RESEARCH ARTICLE

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Electrochemical evaluation of corrosion inhibition of SAE 1010 carbon steel in 1M HCl by galactomannans

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ABSTRACT

The inhibition properties of galactomannans (GM) on low carbon steel samples immersed in 1M HCl were judged by advanced electrochemical assessments. The electrochemical results obtained by potentiodynamic polarization and electrochemical impedance spectroscopy of the inhibited electrodes were evaluated in contrast to the electrodes prone to corrosive solution and GM's character in inhibition of corrosion was perceived. The results, qualitative and quantitative thus derived prove GM to be effective for corrosion protection of SAE 1010 carbonsteel in 1 M HCl.

INTRODUCTION

As the chromates/arsenates were restricted, corrosion prevention with ecological green compounds (nontoxic inhibitors) in oil and gas industry were fabricated to efficiently reach the safety levels and save the metals and their service life. In general, most of these efficient corrosion inhibitors are organic compounds containing hetero atoms such as S, N, O, P and many bonds/aromatic rings. Lone pairs of electrons and π- electrons which are loosely bound in their functional groups determine their activity. These biocompatible substances might be of plants and animal origin. In the past two decade, the researchers sought after the ''green'' or "eco-friendly" corrosion inhibitors to use cheap, effective compounds at low or ''zero'' effect on nature Abbout *et al*., 2018; Abdallah, 2004; Al-Otaibi *et al*., 2014; Chellouli *et al*., 2016; Jano, Lame, & Kokalari, 2012; Umoren & Eduok, 2016; Zouarhi *et al*., 2018. The ever increasing publications on green corrosion inhibition indicate the interest in exploring the new inhibitors to control the corrosion of various metals. This article evaluates the role of galactomannans (GM) to prevent metallic corrosion in 1M HCl through electrochemical investigations (Figure 1).Galactomannans are frequently utilized in food products to enhance the water phase viscosity. Galactomannans consist of a backbone of mannoseand side groups of galactose (specially, a (1-4)-linked β-D-mannopyranose backbone with branchings from their 6thpositions linked to α-D-galactose, (i.e. 1-6-linked α-D-galactopyranose).

MATERIALS AND METHODS

Preparation of Electrolyte

The corrosive solution or blank solution was 1M HCl aqueous solution. The electrolyte contained various concentrations of GM from 100 to 500 ppm. The galactomannan powder was obtained commercially by Sigma-Aldrich,India. The effect of adding GM (100-500 ppm) on the SAE-1010 carbon steel (SCS) corrosion was studied at room temperature. The experiments were conducted in 1M HCl in air without stirring.

The Working Electrode

The compositional weight of commercially obtained SCS was 0.49% carbon, 0.46% manganese, 0.16% silicon,

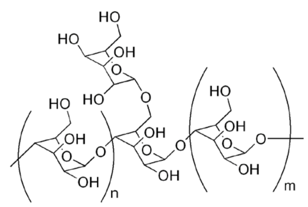

Figure 1. Chemical structure of galactomannan

0.27% chromium, and remaining percentage of iron. The testcoupons from SCS were abraded mechanically using different grades of silicon carbide paper (#600 - #2000). Later they were rinsed with running water, dipped in acetone and dehydrated prior to their installation as working electrodes in electrochemical set up.

Electrochemical Investigations

Potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) was carried outusing tri electrode system in Gamry PGSTAT instrument. The corrosion cell setup comprised of Ag/AgCl; reference electrode, a platinum; counter electrode (Pt) and a SCS: working electrode with the surface area of 0.785 cm^2.

PDP or Potentiodynamic polarization

For potentiodynamic polarization (PDP) evaluation, firstly the cathodic and later the anodic scanning of WE (working electrode) was carried out at the scan rate of 1 mV/s within the potential range of −250 to +250 mV against E_{corr}. Potentiodynamic results were computed on extrapolation of the Tafel plots' linear values. The values of the cathodic Tafel curve (β_c), the anodic Tafel curve (β_a), the corrosion potential (E_{corr}) and corrosion current density (i_{corr}), were obtained by these quantifications. The anodic and cathodic Tafel graphs were analysed in EchemAnalyst™ 3.0 software. The results of R_p or resistance polarization were computed using Stern Geary's equation (1):

$$i_{corr} = \frac{\beta a\ \beta c}{2.303\,(\beta a+\beta c)}\frac{1}{R_P} i_{corr} = \frac{\beta a\ \beta c}{2.303\,(\beta a+\beta c)}\frac{1}{R_P} \quad (1)$$

The calculated $i_{cor\,r}$ results yielded the inhibition efficiency or η (%) relative to equation (2).

$$\eta_{PDP}(\%) = \frac{i_{corr} - i^{i}_{corr}}{i_{corr}} \times 100 \quad (2)$$

where, i_{corr} and i^{i}_{corr} represented the corrosion current density in the presence and absence of GM.

