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Corrosion Inhibition of Naturally Occurring Gum Exudates of *Araucaria columnaris* on Mild Steel in 1 M H_2SO_4

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Abstract

The corrosion inhibitive performance of naturally occurring gum exudates of Araucaria columnaris (AC) and its synergistic effect with halides and metal cations on mild steel in 1 M H_2SO_4 has been studied using weight loss and electrochemical methods. The inhibition efficiency was found to increase with increase in concentration and decrease with temperature. The adsorption of AC gum on the mild steel obeys Langmuir adsorption isotherm. Potentiodynamic polarization studies showed that AC gum acting as mixed type of inhibitor. The formation of protective layer on mild steel surface is confirmed by SEM analysis.

Keywords: Gum exudates of Araucaria columnaris (AC), Mild steel, Synergism, Electrochemical methods, SEM.

Introduction

Mild steel has remarkable economic and attractive materials for industries owed to its low cost and easy availability. To prevent the metal dissolution and minimize acid consumption, inhibitors are added to the corrosive environment[1-3]. The most widely used inhibitors are organic compounds containing oxygen, nitrogen and sulphur[4,5]. Lots of work related to green corrosion inhibitors have been reported and this may be due to the presence of complex organic species such as tannins, alkaloids, carbohydrates and proteins as well as their acid hydrolysis products[6-8]. Several researchers reported that even polysaccharides are more efficient corrosion inhibitors due to their solubility in water, abundant availability and less expensive[9]. Some investigations have been reported using gum exudates of *Pachylobus edulis and Raphia hookeri, Dacroydes edulis, Acacia seyal var seyal*[10-13] for the corrosion inhibition of various metals. In the present investigation of natural corrosion inhibition materials, gum exudates of *Araucaria columnaris* is used as safe and cheap corrosion inhibitor for mild steel in acidic medium by weight loss and electrochemical methods.

Material and Methods

Mild steel specimen: Mild steel specimens of the following composition have been used all over the present investigations (Carbon: 0.07 %, Sulphur: Nil, Phosphorous: 0.008%, Manganese: 0.34%, remaining ferrous). Mild steel with the dimensions 2.5 cm x 1.0 cm x 0.1 cm were used for weight loss measurements. The mild steel specimens were polished with different grades of emery papers (1/0, 2/0, 3/0 and 4/0), washed with double distilled water, dried, degreased with acetone. AR grade sulphuric acid was used for preparing the test solution.

Purification of gum: The gum exudates of *Araucaria columnaris* (AC) were collected locally and dissolved in doubly distilled water and filtered to remove insoluble dust and impurities. It is then dried in a desiccator to obtain a glassy mass of purified gum.

Electrochemical measurements: Electrochemical experiments were conducted in a three-electrode glass cell of 100 ml capacity. A platinum counter electrode and a saturated calomel electrode (SCE) as reference electrode are used. The SCE was connected via Luggin's capillary.

The electrochemical impedance measurements were carried out over the frequency range of 10 KHz to 0.01 Hz carried with AC signal amplitude of the 10 mV at the corrosion potential. The measurements were automatically controlled by Z_{view} software and the impedance diagrams were given as Nyquist plots. From the plots the electrochemical parameters such as double layer capacitance (C_{dl}) and charge transfer resistance (R_t) were calculated. The potentiodynamic polarization measurements were made for a potential range of -200 mV to +200 mV with respect to open circuit potential, at scan rate of 1 mV/sec. From the plot of E Vs log I, the corrosion potential (E_{corr}), corrosion current (I_{corr}) were obtained. Tafel slopes b_a and b_c were obtained in the absence and presence of inhibitors.

Surface analysis: The surface of the mild steel immersed in the absence and presence of inhibitors were examined using scanning electron microscopy (JEOL-JSM-35-CF).

Results and Discussion

Weight loss measurements: The corrosion inhibition of 1 M H_2SO_4 in the presence of AC gum has been studied by weight loss measurements. The inhibition efficiency and corrosion rats of AC gum with different concentrations (50 ppm to 600 ppm) have been evaluated and the results are given in table-1. Analysis of table-1 shows that the inhibition efficiency increases with increase in concentration of the AC gum. The highest inhibition efficiency is obtained at 400 ppm and any further increase in concentration does not affect the performance of the inhibitor.

