



Thermodynamic Study of Chitosan as a Corrosion Inhibitor for Carbon Steel in Chloride Solutions (NaCl and HCl) at Various Temperatures and Concentrations

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Abstract

This research investigates the thermodynamic characteristics of chitosan as a corrosion inhibitor for carbon steel in chloride electrolyte environments, specifically saturated sodium chloride and 1 M hydrochloric acid, across different temperatures and concentrations. The study aimed to evaluate the effectiveness of chitosan in preventing corrosion and to examine the thermodynamic characteristics of the adsorption process. The results revealed that chitosan achieved the highest inhibition efficiency of 90.07% in a 1 M hydrochloric acid solution with a concentration of 250 mg/L at 303.15 K. In contrast, the maximum inhibition efficiency in a saturated sodium chloride solution was 50.50% at the same concentration of 250 mg/L and 303.15 K. Thermodynamic analysis showed that the adsorption of chitosan is spontaneous and exothermic in both media. The standard free energy of adsorption was found to be -38.63 kJ/mol at 303.15 K, decreasing to -43.69 kJ/mol at 343.15 K in saturated NaCl, and -42.40 kJ/mol at 303.15 K, decreasing to -48.65 kJ/mol at 343.15 K in 1 M HCl. The enthalpy of adsorption was -0.24976 kJ/mol in NaCl and 4.93560 kJ/mol in HCl, while the entropy of adsorption was -0.12661 J/mol·K in NaCl and -0.15610 J/mol·K in HCl. Additionally, the activation energy for corrosion increased from 1.61 kJ/mol at 0 mg/L to 6.96 kJ/mol at 250 mg/L chitosan in NaCl and from 4.10 kJ/mol at 0 mg/L to 23.79 kJ/mol at 250 mg/L chitosan in HCl. SEM analysis confirms the formation of a protective chitosan film, significantly reducing corrosion damage compared to uninhibited conditions. These findings indicate that chitosan is a highly effective corrosion inhibitor with favorable thermodynamic characteristics for applications in chloride-containing environments.

1. Introduction

Corrosion, defined as the degradation or destruction of materials through chemical interactions with their environment, leads to structural and chemical changes on the metal surface [1, 2]. The corrosion process involves the oxidation of metals by elements such as oxygen, water, and other chemical compounds and includes a series of electrochemical reactions influenced by environmental composition and the properties of the metal material [3]. In the chloralkali industry, corrosion of carbon steel pipes and storage tanks that interact with sodium chloride (NaCl) and hydrochloric acid (HCl) solutions can cause severe damage, threaten structural

integrity, induce leaks, and increase the cost of equipment replacement and production downtime [4]. One of the mechanisms that mitigate corrosion involves the formation of a protective layer on the metal surface, which disrupts the progression of corrosion reactions [5]. Therefore, understanding corrosion mechanisms and applying prevention strategies are crucial to reduce material, structural, and economic losses [6].

Corrosion prevention involves several technical methods, including coating techniques, cathodic protection, and corrosion inhibitors. These inhibitors are chemical compounds aimed at slowing down the corrosion rate on metals by interacting with the metal

surface, forming protective layers, or modifying electrochemical properties that inhibit corrosion. This approach has proven effective in maintaining the structural integrity of metals and provides both theoretical and practical foundations for developing more advanced corrosion prevention strategies [7].

Previous studies have tested various corrosion inhibitors, such as Ofloxacin, in HCl environments. The effect of ofloxacin as a corrosion inhibitor can be detected by monitoring changes in R_p (resistance polarization) and C_{dl} (double-layer capacitance) values. At higher concentrations, the R_p value increases, and the C_{dl} value decreases, signaling the creation of an adsorption layer that shields the steel surface from corrosion [8]. Additionally, Sulfathiazole on copper in NaCl solution exhibited an inhibition efficiency of 80.37% [9], and Metformin on steel in HCl environment showed an inhibition efficiency of 86.06% [10]. Furthermore, a mixture of pyridine, quinoline quaternary ammonium salts, and thiourea on X70 steel in a 3.5% NaCl solution with CO_2 at 60°C demonstrated an efficiency of 95.62% [11], and Terazosin at 150 ppm in 1.0 M HCl was also effective, with an efficiency of 94.8% [12].

