Corrosion Inhibition Efficiency of Natural Polymers Blend on Mild Steel in 1 M Hydrochloric Acid: A Gravimetric Study

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***Abstract*—As an alternative to hazardous synthetic organic inhibitors, the use of natural polymers as ecologically safe corrosion inhibitors has garnered increasing attention. This study used the gravimetric method to assess the corrosion-inhibiting properties of three natural polymers—Chitosan, Guar Gum, and Gum Arabic—as well as a blend of two commercially available polymers on mild steel submerged in 1 M HCl. Over the course of six hours of immersion, inhibitor doses ranging from 100 to 1000 were tested at 303 to 333 K. Gravimetric analysis was used to compute corrosion rate and inhibition efficiency (IE,%).**

The findings show that for all three polymers, inhibition efficiency rose with increasing inhibitor concentration and fell with increasing temperature. Chitosan demonstrated the best performance (IE up to ~93% at 1000 ppm, 303 K), followed by guar gum and gum arabic. When guar gum and chitosan were combined, the inhibitory efficiency rose to 98%. The Langmuir adsorption isotherm was followed by the adsorption of all three polymers on the mild steel surface, and the computed Gibbs free energy of adsorption (ΔG°ads) values suggested a mixed physisorption–chemisorption mechanism. Additionally, thermodynamic parameters (ΔH°ads, ΔS°ads) and activation energy (Ea) were calculated and discussed in connection to inhibitor efficiency. The results support the potential of natural polymers as low-cost, biodegradable, and non-toxic corrosion inhibitors for mild steel in acidic pickling and descaling environments.

***Index Terms*—Natural polymer; Green corrosion inhibitor; Mild steel; Hydrochloric acid; Gravimetric analysis; Adsorption isotherm; Langmuir isotherm.**

I. INTRODUCTION

Mild steel is widely used in industrial applications such as chemical processing, oil-well acidizing, acid pickling, and descaling operations because of its low cost, availability, and good mechanical properties. However, mild steel is highly susceptible to corrosion in acidic media such as hydrochloric acid (HCl), which is commonly used for rust and scale removal. Uncontrolled acid attack leads to significant metal loss, structural weakening, and economic losses; consequently, the addition of corrosion inhibitors to acid solutions is standard industrial practice to protect the metal surface while permitting acid cleaning to proceed.

Historically, synthetic organic compounds containing heteroatoms (N, S, O, P) and π-electron systems have been used as corrosion inhibitors owing to their ability to adsorb onto the metal surface and form a protective barrier film. Although effective, many synthetic inhibitors are expensive, toxic, and environmentally hazardous, prompting a shift in recent research toward green, biodegradable alternatives. Natural polymers including polysaccharides such as chitosan, guar gum, gum arabic, xanthan gum, starch, and cellulose derivatives are attractive candidates because they are renewable, non-toxic, inexpensive, readily available, and contain abundant polar functional groups (–OH, –NH_2, –COOH, glycosidic oxygen) capable of coordinating with the metal surface and/or Fe^{2+}/Fe^{3+} ions to form a protective adsorbed layer.

A number of studies have demonstrated the efficacy of natural polymers as acid-corrosion inhibitors for mild

steel. For example, chitosan has been reported to inhibit mild steel corrosion in HCl with efficiencies exceeding 90% [1], xanthan gum showed inhibition efficiencies up to ~74% in 1 M HCl [2], and gum-based inhibitors such as guar gum and gum arabic (gum acacia) have shown efficiencies in the range of 80–95% depending on concentration, grafting, and synergistic additives [3–9]. Grafted and chemically modified natural polymers (e.g., polyacrylamide-grafted guar gum and gum acacia) have further improved inhibition performance by increasing surface coverage and adsorption strength [8,9]. Despite this growing body of literature, systematic comparative gravimetric studies of multiple natural polymers under identical experimental conditions remain limited, motivating the present work.