The corrosion inhibition of mild steel by AC gum is due to the adsorption at the electrode/solution interface. AC gum is a polysaccharide consisting of 1,2-benzenedicarboxylic acid, bis (2-ethylhexyl) ester, diisooctyl-phthalate, phthalic acid, isobutyl and isopropyl ester[14]. The presence of hetero oxygen atom and carboxylate anions in the structure of AC gum forms a co-ordinate type linkage with the mild steel surface through the transfer of lone pairs of electron of oxygen atoms, giving a stable chelate with ferrous ions. The simultaneous adsorption of oxygen atoms, forces the AC gum molecule to be horizontally oriented at the metal surface, which led to increase the surface coverage, resulting in an increase in the inhibition efficiency.

Effect of synergism: It has been reported that halide ions have the most adsorbable character of steel. Addition of I^-, Cl^- and Br^- to an inhibitor enhances the inhibitory action. Analysis of table-2 indicates that the inhibition efficiency of AC gum is enhanced by the addition of halides.

The addition of Iodide ions to the inhibiting solution is found to have highest inhibition efficiency when compared to the addition of bromide and chloride ions. The maximum inhibition efficiency caused by I^- can be explained as follows.

In general, the presence of halide ions in acidic medium has synergistically increased the inhibition efficiency of most of the organic compounds. The halide ions increases the adsorption of the organic cations by forming intermediate bridges between the organic inhibitor and charged metal surface.[15] The synergistic effect of AC gum with halides is studied using weight loss methods and electrochemical impedance spectroscopy. Analysis of the result shows that the inhibition efficiency of AC gum is enhanced by the addition of halides. The synergistic ability of halides increased in the order $Cl^- < Br^- < I^-$ and similar observation has been reported by several researchers[16,17]. The highest synergistic inhibition efficiency influenced by iodide ion is attributed to its large ionic radius, higher hydrophobicity and low electro negativity compared to other halide ions.

The effect of metal cations on corrosion of mild steel in 1M H_2SO_4 is studied with and without the addition of AC gum. The calculated values of inhibition efficiencies and corrosion rates are given in table-2.

Table-1
Inhibition efficiencies of AC gum on mild steel in 1M H_2SO_4 from weight loss measurement at room temperature

Inhibitor Concentration (ppm)	Inhibition Efficiency (%)	Corrosion Rate (mmpy)	Degree of Coverage (θ)	$-\Delta G_{ads}$ (kJ/ mol)
Blank	--	0.0561	--	--
50	42.0	0.0325	0.420	16.85
100	46.2	0.0302	0.462	15.50
200	47.5	0.0294	0.475	13.92
400	55.1	0.0251	0.551	12.94
600	54.4	0.0255	0.544	11.85

Table-2
Synergistic effect of halides and metal cations on corrosion inhibition of AC gum on mild steel in 1M H_2SO_4 from weight loss measurement at room temperature

Inhibitor Concentration	Inhibition Efficiency (%)	Corrosion Rate (mmpy)	Degree of Coverage (θ)
Blank	--	0.0931	--
0.1 mM KI	93.3	0.0061	0.933
0.1 mM KI+400 ppm AC gum	97.5	0.0023	0.975
0.1 mM KCl	75.2	0.0231	0.752
0.1 mM KCl+ 400 ppm AC gum	80.1	0.0184	0.801
0.1 mM KBr	82.6	0.0167	0.826
0.1 mM KBr+ 400 ppm AC gum	88.4	0.0118	0.884
0.1 mM Zn^{2+}	50.1	0.0259	0.501
0.1 mM Zn^{2+}+400 ppm AC gum	82.6	0.0089	0.826
0.1 mM Ni^{2+}	72.9	0.0139	0.729
0.1 mM Ni^{2+}+ 400 ppm AC gum	84.3	0.0081	0.843

It is evident from the table that Zn^{2+} and Ni^{2+} ions enhance the inhibition efficiency of AC gum remarkably. When we compare the effect of Zn^{2+} ions on the corrosion of mild steel with Ni^{2+} ions, the Ni^{2+} ions have enhanced inhibition efficiency. The improvement in the corrosion inhibition efficiency can be endorsed to the formation of complex between metal cations and AC gum. Therefore, the inhibitor molecules are readily transported from the bulk to the metal surface[18].Remarkably, inhibition efficiency is found to more pronounced even at higher temperatures.

