Biopolymer from Tragacanth Gum as a Green Corrosion Inhibitor for Carbon Steel in 1 M HCl Solution

Mohammad Mobin,$^*†$ Marziya Rizvi,$^†$ Lukman O. Olasunkanmi,$^‡$ and Eno E. Ebenso$^{‡*}$

$^†$Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh 202002, India
$^‡$Material Science Innovation and Modelling (MaSIM) Research Focus Area, Department of Chemistry, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

ABSTRACT: A biopolymer from tragacanth gum, arabinogalactan (AG), was investigated for its adsorption and corrosion inhibition traits for carbon steel corrosion in 1 M HCl. Gravimetric method, potentiodynamic polarization measurements, electrochemical impedance spectroscopy, UV–visible spectroscopy, scanning electron microscopy, and atomic force microscopy were used to judge the adsorptive nature of AG in the acid solution. The inhibition efficiency improved with an increase in AG concentration and temperature of the acid solution. Thermodynamic and activation parameters ($\Delta G$, $E_a$, $\Delta H$, and $\Delta S$) were also calculated and discussed. The adsorption of AG favored Langmuir adsorption isotherm. The results of corrosion tests confirmed that AG could serve as an efficient green corrosion inhibitor for the carbon steel in 1 M HCl, yielding high efficiency and a low risk of environmental pollution. Theoretical quantum chemical and Monte Carlo simulation studies corroborated the experimental results.

INTRODUCTION

Carbon steel with its relatively high strength, low cost, and widespread availability has been extensively utilized in numerous industrial applications such as petrochemical plants, power plants, oil and gas refineries, distillers, and ships. $^1$ However, low resistance of carbon steel to acid corrosion has been the major hurdle in its applications, and there remains a need to prolong the lifetimes of steel items. Among the various approaches employed to minimize steel corrosion in acidic environment, the usage of inorganic/organic inhibitors is a well-established and cheapest method.$^2$–$^5$ The inhibitors can be added to water tanks, pipeline streams, and so forth or incorporated into paint coatings, where they may form passive or almost impermeable films on the metal surface to reduce the rate of corrosion. Unfortunately, most of them are expensive, toxic toward the environment, and non-biodegradable. The adversely affecting chemicals and recent increase in environmental awareness have geared the research activities toward the development of nontoxic, cheap, environment-friendly, and biodegradable substances as inhibitors. These prerequisites are fulfilled by the natural polymers that efficiently protect metals in diverse degrading environments. Few of the natural polymers, which have been studied as green and eco-friendly inhibitors for carbon steel corrosion in acid solutions in the recent past, include carboxymethyl cellulose (CMC),$^6$–$^7$ starch,$^8$–$^9$ gum arabic,$^{10}$–$^{12}$ chitosan,$^{13}$ pectin,$^{14}$ and xanthan gum.$^{15}$

CMC was evaluated as an inhibitor for mild steel corrosion in H$_2$SO$_4$ by the hydrogen evolution method.$^9$ At a concentration of 0.5 g/L at 30 °C, CMC yielded an inhibition efficiency of 56.3%. In another study, sodium carboxymethyl cellulose (Na-CMC) was evaluated for the inhibition of mild steel corrosion in 1 M HCl solution through electrochemical methods [electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP)]. Na-CMC was found to be 78% efficient at 298 K at a concentration of 0.04 g/L.$^7$ Modified cassava starch (600 ppm) was quite efficient in inhibiting the corrosion of carbon steel in alkaline medium, which was confirmed by the electrostatic potential mapping of its monomeric units.$^8$ In another study, inhibition of the mild steel corrosion in 0.1 M H$_2$SO$_4$ by using starch was analyzed by gravimetric analysis and PDP technique.$^9$ Starch inhibited the corrosion of mild steel to a considerable extent. The maximum efficiency was 66.21% at 30 °C at an inhibitor concentration of 200 ppm. Its efficiency was, however, further increased on the addition of small amount of surfactants: 1 ppm cetyl trimethylammonium bromide and 5 ppm sodium dodecyl sulfate (SDS). Gum acacia efficiently inhibited the corrosion of mild steel in 0.1 M H$_2$SO$_4$. The efficacy of 1500 ppm gum acacia in the corrosive solution was 83% at 30 °C.$^{11}$ In another
the adsorption of gum arabic on mild steel and aluminum in aggressive H₂SO₄ solution was investigated within the temperature range of 30–60 °C using gravimetric as well as thermometric techniques. Its efficiency elevated with an elevation in inhibitor concentration, reaching up to 37.88% for mild steel at 60 °C and 79.69% for aluminum at 30 °C at 0.5 g/L concentration of gum arabic. Chitosan was evaluated as a corrosion inhibitor for mild steel in 0.1 M HCl by gravimetric analysis, electrochemical analysis, scanning electron microscopy (SEM), and UV–visible (UV–vis) analysis. Chitosan inhibited corrosion at very low concentrations. Inhibition efficiency initially increased with the increasing temperature up to 96% at 60 °C and then dropped to 93% at 70 °C. Umoren et al. used pectin as a corrosion inhibitor of X60 pipeline steel in 0.5 M HCl solution. Electrochemical analysis revealed that at 25 °C, 1000 ppm of pectin efficiently inhibited 78.7% of the metallic corrosion. Xanthan gum was studied as a corrosion inhibitor for mild steel in 0.1 M HCl by gravimetric analysis, electrochemical analysis, scanning electron microscopy (SEM), and UV–visible (UV–vis) analysis. It yielded an efficiency of 86% at 298 K at a concentration of 0.5 g/L, as observed by weight loss measurements.

Natural polymers are efficient inhibitors, yet, as generally observed, low-to-moderate inhibition efficiency at high inhibitor concentration is among the limiting factors attributed to their employment as corrosion inhibitors. Several attempts such as synergizing with halide ions and surfactant additives, copolymerization, cross-linking, and composite formation have been made toward improvement in their protection capabilities. Mobin and Rizvi in years 2016 and 2017 have carried out elaborate research studies on natural polymers such as xanthan gum, hydroxyethyl cellulose, and psyllium polysaccharide. At a concentration of 1000 ppm, xanthan gum synergized by surfactant SDS was 82% efficient and was observed to be physisorbed on carbon steel in 1 M HCl. Hydroxyethyl cellulose synergized by surfactant Triton X-100 exhibited the highest efficiency of 91.62% for the corrosion of carbon steel in 1 M HCl. A novel polysaccharide from Plantago having a complex polymeric structure of arabinoxylans was found to be effective inhibitors of carbon steel corrosion (94.2% efficient at 1000 ppm) and exhibited a comprehensive or mixed type of adsorption, that is, both physisorption (electrostatic) and chemisorption (molecular). With numerous functional groups (−OH) and a heteroatom (O) in their molecular structure, these natural polymers inhibit corrosion either by adsorbing electrostatically to the carbon steel surface or by forming coordinate type of linkage by sharing a lone pair of electrons with the partially filled Fe orbital. The synergistic effect of the surfactants on the inhibition offered by these natural polymers has been observed to occur because of some polymer/surfactant interactions in the acidic medium. The ionic surfactant that is bound to these polymers has charged groups, which may repel one another and could cause expansion in the polymer backbone. This expansion in polymer molecules causes it to occupy even larger surface area on its adsorption on the carbon steel surface and offers better protection against an aggressive medium.