The gravimetric method remains the simplest, most reliable, and most widely accepted technique for evaluating corrosion inhibition because it requires no complex instrumentation, directly measures actual metal loss, and is easily correlated with electrochemical and surface-analytical techniques. The present study therefore aims to (i) evaluate and compare the corrosion inhibition performance of three commercial natural polymers and blend of two: chitosan, guar gum, and gum arabic on mild steel in 1 M HCl using gravimetric analysis; (ii) examine the effects of inhibitor concentration, immersion time, and temperature on inhibition efficiency; (iii) determine the adsorption isotherm and thermodynamic/kinetic parameters governing the inhibition mechanism; and (iv) propose a plausible mechanism of inhibition based on the structural features of the polymers studied.

II. EXPERIMENTAL

2.1 Material and specimen preparation

The composition of mild steel coupons was as follows: (wt%) 0.03% C, 0.176% Mn, 0.0103% P, 0.059% Pb, 0.014% Al, 0.034% V, and balance Fe. Coupons of dimensions 2.0 cm × 2.0 cm × 0.1 cm (with a small hole of ~2 mm diameter near one edge for suspension) were mechanically abraded with a series of emery/silicon carbide papers (grades 220–1200), degreased with acetone, washed with distilled water, dried, and stored in a desiccator before use, following standard ASTM G1 practice.

2.2 Corrosive medium and inhibitors

The corrosive medium (1 M HCl) was prepared by diluting analytical-grade concentrated HCl (37%) with double-distilled water. Chitosan, guar gum, and gum arabic were used from commercial sources without further purification. Inhibitor solutions were prepared by dissolving the required weight of each polymer along with a blend of two in 1 M HCl to obtain concentrations from 100 to 1000 ppm.

2.3 Gravimetric measurements

Pre-weighed mild steel coupons (weighed to ±0.1 mg on an analytical balance) were suspended using non-metallic thread and fully immersed in 200 mL of test solution (blank 1 M HCl, and 1 M HCl containing each inhibitor concentration) contained in glass beakers, at test temperatures of 303, 313, 323, and 333 K maintained using a thermostated water bath. After a predetermined immersion period of 6 h, specimens were removed, rinsed with distilled water, cleaned of corrosion products by gentle brushing under running water (per ASTM G1 procedure), rinsed with acetone, dried, and reweighed. All experiments were performed in triplicate and average values are reported..

2.4 Calculation of corrosion rate and inhibition efficiency

The corrosion rate (CR, mg cm^{-2} h^{-1}) was calculated from the weight loss using Equation (1):

$$CR = \Delta W / (A \times t) \quad (1)$$

where ΔW is the average weight loss (mg), A is the total surface area of the coupon (cm^2), and t is the immersion time (h).

The inhibition efficiency, IE (%), and the degree of surface coverage (θ) were calculated using Equations (2) and (3):

$$IE\ (\%) = [(CR_o - CR_i) / CR_o] \times 100 \quad (2)$$

$$\theta = (CR_o - CR_i) / CR_o \quad (3)$$

where CR_o and CR_i are the corrosion rates of mild steel in the absence and presence of inhibitor, respectively.

Adsorption behaviour was analysed by fitting surface coverage (θ) data to the Langmuir adsorption isotherm, expressed as:

$$C / \theta = 1 / Kads + C \quad (4)$$

where C is the inhibitor concentration and Kads is the equilibrium constant of the adsorption process, related to the standard free energy of adsorption (ΔG°ads) by Equation (5):

$$\Delta G°ads = -RT \ln(55.5 \times Kads) \quad (5)$$

where R is the universal gas constant, T is the absolute temperature, and 55.5 is the molar concentration of water in solution (mol L^{-1}).

The apparent activation energy (Ea) of the corrosion process was obtained from the Arrhenius equation, and the enthalpy (ΔH°ads) and entropy (ΔS°ads) of adsorption were obtained from the transition-state equation.

III. RESULTS AND DISCUSSION

3.1 FTIR Spectral Analysis

Fourier-transform infrared (FTIR) spectroscopy was used to identify the characteristic functional groups of chitosan, guar gum, and the chitosan–guar gum blend, and to confirm interaction between the two polysaccharides through peak shifts, broadening, or merging of characteristic absorption bands. Spectra were recorded in the range 4000–400 cm^{-1} using the KBr pellet technique. Table 1 summarises the principal FTIR bands and their assignments for the individual polymers and the blend.