Effect of temperature: The effect of temperature (303 - 323 K) on the corrosion behavior of mild steel in the presence of AC gum with halides and metal cations are investigated by weight loss techniques. Data in table-3 indicate that the corrosion rate is not significantly affected with rise in temperature. This behavior reveals that the AC gum acting as an efficient corrosion inhibitor in the temperature range studied. Organic compounds containing hetero atoms are used as inhibitors as they adsorbed onto the metal/solution interface. Adsorption of the inhibitor on the mild steel specimen mainly depends on its chemical structure, chemical composition of the test solution, the nature of the electrode, temperature and electrochemical potential at the metal-solution interface. The adsorption provides information about the, adsorbed molecules as well as their interaction with the metal surface. The surface coverage (Θ) of the inhibitors at different concentrations is used to obtain the best adsorption isotherm. The θ values have been calculated using the following equations (1 and 2):

$$\Theta = 1 - \frac{W_{(inh)}}{W} \quad (1)$$

Where: $W_{(inh)}$ = weight loss obtained in the presence of inhibitor and W = weight loss obtained for blank.

It is well known that the adsorption isotherms are useful to understand the mechanism of corrosion inhibition. The present experimental data fit to Langmuir adsorption isotherm and it is shown in figure-1. The Langmuir adsorption isotherm is expressed as:

$$\Theta = \frac{KC}{(1+KC)} \quad (2)$$

Where: K is the equilibrium constant for the adsorption process and C is the concentration. The above equation may be modified as:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (3)$$

The plot of C/θ versus C gives a straight line with slope equal to unity. The present experimental data fit to Langmuir adsorption isotherm. Free energy of adsorption (ΔG_{ads}) is calculated using the equation (4) and the values are included in table-1.

$$\Delta G_{ads} = -RT \ln(55.5\ K) \quad (4)$$

The values of ΔG_{ads} obtained for AC gum point out the spontaneity of the adsorption process. In the present study, ΔG_{ads} values of AC gum lies below -20 kJ/ mol, indicating the operation of physisorption mechanism. The activation energy (E_a) is calculated from the plot of log (corrosion rate) versus 1000 / T by using the formula and its representative curves are given in the figures-2(a)(b), 3.

The activation energies (E_a) obtained for the inhibited solutions are found to be higher than the E_a of blank. The higher value of E_a in the inhibiting solution supports the physisorption mechanism. The energy barrier increases with increase in concentration of inhibitors, which results in increase in activation energy[19].

$$\log CR = -\frac{E_a}{2.303\ R} + \log A \quad (5)$$

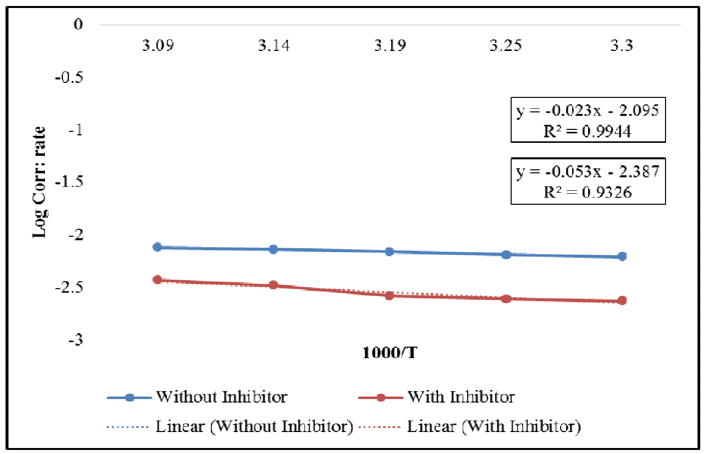

Figure-1
Langmuir adsorption isotherm for the AC gum on mild steel in 1 M H_2SO_4 at room temperature