Similarly, Bepotastine-B exhibited a maximum inhibition efficiency of 94.6% at a concentration of 300 mg/L [13], and N-(benzo[d][1,3]dioxol-5-ylmethylene)pyridin-2-amine showed an inhibition efficiency of 14.28% in 2 N HCl at a concentration of 1%, with an optimum corrosion rate of $1.2 \text{ mg cm}^{-2} \text{ day}^{-1}$ after a 4-hour immersion period [14]. Novel pyrazolo-pyrimidine compounds (C1 and C2) effectively inhibit zinc corrosion in 1 M HNO_3 , with maximum efficiencies of 92.06% for C1 and 79.36% for C2 at 700 ppm, acting as anodic inhibitors by forming a protective surface layer [15]. These studies indicate variations in inhibition efficiency based on the type of metal, the corrosion medium, and the specific inhibitor used.

Other studies also emphasize the importance of research on chitosan as an environmentally friendly corrosion inhibitor. Chitosan, with its abundant hydroxyl and amino groups, has significant potential to control the corrosion rate by forming strong protective layers resistant to corrosion [16]. Research on chitosan-montmorillonite nanocomposite as a corrosion inhibitor for mild steel in 1.0 M HCl solution shows that inhibition efficiency increases with the rise in inhibitor concentration, reaching a maximum value of 74.08% at a concentration of 0.5 g/L [17]. A deep understanding of the characteristics of each inhibitor is crucial for developing effective corrosion prevention strategies.

Several factors influencing the rate of corrosion have been identified in previous research, including the increase in environmental temperature, which significantly accelerates the corrosion reaction by increasing the kinetic energy of molecules and the conductivity of the electrolyte, thereby speeding up electrochemical reactions in the corrosion phenomenon [18]. In this context, further research is needed to understand the impact of these factors on corrosion and

to strengthen the scientific basis for developing more effective prevention methods.

This research presents novelty by deepening the thermodynamic analysis of corrosion and investigating the interactions between chitosan and carbon steel surfaces in specific electrolyte environments. The potentiodynamic polarization method is employed to analyze the corrosion rate and electrochemical properties of the metal. This technique yields electrochemical kinetic parameters, including corrosion current density, corrosion potential, and Tafel slopes (β_a and β_c) [11].

This research aims to investigate the effectiveness of chitosan as a corrosion inhibitor for carbon steel-saturated NaCl (300 g/L) and 1 M HCl solutions. In the chlor-alkali industry, known for its highly corrosive environment, saturated NaCl solutions with a concentration of 300 g/L are used as the primary raw material in the electrolysis process. This concentration was selected as it closely approximates the maximum solubility of NaCl in water, allowing for optimal electrolysis efficiency. Therefore, this study replicates real-world industrial conditions by employing saturated NaCl (300 g/L) as one of the test media. This approach aims to evaluate the effectiveness of chitosan as a corrosion inhibitor under operational conditions relevant to practical applications in the industry.

The study focuses on analyzing the influence of electrolyte solutions, temperature, and chitosan concentration on the corrosion rate while also evaluating inhibitor efficiency, adsorption mechanisms, thermodynamic parameters, and activation energy in the corrosion process. With a deeper understanding of these factors, the results are expected to contribute significantly to developing more effective and sustainable corrosion prevention strategies for industrial and environmental applications.