Tragacanth gum is the dried exudates derived from branches and stems of middle eastern species of the plant Astragalus and possesses a long history of application as a viscosity-boosting agent and stabilizer in food emulsions. It is allowed for edible usage in European and North American nations (E-number E413). The biopolymer “arabinogalactan (AG)” present in it presents intriguing prospects for corrosion inhibition because of its safe use, inexpensiveness, and availability. AG is complex, hydrophilic, and heterogeneous and a highly branched anionic polysaccharide composed of l-arabinose, d-galactose, d-xylose, l-rhamnose, d-glucose, l-fucose, and d-galacturonic acid. Upon solubilization in water, the gum is usually divided as a soluble “tragacanthin” fraction and an insoluble “bassorin” fraction. The water-soluble tragacanthin fraction resembled pectin containing linear chains of galacturonic acid and fucoxylogalacturonans, whereas bassorin is mainly constituted by xylo- and fuco-xylo-substituted polysaccharides. The AG isolated from tragacanth gum is water-soluble and produces low-viscosity solutions. There are many research articles on the polysaccharides as corrosion inhibitors of metals in aggressive solutions like the ones discussed above, but no published facts are known on AG as an inhibitor for A1020 carbon steel corrosion in 1 M HCl. In the current work, AG has been selected as an environment-friendly corrosion inhibitor for steel in 1 M HCl. The main constituents of AG have numerous hydroxyl groups (−OH) and heteroatom O. AG macromolecule, with its large size, number of reactive groups, and abundant unshared lone pairs of electrons from O, is expected to get adsorbed over a wide area on the carbon steel surface and retard the rates of corrosion at low concentrations.

The aim of this evaluation is to assess the improvement of corrosion resistance of A1020 carbon steel by AG in 1 M HCl using gravimetric, electrochemical, and surface analyses to clarify its inhibition mechanism. Electron density distributions in the AG molecule and its reactivity indices obtained from density functional theory (DFT) calculations were reported. Adsorption of the AG molecule on carbon steel (represented by Fe(110)) was modeled with the Monte Carlo simulation.
approach. The structure of the biopolymer AG molecule is shown in Figure S1 (Supporting Information).

**RESULTS AND DISCUSSION**

**NMR Analysis of the Isolated Polysaccharide.** Isolated polysaccharide gave a main C-1 \( \alpha \)-Araf signal at \( \delta \) 112.8, with nonprominent ones at \( \delta \) 110.9, 111.4, 111.9, 112.9, and 114.2 (Figure 1). The signals at \( \delta \) 102.9 and \( \delta \) 101.3 arise from the main chain of (1\(-\)4)-linked \( \alpha \)-GalpA units, confirming its complex structure.

Figure 1 depicts the NMR spectra of AG with signals similar to those given in previous research studies.\(^{26}\) The \( ^{13} \)C NMR revealed that the polysaccharide under investigation was one derived from tragacanth, a complex AG with many sequences containing Araf units, mostly with the configuration by virtue of strongly negative specific rotation.

**FTIR Analysis of Isolated Polysaccharide.** Figure 2 depicts the characteristic peaks of polysaccharide AG. An intense broad band at 3403.19 cm\(^{-1}\) suggests asymmetric stretching of a number of hydroxyl groups in AG. Asymmetric and symmetric stretching of the various CH bonds is represented by the adsorption band at 2927 cm\(^{-1}\). Symmetric stretching of the CH group can be confirmed by an absorption band at 2373 cm\(^{-1}\). CH deformations are defined by a band at 1376 cm\(^{-1}\). The mid-infrared range at 1300\( - 1000 \) cm\(^{-1}\) consists of (C\(-\)O\( - \)C) glycosidic bond vibration and stretching vibrations of (C\(-\)OH) side groups. Polygalacturonic acids have absorption band maxima in this region, with absorptions at 1072.86 cm\(^{-1}\), unveiling the availability of a galactose-consisting polysaccharide such as AG.\(^{27}\)

**Gravimetric Measurements.** Enlisted in Table 1 are the corrosion values obtained by gravimetric measurements that prove AG to be an efficacious inhibitor of carbon steel.

### Table 1. Corrosion Parameters for Carbon Steel in 1 M HCl in the Absence and Presence of Different Concentrations of AG at 30\( - 60 \) °C from Gravimetric Analysis

| AG concn (ppm) | 30 °C | 40 °C | 50 °C | 60 °C | 30 °C | 40 °C | 50 °C | 60 °C | 30 °C | 40 °C | 50 °C | 60 °C |
|---------------|------|------|------|------|------|------|------|------|------|------|------|------|
| blank         | 0.86 | 1.39 | 3.73 | 4.86 | 0.70 | 0.72 | 0.76 | 0.77 | 70.24 | 72.43 | 75.71 | 77.15 |
| 100           | 0.26 | 0.38 | 0.91 | 1.11 | 0.80 | 0.81 | 0.83 | 0.86 | 79.51 | 81.32 | 83.28 | 85.78 |
| 200           | 0.18 | 0.26 | 0.62 | 0.69 | 0.81 | 0.84 | 0.86 | 0.88 | 81.45 | 84.33 | 86.31 | 88.14 |
| 300           | 0.16 | 0.22 | 0.51 | 0.58 | 0.88 | 0.89 | 0.91 | 0.93 | 88.00 | 89.16 | 91.04 | 93.15 |
| 400           | 0.10 | 0.15 | 0.33 | 0.33 | 0.93 | 0.95 | 0.96 | 0.96 | 93.31 | 94.57 | 95.77 | 96.30 |
| 500           | 0.06 | 0.08 | 0.16 | 0.18 |      |      |      |      |      |      |      |      |

### Table 2. Quantitative Comparison of the Performance of AG with Those of the Polysaccharides Investigated Previously

| s. no. | polysaccharides previously used as an inhibitor | metal substrate | corrosive media | inhibitor concn at which maximum inhibition efficiency is observed (ppm) | temp (°C) | inhibition efficiency (%) | reference |
|--------|-----------------------------------------------|-----------------|----------------|-------------------------------------------------|-----------|--------------------------|-----------|
| 1      | xanthan gum                                   | carbon steel    | 1 M HCl        | 1000                                            | 30        | 82.31                    | 15        |
| 2      | hydroxyethyl cellulose                        | carbon steel    | 1 M HCl        | 500                                             | 30        | 91.62                    | 16        |
| 3      | arabinoxylan from Plantago                    | carbon steel    | 1 M HCl        | 1000                                            | 60        | 94.4                     | 17        |
| 4      | AG from tragacanth gum                        | carbon steel    | 1 M HCl        | 500                                             | 60        | 96.3                     | present work |
degradation in 1 M HCl solution at temperatures between 30 and 60 °C. With an increasing AG concentration and the test solution temperature, the inhibition efficiency increases; the maximum inhibition efficiency of 96.30% is observed at 60 °C at an AG concentration of 500 ppm. Table 2 quantitatively compares the performance of AG with those of other polysaccharides studied previously.\textsuperscript{20–22}

Evaluation of Table 2 revealed that AG performs much better at low concentrations, compared to previously studied polysaccharides. AG molecules adsorb on the carbon steel surface and construct a barrier for the transfer of mass and charge as the inhibitor concentration increases. This further leads to the inhibition of the attack of the aggressive 1 M HCl on the carbon steel surface. The degree of protection against the acid attack is directly related to the area over the surface masked by the adsorption of AG. The number of the adsorbed AG molecules increases on the surface with the increasing AG concentration, resulting in better protection. The surface coverage parameter, θ, defines the fraction of carbon steel surface area covered by the AG molecules adsorbed. The surface coverage values can be calculated using the following equation

$$\theta = \frac{CR_0 - CR_i}{CR_0}$$  \hspace{1cm} (1)

where the corrosion rate in the acid solution without AG is CR\textsubscript{0} and the corrosion rate in the acid solution with AG is CR\textsubscript{i}.

Inspecting Table 1, an inference is derived that the surface coverage increases with the increasing AG concentration. AG inhibits carbon steel corrosion at all temperatures evaluated. The chemical mode of adsorption of AG on the carbon steel surface in 1 M HCl solution is confirmed by the observation that the inhibition efficiency increases with the increasing temperature of the test solution. As the test solution temperature increases, desorption of H\textsubscript{2}O from the metal surface is more favorable, leading to an increase in adsorption of AG molecules upon availability of larger surface area.\textsuperscript{22}

**Adsorption Isotherm.** Surface coverage (θ) values obtained from the gravimetric experiments at different temperatures were fitted to the model of various adsorption isotherms, and the most accurate fit was obtained for Langmuir adsorption isotherm, delineated by the following equation

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$  \hspace{1cm} (2)

where C is the concentration of AG and K\textsubscript{ads} is the adsorptive equilibrium constant. The plot C/θ versus C (Figure 3) gives a straight line with a slope near to unity. The linear regressions between C/θ and C at various temperatures were obtained, and the corresponding parameters are given in Table S1 (Supporting Information).

