

APPLICATION OF SILK PROTEIN HYDROLYSATE AS A POTENT ANTI-CORROSIVE AGENT FOR MILD STEEL IN HCl SOLUTION

V. Nijarubini and J. Mallika 

Department of Chemistry, PSG College of Arts and Science,
Coimbatore - 641014, Tamil Nadu, India

 Corresponding Author: mallika@psgcas.ac.in

ABSTRACT

The study focuses on broadening the application of Silk Protein Hydrolysate (SPH) towards conventional metal protection of metallic materials. The inhibitory potentials of SPH against corrosion of mild steel in 1 N HCl media are analyzed through weight loss, electrochemical, and surface morphological techniques. The assessment of the inhibitor effectiveness, kinetic and thermodynamic variables was done at the temperature of 303 – 333 K. The studies exhibited superior anti-corrosion efficacy of 93 % for 10 ppm SPH at 303 K and good maintenance in corrosion control is seen with temperature rise. The SPH assimilation at the metal surface follows the Langmuir adsorption model with free energy values lower than -20 KJ/mol. Potentiodynamic polarization studies evince the mode of corrosion protection to be mixed overall with cathodic predominance. Electrochemical impedance spectroscopy describes the resistive and capacitive behavior through R_{ct} and C_{dl} values signifying the physical barrier prevailing on the metal surface. Surface monitoring through SEM-EDS reveals the firm adherence of SPH to the metallic surface, XRD study characterizes the corrosion products formed in the process. The roughness variables derived from AFM imaging remark the stable protective layer formed by the SPH molecules. The defensive film formed smoothes the metal surface leading to an enhanced water contact angle.

Keywords: Silk Protein Hydrolysate, Mild Steel, Corrosion, Potentiodynamic Polarization, Electrochemical Impedance Spectroscopy, SEM-EDS, AFM, XRD.

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INTRODUCTION

The widespread applications of mild steel continue to grow over the years for its high mechanical strength, ductility, malleability, and toughness.^{1,2} Moreover, the major issue faced by industries is the damaging effects of the metal and the economic loss that has been incurred by employing acids for scrapping off mill scale and rust from the metal surface. The most prominent method of offering metal protection is with the addition of inhibitors in the acidizing process which controls metal dissolution. Numerous corrosion inhibitors are reported by researchers, of which organic compounds are of special interest, which either physically or chemically associate with the metallic surface and retard the metal dissolution in the corrosive environment.^{3,4} However, the novel perspective of using green inhibitors towards controlling the corrosion process is on the higher end in the past decades as they are non-toxic to the environment and mankind. Several natural substances have been recorded as promising corrosion inhibitors, involving plant extracts with active phytochemical constituents^{5,6}, plant-based gums⁷⁻⁹, animal proteins, and biopolymers.¹⁰⁻¹² Silk protein fall under the class of biopolymers exhibiting promising applications in the biomedical and pharmaceutical industries. The versatile material has been reported for its use as silk composites, coatings & films, micro-patterning and microfluidics, and implant applications, etc.¹³ J. G. Hardy & T. R. Scheibel studied the various silk protein composites and their applications in the textile industry, tissue scaffolds and in drug delivery.¹⁴ Despite its use in several areas of research, the paper presents the investigation of the inhibition performance of Silk Protein Hydrolysate toward controlling mild steel corrosion in a 1 N HCl medium. Conventional weight loss, electrochemical and surface analysis were performed to understand its effectiveness towards the corrosion process. Promising inhibition efficacies observed with low amounts of SPH mark its superiority and cost-effectiveness.

EXPERIMENTAL

Sample Preparation

Mild steel comprising of the following composition C - 0.069, Si - 0.077, Mn - 0.29, P - 0.016, S - 0.014, Cr - 0.011, Cu - 0.007, Al - 0.01, and Fe in balance (wt %) was machined to strips of dimension 30 mm×10 mm×1mm for mass loss measurements. Similarly for electrochemical investigation, the epoxy-coated mild steel with a specific area being exposed serves as the working electrode. Surface preparation involves abrading the metal substrate with different grades of emery sheets ranging from 120, 150, 220, 400, and 600. Thereafter, cleansed thoroughly with doubly deionized water, and ethanol, dried, and stored in a vacuum desiccator.

Inhibitor and Test Media Details

Silk Protein Hydrolysate procured from Suboneyo Pharmaceuticals is used as received. HPLC analysis reveals the comprehensive profile of SPH viz. glutamic acid, aspartic acid, tyrosine, glycine, lysine valine, serine, tryptophan, isoleucine, phenylalanine, leucine, and methionine.¹⁵ The electrolytic medium (1N HCl) is prepared with 37 % HCl using double distilled water and the volume employed for the studies is 100 ml. The inhibitor concentration is expressed in ppm due to the molecular complexity of the inhibitor system.

Weight Loss Analysis

The most reliable method of calculating the corrosion rates is through weight loss measurements. The weighed metal coupons were submerged as triplicates in 100 ml electrolyte inclusive and exclusive of inhibitor with 1, 2, 4, 8, and 10 ppm concentrations for 1, 2, 3, 6, 12, and 24 h immersion at room temperature. The inhibitor action at elevated temperatures was studied for 1 h immersion. The test samples retrieved from the HCl medium after a specific duration was post-treated following the cleaning procedure, discussed under the sample preparation section. The initial and final weight difference presents the weight lost during the electrochemical reaction, from which the rate of corrosion and the percentage inhibition efficiency was evaluated through equation (1) and (2) respectively.^{16,17}

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

Where, W , ρ , A , t . refers to weight loss in grams, the density of the mild steel specimen in gcm^{-3} , the total surface area of the metal in cm^2 , and the time of immersion in hours.