2. Experimental

2.1. Materials and Tools

The materials and equipment used in this study are essential for conducting the experiments and analyzing the results. Chitosan, purchased online, served as the primary corrosion inhibitor for the experiments. Carbon steel samples from Mojokerto, Jawa Timur, including the SS41 type, were used as test electrodes. The SS41 grade primarily comprises iron (Fe) at 98.87% and carbon (C) at 0.243%. Other alloying elements, such as manganese, silicon, and others, are present in smaller amounts and contribute to the material's overall properties. Sodium chloride (NaCl), acquired from a chemical store in Surabaya, Jawa Timur, prepared a saturated NaCl solution with a concentration of 300 g/L. Hydrochloric acid (HCl) from the same store was used to prepare a 1 M HCl solution for corrosion testing. Distilled water obtained from the chemical store in Surabaya was utilized for solution preparation and dilution. Acetic acid, also obtained from Surabaya, was employed to dissolve chitosan, creating chitosan solutions at concentrations of 0, 50, 150, and 250 mg/L.

In addition to the materials mentioned, standard laboratory equipment such as beakers, pipettes, a thermometer, a hot plate, sandpaper, a saw, a ruler, volumetric flasks, graduated cylinders, a spatula, and an analytical balance were used for the preparation, and handling of solutions and materials. Electrochemical testing was performed using an electrochemical cell with a carbon steel working electrode, a platinum electrode serving as the counter electrode, and a calomel electrode as the reference, connected to an Autolab potentiostat and controlled by software for data acquisition and analysis.

2.2. Material Preparation

The carbon steel specimens were sized to measure 4 cm × 1 cm × 0.3 cm and sanded with grit 120 and 800 sandpaper to achieve a smooth surface. One end of each sample was coated with epoxy adhesive to isolate the non-exposed area, leaving a 1 cm² area exposed for interaction with the test solutions. The samples were then rinsed with distilled water and dried.

2.3. Solution Preparation

A saturated NaCl solution was prepared by dissolving 300 grams of NaCl in distilled water until complete dissolution, then adjusting the total volume to 1000 mL. A 1 M HCl solution was diluted with 83 mL of 37% HCl with distilled water to a final volume of 1000 mL. Chitosan solutions at concentrations of 0, 50, 150, and 250 mg/L were prepared by dissolving chitosan in acetic acid and mixed with NaCl and HCl solutions to a total volume of 500 mL. The presence of acetic acid in the corrosion testing system is minimal. Acetic acid is used in a very small amount, with a concentration of 1% (v/v), and the volume used is only around 3 mL in the total solution volume. The dissolution of chitosan takes approximately 5 minutes to ensure complete dissolution in the acetic acid solution, which is then mixed with NaCl and HCl solutions.

2.4. Testing Process

The carbon steel electrodes were inserted into an electrochemical cell equipped with a platinum counter electrode and a saturated calomel reference electrode. The cell was connected to an Autolab potentiostat controlled by software to measure the polarization curves. Measurements were conducted at 303.15 K, 323.15 K, and 343.15 K using a hot plate and thermometer. The polarization measurements were performed within an electrode potential range of -0.6 V to -0.2 V, with a scanning rate of over 120 seconds.

2.5. Data Analysis

Polarization curves obtained from the electrochemical tests were analyzed to determine corrosion parameters, including corrosion current density (I_{corr}), corrosion potential (E_{corr}), anodic (β_a), and cathodic (β_c) Tafel constant. The thermodynamic parameters such as activation energy (E_a), Gibbs free energy of adsorption (ΔG°_{ads}), adsorption enthalpy (ΔH°_{ads}), and adsorption entropy (ΔS°_{ads}) were calculated

to evaluate the effectiveness of chitosan as a corrosion inhibitor.

3. Results and Discussion

3.1. Effect of Corrosion Inhibitor

The experimental results reveal that adding chitosan as a corrosion inhibitor significantly affects the corrosion rate and inhibition efficiency of carbon steel in saturated NaCl and 1 M HCl media at various temperatures and inhibitor concentrations. In the saturated NaCl medium, the efficiency of chitosan increased with its concentration but varied with temperature.