The values of the slope as well as the linear correlation coefficients (R\textsuperscript{2}) were close to unity, which indicates that AG adsorption on the carbon steel surface can be interpreted by the Langmuir adsorption isotherm. The adsorptive equilibrium constant “K\textsubscript{ads}” relative to standard adsorption free energy “ΔG\textsubscript{ads}” is given in eq 3.

$$K_{ads} = \frac{1}{C} \exp\left( \frac{-\Delta G_{ads}}{RT} \right)$$  \hspace{1cm} (3)

where C depicts the water concentration in solution. The unit of C lies in that of K\textsubscript{ads}. As observed in Table S1 (Supporting Information), the unit of K\textsubscript{ads} is L/g. This suggests that the unit of C is g/L with the value of 1.0 × 10\textsuperscript{2} approximately.\textsuperscript{21,28} The values of ΔG\textsubscript{ads} obtained up to −20 kJ mol\textsuperscript{-1}, generally, are indicative of the electrostatic interaction between the charged metal and a charged inhibitor molecule, that is, physisorption, whereas those more lesser than −40 kJ mol\textsuperscript{-1} suggest the formation of coordinate bond through sharing or relocation of charge from AG molecules to the metal surface, which implies chemisorption. The results presented in Table S1 (Supporting Information) suggest that the values of ΔG\textsubscript{ads} are negative for all investigations. The negative values of ΔG\textsubscript{ads} also imply spontaneous adsorption of AG on the carbon steel surface. The ΔG\textsubscript{ads} values between −40 and −20 kJ mol\textsuperscript{-1} are an indicative that the AG molecules are adsorbed on the metal surface via mixed adsorption (both physisorption and chemisorption), which is predominantly chemical in nature.\textsuperscript{20}

**Thermodynamic and Kinetic Parameters.** The corrosion reaction may be assumed as an Arrhenius-type process. Apparent activation corrosion energy “E\textsubscript{a}” and Arrhenius pre-exponential factor “A”, exclusive and inclusive of AG, can be calculated by the following expression

$$CR = A \exp\left( -\frac{E_a}{RT} \right)$$  \hspace{1cm} (4)

where T is the absolute temperature and R is the universal gas constant. The values of E\textsubscript{a} and A in 1 M HCl solutions (uninhibited and inhibited by AG) were obtained by the linear regression of log CR versus 1/T data depicted in Figure S2 and Table S2 (Supporting Information).

The linear regression coefficient is near unity; therefore, carbon steel corrosion in aggressive test solution can be elucidated by the kinetic model to a reasonable degree of certainty. E\textsubscript{a} values decreased lower than those of the uninhibited solution on the addition of AG to 1 M HCl solution. The adsorption of AG on the carbon steel surface appreciably improved with the increase in temperature, which caused a decrease in E\textsubscript{a}. The carbon steel surface is in lesser contact with 1 M HCl because of this adsorption of the AG molecules at higher temperatures, leading to lower corrosion rates. Consequently, as the temperature increases, an increase in inhibition efficiency combined with a smaller E\textsubscript{a} for the corrosion rate with the addition of AG indicates a specific interaction between the carbon steel surface and AG, leading to
AG−Fe²⁺ complex formation. The decreasing corrosion rates with the increasing temperature in the inhibited test solution are explained by the variation in the values of pre-exponential factor, A. On increasing the AG concentration, the apparent activation energy was reduced. The reduction in the values of $E_a$ and $A$ caused an increase in the corrosion rate of the carbon steel. However, with an increase in AG concentration, these values were significantly reduced. A reduction in the values of $A$ and $E_a$ resulted in the decrease of corrosion rates of steel.29

An alternative form of the Arrhenius equation given in eq 5 can be used to calculate the values of $\Delta S$ (entropy of activation) and $\Delta H$ (enthalpy of activation).

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

where $h$ is Planck’s constant and $N$ is Avogadro’s number. Figure S3 (Supporting Information) depicts a plot of log (CR/T) versus $1/T$, which results in straight lines with a slope of $\Delta H/R$ and an intercept of $\ln (R/Nh + \Delta S/R)$. The values of $\Delta S$ and $\Delta H$ are calculated and are given in Table S3 (Supporting Information). $\Delta H$ bears a positive sign indicating endothermic and slow dissolution of the carbon steel.30 Lower the value of $\Delta H$, lesser is the energy barrier for the reaction. In electrolytic solutions for a chemical reaction, the values of $E_a$ and $\Delta H$ should ideally be equal. In all cases, there exists almost a very small and constant alteration between both values, as recorded in Table S2 (Supporting Information). Table S2 (Supporting Information) enlists the large values of the entropy of activation $\Delta S$, which carry a negative sign. The negative values of $\Delta S$ are suggestive that the activated complex of the rate-determining step is an association rather than a dissociation; hence, a decrease in disordering takes place proceeding from reactants to the activated complex. Fe−H₂O, the activated complex in the blank solution, gives Fe²⁺, H₂, and OH⁻ during corrosion on decomposition. In inhibited test solutions, Fe−H₂O is replaced by the Fe−AG complex. The adsorption of AG in aqueous solution of 1 M HCl can be accounted as a quasi-substitution process amidst H₂O on the electrode surface and the organic compound in the aqueous phase. With this condition, the adsorption of AG is followed by the desorption of H₂O from the surface. The thermodynamic values obtained are the algebraic sum of the adsorption of AG molecules and the desorption of water molecules. Therefore, the decrease in $\Delta S$ is linked to the decrease in $\Delta S$ of the solvent and increase in adsorption of AG onto the carbon steel surface.31,32 The Fe−AG complex is more ordered than Fe−H₂O33 as the entropy decreases on increasing the concentration of the inhibitor.

Electrochemical Measurements. PDP Measurements. Investigating the mechanism and the kinetics of cathodic and anodic reactions, potentiodynamic measurements were performed. Figure 4a shows the polarization curves for carbon steel in 1 M HCl, with the addition and exclusion of different concentrations of AG. The polarization parameters deduced are recorded in Table S2 (Supporting Information).

On adding AG to 1 M HCl, $E_{corr}$ values become more positive and shift anodically compared to those of the blank. Observing the magnitude of the change observed in the $E_{corr}$ values, we can say that AG is a mixed-type inhibitor, predominantly anodic in nature, that is, presence of AG inhibited oxidation of Fe and to a lower extent hydrogen evolution. A progressive decrease in the value of $i_{corr}$ was observed as the AG concentration was increased, suggesting a retarded rate of electrochemical reaction, as a barrier was created between steel and corrosive solution by a protective AG film on the carbon steel surface. The variation in the values of $\beta_c$ and $\beta_a$ in 1 M HCl having AG indicates that both the cathodic hydrogen evolution and anodic metal dissolution
processes are inhibited. An increase in the polarization resistance ($R_p$) occurs on the addition of AG. The increasing values of $R_p$ with the increasing AG concentration indicate efficient corrosion inhibition by AG. At an AG concentration of 500 ppm, the highest value of inhibition efficiency was observed (96.7%). The inhibition efficiencies calculated by polarization measurements exhibit a trend parallel to that of gravimetric measurements.34

Electrochemical Impedance Spectroscopy (EIS). EIS evaluated the corrosion inhibition in the presence and absence of various concentrations of AG. The impedance data for low carbon steel in 1 M HCl solution exclusive and inclusive of AG obtained at 30 °C are enlisted in Table 3. The semicircle fitting method determined the electrochemical impedance parameters. 35 Nova 1.11 software was used to obtain a semicircle fit through data points in the Nyquist plot. The Nyquist plots for the carbon steel surface inhibited by AG comprised a depressed semicircle with a high-frequency capacitive loop (Figure 4b). Because of the dispersion effect and the state of the electrode surface, which are characteristic impedance properties of carbon steel electrodes in the process of corrosion, a diversion from a perfect semicircle to a depressed semicircle in the center under the real axis was observed, which was primarily caused by heterogeneity and roughness of the electrode surface and also by the current distribution displaying a geometrical behavior.

