



## Efficacy of Corrosion Inhibitive Properties of Gum exudates of *Azadirachta indica* on Carbon steel in 1N hydrochloric acid

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### ABSTRACT

Corrosion mitigation of carbon steel by neem gum (gum exudates of *Azadirachta indica*) was investigated in 1N HCl medium. Effect of temperature and immersion period towards the mitigation process is studied using weight loss method. Electrochemical studies indicate that corrosion reaction is inhibited by adsorption of gum molecules. Adsorption process is consistent with Langmuir isotherm. The inhibitor behaves as mixed type for carbon steel corrosion in 1N HCl. Surface morphology studies reveal adsorption on the metal surface.

**Keywords:** Corrosion inhibition, Gum exudates of *Azadirachta indica*, Carbon steel, HCl, SEM.

### INTRODUCTION

Carbon steel (CS) is extensively used in constructions as well as in industrial applications<sup>1,2</sup>. Under different working environments, CS is liable to undergo corrosion. Though many ways are available for corrosion inhibition of metals, use of inhibitors to arrest the corrosion process is considered the best<sup>3</sup>. Many synthetic organic compounds are reported as corrosion inhibitors<sup>4</sup>. Due to their environment and health constraints<sup>5</sup>, use of natural plant products as corrosion inhibitors are extensively studied<sup>6</sup>. Since gum exudates of plants and trees have the potential to act as corrosion inhibitors, many naturally occurring gum exudates were studied as corrosion inhibitors<sup>7-9</sup>. The complexity of constituents, tendency

to form complexes with metal ions and eco-friendly nature make the gum exudates good corrosion inhibitors<sup>10</sup>.

A survey of literature showed that the neem gum i.e., gum exudates of *Azadirachta indica* (GAI) has not been employed towards corrosion mitigation of carbon steel in hydrochloric acid medium. *Azadirachta indica* gum is reported to contain D- glucose, D-glucuronic acid, L-arabinose, L-fucose, mannose, xylose, rhamnose, D-glucosamine, aldobiuronic acid, serine, threonine and aspartic acid<sup>11,12</sup>. Considering the above mentioned advantages of gum exudates towards corrosion inhibition and the presence of complex organic constituents in GAI, the current investigation is aimed to examine



the possibility of gum exudates of *Azadirachta indica* as a CS corrosion inhibitor in HCl solution. The inhibition efficiency has been tested using the following methods: weight loss, Polarization and AC impedance methods. The effect of temperature (303-328±1 K) and immersion time 1,2,4,5,6 and 8 h on the corrosion performance of CS was also analyzed using weight loss method. The carbon steel surface in the absence and presence of inhibitor has been examined using scanning electron microscopy.

### MATERIALS AND METHOD

Neem gum obtained from local area was purified. Analar grade sulphuric acid solution was used as corrosive medium. All solutions were prepared using double distilled water. The Carbon steel coupons of composition 0.37 % C, 0.680 % Mn, 0.230 % Si, 0.160 % Cu, 0.077 % Cr, 0.059 % Ni, 0.015 % S, 0.011 % Ti, 0.009 % Co, remaining Fe having dimensions of 25 x 10 x 1 mm was used to carry out weight loss experiments on the basis of ASTM practice standard G-3114.

Following equations (1),(2) and (3) were used for calculation purpose.

$$\text{Corrosion rate (mmpy)} = 87.6 \times \frac{W}{\rho A t} \quad (1)$$

$$\text{Inhibition efficiency (\%)} = \frac{W_0 - W_i}{W_0} \times 100 \quad (2)$$

$$\text{Surface Coverage } \theta = 1 - \frac{W_i}{W_0} \quad (3)$$

Where  $W$ ,  $\rho$ ,  $A$ ,  $t$ ,  $W_i$  and  $W_0$  represents weight loss in g, density of CS coupon in g cm<sup>3</sup>, area of the coupon in cm<sup>2</sup>, time of immersion in h, loss of weight in inhibited and free acid solutions respectively.