The corrosion rate in Table 1 is determined using potentiodynamic measurements, which generate a polarization curve linking potential and current density. The corrosion current density (I_{corr}) is obtained by extrapolating the log current versus the potential curve at the corrosion potential (E_{corr}). This intersection provides the corrosion current, which is used to calculate the corrosion rate. The data shows that the shift in E_{corr} with the inhibitor compared to the blank is less than 0.085 V, indicating that the corrosion protection type of the inhibitor for carbon steel is a mixed anodic and cathodic protection [19].

The Tafel polarization curves obtained during testing have been utilized to determine key electrochemical parameters, including the corrosion current density (I_{corr}), forming the basis for this study's analysis. Although the curves are not directly presented in the manuscript, the derived data have been processed to calculate the corrosion rate and inhibition efficiency (%IE) of chitosan as a corrosion inhibitor. The I_{corr} values provide quantitative insight into the ability of chitosan to mitigate corrosion on carbon steel. Using I_{corr} , the corrosion rate was calculated through Faraday's equation, ensuring a relevant and comprehensive analysis [20].

This approach is further supported by additional electrochemical methods, such as electrochemical impedance spectroscopy (EIS), to enrich the analysis and validate the results. The combination of I_{corr} with parameters like R_p enhances the understanding of the corrosion inhibition mechanism by chitosan [21]. Thus, even though the Tafel curves are not explicitly shown, the data derived from them have been fully utilized to ensure the accuracy and relevance of the study's findings. This demonstrates that analysis based on I_{corr} can provide significant insights into inhibitor performance across different corrosion conditions.

Table 1 shows that at 303.15 K, the inhibitor efficiency increased from 15.44% at 50 mg/L to 50.50% at 250 mg/L. However, at higher temperatures, such as 343.15 K, the efficiency decreased from 50.50% to 36.76% at the same concentration. The decrease in %IE at 343.15 K in saturated NaCl medium is due to the desorption of chitosan from the carbon steel surface caused by high kinetic energy, thermal degradation of chitosan, and the dominance of Cl⁻ ions that accelerate corrosion. This reflects the sensitivity of the physisorption mechanism of chitosan to high temperatures [22].

Table 1. Inhibition efficiencies and corrosion rates for various concentrations of chitosan in saturated NaCl and 1 M HCl at different temperatures

Medium	Temperature, T (K)	Inhibitor Concentration, C (mg/L)	Corrosion Potential, E_{corr} (V)	Corrosion Current Density, I_{corr} (A/cm ²)	Anodic Tafel Constant, β_a (mV)	Cathodic Tafel Constant, β_c (mV)	Corrosion Rate, CR (mpy)	Inhibitor Efficiency, IE (%)
NaCl	303.15	Blank	-0.40285	0.0000369	572.80	120.24	0.427390	-
		50	-0.41552	0.0000313	489.40	113.84	0.361410	15.44
		150	-0.41224	0.0000266	475.77	113.61	0.268640	37.14
		250	-0.40814	0.0000182	460.51	109.60	0.211540	50.50
	323.15	Blank	-0.43482	0.0000390	556.31	122.95	0.447640	-
		50	-0.41468	0.0000340	536.63	115.99	0.384390	14.13
		150	-0.43148	0.0000275	450.07	113.45	0.303720	32.15
		250	-0.38366	0.0000231	958.75	111.79	0.267460	40.25
	343.15	Blank	-0.39010	0.0000430	250.35	123.26	0.460366	-
		50	-0.40997	0.0000321	301.54	120.04	0.398290	13.48
		150	-0.41858	0.0000278	448.45	110.62	0.320160	30.46
		250	-0.42606	0.0000242	426.83	111.16	0.291140	36.76
303.15	Blank	-0.46173	0.000041	124.17	331.62	0.424182	-	
	50	-0.48071	0.000017	81.80	236.34	0.208770	50.78	
	150	-0.53519	0.000011	97.37	103.99	0.127880	69.85	
	250	-0.47805	0.000004	100.46	141.85	0.042118	90.07	
HCl	323.15	Blank	-0.48595	0.000035	86.84	332.30	0.468970	-
		50	-0.48853	0.000020	82.23	218.68	0.235410	49.80
		150	-0.47564	0.000014	82.13	253.56	0.159010	66.09
		250	-0.40781	0.000005	107.31	141.63	0.088012	81.23
	343.15	Blank	-0.48801	0.000027	84.78	308.97	0.512800	-
		50	-0.47865	0.000023	83.35	312.67	0.256050	50.07
		150	-0.48448	0.000016	78.61	230.54	0.190720	62.81
		250	-0.51767	0.000011	88.21	126.09	0.125730	75.48