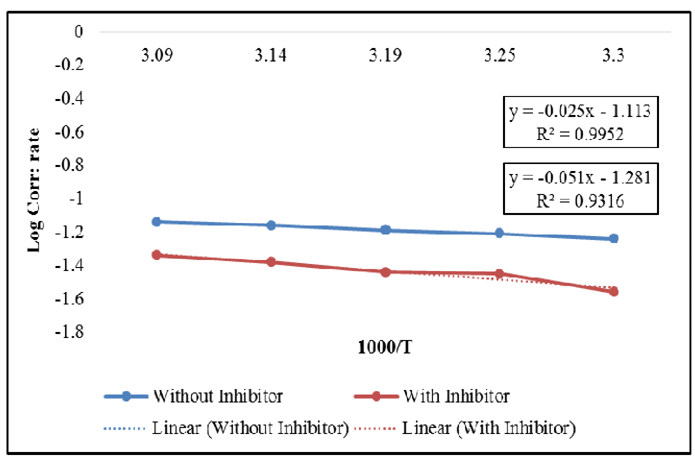

Figure-2
Arrhenius plot for AC gum with Zn^{2+} on mild steel in 1 M H_2SO_4 (b) Arrhenius plot for AC gum with Ni^{2+} on mild steel in 1 M H_2SO_4

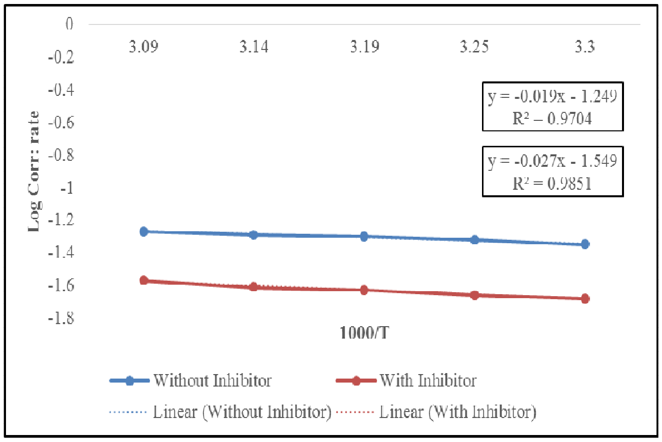

Figure-3
Arrhenius plot for AC gum with KI on mild steel in 1 M H_2SO_4

Potentiodynamic polarization studies: The potentiodynamic polarization curves for mild steel in 1 M H_2SO_4 in the absence and presence of AC gum with halides and metal cations are given in figures-4 to 6. The addition of inhibitors causes a remarkable decrease in the corrosion rate, i.e., shifts both anodic and cathodic curves to lower current densities. Electrochemical parameters like corrosion potential (E_{corr}), and corrosion current density (I_{corr}), Tafel constant b_a and b_c are listed in tables-5 and 6. The addition of inhibitors causes a remarkable decrease in the corrosion rate, i.e., shifts both anodic and cathodic curves to lower current densities. In other words, both the anode and cathodic reactions of mild steel is drastically inhibited by the inhibitors. I_{corr} values significantly decreases as additives are added to the corrosive medium and this indicates the inhibiting nature of the gum. It is clear from the tables-5 and 6 that the I_{corr} decreased considerably in the presence of inhibitors while no definite trend was observed in the shift of E_{corr}. The AC gum adsorbed onto the mild steel surface suppresses both the anodic and cathodic reaction and thereby hindering the active sites, and these results suggested that the addition of inhibitors reduces the anodic dissolution and also retards the cathodic hydrogen evolution reaction, indicating that these inhibitors act as mixed type of inhibitor.