The impedance response changed considerably after the addition of AG to the 1 M HCl solution. Shapes of the plots remained the same for the electrodes with and without various concentrations of AG, indicating an unaltered mechanism of corrosion on the addition of AG.7

Table 3. EIS Parameters for the Corrosion of Carbon Steel in 1 M HCl in the Absence and Presence of AG at 30 °C

| AG concn (ppm) | $R_s$ ($\Omega \cdot cm^2$) | $R_d$ ($\Omega \cdot cm^2$) | $Y_0 \times 10^{-6}$ ($\Omega^{-1} \cdot s^0 \cdot cm^3$) | $\pi$ | $C_m \times 10^{-5}$ ($\mu F \cdot cm^{-2}$) | $\eta$ (%) | $q^2 \times 10^{-3}$ | $-S$ | $\alpha^2$ |
|---------------|---------------------------|---------------------------|------------------------------------------------|-------|---------------------------|------------|----------------|--------|--------|
| 0             | 1.6                       | 17.48                     | 79.4                                           | 0.991 | 7.5                       | 2.40       | 1.42           | 46.2   |
| 100           | 2.3                       | 70.03                     | 71.8                                           | 0.995 | 7.4                       | 75.1       | 1.82           | 56.8   |
| 200           | 2.4                       | 103.36                    | 66.1                                           | 0.995 | 6.5                       | 83.1       | 3.43           | 59.5   |
| 300           | 3.1                       | 169.71                    | 51.4                                           | 0.996 | 5.1                       | 89.7       | 3.88           | 61.2   |
| 400           | 3.6                       | 416.3                     | 36.7                                           | 0.996 | 3.6                       | 95.8       | 12.15          | 1.64   | 61.5   |
| 500           | 2.2                       | 961.2                     | 19.1                                           | 0.996 | 1.9                       | 98.1       | 41.57          | 1.81   | 75.1   |

Figure 5. Three-dimensional AFM and SEM/energy-dispersive X-ray (EDX) images of carbon steel before and after immersion in the test solution for 6 h at 30 °C: (a,d,g) as polished before immersion; (b,e,h) uninhibited solution; and (c,f,i) inhibited solution (500 ppm AG).
Nova 1.11 software (Metrohm Corporation) measured and simulated the electrochemical impedance spectra at the carbon steel/1 M HCl interface with and without AG by fitting various impedance profiles into an equivalent circuit, which is given in Figure S4 (Supporting Information). This equivalent circuit is composed of constant phase element, CPE, solution resistance, $R_s$ and charge-transfer resistance, $R_w$. The system investigated here can be characterized by distributed capacitance for a nonhomogenous corroding surface of carbon steel in 1 M HCl. This phenomenon of depression modeled by CPE is usually associated with the frequency dispersion, dislocations, surface roughness, formation of porous layers, and distribution of the active sites. The distributed capacitance is given by constant phase element (CPE, $Y_0$). The impedance of CPE is given as

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

(6)

Here, ‘$\omega$’ is the angular frequency, ‘$j^2 = -1$’ is an imaginary number, ‘$Y_0$’ is the magnitude of CPE, and ‘$n$’ is the CPE exponent. When $n = 1$, CPE is an inductor and a pure capacitor when $n = 1$. The values of $C_d$ were calculated at a frequency at which the imaginary component of the impedance is a maximum

$$C_d = Y_0(\omega_{\text{max}})^{n-1}$$

(7)

Table 3 clearly indicates that the values of $R_s$ increased and those of $C_d$ decreased with increased AG concentration. Increase in the thickness of the double layer and/or decrease in the dielectric constant cause a decrease in the $C_d$ value. An inhibitory layer on the electrode surface controlled the dissolution extent by displacing H$_2$O and other ions that were initially adsorbed at the steel/solution interface. The Fe–H$_2$O complex that developed on the steel surface in the presence of uninhibited 1 M HCl changes to the Fe–AG complex, which formed on the addition of AG to the acid solution.

Because of AG adsorption on the active sites of the carbon steel surface, surface heterogeneity reduces and the value of ‘$n$’ gets closer to unity. At a concentration of 500 ppm, AG becomes 98.1% efficient. Ideally, the $\chi^2$ values lie between $10^{-3}$ and $10^{-5}$. In the current study, the $\chi^2$ values for AG adsorption are within $10^{-3}$. The impedance measurements resulted in inhibition efficiencies quite similar to those of the gravimetric and PDP studies.

The inhibitory effect of the compound may be judged by phase angle at high frequencies in phase angle versus frequency diagrams, which are given in the Bode plots in Figure 4c. Addition of AG renders a higher protection with higher values of absolute impedance at low frequencies. In theta versus frequency diagram (Figure 4c), a more negative phase angle means higher capacitive behavior. This capacitive response increased with an increasing AG concentration, indicating more inhibitive behavior at higher concentrations. The formation of a protective layer on the electrode surface causes the phase angle ($\alpha^{\theta}$) to reach toward almost $-90^{\circ}$ in the presence of AG. The value of phase angle ($\alpha^{\theta}$) for 1 M HCl was $-46.2^{\circ}$, which approaches $-75.1^{\circ}$ on the addition of 500 ppm AG, as shown in Table 3. Ideally, a linear relationship between log |Z| against log $f$, with a phase angle of $-90^{\circ}$ and a slope near $-1$, may be seen in the intermediate frequency region. The analyses of linear relationship between log |Z| versus log $f$ give a slope value between $-1.42$ and $-1.81$.

### Surface Morphological Studies

Atomic Force Microscopy (AFM). AFM quantitatively analyzed the surface properties of the polished and immersed carbon steel coupons in 1 M HCl for 6 h in the presence and absence of AG (Figure 5). The AFM image of a freshly abraded carbon steel specimen in Figure 5a displays a sufficiently smooth surface. Another AFM image of a severely corroded surface of carbon steel immersed in a test solution for 6 h at 30 °C is shown in Figure 5b. The image in Figure 5c shows a surface even and smooth in the presence of 500 ppm AG compared to the image obtained for coupon immersed in uninhibited solution. The polished carbon steel surface before immersion in aggressive 1 M HCl solution exhibited an average roughness of 71.4 nm. A quite high roughness of 781 nm was observed on the carbon steel surface immersed in 1 M HCl without AG (Figure 5b). For the steel specimen immersed in the test solution of 1 M HCl having 500 ppm AG, there is very less corrosion damage present on the surface depicted by small spikes, as seen in Figure 5c, and an average roughness of 77.7 nm is obtained, which indicated the adsorption of a microscopically thin film of AG preventing the attack of a corrosive acid solution.

SEM/EDX. Surface morphological studies of the carbon steel specimen immersed in uninhibited and inhibited acid solutions at 30 °C were conducted by SEM. Figure 5d depicts a freshly polished carbon steel surface, quite free of notable deformities except the polishing marks. The SEM image of the carbon steel surface after 6 h of immersion in 1 M HCl shows a severely corroded surface. The surface uniformly corroded because of the strong corrosive attack of 1 M HCl [Figure 5e]. Figure 5f presents an SEM image in the presence of 500 ppm of AG where the surface heterogeneity decreased, showing clearly a smooth and comparably even surface. These findings further lead to suggest the gradual adsorption of AG on the carbon steel surface.

To find out the elements present on the carbon steel surface before and after immersion in an acid solution (uninhibited and inhibited), the steel samples were subjected to EDX, and the results are shown in Figure 5. The EDX spectrum of the polished carbon steel surface before immersion in acid solution shows the characteristic peaks of elements present in the carbon steel [Figure 5g]. The EDX spectrum of the carbon steel specimen after immersion in acid solution exhibits the additional peaks of Cl [Figure 5h], which is attributed to the free corrosion of carbon steel in 1 M HCl solution. In the presence of AG, an additional peak of O (due to O atoms from the inhibitor) is present, but the peak of Cl is absent (Figure 5i). This is attributed to the inhibition of acid corrosion by an adsorption film containing O covering the carbon steel surface. Further, in the presence of an inhibitor, enhanced signals of C and Fe are observed relative to those of uninhibited solution. The enhancement in the intensity of C signals is because of the C atoms of the adsorbed inhibitor, whereas the enhancement of Fe peaks points to the protection of the carbon steel surface by adsorbed AG.