The electrochemical tests were carried out using a conventional three electrode system at room temperature. Along with the CS working electrode, saturated calomel electrode and platinum electrodes were used as reference and counter electrodes respectively. Scan rate in the case of polarization studies was 1mV s<sup>-1</sup> and the potential range studied was +200 to -200mV. Frequency range of 10 KHz to 0.01 Hz was set for impedance studies while 10 mV amplitude AC signals were employed for OCP

with prior immersion of 30 minutes.  $Z_{view}$  software was used to obtain impedance data as Nyquist plots from which the  $R_{ct}$  values were found. JEOL-JSM-35-CF SEM instrument was employed to analyze the exterior surface of inhibited and uninhibited carbon steel specimens.

### RESULTS AND DISCUSSION

#### Effect of inhibitor concentration

Effect of GAI on the corrosion process of CS in 1N HCl medium was studied at 303±1 K using gravimetric measurements for different immersion periods up to 8 hours. Table 1 shows the calculated values of corrosion rate (CR), inhibition efficiency (IE) and surface coverage ( $\theta$ ). Analysis of Table 1 indicates that there was a gradual decrease in corrosion rate with increase in GAI concentration showing the concentration dependence of corrosion rates. Beyond 80 ppm concentration, no considerable inhibition performance of GAI was observed which specifies the optimum concentration as 80 ppm. The gum showed the maximum inhibition efficiency of 83.04% for 1 h immersion period at an optimum concentration of 80 ppm. Primarily the protection act was due to GAI accumulation on to the CS surface which reduces the acid contact of the metal. The high outcome for relatively longer immersion period could be due to insoluble filmy coat or corrosion product formed on CS surface which prevents the penetration of Cl<sup>-</sup> ions of aggressive medium and inward diffusion of oxygen, thereby decreasing the corrosion rate<sup>16</sup>.

#### Effect of Immersion Period

Stability of GAI on CS surface is evaluated by carrying out weight loss measurements in the inhibited and uninhibited solutions for immersion periods of 1,2,4,5,6 and 8 h at 303 K and the obtained corrosion parameters are given in the Table1. On close inspection of the table it can be understood that efficiency of the inhibitor increased with immersion period revealing the protective layer formation on CS due to strong adsorption of GAI. There was a linear relationship of weight loss with immersion period. As the immersion period and the GAI concentration increases, a chemical mode of adsorption was expected<sup>17</sup>. The inhibitor efficiency increases gradually attaining maximum for 5 h immersion time suggesting that the stability and effectiveness of the inhibitor withstands over a period of 5 hour. After an immersion period of 5 h, it can be noticed that the inhibition efficiency slowly started to decrease.

**Table 1: Effect of different concentrations of GAI on CS in 1N HCl for various immersion periods at 303K**

C ppm	1 h			2 h			4 h		
	CR mmpy	I E (%)	$\theta$	CR mmpy	I E (%)	$\theta$	CR mmpy	I E (%)	$\theta$
Blank	46.11			49.27			52.21		
5	32.1	30.39	0.3039	31.87	35.32	0.3532	31.08	40.48	0.4048
10	28.03	39.22	0.3922	26.44	46.33	0.4633	25.65	50.87	0.5087
20	23.51	49.02	0.4902	21.47	56.42	0.5642	21.36	59.09	0.5909
40	18.08	60.78	0.6078	16.95	65.6	0.656	15.93	69.48	0.6948
60	14.47	68.63	0.6863	13.11	73.39	0.7339	11.98	77.06	0.7706
80	13.56	70.59	0.7059	9.49	80.73	0.8073	7.8	85.06	0.8506
100	14.92	67.65	0.6765	9.27	81.19	0.8119	7.57	85.5	0.855
120	13.11	71.57	0.7157	9.04	81.65	0.8165	7.23	86.15	0.8615
C ppm	5 h			6 h			8 h		
	CR mmpy	I E (%)	$\theta$	CR mmpy	I E (%)	$\theta$	CR mmpy	I E (%)	$\theta$
Blank	55.07			58.26			60.03		
5	28.4	48.43	0.4843	32.04	45	0.45	34.67	42.24	0.4224
10	25.16	54.31	0.5431	29.61	49.18	0.4918	31.82	46.99	0.4699
20	20.87	62.11	0.6211	24.18	58.49	0.5849	31.1	48.19	0.4819
40	14.09	74.42	0.7442	21.53	63.05	0.6305	28.07	53.24	0.5324
60	11.38	79.34	0.7934	19.49	66.54	0.6654	27.3	54.52	0.5452
80	9.34	83.04	0.8304	18.36	68.48	0.6848	25.09	58.21	0.5821
100	9.42	82.9	0.829	15.93	72.65	0.7265	22.78	62.05	0.6205
120	9.57	82.63	0.8263	14.92	74.39	0.7439	22.92	61.82	0.6182