Table-3
Inhibition efficiencies of AC gum with halides at different temperatures for 1 M H_2SO_4

Inhibitor concentration	303 K	308 K	313 K	318 K	323 K
400 ppm AC gum	55.1	52.1	48.3	44.9	43.1
0.1 mM KCl	75.2	70.9	69.1	66.3	64.2
0.1 mM KCl+ 400 ppm AC gum	80.1	78.4	75.8	73.5	70.9
0.1 mM KBr	82.6	80.2	79.2	76.1	73.8
0.1 mM KBr+ 400 ppm AC gum	88.4	85.6	81.4	76.1	74.0
0.1 mM KI	93.3	90.3	89.1	88.3	87.4
0.1 mM KI+ 400 ppm AC gum	97.5	97.1	96.4	95.3	94.3
0.1 mM Zn^{2+}	51.2	50.9	49.4	45.1	43.4
0.1 mM Zn^{2+}+ 400 ppm AC gum	70.91	70.1	68.9	66.3	64.2
0.1 mM Ni^{2+}	46.94	43.1	41.2	39.3	38.7
0.1 mM Ni^{2+}+ 400 ppm AC gum	71.45	70.1	68.2	67.2	64

Table-4
Energy of activation parameters in the presence of AC gum with halides and metal cations

Composition	E_a (kJ/mol)	
	Blank	With 400ppm AC gum
H_2SO_4	0.36	0.51
H_2SO_4 + halides	0.44	1.01
H_2SO_4+ Zn^{2+}	0.48	0.97
H_2SO_4 + Ni^{2+}	0.49	1.20

Table-5
Potentiodynamic polarization parameters for the corrosion inhibition of mild steel in 1 M H_2SO_4 with and without inhibitors

Inhibitor Concentration	I_{corr} (mA cm^{-2}) × 10^{-4}	E_{corr} (mV/SCE)	b_a (mV/dec)	b_c (mv/dec)	Corrosion rate (mmpy)	Inhibition efficiency (%)
Blank	0.93	-0.51	0.086	0.129	14.1	--
400 ppm AC gum	0.57	-0.49	0.075	0.135	8.7	38.7
0.1 mM KCl+ 400 ppm AC gum	0.63	-0.49	0.076	0.119	9.4	33.3
0.1 mM KBr+400 ppm AC gum	0.56	-0.50	0.076	0.122	8.6	39.7
0.1 mM KI+400 ppm AC gum	0.15	-0.48	0.066	0.128	2.4	83.8

Table-6
Potentiodynamic polarization parameters for metal cations on corrosion inhibition of mild steel in 1M H_2SO_4 with and without inhibitors

Inhibitor Concentration	I_{corr} (mA cm^{-2}) x 10^{-4}	E_{corr} (mV/SCE)	b_a (mV/dec)	b_c (mV/dec)	Corrosion rate (mmpy)	Inhibition efficiency (%)
Blank	0.93	-0.508	0.086	0.129	14.1	--
400 ppm AC gum	0.57	-0.495	0.075	0.135	8.7	38.7
0.1 mM Zn^{2+}	0.74	-0.506	0.081	0.112	10.4	20.4
0.1 mM Zn^{+}+400 ppm AC gum	0.29	-0.492	0.064	0.137	4.3	68.8
0.1 mM Ni^{2+}	0.68	-0.522	0.063	0.105	10.3	26.8
0.1 mM Ni^{2+}+400 ppm AC gum	0.25	-0.4989	0.061	0.108	3.82	63.2

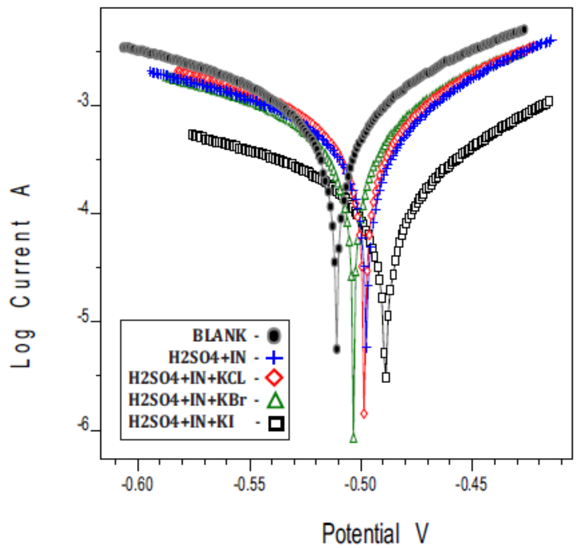

Figure 4
Potentiodynamic polarization curves for AC gum on mild steel in presence of halide ions in 1 M H_2SO_4