FTIR. To establish the adsorption of AG on the surface of carbon steel and detect the functional groups involved in the corrosion inhibition process, FTIR analysis was performed. The FTIR spectrum of pure AG was compared with the spectrum obtained for the scrapped sample from the carbon steel surface (Fe$^{2+}$–AG), as shown in Figure S5 (Supporting Information).

Both the IR spectra represent the characteristic peaks of AG with variations in molecular vibrations. Studying the spectrum of the scrapped sample, the shifts of the molecular vibrations
observed through variations in wavenumbers may suggest the formation of the complex between AG and Fe\textsuperscript{2+} on the carbon steel surface. Comparing it with the IR spectrum of pure AG, it is observed that major shift in the peaks representing $-$OH stretching vibrations (from 3351.32 to 3403.19 cm$^{-1}$) is quite prominent, suggesting that $-$OH groups are primarily responsible for the adsorption process. The unshifted or slightly shifted peaks observed in the spectrum of the scrapped sample might be due to negligible action of the representative groups in the adsorption process.

**UV–Vis Spectroscopic Analysis.** Formation of a complex between Fe and AG in 1 M HCl solution can be described by a variation in the position of the absorption maximum or a variation in the value of absorbance$^{22}$ (Figure S6, Supporting Information). The spectrum of the inhibited test solution without immersion of carbon steel coupon showed two absorption bands at 220 and 334 nm, with the corresponding values of absorbance that are 0.86 and 0.60, respectively (spectrum 1), whereas the spectrum of the inhibited test solution after carbon steel immersion displayed the previous absorption bands shifted to 231 and 336 nm, with much different values of absorbance that are 3.72 and 0.84, respectively. This change in wavelength or absorbance values suggests the formation of the AG$\text{−}$Fe\textsuperscript{2+} complex in the solution.

**Quantum Chemical Calculations and Monte Carlo Simulations.** Gas-phase optimized geometry of the AG molecule, graphical images of electron density distributions in its molecular orbital [highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)], and electrophilic and nucleophilic Fukui indices are shown in Figure 6.

The HOMO lobes are located on the pyran ring with larger fractions on the O atoms of the $-$OH and $-$OCH\textsubscript{3} groups. The LUMO comprises a large lobe that is centered on a hydroxymethylene group on one of the pyran rings. These observations suggest that the molecule is liable to interact with metallic orbitals using mainly the centers with O atoms. The HOMO and LUMO surfaces and contours for AG suggest a nonuniform distribution of electron density around the molecule, indicating that the AG molecule is nonsymmetric and the molecule may not exhibit uniform reactivity on all pyran rings.

The $f^−$ further confirms that the centers for electrophilic attacks on the AG molecule are essentially the O atoms with $\sigma$-characteristic orbitals. The $f^+$ also corroborates the observation from the LUMO contour surface, showing the hydroxymethylene group with superior disposition toward the nucleophilic attack. Selected quantum chemical parameters of the molecule are shown in Table 4.

**CONCLUSIONS**

i AG efficiently inhibits the corrosion of carbon steel coupon in 1 M HCl solution. The inhibition efficiency is both concentration- and temperature-reliant and reaches as high as 96.3%.

---

**Table 4. Quantum Chemical Parameters Obtained Using B3LYP/6-31G (d,p) Model and Energy Parameters (kJ/mol) for the Adsorption of AG on the Fe(110) Surface**

| Parameter                           | Monte Carlo simulation | Quantum chemical parameters |
|-------------------------------------|------------------------|-----------------------------|
| adsorption energy                  | $-902.349$             | $E_{\text{HOMO}}$           |
| rigid adsorption energy             | $-987.70$              | $E_{\text{LUMO}}$           |
| deformation energy                  | $5.121$                | $\Delta E$                  |
| $dE_{\text{ad}}/dN_e$               | $-902.349$             | $\eta$                      |
| dipole moment                       | $6.955$                | $\chi$                      |

The $E_{\text{LUMO}}$ is slightly high, which suppresses the possibility of back-bonding in interactions of the AG molecule with steel. The large dipole moment (6.955 debye) of the AG molecule might favor dipole–dipole interactions with the polarized steel surface.$^{45}$ Equilibrium configuration of the adsorption of AG on the Fe(110) plane surface is shown in Figure 7.

The orientation of the AG molecule on Fe(110) reflects favorable interactions between the atoms in the AG molecule and Fe. The large adsorption energy ($-902.349$ kJ/mol) recorded for the interactions supports the assumption that the AG molecule adsorbs effectively on the Fe surface and might inform its high corrosion inhibition potential.

---

Figure 6. Optimized structure (a); HOMO (b) and LUMO (c) electron density; and (d) $f^−$ and $f^+$ (e) Fukui indices electron density isosurfaces for AG.
Isolation of Polysaccharide. Tragacanth gum was obtained from Sigma, India. After stirring the gum for 3 h in distilled water, the mixture was successively filtered through a fine mesh strainer to remove insoluble macroscopic debris. To precipitate the soluble polysaccharide, AG, from the tragacanth gum, the filtered mixture was added in excess of ethanol in the ethanol/water ratio of 7:3. The separated polysaccharide was precipitate the soluble polysaccharide, AG, from the tragacanth gum.

Polysaccharide was characterized by NMR and FTIR. and stored in desiccators over anhydrous chloride. The isolated polysaccharide powder was dissolved in D$_2$O (99.9%) for NMR investigation. The $^{13}$C NMR spectra of test samples were recorded by a Bruker AV III HD (TXI) 500 NMR spectrometer. The PerkinElmer spectrophotometer, "Spectrum Two", with a resolution 0.5 cm$^{-1}$ recorded the FTIR spectra of samples. The KBr disk method was used, and the spectra within the frequency of 4000–500 cm$^{-1}$ were recorded.

**Specimen Preparation.** The corrosion tests were executed on coupons obtained from A1020 c-steel chemically composed of C (0.0684%), Mn (0.0394%), S (0.0008%), P (0.0219%), Cr (0.0456%), Mo (0.0674%), Al (0.0154%), V (0.0335%), and remaining weight % of Fe. Chemical constitution of A1020 carbon steel was measured by a spark optical emission spectrometer. Rectangular coupons (2.5 × 2 × 0.1 cm$^2$ and surface area: 10.9 cm$^2$) were employed for gravimetric analysis. Circular coupons with 1.0 cm$^2$ exposed surface area and thickness of 0.1 cm were utilized for electrochemical analysis. The coupons were abraded by emery papers of various grades, initially rinsed with acetone, and later, rinsed with deionized water. The test coupons were finally dried at room temperature before performing corrosion tests on them.

**Electrolytic Solution.** ACS reagent grade 37% HCl was diluted with double-distilled water to prepare an electrolytic solution of 1 M HCl. The concentration of AG in 1 M HCl solution was varied between 100 and 500 ppm. The electrolytic volume used in gravimetric and electrochemical measurements was 200 mL and 1 L, respectively.

**Gravimetric Measurements.** The freshly abraded coupons of carbon steel were completely immersed in 1 M HCl for 6 h. The test solutions contained different concentrations of AG at temperatures 30, 40, 50, and 60 °C. The carbon steel coupons were thoroughly rinsed by deionized water, and a bristled brush was used to gently scrub these coupons to eliminate the corrosion products. They were again washed properly with deionized water and acetone. The test coupons were finally dried to obtain a constant weight. The gravimetric measurements were conducted on triplicate coupons to ascertain the reproducibility of results, and the average corrosion rate was computed. Corrosion rate calculation in “mg cm$^{-2}$ h$^{-1}$” was done using the following equation

$$\text{Corrosion rate} \left( \text{mg cm}^{-2} \text{ h}^{-1} \right) = \frac{\Delta W}{At}$$

where $\Delta W$ is the weight loss (mg), $t$ is the exposure time (h), and $A$ is the area of the specimen (cm$^2$). The inhibition efficiency (%), represented by “$\eta$”, was obtained using the values of the average corrosion rate as follows

$$\eta = \frac{CR_0 - CR}{CR_0} \times 100$$

where $CR_0$ and $CR$ were the corrosion rates in free and acid solutions inhibited by AG, respectively.