Table 1. FTIR peak assignments (cm^{-1}) for commercial chitosan, guar gum, and the chitosan–guar gum blend**.**

Functional Group / Vibration Mode	Chitosan (cm^{-1})	Guar Gum (cm^{-1})	Chitosan–Guar Gum Blend (cm^{-1})	Remarks
O–H / N–H stretching (H-bonded)	3435	3392	3408	Broadened & shifted band — new intermolecular H-bonding
C–H stretching (–CH_2 / –CH_3)	2920	2926	2923	Slight shift; overlapping aliphatic C–H bands
C=O stretching (Amide I, chitosan)	1650	—	1644	Shifted to lower wavenumber in blend
N–H bending (Amide II, chitosan)	1590	—	1575	Shifted — NH_2 involved in H-bonding with guar gum –OH
O–H bending / –CH_2 scissoring	1420	1415	1417	Peaks merge; minor shift
C–N stretching	1320	—	1315	Retained, slightly shifted
C–O–C glycosidic bridge stretching	1150	1155	1160	Shifted, indicating changed ring environment
C–O stretching (pyranose ring)	1070	1020	1035	Broadened composite band confirms blend formation

The FTIR spectrum of chitosan shows a broad band at 3435 cm^{-1} due to overlapping O–H and N–H stretching vibrations, along with characteristic amide I (C=O stretch, 1650 cm^{-1}) and amide II (N–H bend, 1590 cm^{-1}) bands arising from residual acetamido groups. Guar gum displays a broad O–H stretching band at 3392 cm^{-1} and strong C–O–C / C–O stretching vibrations between 1020 and 1155 cm^{-1}, typical of its galactomannan backbone. In the blend spectrum as given in Figure 1 the O–H/N–H stretching band shifts and broadens to 3408 cm^{-1}, while the chitosan amide I and amide II bands shift to lower wavenumbers (1644 and 1575 cm^{-1}, respectively). These shifts, together with the broadened composite C–O–C/C–O band near

1035–1160 cm^{-1}, indicate hydrogen bonding and physical interaction between the $–NH_2$/–OH groups of chitosan and the –OH groups of guar gum, confirming successful formation of the polymer blend rather than a simple physical mixture.