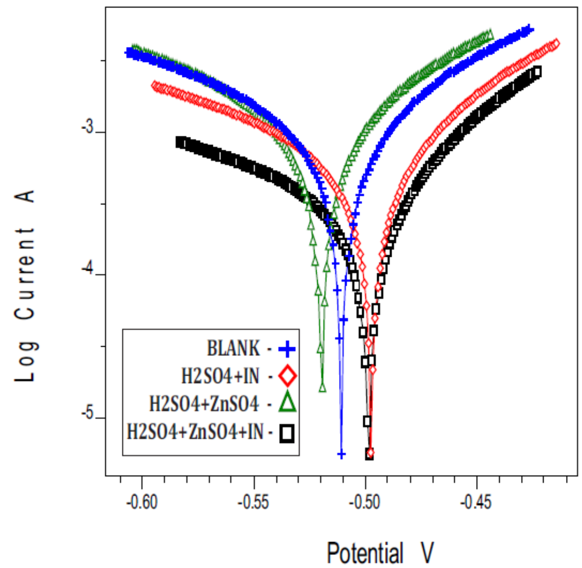

Figure-6
Potentiodynamic polarization curves for the AC gum on mild steel in presence of Zn^{2+} ion in 1 M H_2SO_4

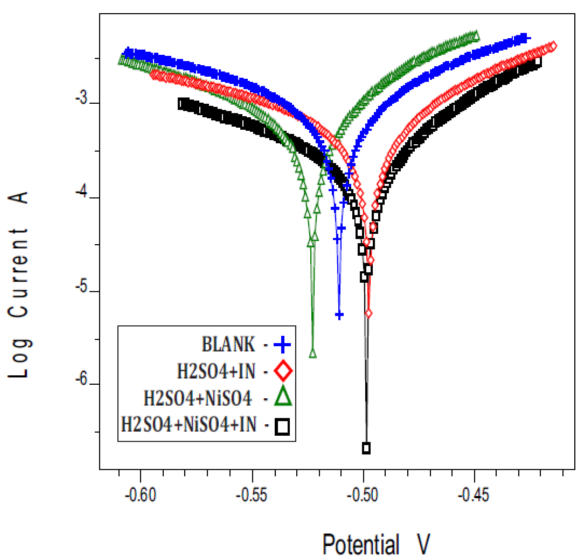

Figure-5
Potentiodynamic polarization for AC gum on mild steel in presence of Ni^{2+} ion in 1 M H_2SO_4

Electrochemical impedance spectroscopic studies: The corrosion inhibition of mild steel in 1 M H_2SO_4 in absence and presence of AC gum with halides and metal cations are investigated by electrochemical impedance spectroscopic method at 303 K. The recorded Nyquist plots are given in figures-7 to 9. The electrochemical parameters such as R_t, C_{dl} and inhibition efficiency are calculated and presented in table-7. The semicircular nature of Nquist plots indicates that the corrosion of mild steel is controlled by a charge transfer process, and the presence of the inhibitor does not affect the mild steel dissolution[20]. The R_t values were calculated from the difference in impedance at low and high frequencies. The double layer capacitance values are obtained from the frequency at which imaginary Z'' component of the impedance (-Z''$_{max}$) is maximized. The relationship used is:

$$F_{(-Z''max)} = \frac{1}{2\pi C_{dl} RT} \quad (6)$$

It is evident from the table 7 that R_t value increases with the addition of AC gum (400 ppm) with halide ions and metal cations. The data also indicate that C_{dl} value decreases with the addition of AC gum with halide ions and metal cation. The decrease is due to the adsorption of gum exudates of AC on the metal surface. The inhibition efficiency of the gum is calculated directly by using the following relationship

$$\text{Inhibition efficiency (\%)} = \frac{R_t^{-1} - R_{t\,(inh)}^{-1}}{R_t^{-1}} \qquad (7)$$

Where, $R_{t\,(inh)}^{-1}$ is the charge transfer resistance of the inhibited solution and R_t^{-1} is the charge transfer of the uninhibited solution.