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

W_o and W_i correspond to the mass loss of mild steel in corroding electrolytes without and with varying amounts of the inhibitor.

Electrochemical Investigation

Electrochemical experiments involving potentiodynamic polarization and impedance spectroscopy studies were performed in a cell assembly comprising of mild steel specimen (working electrode), a platinum electrode (auxiliary electrode), and the saturated calomel electrode (reference electrode). A 0.3 cm^2 surface area of the mild steel electrode was exposed to the electrolyte and allowed to achieve the equilibrium potential, before preceding the polarization measurements. From the current-potential curves, the parameters viz. corrosion potential (E_{corr}), corrosion current density (i_{corr}), and anodic and cathodic Tafel slopes b_a and b_c were measured in the electrolyte medium without and with selective inhibitor concentrations. The same experimental set-up equipped for polarization technique was used to study Electrochemical impedance spectroscopy. It measures the charge transfer resistance (R_{ct}) double-layer layer capacitance (C_{dl}) at the electrode-electrolyte interface. The percentage inhibition efficiency was calculated employing equation (3).¹⁸

$$\text{IE (\%)} = \frac{R_{\text{ct}}(\text{inhibitor}) - R_{\text{ct}}(\text{blank})}{R_{\text{ct}}(\text{inhibitor})} \times 100 \quad (3)$$

Surface Examination

Examination of the metal surface provides deep insights into the protective film formed. The pretreated metal plates were submerged in 1 N HCl for 6 h without and with 10 ppm SPH, afterward dried and subjected to surface analysis. XRD studies characterize the nature of the corrosion products formed over the mild steel surface. SEM-EDS analysis helps to examine the elements present in uninhibited and

inhibited metal surfaces. The roughness analysis is investigated through AFM which exhibits 2-Dimensional and 3-Dimensional images of the metal surface with statistical roughness parameters in nanoscales, affording an excellent understanding of corrosion protection. The static water contact angle measures the wetting properties of the protected and unprotected metal surface and was performed thrice to check its accuracy.

RESULTS AND DISCUSSION

Influence of Immersion Time on Inhibition Efficiency At Room Temperature

At low concentrations of SPH, limited amounts of the inhibitor species coherently participate in adsorption at the metal-active sites. However, with increasing inhibitor concentrations and contact time, adequate amounts of SPH molecules are well adsorbed at the deficit area, masking the overall metal surface, and exhibiting an increased inhibition action. The progress in the adsorption gradient under these circumstances shows an upright inhibition efficiency (Fig.-1). The constancy in the %IE beyond 12 h dictates the stability of the adhered SPH molecules in the corrodent solution for a longer exposure time. The observations emphasize the collective interaction of the amino acid assembly, strengthening the surface adsorption and barricading the metal to dissolve from the free metal surface and entering into the acidic media.

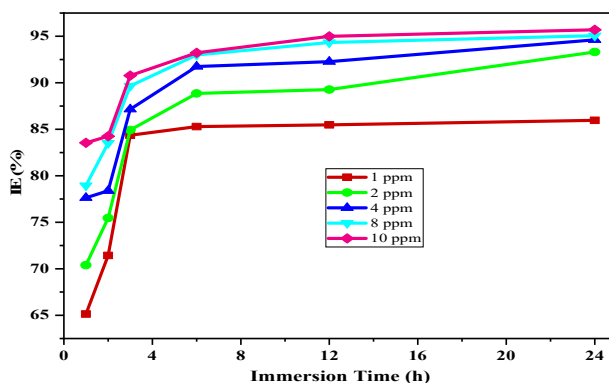


Fig.-1: Variation of IE with Respect to Contact Time for a Period of 24 Hours at 303K

Temperature Influence on Inhibition Efficiency

Table-1 displays the variations in the corrosion rate and inhibition efficiency observed in weight loss measurements. The temperature being a key factor influencing the inhibitor adsorption process brings remarkable changes in the metal surface.¹⁹ At the operating temperatures of 313 and 323 K, the strength of the metal-inhibitor interaction begins to fall showing a rise in the dissolution efficiency. The acceleration in the corrosion rates is more pronounced at these temperatures for 1 ppm SPH, whereas 2, 4, 8, and 10 ppm concentrations show significant stability in inhibition efficiencies. At 333 K, the shielding capacity of the inhibitor decreases even for higher SPH concentrations. The desorption rate predominates over the adsorption rate, facilitating the acid attack on the metal substrate, leading to an increased charge/mass transfer. The progressive increase in efficiency with lowering temperatures and higher corrosion rates with temperature rise suggest that inhibitor adsorption over the metal surface occurs perhaps through a physical adsorption process.²⁰

Table-1: Corrosion Rates (mmpy) and Inhibition Efficiencies (%) for Various SPH Concentrations at Different Temperatures

Temperature (K)		Inhibitor concentration (ppm)					
		Blank	1	2	4	8	10
303	CR	0.0564	0.0197	0.0167	0.0126	0.0119	0.0093
	IE	-	65.13	70.39	77.63	78.95	83.55
313	CR	0.1332	0.0516	0.0367	0.0293	0.0226	0.0215
	IE	-	61.28	72.42	77.99	83.01	83.84
323	CR	0.2536	0.0983	0.0686	0.0486	0.0382	0.036
	IE	-	61.26	72.95	80.85	84.94	85.82
333	CR	0.2868	0.1302	0.0909	0.069	0.0612	0.0531
	IE	-	54.59	68.31	75.94	78.65	81.5