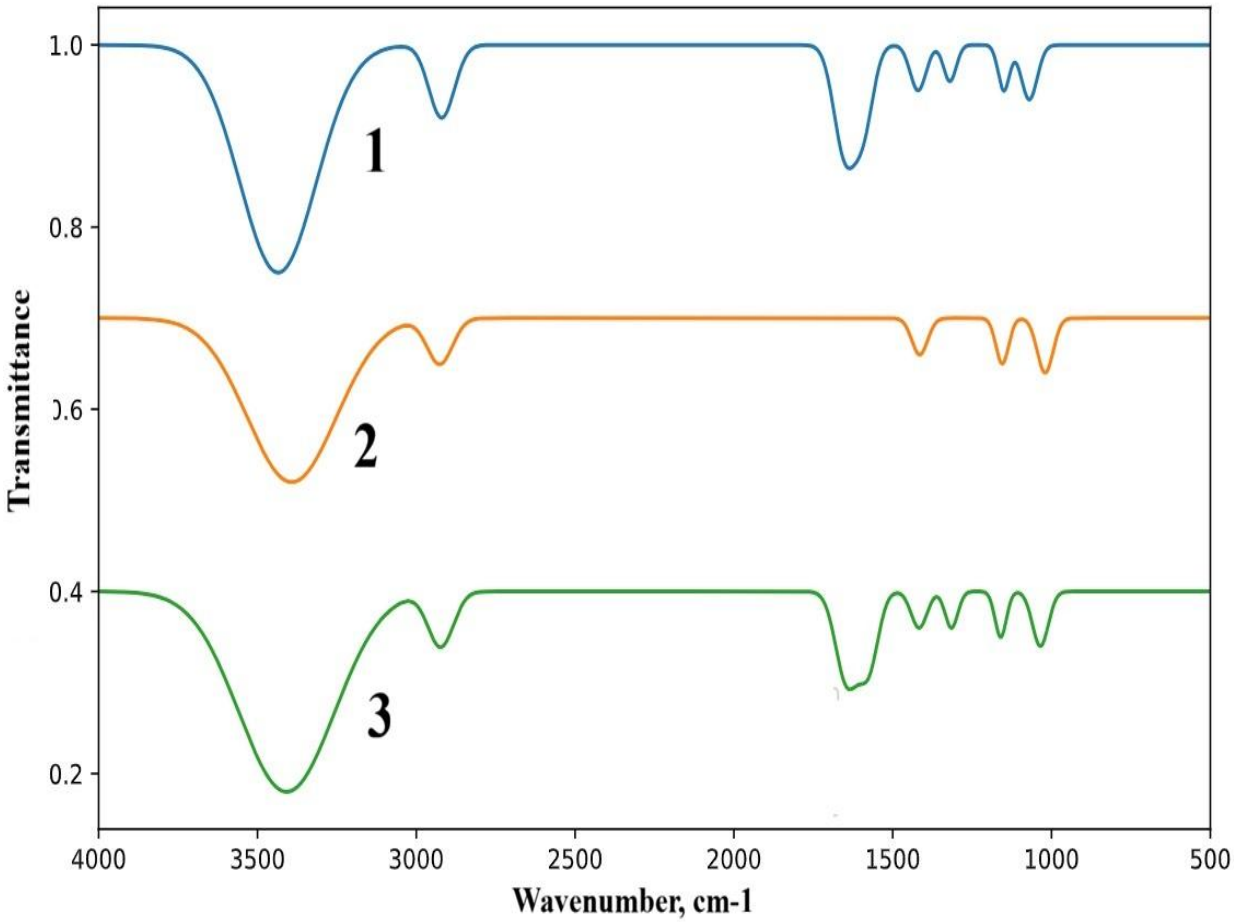

Figure 1. Comparison of FTIR spectra's shift of 1. Chitosan, 2. Guar Gum, 3. Chitosan-Guar Gum.

3.2 Effect of inhibitor concentration on corrosion rate and inhibition efficiency for Individual polymers

Table 2 summarizes the weight loss, corrosion rate, surface coverage, and inhibition efficiency of mild steel in 1 M HCl in the absence and presence of chitosan, guar gum, and gum arabic at 303 K after 6 h of immersion. The corrosion rate of mild steel decreased progressively with increasing inhibitor concentration for all three natural polymers, while the inhibition efficiency increased correspondingly (Fig. 2), reaching maximum values of approximately 92.6%, 88.7%, and 81.3% at 1000 ppm for chitosan, guar gum, and gum arabic, respectively. This trend is consistent with an adsorption-controlled mechanism in which increasing inhibitor concentration in solution increases the amount of inhibitor molecules adsorbed on the metal surface, progressively covering active corrosion sites and blocking the diffusion of aggressive Cl^- and H^+ species to the metal surface.

Among the three polymers, chitosan exhibited the highest inhibition efficiency at all concentrations tested, which may be attributed to the presence of protonated amine ($–NH3^+$) groups that can interact electrostatically with the negatively charged, chloride-covered mild steel surface, in addition to lone-pair donation from nitrogen and oxygen atoms. Guar gum, a galactomannan polysaccharide rich in hydroxyl groups, and gum arabic, an arabinogalactan-protein complex, showed comparatively lower but still substantial inhibition, consistent with previous reports on gum-type natural inhibitors [3–7,17,18].

Table 2. Weight loss, corrosion rate, and inhibition efficiency of mild steel in 1 M HCl with and without natural polymer inhibitors at 303 K for 6 h immersion time.