The inhibition efficiency calculated by electrochemical measurements follows the same trend as a weight loss method.

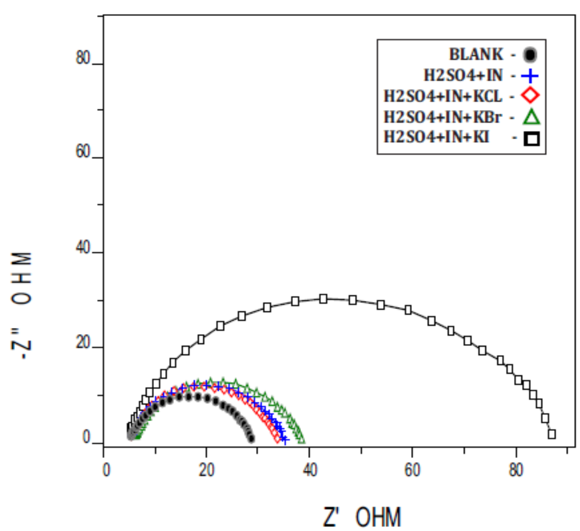

Figure-7
Nyquist plots for AC gum on mild steel in presence of halide ions in 1 M H_2SO_4

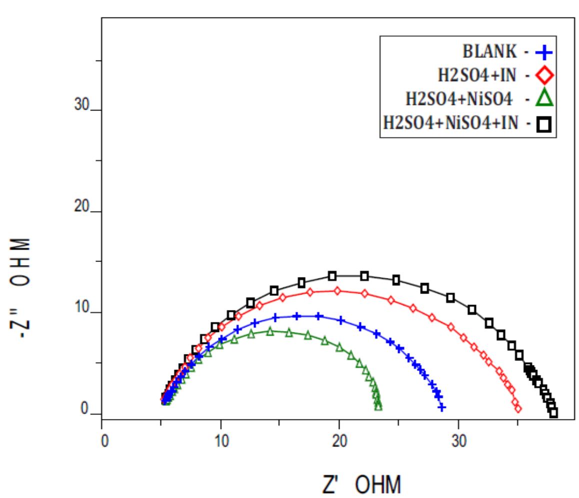

Figure-8
Nyquist plots for AC gum on mild steel in presence of Ni^{2+} in 1 M H_2SO_4

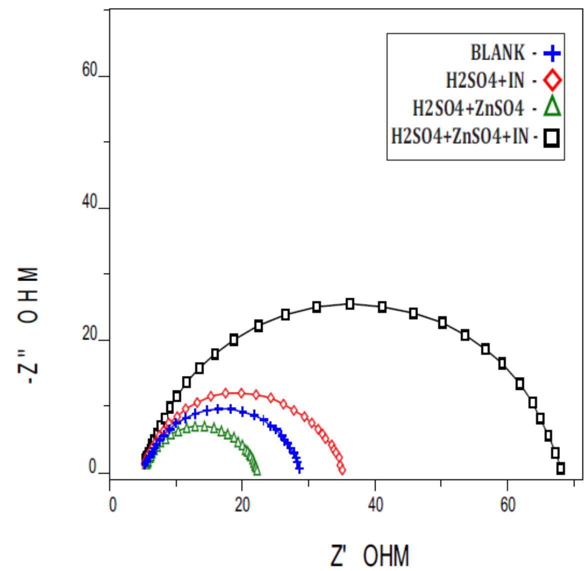

Figure 9
Nyquist plots for the AC gum on mild steel in presence of Zn^{2+} in 1 M H_2SO_4

SEM Micrographs: The SEM micrographs of corroded mild steel in the presence of 1M H_2SO_4 are shown in figure-8. The faceting seen in the figures in a result of pits formed due to the exposure of mild steel to the acid. figure-9 shows the SEM micrograph of the mild steel in 1M H_2SO_4 in the presence of AC gum. The faceting observed in figure-8 disappeared and the surface is free from pits and it is smooth. It can be concluded from figure-9, the corrosion does not occur in the presence of inhibitor and hence corrosion was inhibited strongly in the presence of inhibitors.