Thermodynamic Parameters

The kinetic and thermodynamic parameters of the corrosion process are calculated from weight loss values. The logarithm of CR vs $1000/T$ reveals the effect of temperature on the inhibition performance, expressed through the Arrhenius equation (4).²¹

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

CR - corrosion rate, A - Arrhenius pre-exponential factor, E_a - apparent activation energy and R is the universal gas constant. The activation energies for different concentrations of SPH are calculated with the slope ($-E_a/2.303R$) of the Arrhenius plots (Fig.-2) through the expression $E_a = -(\text{slope}) \times 2.303R$. The E_a values displayed in Table-2, are high for the inhibitor-treated system than the uninhibited system and decrease with increasing inhibitor concentration. However, the experimental values are less than 80 KJ/mol, suggesting the metal-inhibitor interaction to presume through the physisorption mechanism.²²

The enthalpy and entropy of activation (ΔH°), (ΔS°) were evaluated using the equation (5).²³

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

The values of ΔH° & ΔS° are derived from the slope ($-\Delta H^\circ/2.303R$) and intercept [$\log(R/Nh) + (\Delta S^\circ/2.303R)$] of the linear transition plot (Fig.-3). The positive ΔH° values dictate the endothermic metal dissolution, which is indeed a slow process in the presence of the inhibitor.²⁴ The sequential variation noticed with E_a and ΔH° values display an average difference of 2.64 KJ/mol for $E_a - \Delta H^\circ$, which exactly matches the product of gas constant (R) and the average experimental temperature^{25,26} confirming the unimolecular corrosion process involving a gaseous reaction. The negative ΔS° values claim the lowering in disorderliness taking place during the transition of the free inhibitor to its adsorbed state.²⁷ The entropy observed is characteristic of both water desorption and inhibitor adsorption. The large negative values of ΔS° compared to the inhibitor-free system can be explained as: The activated complex in the absence of an inhibitor involves $\text{Fe-H}_2\text{O}$ which dissociates into Fe^{2+} , H_2 , and OH^- ions. However, in the presence of SPH, the water molecules are gradually replaced and a well-ordered array of Fe-inhibitor matrix is developed, which retards the acid attack and their subsequent reactions involving the discharge of the hydrogen ions and the generation of adsorbed hydrogen molecules at the mild steel surface.²⁸

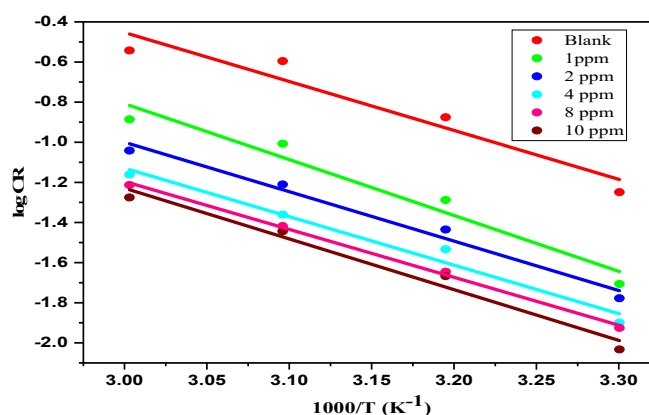


Fig.-2: Arrhenius Plot for Mild Steel Without and with Different SPH Concentrations in 1 N HCl

Table 2: Activation Parameters for Mild Steel Observed in the Absence and Presence of Different SPH Concentrations

Inhibitor concentration	E_a (KJ mol ⁻¹)	ΔH° (KJ mol ⁻¹)	ΔS° (JK ⁻¹ mol ⁻¹)
Blank	46.71	44.06	-122.35
1 ppm	53.33	50.69	-109.25
2 ppm	47.18	44.53	-131.41
4 ppm	46.29	43.65	-136.53
8 ppm	45.74	43.10	-139.45
10 ppm	48.43	45.78	-132.04

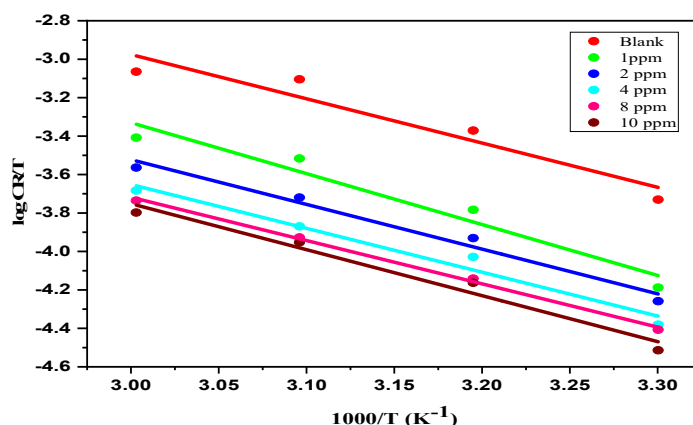


Fig.-3: Transition Plot for Mild Steel in 1 N HCl in the Absence and Presence of SPH

Adsorption Isotherm

The surface coverage (θ) helps to determine the inhibitor adsorption characteristics, it symbolizes the number of reactive centers occupied by the inhibitor molecules, calculated using the equation $\theta = \% \text{ IE} \times 100$. Application of Langmuir model adsorption isotherm offers linear fits with regression coefficient close to unity. The isotherm relates the degree of surface coverage and inhibitor concentration through equation (6)²⁹