### Thermodynamic considerations

Influence of temperature on inhibition behavior of GAI for CS corrosion in 1N HCl was studied at the temperatures 303K, 313 K and 323 K and the obtained results were shown in Table 2. With increase in temperature, corrosion rate increases in the presence and absence of GAI due to increase in the kinetic energy of the reacting entities. Corrosion rate at any given concentration decreases in case of inhibited acid solution compared to that of uninhibited solution in all temperature range studied. It was as a result of mitigating effect of the gum on the corrosion reaction of CS. With increase in temperature, a linear but a slight increase in inhibition efficiency was observed. At all temperatures studied, inhibition performance lowered or remained similar after 80 ppm GAI. The adsorption process may be either physical or chemical adsorption<sup>18</sup>. The fact is decided by nature and structure of the inhibitor, pH and temperature of the system and character and charge of the metal<sup>18</sup>.

Based on the Arrhenius equation<sup>19</sup>, the apparent activation energy ( $E_a^*$ ) was evaluated

using frequency factor A from the equation (4). A plot (Fig. 1) was made between log CR and  $1/T$  resulting in the slope of  $-E_a^*/2.303R$  and intercept A from which  $E_a$  and A were obtained. The enthalpy and entropy parameters  $\Delta S^*$  and  $\Delta H^*$  were obtained using equation 5. A transition state curve between  $\log(CR/T)$  versus  $1/T$  is plotted. This plot Fig. 2 gave a straight line with slope  $(-\Delta H^*/2.303 R)$  and intercept  $\log (R/Nh) + \Delta S^*/2.303 R$ .

$$\log CR = \log A - \frac{E_a^*}{2.303RT} \quad (4)$$

$$CR = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \quad (5)$$

Table 3 displays the obtained values for  $E_a$ ,  $\Delta H^*$  and  $\Delta S^*$ . Activation energy ( $E_a$ ) for free acid solution is 72.83 KJmol<sup>-1</sup> which decreases to 58.26 KJmol<sup>-1</sup> in the presence of GAI. This indicates that GAI is adsorbed chemically which in turn reduces the corrosion rate<sup>20-22</sup>. For any given concentration  $E_a$  value is larger than  $\Delta H^*$  value. Decrease in  $\Delta H^*$  value for the inhibited solution compared to blank also supports the chemical nature of adsorption.

Endothermic nature of CS dissolution is confirmed by positive enthalpy values ( $\Delta H^*$ )<sup>23,24</sup>. The free acid solution has entropy value ( $\Delta S^*$ ) of  $19.17 \text{ JK}^{-1} \text{ mol}^{-1}$