EIS or Electrochemical Impedance Spectroscopy

The corrosion cell arranged in thisstudy was similar to PDP investigation. The open circuit potential was recorded and a steady state achieved after 2h of dipping in the corrosive solution ahead of every assessment. EIS was carried out at acorrosion potential (E_{corr}) of 10 mV peak-to-peak amplitude signal with a 30 mHz to 100 kHz frequency range (Gerengi *et al.*, 2018). The conclusive values were interpretedusing software called ZsimpWin 3.21. The % percentage inhibition efficiency 'η_{EIS}' is based on the R_{ct} parameters following the equation (3).

$$\eta_{EIS}(\%) = \frac{R_{ct}^{(i)} - R_{ct}}{R_{ct}^{(i)}} \times 100 \quad (3)$$

Where $R_{ct}^{(i)}$ is the resistance value for charge transfer on gradual and measured addition of GM while R_{ct} represents the value in corrosive solution without GM, respectively.

RESULTS AND DISCUSSION

PDP measurements

PDP measurements evaluated the process of cathodic and anodic potentials of corrosion process. The Tafel graphs for SCS in electrolyte both in the presence and absence of GM are displayed in Figure 2. The polarization values conclusive of the plots have been documented in Table 1. Compared to blank, the βa andβc values first increase on adding the inhibitor and later diminish after adding more concentration of GM. This reduction in anodic and cathodic values is due toincrease in thickness of electrical double layer by hydroxylic groups. For the anodic slope it is important to remember that it is associated with dissolution of steel. When inhibitors are added in low concentrations they might get lost them self in the electrolyte or even get adsorb on the steel surface, masking of small fraction of the substrate causes initial increasing in βa values (Zhang *et al.*, 2018). The values of can be according to a particular adsorption of GM,because I_{corr} are depleting on the increasing GM concentration.

The extent of change seen in the corrosion potential values, which should be E_{corr}≤s85mV, point towards a mixed type of inhibition. The maximum difference of potential was observed at maximum GM concentration of 500ppm and it was ΔE_{corr} = 85mV. On increasing concentration of GM in the 1M HCl a constant depletion in values of i_{corr} was observed. This suggested building up of a protective film between metal and corrosive solution by GM hence decreasing the electrochemical reaction rate (Aslam, Mobin, Aslam, & Lgaz, 2018). The inhibition efficiency or 'η_{PDP}' values approach 92.5 % on adding 500 ppm of GMto the electrolyte.

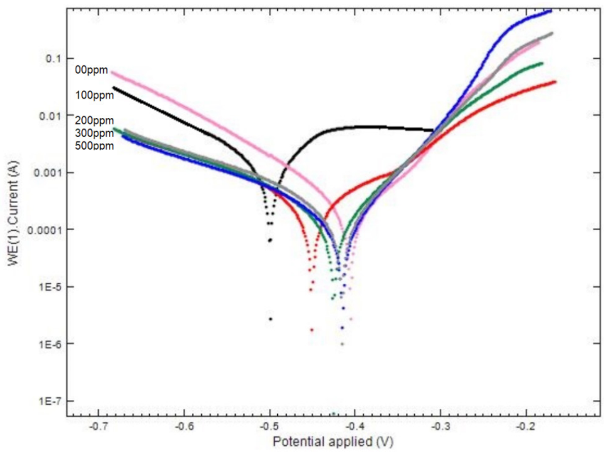

Figure 2: Tafel plots for SCS sample in 1M HCl solution in presence and absence of various GM concentrations

Table 1: Potentiodynamic polarization parameters for SCS sample in 1M HCl solution in presence and absence of various GM concentrations at room temperature.

Inhibitor concentration (ppm)	E_{corr} *(mV/Ag/AgCl)*	i_{corr} *(μA/cm²)*	β_a *(mV/dec)*	β_c *(mV/dec)*	η_{PDP} *(%)*
0	-500.1	1208.5	103.5	82.8	
100	-451.4	457.7	200.5	206.9	62.1
200	-406.1	240.4	91.8	106.1	80.1
300	-416.1	123.5	94.4	68.0	89.8
400	-425.6	112.7	91.7	73.3	90.7
500	-415.5	90.2	88.8	58.3	92.5

Table 2: EIS parameters for SCS sample in 1M HCl solution in presence and absence of various GM concentrations at room temperature.

Concentration (ppm)	*Rs (Ω cm²)*	Y_o *(μWsⁿ m⁻²)*	*n*	R_{ct} *(Ω cm²)*	$\%\eta_{EIS}$	*-α°*
0	1.56	78.892	0.991	17.476	-	43
100	0.21	90.885	0.994	75.004	76.71	47
200	0.79	196.59	0.995	93.955	81.41	51
300	0.39	137.88	0.996	123.82	85.89	54
400	2.07	160.94	0.997	137.43	87.29	67
500	5.92	122.9	0.997	184.67	90.54	69

Electrochemical impedance spectroscopy (EIS)

Figure 3 shows the impedance graph for SCS corrosion in 1M HCl solution with and without adding the GM. As seen in Figure 3, high-frequency capacitive loops and depressed semicircles obtained as Nyquist plots on adding varying concentration of GM to corrosiveelectrolyte.