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (6)$$

θ - degree of surface coverage, C - inhibitor concentration, and K_{ads} - equilibrium constant for the adsorption/desorption process. The K_{ads} values for the studied temperatures are calculated from the intercept of the Langmuir plot. Equation (7)³⁰ presents the relation between K_{ads} and standard free energy of adsorption ΔG°_{ads} ,

$$\Delta G^\circ_{ads} = -2.303 RT \log(55.5 \times K_{ads}) \quad (7)$$

Where R - Universal gas constant, T - Absolute temperature, and 55.5 is the concentration of water in solution in mol L^{-1} . Fig.-4 depicts the plots of C/θ Vs C. Table-3 presents the adsorption parameters derived from the plot. A substitutional adsorption phenomenon is expected to take place, whereby the water molecules are replaced by the inhibitor at the interface region. The Langmuir interaction signifies the proportionality of the inhibitor to the surface reactive sites, exhibiting a homogeneous dispersion of inhibitor molecules.³¹ At low inhibitor concentrations, the surface coverage is low and metal dissolution occurs at the inhibitor-free surface. However, with high SPH concentrations, the metal surface is sufficiently occupied, offering a substantial monolayer coverage to the surface of the metal substrate. Additionally, interactions among inhibitor molecules also arise due to high surface coverage.^{32,33} The K_{ads} values postulate the ease of the inhibitor adsorption to the mild steel surface. Its high values at low temperatures represent the strong adhesion of the inhibitor to the metal substrate, indicating that the SPH molecules are less prone to the acid attack thereby exhibiting a higher % IE.³⁴ Also, with the rise in temperature, the inhibitor molecules experience feeble interactions with the metal surface, and it eventually desorbs. The results are significant with the trend observed in the activation energy. Moreover, a comprehensive adsorption phenomenon is expected to occur based on the maintenance of inhibition efficiency values. But the ΔG°_{ads} values fall below -20 KJmol^{-1} , showing the dominance of physisorption³⁵⁻³⁷, which is also evident from the inhibition performance recorded beyond 323 K.

Table-3: Adsorption Parameters Obtained From Langmuir Isotherm Plots

Temperature (K)	Slope	K_{ads}	R^2	ΔG°
303	1.1	2.18	0.9983	-12.09
313	1.0	0.69	0.9735	-9.50
323	1.1	1.95	1	-12.59
333	1.1	1.61	0.9995	-18.82

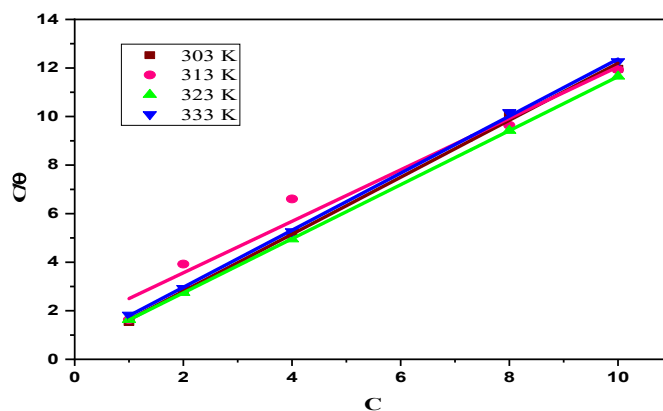


Fig.-4: Langmuir Isotherm Plot of Mild Steel in 1 N HCl Containing Different SPH Concentrations at Different Temperatures

Potentiodynamic Polarization

The polarization profiles of mild steel in 1 N HCl without and with various concentrations of SPH are shown in Fig.-5. Table-4 displays the parameters obtained from the Tafel plots. The lowering rate of corrosion (CR) and corrosion current density (i_{corr}) with the increase of SPH concentration in the corrosive medium suggests molecular diffusion through the charged interface followed by its adsorption onto the electrode surface. The displacement of corrosion potential (E_{corr}) to more negative values implies the predominant cathodic protection offered by the inhibitor.³⁸ This can be explained as in the acid media the amino acid units are rapidly protonated and through electrostatic interactions, these cationic species are adsorbed to the electron-rich centers whereby blocking the cathodic sites.³⁹ However, the E_{corr} difference measured falls below 85 mV suggesting the mixed mode of corrosion protection offered by SPH in controlling both cathodic and anodic reactions.⁴⁰ The curvature observed in the anodic branches owes to the corrosion products deposited over the surface forming a non-passive film.⁴¹ It is obvious that the inhibitor addition equally reduced the anodic and cathodic current densities. Also, the variation in the cathodic (β_c) and anodic (β_a) tafel slopes are not much specific, representing the inhibitor adsorption at the electrode/electrolyte interface, blockading the reactive centers and slow down the corrosion reaction by suppressing both metal dissolution and inhibitor desorption without altering the corrosion mechanism.⁴² The polarization resistance (R_p) characterizes the resistance developed against the applied potential and it increases with inhibitor concentration⁴³ ensuring the presence of the physical barrier contributing towards corrosion protection.