**Electrochemical Measurements.** The electrochemical measurements were executed on an Autolab 128N potentiostat/galvanostat. A three-neck corrosion cell from Autolab (a capacity of 1 L) that includes the test coupon of a vulnerable specimen. The PDP method was used, and the spectra within the frequency of 4000–500 cm$^{-1}$ were recorded.

**Specimen Preparation.** The corrosion tests were executed on coupons obtained from A1020 c-steel chemically composed of C (0.0684%), Mn (0.0394%), S (0.0008%), P (0.0219%), Cr (0.0456%), Mo (0.0674%), Al (0.0154%), V (0.0335%), and remaining weight % of Fe. Chemical constitution of A1020 carbon steel was measured by a spark optical emission spectrometer. Rectangular coupons (2.5 × 2 × 0.1 cm$^2$ and surface area: 10.9 cm$^2$) were employed for gravimetric analysis. Circular coupons with 1.0 cm$^2$ exposed surface area and thickness of 0.1 cm were utilized for electrochemical analysis. The coupons were abraded by emery papers of various grades, initially rinsed with acetone, and later, rinsed with deionized water. The test coupons were finally dried at room temperature before performing corrosion tests on them.

**Electrolytic Solution.** ACS reagent grade 37% HCl was diluted with double-distilled water to prepare an electrolytic solution of 1 M HCl. The concentration of AG in 1 M HCl solution was varied between 100 and 500 ppm. The electrolytic volume used in gravimetric and electrochemical measurements was 200 mL and 1 L, respectively.

**Gravimetric Measurements.** The freshly abraded coupons of carbon steel were completely immersed in 1 M HCl for 6 h. The test solutions contained different concentrations of AG at temperatures 30, 40, 50, and 60 °C. The carbon steel coupons were thoroughly rinsed by deionized water, and a bristled brush was used to gently scrub these coupons to eliminate the corrosion products. They were again washed properly with deionized water and acetone. The test coupons were finally dried to obtain a constant weight. The gravimetric measurements were conducted on triplicate coupons to ascertain the reproducibility of results, and the average corrosion rate was computed. Corrosion rate calculation in “mg cm$^{-2}$ h$^{-1}$” was done using the following equation

$$\text{Corrosion rate} \left( \text{mg cm}^{-2} \text{ h}^{-1} \right) = \frac{\Delta W}{At}$$

where $\Delta W$ is the weight loss (mg), $t$ is the exposure time (h), and $A$ is the area of the specimen (cm$^2$). The inhibition efficiency (%), represented by “$\eta$”, was obtained using the values of the average corrosion rate as follows

$$\eta = \frac{CR_0 - CR}{CR_0} \times 100$$

where $CR_0$ and $CR$ were the corrosion rates in free and acid solutions inhibited by AG, respectively.

**Electrochemical Measurements.** The electrochemical measurements were executed on an Autolab 128N potentiostat/galvanostat. A three-neck corrosion cell from Autolab (a capacity of 1 L) that includes the test coupon of a vulnerable specimen. The PDP method was used, and the spectra within the frequency of 4000–500 cm$^{-1}$ were recorded.

**Specimen Preparation.** The corrosion tests were executed on coupons obtained from A1020 c-steel chemically composed of C (0.0684%), Mn (0.0394%), S (0.0008%), P (0.0219%), Cr (0.0456%), Mo (0.0674%), Al (0.0154%), V (0.0335%), and remaining weight % of Fe. Chemical constitution of A1020 carbon steel was measured by a spark optical emission spectrometer. Rectangular coupons (2.5 × 2 × 0.1 cm$^2$ and surface area: 10.9 cm$^2$) were employed for gravimetric analysis. Circular coupons with 1.0 cm$^2$ exposed surface area and thickness of 0.1 cm were utilized for electrochemical analysis. The coupons were abraded by emery papers of various grades, initially rinsed with acetone, and later, rinsed with deionized water. The test coupons were finally dried at room temperature before performing corrosion tests on them.

**Electrolytic Solution.** ACS reagent grade 37% HCl was diluted with double-distilled water to prepare an electrolytic solution of 1 M HCl. The concentration of AG in 1 M HCl solution was varied between 100 and 500 ppm. The electrolytic volume used in gravimetric and electrochemical measurements was 200 mL and 1 L, respectively.

**Gravimetric Measurements.** The freshly abraded coupons of carbon steel were completely immersed in 1 M HCl for 6 h. The test solutions contained different concentrations of AG at temperatures 30, 40, 50, and 60 °C. The carbon steel coupons were thoroughly rinsed by deionized water, and a bristled brush was used to gently scrub these coupons to eliminate the corrosion products. They were again washed properly with deionized water and acetone. The test coupons were finally dried to obtain a constant weight. The gravimetric measurements were conducted on triplicate coupons to ascertain the reproducibility of results, and the average corrosion rate was computed. Corrosion rate calculation in “mg cm$^{-2}$ h$^{-1}$” was done using the following equation

$$\text{Corrosion rate} \left( \text{mg cm}^{-2} \text{ h}^{-1} \right) = \frac{\Delta W}{At}$$

where $\Delta W$ is the weight loss (mg), $t$ is the exposure time (h), and $A$ is the area of the specimen (cm$^2$). The inhibition efficiency (%), represented by “$\eta$”, was obtained using the values of the average corrosion rate as follows

$$\eta = \frac{CR_0 - CR}{CR_0} \times 100$$

where $CR_0$ and $CR$ were the corrosion rates in free and acid solutions inhibited by AG, respectively.
recorded the polarization curves from $-250$ to $+250$ mV according to the steady-state OCP at a scan rate of 0.00166 V/s. The corrosion current density ($i_{\text{corr}}$), anodic Tafel slope ($\beta_a$), cathodic Tafel slope ($\beta_c$), and corrosion potential ($E_{\text{corr}}$) were obtained. Cathodic and anodic Tafel polarization curves were investigated using Nova 1.11 software. The measured values of $i_{\text{corr}}$ helped in the calculation of inhibition efficiency $\eta$ (%) as per the following relationship

$$\eta (\%) = \frac{i_{\text{corr}} - i_{\text{corr}}^0}{i_{\text{corr}}^0} \times 100$$  \hspace{1cm} (10)

where $i_{\text{corr}}$ and $i_{\text{corr}}^0$ represent the corrosion current densities in the presence and absence of AG, respectively. Frequency spectrum from $10^{-2}$ to $10^4$ Hz and ac signals of 10 mV amplitude were employed to conduct the impedance measurements. Nova 1.11 software assisted in obtaining and analyzing the impedance parameters. The % inhibition efficiency $\eta$ was obtained using charge-transfer resistance ($R_{\text{ct}}$) in the impedance data of the Nyquist plots.

$$\eta (\%) = \frac{R_{\text{ct}} - R_{\text{ct}}^0}{R_{\text{ct}}^0} \times 100$$  \hspace{1cm} (11)

Here, $R_{\text{ct}}$ and $R_{\text{ct}}^0$ were the charge-transfer resistance values inclusive and exclusive of AG, respectively.

**Surface Analysis.** To visually assess the corrosion extent on the carbon steel specimens (in terms of heterogeneity of the surface/roughness) immersed in uninhibited and inhibited 1 M HCl solutions, the surface evaluation was performed by AFM and SEM/EDX analyses. These studies were conducted on test specimens obtained from gravimetric experiments inclusive and exclusive of optimum AG concentrations at 30 °C. An SEM/EDX study was conducted using a JEOL JSM-6510LV scanning electron microscope with EDX (model: INCA, Oxford). The instrument incorporated to conduct AFM of uninhibited and inhibited carbon steel specimens was “Dimension Icon ScanAsyst” having a spring constant of 42 N m$^{-1}$ and a tip radius of 10 nm. A scan rate of 0.4 Hz was used for studying an area of 50 × 50 μm$^2$ of test coupon in the tapping mode. The data obtained were analyzed by NanoScope V software.