Conversely, in the 1 M HCl medium, the inhibitor efficiency increased with the chitosan concentration, showing a more consistent trend at higher temperatures. At 303.15 K, the efficiency rose from 50.78% at 50 mg/L to 90.07% at 250 mg/L. At 343.15 K, the efficiency remained high, reaching 75.48% at 250 mg/L. These results indicate that chitosan is a more effective corrosion inhibitor in HCl medium than NaCl saturated medium and that inhibitor efficiency is influenced by temperature and concentration. The inhibition efficiency (IE) can be calculated using the Equation (1).

$$\%IE = \frac{CR_{blank} - CR_{inhibitor}}{CR_{blank}} \times 100\% \quad (1)$$

Where, %IE is the inhibitor efficiency, CR_{blank} is the corrosion rate without the inhibitor (mpy), and $CR_{inhibitor}$ is the corrosion rate with the inhibitor (mpy) [23].

In previous studies, chitosan and its derivatives have demonstrated significant potential as corrosion inhibitors due to their adsorption capability on metal surfaces, which forms a protective barrier and alters electrochemical properties. For instance, a study on chitosan-montmorillonite nanocomposites showed an increase in inhibitor efficiency with concentration, achieving a maximum of 74.08% at 0.5 g/L in 1.0 M HCl,

emphasizing that higher concentrations enhance corrosion protection [17]. Furthermore, functional groups such as -OH and -NH₂ in chitosan play a crucial role in adsorption, improving its effectiveness in acidic environments like hydrochloric acid. Research on synthesized chitosan-sodium pyruvate (Chi-SP) polymers combined with titanium dioxide (TiO₂ NPs) nanocomposites revealed improved structural, morphological, and electrochemical properties, which make them effective corrosion inhibitors for Cu-Ni alloys in HCl solutions [24]. These studies underscore the importance of chitosan's chemical structure and interaction with metal surfaces in achieving high corrosion inhibition efficiencies, demonstrating its applicability in industrial environments.

The comparison of these results indicates that inhibitor efficiency is greatly influenced by the type of corrosion medium, type of inhibitor, inhibitor concentration, and temperature. This research shows that chitosan is effective as a corrosion inhibitor, particularly in an HCl medium, but its efficiency decreases at high temperatures in a NaCl medium. This is due to the desorption of the inhibitor at high temperatures, which increases the kinetic energy of the molecules [11]. Other studies show increased efficiency

with higher inhibitor concentrations, consistent with this research [9, 10, 17]. However, some studies show that higher temperatures can enhance efficiency, especially with additives like KI in metformin [10]. These differences may be due to the thermal stability of each inhibitor and their specific interactions with the corrosion medium [25]. Combining inhibitors or using more thermally stable inhibitors can improve inhibition efficiency under various conditions.

3.2. Adsorption Isotherms and Thermodynamic Parameters

In this study, the effectiveness of chitosan as a corrosion inhibitor was analyzed using the Langmuir isotherm model to understand the adsorption behavior of chitosan on the carbon steel surface. The Langmuir model, used to describe the interaction between chitosan and the metal surface, assumes that adsorption occurs at active sites that can hold only one inhibitor molecule per site, forming a monolayer on the metal surface [26]. The Langmuir equation utilized in this analysis is presented in Equation (2).