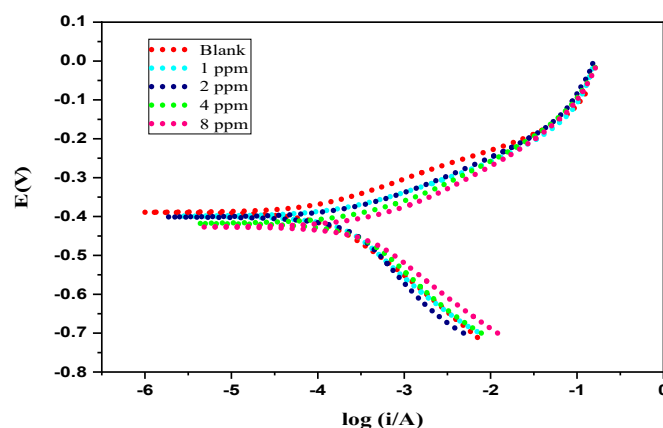


Fig.-5: Tafel Plots for Mild Steel in 1 N HCl With and Without Inhibitor at 303K

Electrochemical Impedance Spectroscopy

The electrochemical behavior of mild steel in 1 N HCl medium with various concentrations of SPH is studied through EIS and the respective Nyquist, bode modulus, and phase angle plots recorded are depicted in Fig.-6a-c. Table-5 displays the charge transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}) values obtained from the impedance analysis. The varying diameter of the Nyquist semicircle explains the resistance to mild steel corrosion. The depressed capacitive loops observed are due to the damage incurred

on the electrode surface during the electrochemical process causing surface roughening. The R_{ct} and C_{dl} values describe the surface interactions at the metal-electrolyte interface. For the system under the influence of the SPH, the inhibitor molecules penetrate through the diffusion layer and facilitate its adsorption at the mild steel surface. However, with increasing SPH concentrations, the charged surface active sites remain thickly populated with the inhibitor molecules.

Table-4: Corrosion Parameters Obtained from Polarization Curves Without and with Different Inhibitor Concentrations at 303 K

Inhibitor Concentration	E_{corr} (V)	i_{corr} ($\mu A\ cm^{-2}$)	b_a (V dec $^{-1}$)	b_c (V dec $^{-1}$)	CR (mpy)	R_p Ω
Blank	-0.3902	3.38×10^{-4}	12.707	6.543	5.143	83
1 ppm	-0.3988	2.64×10^{-4}	12.973	5.079	4.021	106
2 ppm	-0.4006	2.13×10^{-4}	11.522	4.473	3.247	127
4 ppm	-0.4178	1.8×10^{-4}	10.189	5.270	2.740	134
8 ppm	-0.4272	9.71×10^{-5}	9.678	5.005	1.479	232

The dense layers of the adsorbed amino acid entities act as a potential barrier, controlling the acidic species to come into contact with the metal surface and hinder both oxidation and reduction reactions. Therefore, the transport of the charge and mass transfer being resisted is reflected with higher R_{ct} values for the inhibitor-treated HCl compared to the inhibitor-free system.⁴⁴ As the inhibitor approaches, the H_2O molecules adhering to the metal surface flip-flop their orientation during their dislocation which subsequently reduces the dielectric constant and the C_{dl} values.⁴⁵ The shapes of the Bode modulus and phase angle plot are significant with the corrosion inhibition process at the electrode surface. The single maxima in the phase angle plots are ascribed to the single time constant and the relative increase in the peak height with SPH concentration signifies the apparently smoothed surface serving as an intact layer at the metal-acid boundary.^{46,47} The intermediate frequency signaled in the Bode modulus plot is correlated to the capacitive behavior at the interface region.⁴⁸

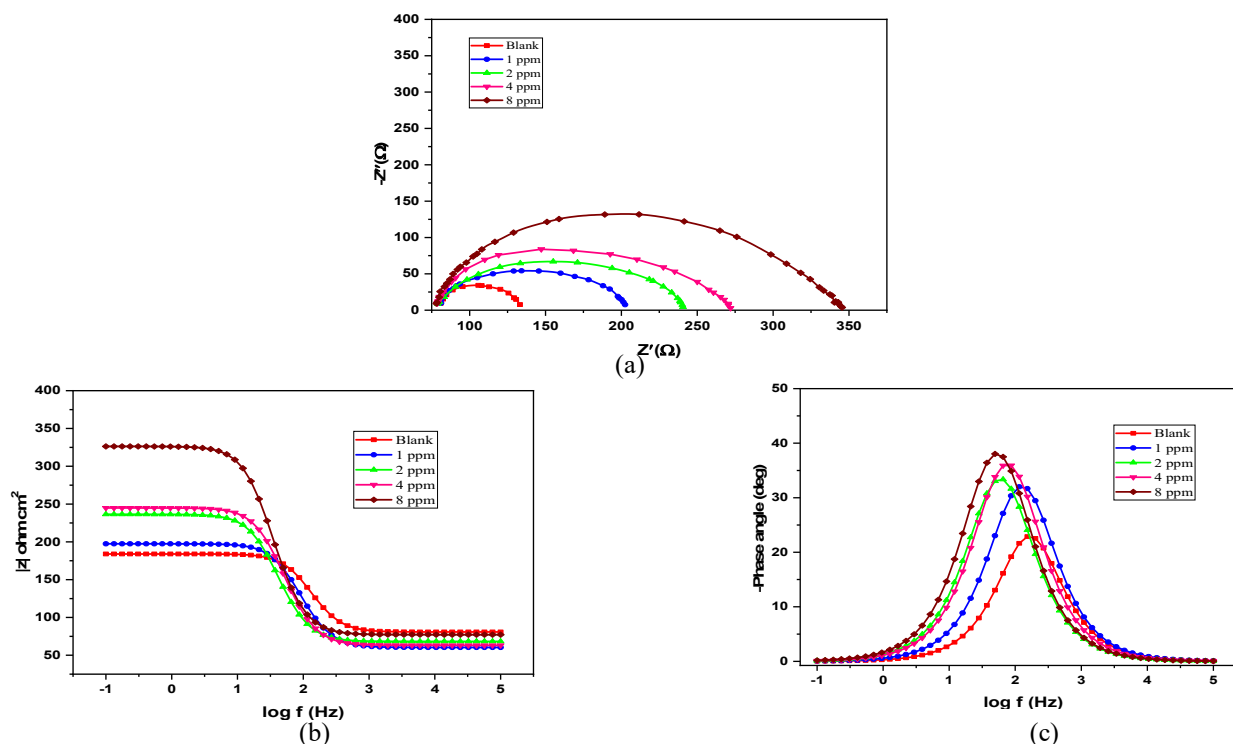


Fig.-6: (a) Nyquist Plot, (b) Bode Modulus and (c) Bode Phase Angle Plot for Mild Steel in 1 N HCl Without and With Various SPH Concentrations at 303 K