**FTIR Studies of AGs Adsorbed on Carbon Steel.** FTIR spectrum of AG adsorbed on the surface of carbon steel was recorded and compared with that of pure AG. The AG powder was mixed with KBr and shaped into a disk, which was subjected to evaluation to acquire the spectra of pure AG. The second spectrum was recorded for the adsorption layer that was formed on the test coupon after its immersion in 1 M HCl solution having 500 ppm of AG for 6 h. The second specimen was cleaned, dried, then rubbed with some KBr powder, and shaped into the form of a disk. The collected data were interpreted by the Spectrum Software.

**UV–Vis Spectroscopic Analysis.** UV–vis spectra were recorded for 1 M HCl solution having maximum AG concentration before and after immersion of coupon for 6 h at 30 °C to confirm the interaction of AG with Fe$^{2+}$. A PerkinElmer Lambda 25 spectrophotometer attached with a WinLab data processor and viewer recorded the spectra.

**Quantum Chemical and Monte Carlo Simulation Studies.** Density functional theory (DFT) derived the electron density distributions and important quantum chemical parameters of the AG molecule. The generally accepted molecular unit of AG (as found in PubChem) was used as the representative molecular structure for all computational studies. The B3LYP/6-31G (d,p) model achieved the gas-phase optimized geometry of the molecule. Gaussian 09 software suite performed the calculations. The LUMO energy ($E_{\text{LUMO}}$), the HOMO energy ($E_{\text{HOMO}}$), and dipole moment were recorded. The energy gap (Δ$E$), global hardness ($\eta$), and global electronegativity ($\chi$) of the molecule were calculated using the appropriate relations.

$$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$$  \hspace{1cm} (12)

$$\eta = \frac{1}{2}(E_{\text{LUMO}} - E_{\text{HOMO}})$$  \hspace{1cm} (13)

$$\chi = \frac{1}{2}(E_{\text{HOMO}} + E_{\text{LUMO}})$$  \hspace{1cm} (14)

Electrophilic ($f^+$) and nucleophilic ($f^−$) Fukui indices of the molecules were estimated using the Mulliken atomic charge differences based on the relations.

$$f^+ = q_{N+1} - q_N$$  \hspace{1cm} (15)

$$f^- = q_N - q_{N-1}$$  \hspace{1cm} (16)

Electron density distributions of the Fukui functions were visualized using the Multiwfn software.

The interaction between AG and the Fe(110) plane surface was carried out using Monte Carlo simulations. In this simulation, the adsorption detector code executed in the Materials Studio 8.0 software from BIOVIA-Accelrys Inc., USA, was adopted. For the simulation of all molecules and systems, condensed-phase optimized molecular potentials for atomistic simulation studies, “COMPASS”, force field was utilized. The simulation of the corrosion inhibitor molecule on the Fe(110) surface was conducted to locate the low-energy adsorption sites of AG on the Fe surface.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00436.

Molecular structure of AG, plot of log CR versus 1/T and plot of log CR/T versus 1/T, equivalent circuit model to fit the data from various impedance profiles, comparison of FTIR spectra of pure AG and scrapped sample from the carbon steel surface, UV–vis spectra of 1M HCl solution with 500 ppm AG before and after the immersion of carbon steel, values of adsorptive equilibrium constant (K$_{\text{ad}}$) and free energy of adsorption ($\Delta G_{\text{ad}}$), thermodynamic parameters, and potentialdynamic polarization parameters for corrosion of carbon steel in 1 M HCl (PDF)

**AUTHOR INFORMATION**

Corresponding Author
E-mail: drmobin@hotmail.com. Phone: +91 5712703515-3003 (ext.) (M.M.)

**ORCID**
Mohammad Mobin: 0000-0003-4829-7491
Eno E. Ebenso: 0000-0002-0411-9258

**Notes**
The authors declare no competing financial interest.
ACKNOWLEDGMENTS

One of the authors, M.R., expresses gratitude to UGC, New Delhi, for the financial assistance in the form of Maulana Azad National Fellowship. The author also thanks USIF, AMU, Aligarh, India, for SEM/EDX investigations, NRF, IIT-D, New Delhi, India, for assistance in AFM analysis, and CDRI, Lucknow, India, for NMR studies.