This deflection from the perfection in nyquist semicircle is either attributed to heterogeneity/micro-roughness of metal substrate or non-uniform geometrical nature of current distribution. The result of impedance changed considerably on increasing the concentration of GM to the electrolyte but the semicircular plot shapes remained unaltered for the electrodes suggesting an unaffectedmechanism of corrosion on increasing GM concentration. The process was primarily standardized by a process of charge transfer (Bayol, Gürten, Gürten, & Erbil, 2008). Table 2 lists the impedance results. The impedance data was accurately designed applying the conventional *R(QR)* circuit according to the χ^2 values within 104 range (Figure 4).

R_{ct} is the charge transfer resistance,Q is the constant phase element, R_s is the non-compensated solution resistance and CPE used in place of C_{dl}/double layer capacitance to attribute for behavior deviated from ideal (Solomon, Gerengi, Kaya, & Umoren, 2017) in this equivalent circuit. The CPE can be modeledwith the help of equation (4):

$$Z_{CPE} = Y_o^{-1}(j\omega)^{-n} Z_{CPE} = Y_o^{-1}(j\omega)^{-n} \quad (4)$$

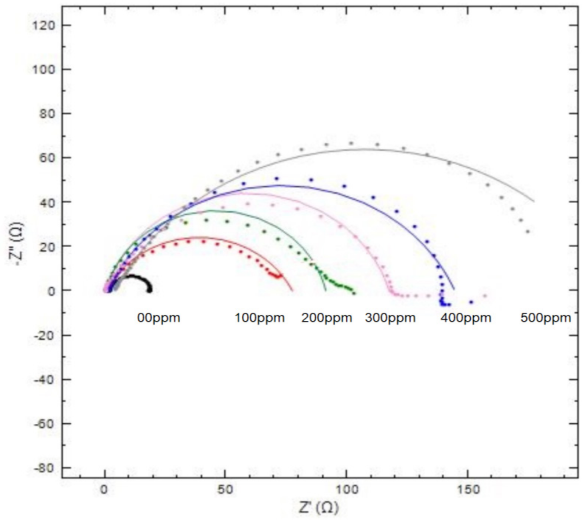

Figure 3. Nyquist plots for for SCS sample in 1M HCl solution in presence and absence of various GM concentrations

where Z_{CPE} stands for impedance, ω signifies the frequency, j denotes the square root of −1, n is for the measurement of the capacitor's non-homogeneity whose value might be ranged between -1 and 1 (n = 0, -1 and 1, the CPE is a pure resistor, an inductor and a pure capacitor, respectively) and $Y_o Y_o$represents proportionality factor and. The R_{ct} increases with increase in concentration of GM. R_{ct} obtained for solution without inhibitor are outcome of the basically water molecules and other ions adsorbed on substrate/HCl junction. They further get displaced by inhibitive GM layer. Significant values of resistance were received even for

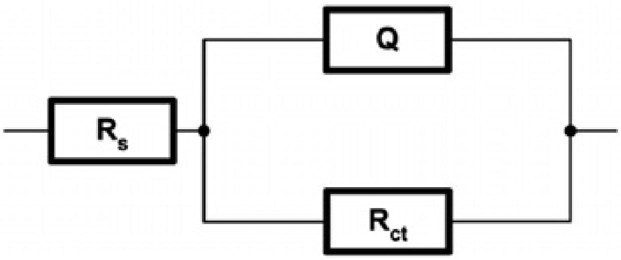

Figure 4: Equivalent circuit applied for EIS evaluation of SCS sample in 1M HCl solution in presence and absence of various GM concentrations

low GM concentration, which substantiate the high attraction of GM to Fe^{2+} atoms. The complex of Fe^{2+}/H_2O firstly developed on SCS in corrosive solution without inhibitor transitioned to Fe^{2+}/GM complex in the protected solution as per the results of EIS. At 500 ppm concentration GM becomes 90.54% effective in prevention corrosion according to the results of impedance measurement.

The effective performance of GM as a corrosion inhibitor was also proved results of phase angle at high frequencies. Angles nearing a -90° suggest an increased capacitive behavior (Lu & Chen, 2012). Such a responseincreased more on adding moreamount of GM. The higher range offrequency attained larger value of phase angle. The phase angle (-α°) increased on addition of GM might be relative to formation of a inhibitive film on working electrode as displayed in Table 2.

CONCLUSIONS

The effect of adding GMs to 1M HCl solution having SCS coupon was elaborated and studied assisted by advanced electrochemical analysis (PDP, EIS). The investigation has led to following conclusions:

GM might prevent90 % ~ 92 % of SCS corrosion in 1M HCl solution whenused at 500 ppm. The efficiency of corrosion inhibition is observed to be increasing on increasing the GM's concentration.

The outcomes of PDP suggest that GM is a mixed type inhibitor as it curbs the rapid corrosion reactions on SCS surface in 1M HCl solution.

The EIS show the presence of protective film barricading the aggresive 1M HCl solution to reach SCS surface.

The studies assure that GM,a polysaccharide of plant origin, is a better alternate to the hazardous corrosion inhibitors for SCS corrosion in 1M HCl.

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