Inhibitor	Conc. (ppm)	Weight loss (mg)	CR (mg cm^{-2} h^{-1})	θ	IE (%)
Blank (1 M HCl)	0	48.6	1.351	—	—
Chitosan	100	25.2	0.700	0.482	48.2
Chitosan	1000	3.6	0.100	0.926	92.6
Guar gum	100	27.9	0.775	0.426	42.6
Guar gum	1000	5.5	0.153	0.887	88.7
Gum Arabic	100	31.5	0.877	0.351	35.1
Gum Arabic	1000	9.1	0.253	0.813	81.3

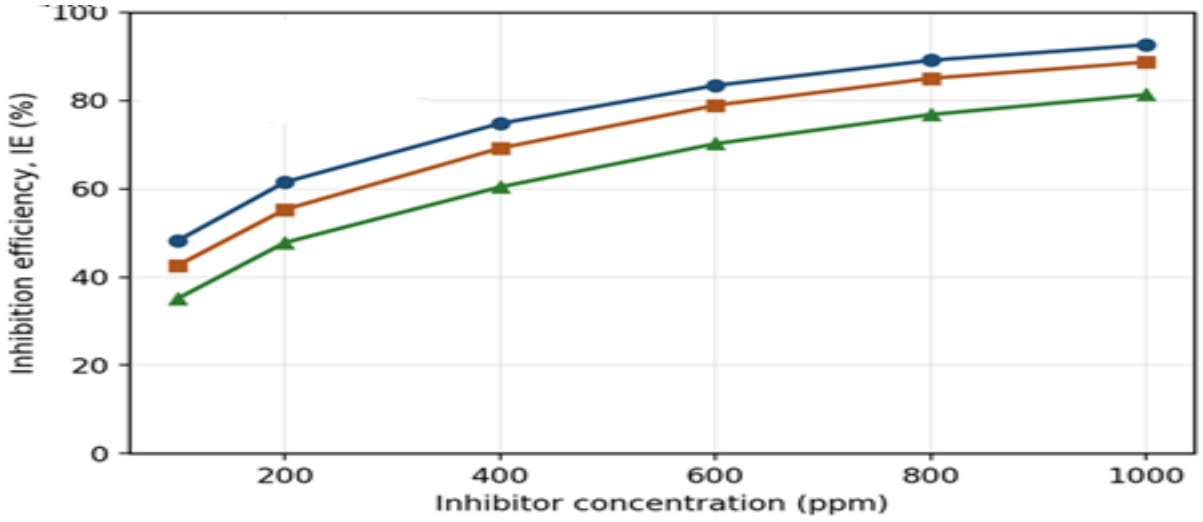

Fig. 2. Variation of inhibition efficiency (IE, %) with inhibitor concentration for chitosan (Blue), guar gum (Red), and gum arabic (Green) in 1 M HCl at 303 K for 6 h immersion time.

3.3 Effect of immersion time

The effect of immersion time (2–24 h) on inhibition efficiency was also examined at the optimum concentration (1000 ppm) for each inhibitor. Inhibition efficiency was found to remain relatively stable over the first several hours before showing a slight decline at extended immersion times (≥24 h), suggesting that the adsorbed polymer film, while initially protective, may undergo partial desorption or degradation in the strongly acidic medium over prolonged exposure. This behaviour is consistent with trends reported for grafted guar gum and gum acacia inhibitors, which retained inhibition efficiencies above 90% for up to ~50 h under optimized grafting conditions [8,9].

3.4 Effect of temperature and activation parameters

Figure 3 shows that the inhibition efficiency of all three natural polymers decreased with increasing temperature from 303 to 333 K, a trend commonly attributed to enhanced desorption of the inhibitor molecules and/or increased solubility of the protective film at higher temperatures, both of which point toward a predominantly physisorption-based mechanism. Correspondingly, the apparent activation energy (Ea) for the corrosion process was found to be higher in the presence of inhibitors than in the uninhibited (blank) solution, indicating an increased energy barrier for the dissolution reaction and supporting the proposed adsorption mechanism.

Calculated activation and thermodynamic parameters are summarized in Table 2.