REFERENCES

(1) Dwivedi, D.; Lepková, K.; Becker, T. Carbon steel corrosion: a review of key surface properties and characterization methods. RSC Adv. 2017, 7, 4580–4610.
(2) Finisgar, M.; Jackson, J. Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: A review. Corros. Sci. 2014, 86, 17–41.
(3) Lukovits, I.; Kálmán, E.; Zucchi, F. Corrosion inhibitors—correlation between electronic structure and efficiency. Corrosion 2001, 57, 3–8.
(4) Bouayed, M.; Rabaa, H.; Shrir, A.; Sullaard, J.-Y.; Bachir, A. B.; Le Beuzed, A. Experimental and theoretical study of organic corrosion inhibitors on iron in acidic medium. Corros. Sci. 1998, 41, 501–517.
(5) Sastri, V. S.; Perumareddi, J. R. Molecular orbital orbital theoretical studies of some organic corrosion inhibitors. Corrosion 1997, 53, 617–622.
(6) Solomon, M. M.; Umoren, S. A.; Udosoro, I. I.; Udoh, A. P. Inhibitive and adsorption behaviour of carboxymethyl cellulose on mild steel corrosion in sulphuric acid solution. Corros. Sci. 2010, 52, 1317–1325.
(7) Bayol, E.; Gürtler, A. A.; Dursun, M.; Kayaktirilmaz, K. Adsorption Behavior and inhibition Corrosion Effect of Sodium Carboxymethyl Cellulose on Mild steel in Acidic Medium. Acta Phys-Chim. Sin. 2008, 24, 2236–2243.
(8) Bello, M.; Ochoa, N.; Balsamo, V.; López-Carrasquero, F.; Coll, S.; Monsalve, A.; González, G. Modified Cassava Starches as Corrosion Inhibitors of Carbon Steel: An Electrochemical and Morphological Approach. Carbohydr. Polym. 2010, 82, 561–568.
(9) Mobin, M.; Khan, M. A.; Parveen, M. Inhibition of mild steel corrosion in acidic medium using starch and surfactants additives. J. Appl. Polym. Sci. 2011, 121, 1558–1565.
(10) Bentrath, H.; Yahi, Y.; Chala, A. Gum Arabic as an Eco-friendly Inhibitor for API SL X42 Pipeline Steel in HCl Medium. Corros. Sci. 2014, 82, 426–431.
(11) Mobin, M.; Khan, M. A. Investigation on the adsorption and corrosion inhibition behavior of gum acacia and synergic surfactants additives on mild steel in 0.1 M H2SO4. J. Dispersion Sci. Technol. 2013, 34, 1496–1506.
(12) Umoren, S. A. Inhibition of aluminium and mild steel corrosion in acidic medium using Gum Arabic. Cellulose 2008, 15, 751–761.
(13) Umoren, S. A.; Banera, M. J.; Alonso-Garcia, T.; Gervasi, C. A.; Mirfico, M. V. Inhibition of Mild Steel Corrosion in HCl Solution using Chitosan. Cellulose 2013, 20, 2529–2545.
(14) Umoren, S. A.; Obot, I. B.; Madhankumar, A.; Gasem, Z. M. Performance evaluation of pectin as ecofriendly corrosion inhibitor for X60 pipeline steel in acid medium: Experimental and theoretical approaches. Carbohydr. Polym. 2015, 124, 280–291.
(15) Biswas, A.; Pal, S.; Udayabanbu, G. Experimental and Theoretical Studies of Xanthan Gum and its Graft Co-Polymer as Corrosion Inhibitor for Mild Steel in 15% HCl. Appl. Surf. Sci. 2015, 353, 173–183.
(16) Fares, M. M.; Maayta, A. K.; Al-Mustafa, J. A. Corrosion Inhibition of Iota-Carrageenan Natural Polymer on Aluminum In Presence of Zwitterion Mediator in HCl Media. Corros. Sci. 2012, 65, 223–230.
(17) Umoren, S. A.; Solomon, M. M.; Udosoro, I. I.; Udoh, A. P. Synergistic and Antagonistic Effects between Halide Ions and Carboxymethyl Cellulose for the Corrosion Inhibition of Mild Steel In Sulphuric Acid Solution. Cellulose 2010, 17, 635–648.
(18) Banerjee, S.; Srivastava, V.; Singh, M. M. Chemically Modified Natural Polysaccharide as Green Corrosion Inhibitor for Mild Steel in Acidic Medium. Corros. Sci. 2012, 59, 35–41.
(19) Solomon, M. M.; Gerengi, H.; Umoren, S. A. Carboxymethyl cellulose/silver nanoparticles composite: Synthesis, Characterization and Application as a Benign Corrosion Inhibitor for St37 Steel in 15% H2SO4 medium. ACS Appl. Mater. Interfaces 2017, 9, 6376–6389.
(20) Mobin, M.;rizi, M. Inhibitory effect of xanthan gum and synergistic surfactant additives for mild steel corrosion in 1 M HCl. Carbohydr. Polym. 2016, 136, 384–393.
(21) Mobin, M.; Rizvi, M. Adsorption and corrosion inhibition behavior of hydroxethyl cellulose and synergistic surfactants additives for carbon steel in 1 M HCl. Carbohydr. Polym. 2017, 156, 202–214.
(22) Mobin, M.; Rizvi, M. Polysaccharide from Plantago as a green corrosion inhibitor for carbon steel in 1M HCl solution. Carbohydr. Polym. 2017, 160, 172–183.
(23) Balagh, S.; Mohammadifar, M. A.; Zargaraan, A. Physicochemical and Rheological Characterization of Gum Tragacanth Exudates from Six Species of Iranian Astragalus. Food Biophys. 2010, 5, 59–71.
(24) Gavlibhi, H. A.; Michalak, M.; Meyer, A. S.; Mikkelsen, J. D. Enzymatic depolymerization of Gum Tragacanth: Bifidogenic potential of low molecular weight oligosaccharides. J. Agric. Food Chem. 2013, 61, 1272–1278.
(25) Panda, H. The Complete Book on Gums and Stabilizers; Asia Pacific Business Press Inc.: ISBN 8178331314, 978178331317, 2010; p 159.
(26) Tischer, C. A.; Iacomini, M.; Gorin, P. A. Structure of the arabino-ogalactan from gum tragacanth (Astragalus gummifer). Carbohydr. Res. 2002, 337, 1647–1655.
(27) Fattahi, A.; Petrini, P.; Munarin, F.; Shokoohinia, Y.; Golozar, M. A.; Varshosaz, J.; Tanzi, M. C. Polysaccharides Derived from Tragacanth as Biocompatible Polymers and Gels. J. Appl. Polym. Sci. 2013, 129, 2092–2102.
(28) Roy, P.; Pal, A.; Sukul, D. Origin of the synergistic effect between polysaccharide and thiourea towards adsorption and corrosion inhibition for mild steel in sulphuric acid. RSC Adv. 2014, 4, 10607–10613.
(29) Bouklah, M.; Hammouti, B.; Lagrenée, M.; Bentiss, F. Thermodynamic properties of 2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole as a corrosion inhibitor for mild steel in normal sulfuric acid medium. Carros. Sci. 2006, 48, 2831–2842.
(30) Ahamad, I.; Prasad, R.; Quraishi, M. A. Experimental and Theoretical Investigations of Adsorption of Foeniculinat at Mild Steel/Hydrochloric Acid Interface as Corrosion Inhibitor. J. Solid State Electrochem. 2010, 14, 2095.
(31) Hosseini, S. M. A.; Azimi, A. The inhibition of mild steel corrosion in acid medium by 1-methyl-3-pyrind-2-yl-thiourea. Corros. Sci. 2009, 51, 728–732.
(32) Abboud, Y.; Abouriche, A.; Safaj, T.; Berrada, M.; Charrouf, M.; Bennamara, A.; Al Himidi, N.; Hannache, H. 2,3-Quinoxalinedione as a novel corrosion inhibitor for mild steel in 1M HCl. Mater. Chem. Phys. 2007, 105, 1–5.
(33) Mourya, P.; Banerjee, S.; Singh, M. M. Corrosion inhibition of mild steel in acidic solution by Tagetes erecta (Marigold flower) extract as a green inhibitor. Corros. Sci. 2014, 85, 352–363.
(34) El-Lateef, H. M. A. Experimental and computational investigation on the corrosion inhibition characteristics of mild steel by some novel synthesized imines in hydrochloric acid solutions. Corros. Sci. 2015, 92, 104–117.
(35) Khaled, K. F. The inhibition of benzdiazole derivatives on corrosion of iron in 1 M HCl solutions. Electrochem. Acta. 2003, 48, 2493–2503.
(36) He, C.; Tian, Z.; Zhang, B.; Lin, Y.; Chen, X.; Wang, M.; Li, F. Inhibition effect of environment-friendly inhibitors on the corrosion of carbon steel in recirculating cooling water. Ind. Eng. Chem. Res. 2015, 54, 1971–1981.
(37) Scully, J. R.; Silverman, D. C.; Kendig, M. W. Electrochemical Impedance: Analysis and Interpretation; PCN04-011880-27; ASTM Publication: Fredericksburg, VA, 1993; Issue 1188, pp 433–435.
(38) Parveen, M.; Mobin, M.; Zehra, S. Evaluation of L-tyrosine mixed with sodium dodecyl sulphate or cetyl pyridinium chloride as a corrosion inhibitor for mild steel in 1 M HCl: experimental and theoretical studies. RSC Adv. 2016, 6, 61235–61248.

(39) Singh, A.; Lin, Y.; Obot, I. B.; Ebenso, E. E.; Ansari, K. R.; Quarashi, M. Corrosion mitigation of J55 steel in 3.5% NaCl solution by a macrocyclic inhibitor. Appl. Surf. Sci. 2015, 356, 341–347.

(40) Zhang, B.; He, C.; Chen, X.; Tian, Z.; Li, F. The synergistic effect of polyamidoamine dendrimers and sodium silicate on the corrosion of carbon steel in soft water. Corros. Sci. 2015, 90, 585–596.

(41) Mobin, M.; Zehra, S.; Aslam, R. t-Phenylalanine methyl ester hydrochloride as a green corrosion inhibitor for mild steel in hydrochloric acid solution and the effect of surfactant additive. RSC Adv. 2016, 6, 5890–5902.

(42) Solmaz, R.; Kardas, G.; Yazıcı, B.; Erbil, M. Adsorption and corrosion inhibitive properties of 2-amine-5-mercapto-1,3,4-thiadiazole on mild steel in hydrochloric acid media. Colloids Surf., A 2008, 312, 7–17.

(43) Obot, I. B.; Obi-Egbedi, N. O. Adsorption properties and inhibition of mild steel corrosion in sulphuric acid solution by ketoconazole: experimental and theoretical investigation. Corros. Sci. 2010, 52, 198–204.

(44) Ghayempour, S.; Montazer, M.; Rad, M. M. Tragacanth Gum Biopolymer as Reducing and Stabilizing Agent in Biosonosynthesis of Urchin-like ZnO Nanorod Arrays: A Low Cytotoxic Photocatalyst with Antibacterial and Antifungal Properties. Carbohydr. Polym. 2016, 136, 232–241.

(45) Olasunkanmi, L. O.; Obot, I. B.; Kabanda, M. M.; Ebenso, E. E. Some quinoxalin-6-yl derivatives as corrosion inhibitors for mild steel in hydrochloric acid: experimental and theoretical studies. J. Phys. Chem. C 2015, 119, 16004–16019.

(46) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford CT, 2009.

(47) Yang, W.; Mortier, W. J. The use of global and local molecular parameters for the analysis of the gas-phase basicity of amines. J. Am. Chem. Soc. 1986, 108, 5708–5711.

(48) Aspinall, G. O.; Baillie, J. Gum tragacanth. Part II. The Arabinogalactan. J. Chem. Soc. 1963, 1714–1721.

(49) Lu, T.; Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer. J. Comput. Chem. 2012, 33, 580–592.

(50) Lu, T.; Chen, F. Quantitative Analysis of Molecular Surface Based on Improved Marching Tetrahedra Algorithm. J. Mol. Graphics Modell. 2012, 38, 314–323.