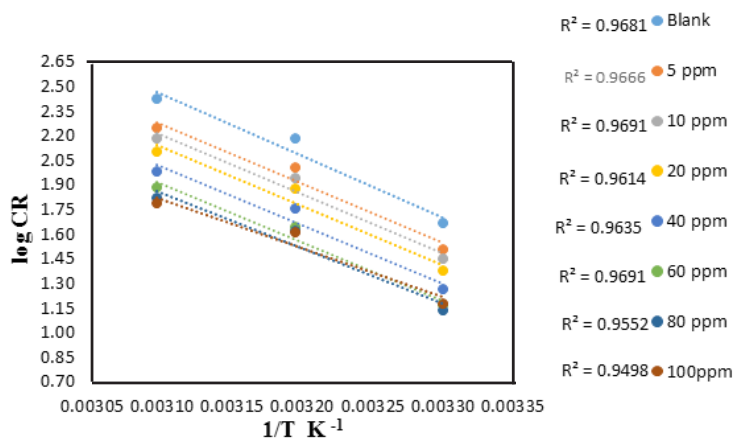
which decreases up to a maximum of  $-38.30 \text{ JK}^{-1} \text{ mol}^{-1}$  in the presence of GAI which actually signifies the conversion of reactants to activated complexes<sup>25</sup>.

**Table 2: Corrosion parameters for different concentrations of GAI on CS in 1N HCl at 303K, 313K and 323 K for 1h immersion period**

C ppm	CR mmpy	303K			313K			323K		
		IE (%)	$\theta$	CR mmpy	IE (%)	$\theta$	CR mmpy	IE (%)	$\theta$	
Blank	46.11			150.08			265.8			
5	32.1	30.39	0.3039	101.26	32.53	0.3253	174.94	34.18	0.3418	
10	28.03	39.22	0.3922	86.79	42.17	0.4217	150.98	43.2	0.432	
20	23.51	49.02	0.4902	74.59	50.3	0.503	125.22	52.89	0.5289	
40	18.08	60.78	0.6078	56.51	62.35	0.6235	95.38	64.12	0.6412	
60	14.47	68.63	0.6863	43.85	70.78	0.7078	75.49	71.6	0.716	
80	13.56	70.59	0.7059	41.14	72.59	0.7259	65.55	75.34	0.7534	
100	14.92	67.65	0.6765	40.68	72.89	0.7289	60.57	77.21	0.7721	
120	13.11	71.57	0.7157	41.59	72.29	0.7229	63.29	76.19	0.7619	

**Table 3: Activation parameters for CS in 1N HCl in the absence and presence of GAI in the temperature range of 303K - 323K for 1h immersion period**

Concentration (ppm)	Ea (kJmol <sup>-1</sup> )	$\Delta H^*$ (kJmol <sup>-1</sup> )	Ea - $\Delta H^*$ (kJmol <sup>-1</sup> )	$\Delta S^*$ (Jmol <sup>-1</sup> k <sup>-1</sup> )
Blank	72.83	70.18	2.66	19.17
5	70.5	67.85	2.66	8.46
10	70.02	67.36	2.66	5.69
20	69.55	66.89	2.66	2.77
40	69.14	66.48	2.66	-0.79
60	68.7	66.04	2.66	-4.18
80	65.51	62.85	2.66	-15.14
100	58.26	55.61	2.66	-38.3
120	65.46	62.8	2.66	-15.46



**Figure 1: Arrhenius plot for GAI on CS in 1N HCl**

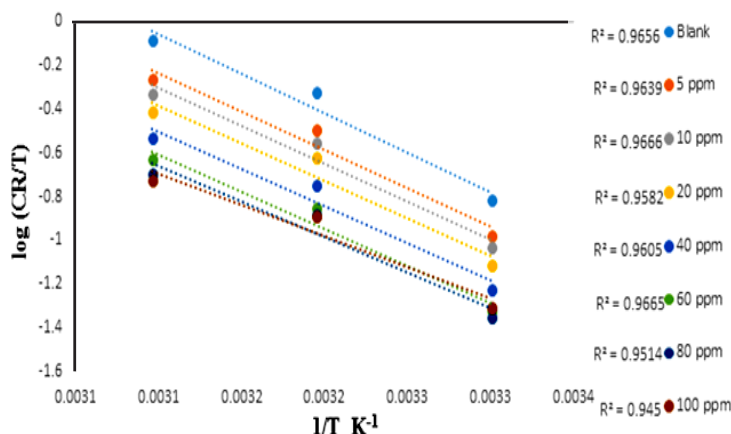


Fig. 2. Transition State plot GAI Carbon steel 1N HCl

**Adsorption Isotherm**

Generally the adsorption process of organic molecules over the metal surface depends on chemical composition of the organic compound, temperature range of study, and electrochemical potential on metal<sup>26,27</sup>. Adsorption isotherms signify the mechanistic path of adsorption. In the present study the Langmuir isotherm model was found as best fitting one. Langmuir isotherm equation relates equilibrium constant  $K_{ads}$  and concentration as in equation (6) and  $\Delta G_{ads}^{\circ}$ , free energy of adsorption is calculated from the equation (7)