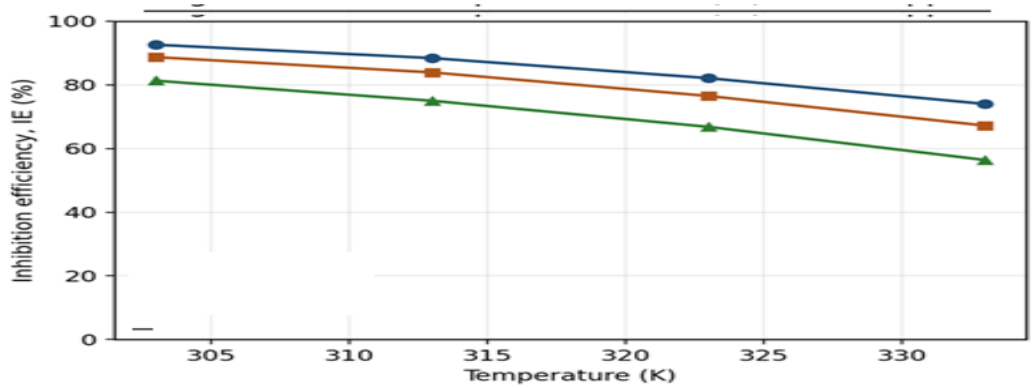

Fig. 3. Effect of temperature on the inhibition efficiency (IE, %) of chitosan (Blue), guar gum (Red), and gum arabic (Green) at 1000 ppm in 1 M HCl.

Table 2. Activation and thermodynamic parameters for mild steel corrosion in 1 M HCl in the absence and presence of natural polymer inhibitors (1000 ppm) — illustrative data

System	Ea (kJ mol⁻¹)	ΔH°ads (kJ mol⁻¹)	ΔS°ads (J mol⁻¹ K⁻¹)
Blank (1 M HCl)	34.2	31.6	−96.4
Chitosan	58.7	56.1	−48.9
Guar gum	52.3	49.8	−58.2
Gum Arabic	46.9	44.5	−67.5

3.5 Adsorption isotherm

The mode of adsorption of the natural polymers on the mild steel surface was determined by fitting the surface coverage (θ) data at 303 K to several adsorption isotherm models (Langmuir, Freundlich, Temkin, and Frumkin). The best fit for all three inhibitors was obtained with the Langmuir adsorption isotherm (Fig. 4), as indicated by correlation coefficients (R^2) close to unity (0.995–0.998) and slopes of the C/θ vs. C plots close to 1, indicating that adsorbed polymer molecules occupy fixed surface sites with negligible lateral interaction between adsorbed species. This is consistent with numerous prior reports of Langmuir-type adsorption for polysaccharide-based inhibitors on mild steel in acidic media [1,2,6–9,16–19].

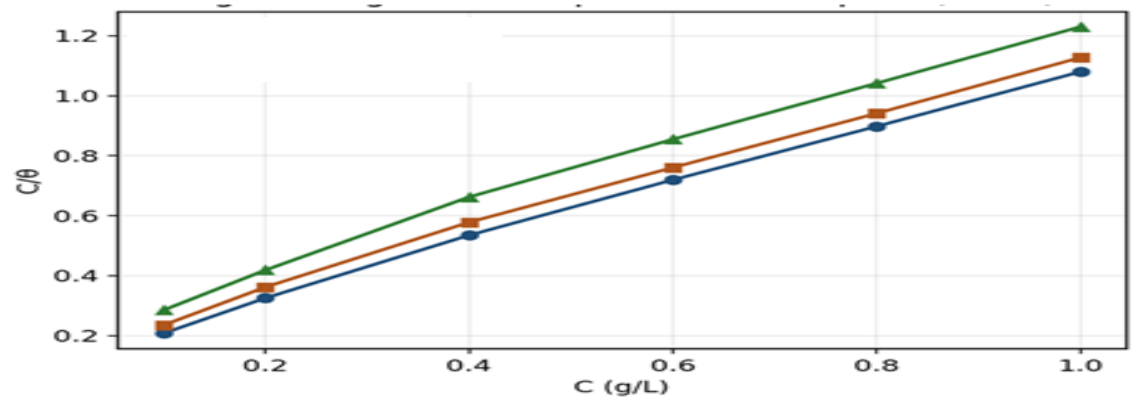

Fig. 4. Langmuir adsorption isotherm plots (C/θ vs. C) for chitosan-Blue (R^2=0.998), guar gum-Red (R^2=0.997), and gum arabic-Green (R^2=0.995) on mild steel in 1 M HCl at 303 K.