Table-5: Impedance Parameters of Mild Steel With Various SPH Concentrations at 303 K

Inhibitor concentration	R_{ct} ($\Omega \text{ cm}^2$)	Cdl ($\mu\text{F cm}^2$)	IE (%)
Blank	22.4	29.7	-
1 ppm	76.7	24.8	70.7
2 ppm	99.80	22.8	77.5
4 ppm	118.6	16.6	81.1
8 ppm	171.7	14.0	86.9

XRD Studies

Fig.-7 presents the X-ray diffraction patterns of the metal immersed in blank and retrieved from inhibited test media. The corrosion products exhibiting peaks at $2\theta = 38.12$, 64.84 are attributed to the formation of iron oxides (Fe_3O_4 , FeOOH), and those at $2\theta = 44.59$, 82.18 are characteristic of iron peaks detected for the mild steel exposure to 1 N HCl.^{49,50} Whereas, the XRD report of the metal under the influence of 10 ppm SPH displays intensities at $2\theta = 44.29$, 82.18 for metallic iron, and 64.84 a characteristic of iron oxy-hydroxide (FeOOH). The absence of Fe_3O_4 and the suppression of the FeOOH peak suggest that the corrosion process is limited in the inhibitor's ambience. Furthermore, the intense peak observed for the elemental iron in the inhibitor-treated system confirms the occurrence of the intact inhibitor layer and its resistance against iron oxide formation.

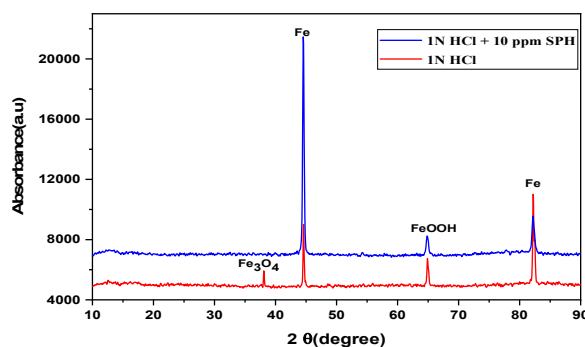


Fig.-7: XRD Pattern of the Corrosion Products Formed Over the Mild Steel Surface in 1 N HCl Without and With 10 ppm SPH

SEM-EDS Analysis

The reports of microscopic imaging are displayed in Fig.-8. The polished metal, prior exposure to the corrodent (image 8a) displays a smooth flat surface with few abrasion streaks. Examination of the metal submerged in the inhibitor-free medium (image 8b) exhibits an uneven surface with oxide layers and the pits developed due to the chloride attack. The flower-like projections seen in image 8c are typical of the adsorbed SPH constituents, fencing the metallic surface and controlling the flow of acid species across it.⁵¹ Furthermore, the protection performance is validated through EDS spectral analysis performed on the selected regions of SEM images (images 8d-f). The disappearance of the Cl peak corroborates the reduced acid attack in the vicinity of SPH. Also, the N, O, and S peaks appeared proves the inhibitor assimilation onto the metal surface.

Atomic Force Microscopy

Figure-9a-f demonstrates the 2D & 3D profiles of polished, inhibitor untreated, and treated mild steel surfaces. The values of average roughness (S_a), the root mean square roughness (S_q), and the maximum peak-to-peak (S_y) derived from AFM images are presented in Table-6. The data explicitly affirms the existence of iron. However, in the acid medium with 10 ppm SPH, the metal experiences minimal roughness, and the values are close to that of polished metal^{52,53} indicating the smoothed surface arising from the accumulation of SPH. The minimal roughness is ascribed to the available nano-level inhibitive layer which isolates the metal from the corrodent, offering substantial surface protection and restricting the metal dissolution behavior. Nevertheless, the roughness observed for polished mild steel is due to the slight atmospheric corrosion.