Table-7
AC Impedance parameters for the corrosion inhibition of mild steel in 1 M H_2SO_4 with and without inhibitors

Inhibitor concentration	R_t (Ω cm^2)	C_{dl} (μF cm^{-2})	Inhibition efficiency (%)
Blank	15.08	0.249	--
400 ppm AC gum	20.62	0.232	26.8
0.1 mM KCl +400 ppm AC gum	19.04	0.250	20.7
0.1 mM KBr +400 ppm AC gum	21.4	0.243	27.6
0.1 mM KI +400 ppm AC gum	62.9	0.145	76.0
0.1 mM Zn^{2+}+ 400 ppm AC gum	49.54	0.204	69.5
0.1 mM Ni^{2+}+ 400 ppm AC gum	23.64	0.246	36.2

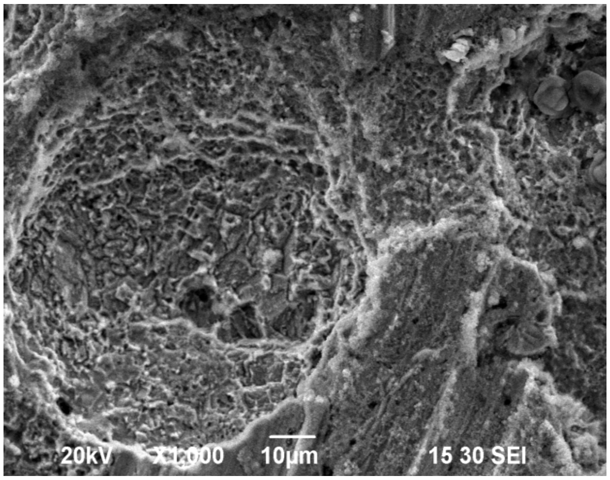

Figure-10
SEM photograph of mild steel in 1 M H_2SO_4

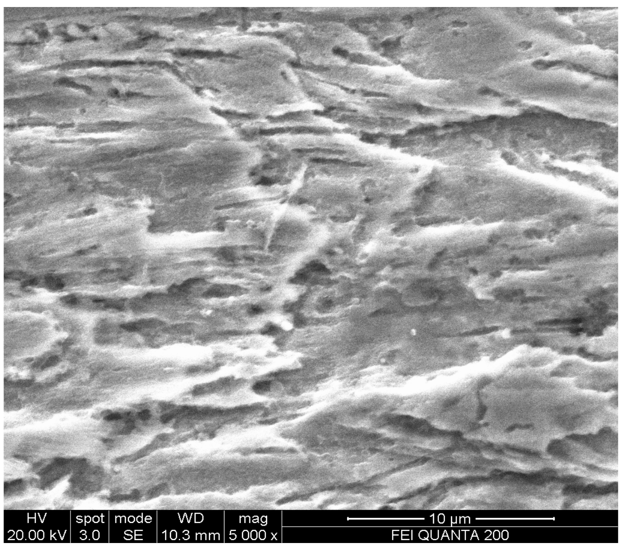

Figure-11
SEM photograph for mild steel in 1 M H_2SO_4 in presence of AC gum

Conclusion

The AC gum act as an effective corrosion inhibitor for the mild steel in 1 M H_2SO_4 acid and maximum inhibition efficiency is achieved at very lower concentration (400 ppm). It has been found that the rate of corrosion is not affected, appreciably up to 323 K, indicating the efficient inhibiting nature in temperature range studied due to the formation of an adherent, protective film on the mild steel surface. The synergistic effect of halides with the AC gum in acidic medium obeys the following order: $I^- > Br^- > Cl^-$. The adsorption of the inhibitor onto the mild steel surface obeys Langmuir adsorption isotherm. From the potentiodynamic polarization studies, it can be concluded that the AC gum acting as a mixed type of inhibitor. The protective layer formed by the AC gum on the mild steel surface is further confirmed by SEM analysis.

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