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{6}$$

$$K = -\log C_{H_2O} - \left( \frac{\Delta G_{ads}^{\circ}}{2.303 RT} \right) \tag{7}$$

Langmuir adsorption plots obtained at different temperatures with various concentrations of GAI is shown in Fig. 3. Strong adsorption is evident from the strong correlation coefficients  $R^2 > 0.99$  at all temperatures. Calculated  $\Delta G_{ads}^{\circ}$  is presented in Table 4. Slope values also confirms the validity of the Langmuir model. Negative  $\Delta G_{ads}^{\circ}$  values shows

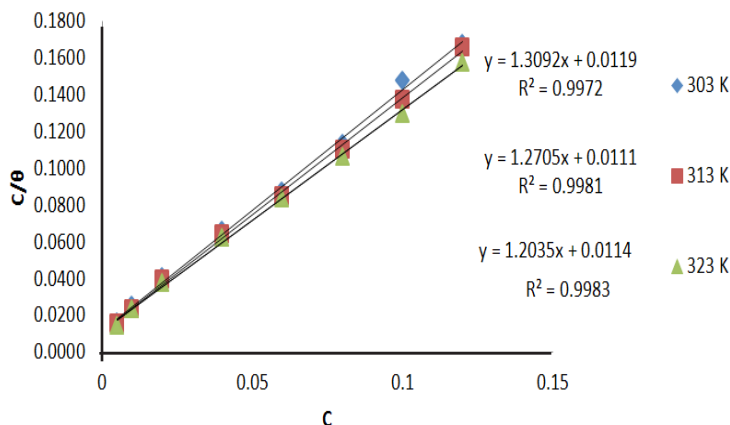


Fig. 3. Langmuir adsorption Isotherm

**Table 4: Adsorption parameters for the different concentration of GAI on CS in 1N HCl in the temperature range of 303-323K**

Temperature K	Slope n	Equilibrium constant ( $K_{ads}$ ) mol <sup>-1</sup>	$-\Delta G_{ads}^{\circ}$ kJmol <sup>-1</sup>
303	1.3	76.527	-21.28
313	1.2	93.52	-21.47
323	1.2	112.138	-21.39

that the adsorption process is spontaneous<sup>28</sup>. Generally,  $\Delta G_{ads}^{\circ}$  around -20 kJ/mol is suggestive of physisorption and around -40 kJ/mol is said to be chemisorption<sup>29</sup>. So it is implicit that  $\Delta G_{ads}^{\circ}$  values presented in Table 4 is reflective of physical nature of adsorption. But the  $E_a$  values reveal that a little of chemical bonding may also be involved in the adsorption process.

### Electrochemical considerations

#### Electrochemical polarization studies

Polarization potential curves applied for the assessment of corrosion mitigation effect of GAI on CS specimen in 1N HCl for 4 h immersion period is presented in Fig. 4. By usual extrapolation method, corrosion current  $I_{\text{corr}}$  and potential  $E_{\text{corr}}$  is evaluated and the inhibition efficiency was assessed by equation (8).

$$IE(\%) = \frac{I_{\text{corr}(0)} - I_{\text{corr}(i)}}{I_{\text{corr}(0)}} \times 100 \quad (8)$$