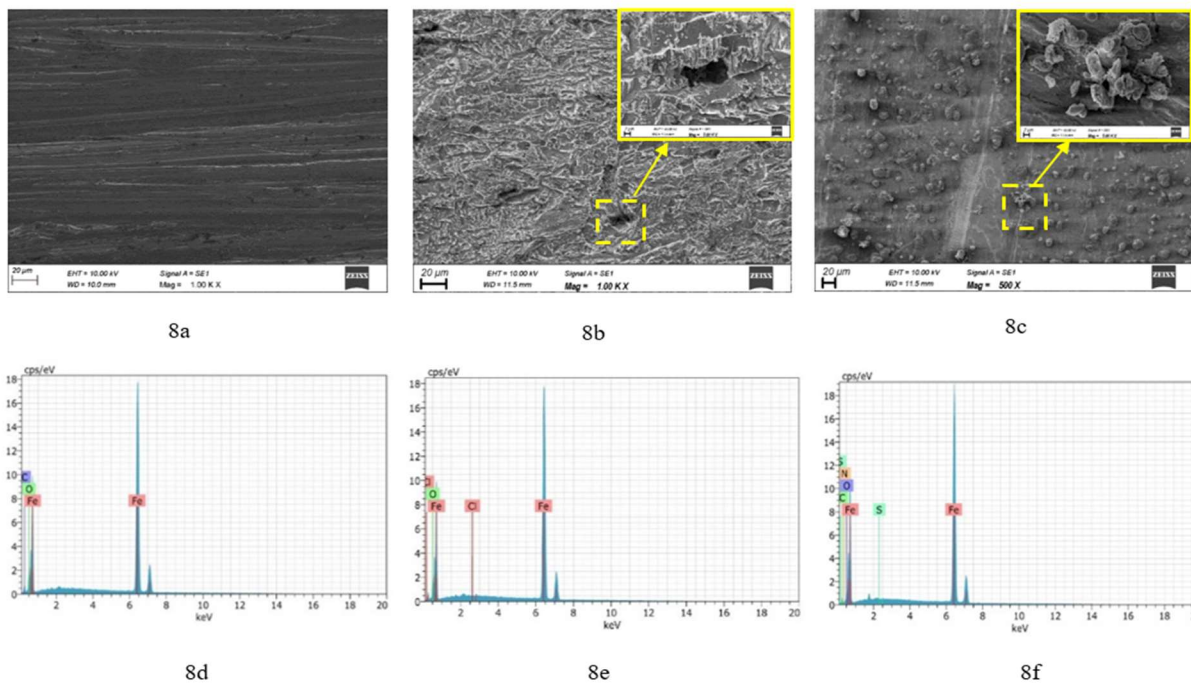


Fig.-8: SEM-EDS Images of Polished Mild Steel, Untreated and Treated with 10 ppm SPH in 1 N HCl

Table-6: AFM Data For Mild Steel Immersed in Uninhibited and Inhibited Solution

Samples	Average roughness (S_a) nm	Root mean square roughness (S_q) nm	Maximum peak to peak height (S_v) nm
Polished Mild steel	34.31	44.05	276.47
Mild steel in 1 N HCl	119.23	153.01	1256.13
Mild steel in 1 N HCl +10 ppm SPH	40.92	51.03	317.44

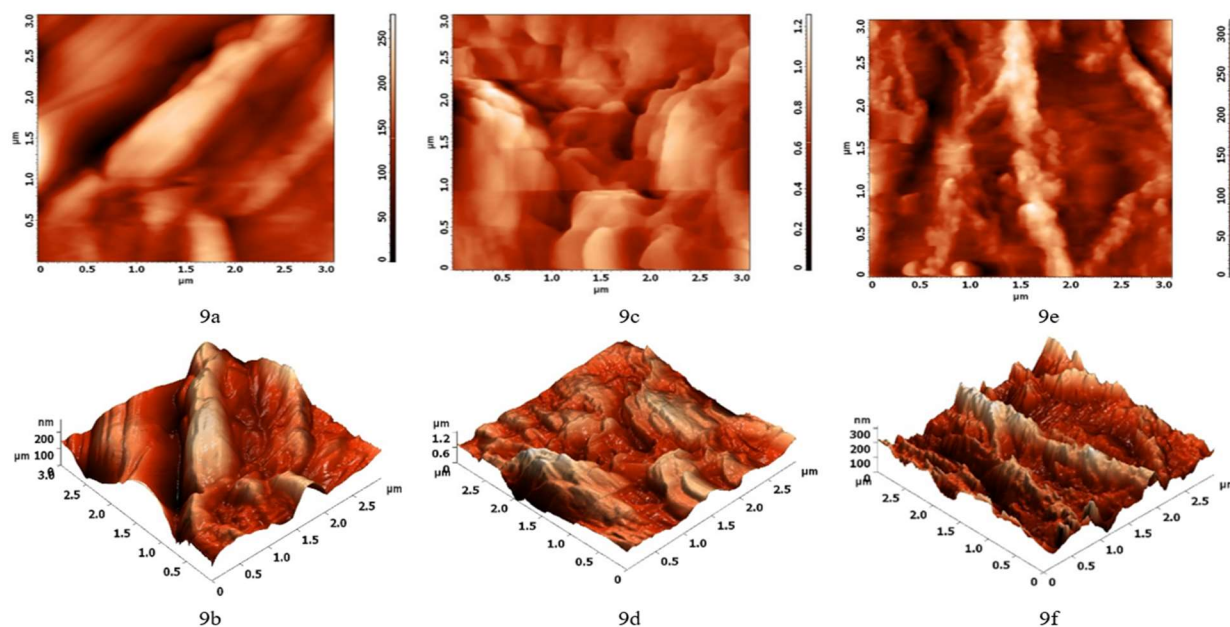


Fig.-9: AFM 2D & 3D Images of Polished Mild Steel (a) & (b), Mild Steel in 1 N HCl (c) & (d), Mild Steel in 10 ppm SPH (e) & (f) for 6 h Immersion at 303 K

Contact Angle Measurement

The morphological images of the contact angle measured for the metal in contact with 1 N HCl and in the presence of 10 ppm SPH are shown in Fig.-10. The measured contact angle (θ) of 31° corresponds to the metal exposed in 1 N HCl (Fig.-10a), on the other hand, a marked increase in angle to 65° is noticed for the metal in the inhibitor system (Fig.-10b). Generally, the lower contact angle value is suggestive of the hydrophilic nature and an inflated angle is ascribed to the hydrophobic character of the metal surface.⁵⁴ The decline in the θ value is specific to the harshly damaged metal substrate, due to the electrochemical dissolution of the mild steel leading to chemical transformation at the metal-acid interface forming corrosion products and its adherence increases the surface roughness. The subsequent rise in the wetting angle owes to the hydrophobic nature imparted by the inhibitor sheath, protecting the metal surface from the acid attack.