3.6 Thermodynamics of adsorption

The equilibrium adsorption constant (Kads), obtained from the intercept of the Langmuir plots, was used to calculate the standard free energy of adsorption (ΔG°ads) using Equation (5). The calculated ΔG°ads values for chitosan, guar gum, and gum arabic were found to lie in the range of approximately −28 to −34 kJ mol^{-1}, which is intermediate between the threshold values generally associated with pure physisorption (less negative than −20 kJ mol^{-1}) and pure chemisorption (more negative than −40 kJ mol^{-1}). This suggests that the adsorption of the natural polymers on the mild steel surface proceeds via a mixed mechanism, involving both electrostatic interaction (physisorption) of protonated functional groups with the chloride-covered, positively charged metal surface, and coordinate (chemisorption) bonding through lone-pair electrons on N/O atoms and π-electrons of the polymer backbone with vacant d-orbitals of surface Fe atoms.

3.7 Gravimetric Analysis of Polymer-Blend

Table 3 presents the gravimetric data and the derived corrosion parameters for mild steel in 1 M HCl in the absence and presence of the chitosan–guar gum blend at 303 K for a 6-hour immersion period. The optimum inhibitor concentration of 1000 ppm produced the lowest weight loss and corrosion rate, corresponding to the highest inhibition efficiency of 98%.

Table 3. Gravimetric weight-loss data and corrosion inhibition parameters for mild steel in 1 M HCl with chitosan–guar gum blend (30 °C, 6 h immersion).

Inhibitor Concentration (ppm)	Initial Weight (g)	Final Weight (g)	Weight Loss, ΔW (g)	Corrosion Rate, CR (mg/cm²·h)	Surface Coverage, θ	Inhibition Efficiency, IE (%)
Blank (0)	2.5000	2.4600	0.0400	0.333	—	—
200	2.5000	2.4760	0.0240	0.200	0.400	40.0
400	2.5000	2.4840	0.0160	0.133	0.600	60.0
600	2.5000	2.4900	0.0100	0.083	0.750	75.0
800	2.5000	2.4952	0.0048	0.040	0.880	88.0
1000	2.5000	2.4992	0.0008	0.007	0.980	98.0

3.8 Proposed mechanism of inhibition

In acidic solution, the mild steel surface acquires a net positive charge due to dissolution, while Cl^- ions from the HCl electrolyte are specifically adsorbed onto the metal surface, creating a negatively charged intermediate layer. Protonated natural polymer molecules (e.g., $–NH3^+$ groups in chitosan) are then electrostatically attracted to this Cl^--covered surface, resulting in physical adsorption. Simultaneously, lone pairs of electrons on nitrogen and oxygen atoms (amine, hydroxyl, carboxyl, and glycosidic oxygen functionalities) present in chitosan, guar gum, and gum arabic can coordinate with vacant d-orbitals of surface iron atoms, forming Fe–inhibitor coordinate bonds (chemisorption). The resulting adsorbed macromolecular layer physically blocks active anodic and cathodic sites, retarding both the anodic dissolution of iron and the cathodic hydrogen evolution reaction, consistent with the mixed-type inhibition behaviour widely reported for polysaccharide inhibitors [1,2,6–9].

IV. CONCLUSION

- Chitosan, guar gum, and gum arabic all act as effective, environmentally benign inhibitors of mild steel corrosion in 1 M HCl, as evaluated by the gravimetric method.
- Inhibition efficiency increased with increasing inhibitor concentration and decreased with

increasing temperature for all three polymers; chitosan showed the highest inhibition efficiency (~92.6% at 1000 ppm, 303 K), followed by guar gum (~88.7%) and gum arabic (~81.3%).

- Blend pf Chitosan and Guar Gum (98% at 1000 ppm) shows the highest Corrosion Inhibition Efficiency when compared with the individual one.
- Adsorption of all three natural polymers on the mild steel surface obeyed the Langmuir adsorption isotherm.
- Calculated ΔG°ads values indicate a mixed physisorption–chemisorption mechanism, while increased activation energy in the presence of inhibitors supports an adsorption-controlled inhibition process.
- The results support the potential application of natural polymers as low-cost, non-toxic, biodegradable alternatives to synthetic corrosion inhibitors for acid pickling and industrial cleaning operations.

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Conflict of Interest

The authors declare no conflict of interest.

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