From Fig. 4, it was clear that corrosion rate decreases in the presence of GAI as a consequence of production of lower current

densities by both anionic dissolution of metals and cationic hydrogen evolution reaction. Change in the Tafel constants prove that GAI affects both anodic and cathodic reaction. Table 5 shows the electrochemical parameters  $I_{\text{corr}}$  and  $E_{\text{corr}}$ , IE(%), Tafel constants  $b_a$  and  $b_c$ . From the table, it is evident that there is decrease in corrosion rate in GAI inhibited solution compared to blank solution. Decrease in  $I_{\text{corr}}$  value shows the retardation of electrochemical reactions. In addition, absence of significant change in  $E_{\text{corr}}$  values is indication of mixed mode type<sup>30</sup>. The inhibition efficiencies obtained in this method follows the similar pattern observed in gravimetric experiments.

**Table 5 : Polarization data of CS in 1N HCl in the presence and absence of GAI**

Concentration (ppm)	$I_{\text{corr}}$ (mA cm <sup>-2</sup> )	$E_{\text{corr}}$ (Mv/SCE)	$b_a$ (mV dec <sup>-1</sup> )	$b_c$ (mV dec <sup>-1</sup> )	IE(%)
Blank	763	-471.28	84.4	133	-
40	312	-433.2	69	150	59.11
60	268	-436.26	72	138	64.88
100	234	-434.91	77	140	69.33

#### AC Impedance Spectroscopy Studies

In order to study the adsorption nature of CS in 1N HCl at room temperature, impedance responses were recorded after 4 h immersion for free acid and inhibited test solutions, which is shown in Fig. 5. This shows Nyquist plots increasing in diameter of semi-circles with GAI concentration which is indicative of the fact that GAI adsorption on to the metal hinders the corrosion process. Difference in the shape of the semicircles can be explained with reference to non-homogeneity of the surface and roughness of the metal<sup>31</sup>. Charge transfer resistance ( $R_{\text{ct}}$ ), double layer capacitance ( $C_{\text{dl}}$ ) and inhibition efficiency values were presented in Table 6. On evaluation of Table 6 shows,  $C_{\text{dl}}$  values were found to decrease with increase in  $R_{\text{ct}}$ . This may be attributed to the fact that the green inhibitor gets adsorbed as thin protective film on the surface of the electrode. The  $C_{\text{dl}}$  value of uninhibited solution is  $45.3 \times 10^{-3} \mu\text{F cm}^{-2}$  which decreases to  $20.8 \times 10^{-3} \mu\text{F cm}^{-2}$  on addition of 100 ppm GAI. Thus there was a decrease in  $C_{\text{dl}}$  values with increase in concentration. This can be accounted by any of the two factors: lowering of dielectric constant and increase of thickness in double layer capacitance<sup>32</sup>. Thus electrical capacity is decreased through the displacement of ions and water molecules on the surface interface<sup>33</sup>. Shapes of the semicircle with and

without inhibitor look alike indicating an unaltered corrosion mechanism on the addition of GAI.

**Table 6: AC Impedance data of CS in 1N HCl in the presence and absence of GAI**

Concentration (ppm)	$R_{\text{ct}}$ ( $\Omega \text{ cm}^{-2}$ )	$C_{\text{dl}}$ ( $\mu\text{F cm}^{-2}$ ) * $10^{-3}$	IE (%)
Blank	12.1	45.1	-
40	51.3	29.7	76.41
60	84.8	23.1	85.73
100	101.3	20.8	88.05

#### Scanning Electron Microscopy

To validate film formation, SEM images of CS coupons exposed to inhibited and uninhibited solutions were documented. Fig. 6a, 6b and 6c show freshly recorded SEM images of polished CS surface, CS surface exposed to uninhibited solution and CS surface exposed to 100 ppm of GAI respectively.

Figure 6a shows plain clear surface, while Fig. 6b depicts severely corroded surface due to acid attack and Fig. 6c represents smooth surface with some scattered pits. This change in the surface of the CS specimen is a supportive feature of formation of adsorbed film. Thus the addition of GAI to 1N HCl has reduced the corrosion of carbon steel specimen significantly.