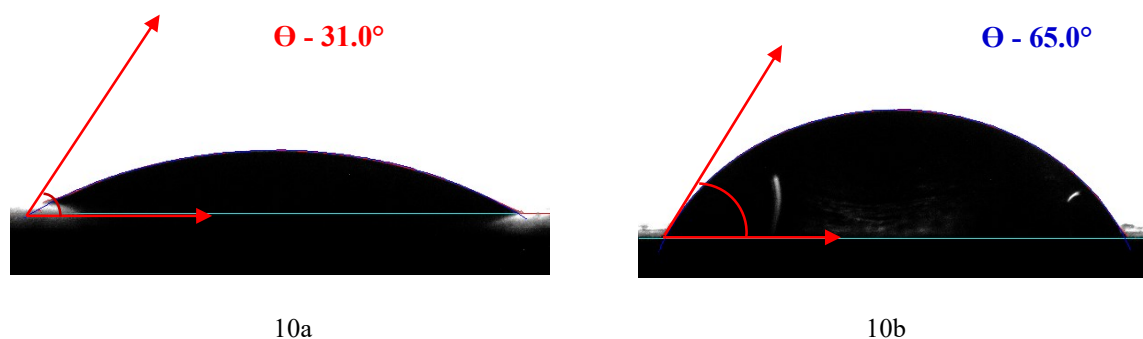


Fig.-10: Contact Angle Values of Mild Steel (a) in 1 N HCl (b) 1 N HCl + SPH System

Inhibition Mechanism

The inhibition action is primarily based on the inhibitor type, its structure, and the charge on the mild steel surface.⁵⁵ The constituents of SPH protonate readily in HCl solution and prevail as cationic species. However, the adsorption of the organic substances might not necessarily occur via the direct interaction with the metal surface, instead the counter ions present may profoundly stimulate the adsorption characteristics.⁵⁶ The mechanistic action of SPH offering surface protection is shown in Fig.-11. The anodic process develops an excessive positive charge on the mild steel surface. These charged centers specifically adsorb the counterions in the electrolyte medium, forming a pool of Cl^- ions. This serves as the potential anchoring site bridging the cationic forms of SPH with the metal surface and interact *via* electrostatic attractions. This mode of metal-inhibitor adsorption through electrostatic interactions ascertains the vertical orientation of the inhibitor species. If the SPH molecules were oriented horizontally during adsorption this would possibly lead to strong interactions forming chemical bonds. However, the variations noticed with E_a and ΔG° evidence the physisorption phenomenon, whereby the inhibitor molecules are aligned perpendicular with respect to the mild steel surface. Cooperative adsorption is likely to occur, favoring the adhesion of the cationic forms of inhibitor molecules over the anion layer.⁵⁷ Additionally, the COO^- terminus of amino acid also interacts with the charged metal ions, forming an inhibitor film at the interface region.⁵⁸ At higher SPH concentrations, the self-assembling property of amino acids favors lateral interaction among themselves through weak forces like van der Waals, and hydrogen bonding and strengthens the inhibitor adsorption process exhibiting supreme inhibition performance with increasing immersion time at 303 K. The inhibitor interaction weakens, the lateral interactions disappear and the surface functionality drops with temperature rise. The SPH molecules subsequently desorb from the mild steel surface developing pores in the protective film, and the aggressive ions migrate through these pores rupturing the lattice structure of the film, promoting the metal dissolution process. Moreover, the increased amounts of oxygen shown in the EDS analysis compliments the XRD report. Also, the considerable amounts of FeOOH present blockade the metal surface and experience surface adsorption with protonated nitrogen atoms through hydrogen bonding.⁵⁹

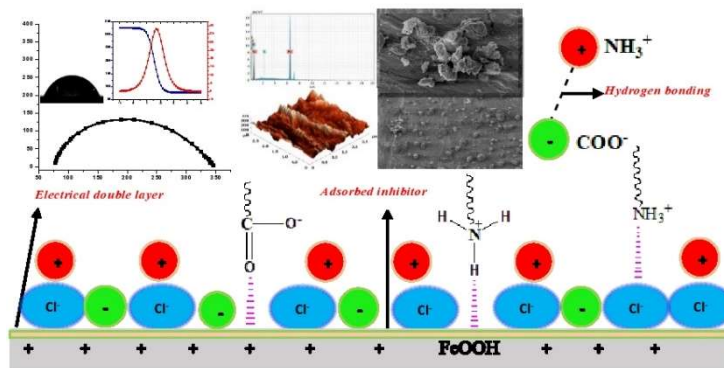


Fig.-11: Mechanistic Action of SPH on Mild Steel Corrosion in 1 N HCl

CONCLUSION

Silk Protein Hydrolysate plays a significant role in mitigating mild steel corrosion in 1 N HCl medium. The inhibition potentiality progresses with a concentration gradient from 1 ppm to 10 ppm SPH. From the insights of thermodynamic and isotherm studies the metal-inhibitor interaction is believed to occur through the physisorption mechanism. The polarization curves propose SPH to function as a mixed inhibitor showing cathodic dominance in controlling mild steel corrosion. The development of the insulating barrier is well exemplified by the increasing diameter of the Nyquist plots. The surface analysis through SEM-EDS, AFM, XRD, and contact angle reports validate the active participation of SPH with the metal surface forming a stable protective layer. These results affirm the excellent anticorrosion behavior of SPH.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

V. Nijarubini  <https://orcid.org/0000-0001-7447-1444>

J. Mallika  <https://orcid.org/0000-0002-5709-2028>

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