 30º C and (B) WL data at 30-60º C.

AFM ANALYSIS

AFM was used to investigate the surface morphology and nature of protective film formed on mild steel surface at nano and micro scale level. AFM provide three dimensional topographical images of the sample. Figure 4(A) displays the AFM image of polished coupon of mild steel with average roughness of 245 nm . Figure 4(B) shows the mild steel coupon in 1 M HCl without inhibitor and Figure 4(C) shows the mild steel coupon in 1 M HCl with desired concentration (500 ppm) of inhibitor. Images prove that the surface roughness is more in 1 M HCl without inhibitor as compared to with inhibitor containing HCl solution . The average roughness of mild steel in 1 M HCl is 627 nm and that of in inhibited acid is 332 nm. The decrease in roughness is attributed by the formation of protective film on mild steel surface in presence of inhibitor.

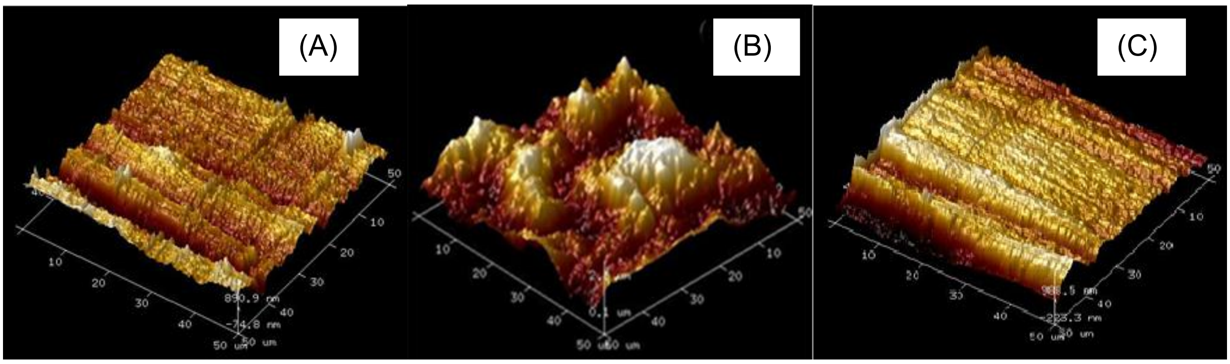

Figure 11. AFM photographs of (A) Polished mild steel coupon with average roughness of 245 nm. (B) Mild steel coupon in 1 M HCl without inhibitor with average roughness of 627nm. (C) Mild steel coupon in 1 m HCl with 500 ppm concentration of inhibitor with average roughness of 332nm.

CONCLUSIONS

The possible inhibiting effect of Boswellia serrata Gum has been studied on mild steel in 1 M HCl. The study reveals that the BSG inhibit mild steel corrosion in 1 M HCl at moderately low concentration and also the inhibition efficiency increases with increasing the concentration but decreased with rise in temperature. The inhibition efficiencies obtained by weight loss, polarization and EIS measurements show good agreement. BSG is found to affect both the anodic and cathodic processes and acts as a mixed-type inhibitor. The corrosion process is inhibited by adsorption of the BSG on the mild steel surface following Langmuir adsorption isotherm. The adsorption of BSG on mild steel surface is mainly physical adsorption. The EIS results confirm the formation of a protective layer over the mild steel surface in presence of BSG. The AFM micrographs showed smooth surface in presence of inhibitor as compared to uninhibited mild steel.

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