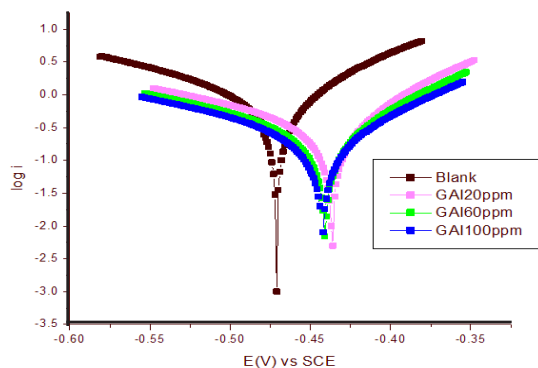


Fig. 4. Polarisation curves for CS in 1N HCl

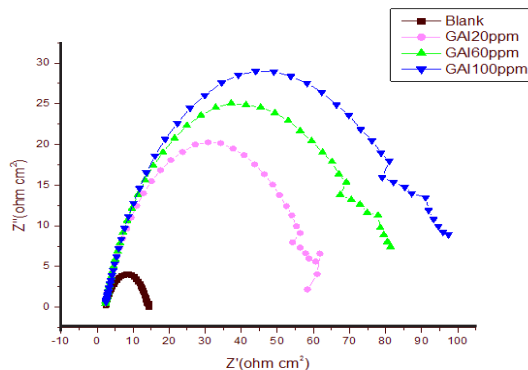
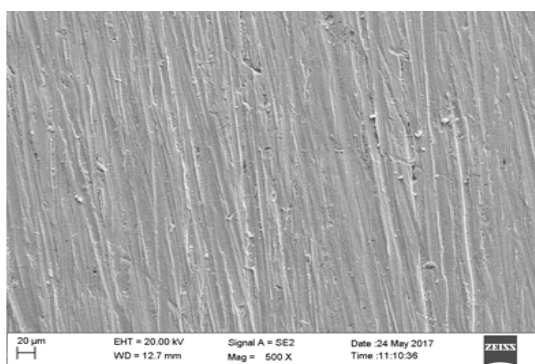
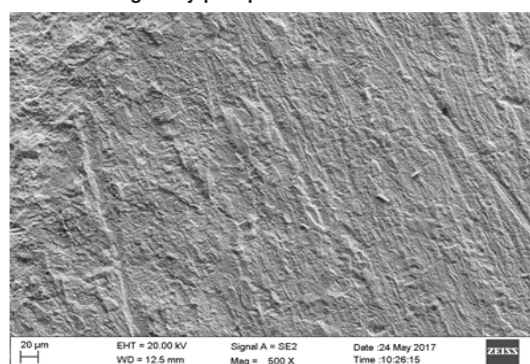


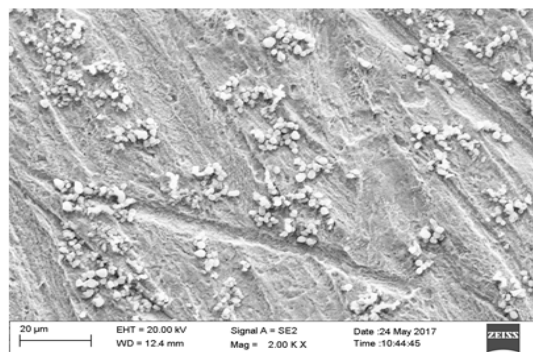
Fig. 5. Nyquist plots of CS in 1N HCl



(a) polished surface



(b) after immersion in 1N HCl solution



(c) after immersion in 100 ppm GAI

Fig. 6. SEM photographs of CS sample

## CONCLUSION

- GAI shows significant corrosion inhibition for CS in hydrochloric acid medium.
- With increase in temperature, inhibition efficiency increases for 1h immersion period.
- Inhibition process takes place through adsorption mechanism  
Langmuir is the best fit isotherm.
- Spontaneity of the adsorption process is shown by thermodynamic parameters.
- The polarization measurements evince the mixed mode nature of GAI.
- The SEM analysis supports protective film formation on carbon steel.

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