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{2}$$

In Equation (2), C represents the chitosan concentration in the solution, θ is the fraction of the carbon steel surface covered by chitosan, and K is the Langmuir adsorption constant reflecting the interaction strength between chitosan and the metal surface. The fit of the data to the Langmuir model was examined by plotting $\frac{C}{\theta}$ against C , which results in a graph with an intercept of $\frac{1}{K}$. Based on this information, K_{ads} is $\frac{1}{intercept}$ [27].

The analysis results show in Figure 1 and Table 2 that the adsorption equilibrium constant, K_{ads} value in saturated NaCl media, decreases as the temperature increases from 303.15 K to 343.15 K. This decrease in K_{ads} indicates that the adsorption capability of chitosan on the carbon steel surface decreases with increasing temperature in NaCl media, which is caused by the increase in molecular kinetic energy at higher temperatures leading to the desorption of chitosan from the metal surface [11].

On the other hand, in 1 M HCl media, there is an increase in K_{ads} with increasing temperature. This finding

indicates that chitosan is more effective in adsorbing onto the carbon steel surface in HCl media at higher temperatures than saturated NaCl. The increase in K_{ads} at higher temperatures in 1 M HCl is likely due to enhanced chitosan diffusion to the metal surface or decreased solution viscosity that improves adsorption efficiency [3].

Furthermore, the standard free energy of adsorption ΔG°_{ads} calculation provides insight into the stability and affinity of chitosan for the carbon steel surface. The standard free energy of adsorption is calculated in Equation (3).

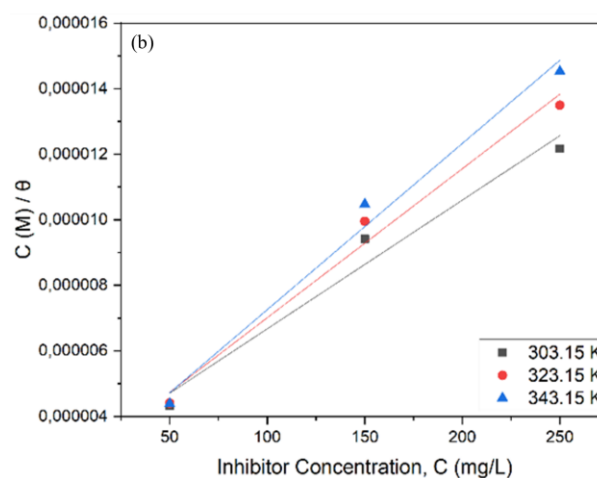
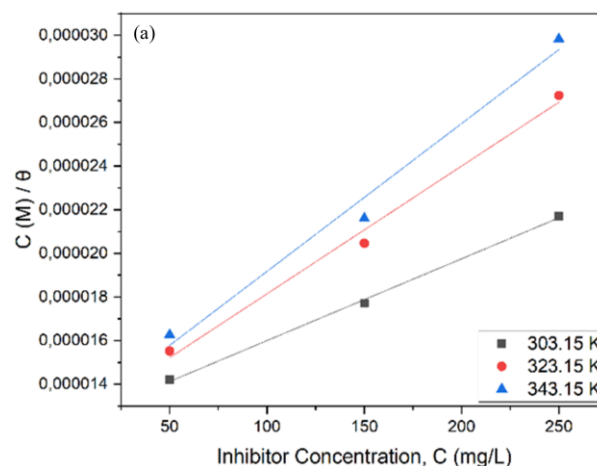


Figure 1. Langmuir adsorption isotherm model and correlation curves for different chitosan concentrations: (a) saturated NaCl solution and (b) 1 M HCl solution

Table 2. The Langmuir adsorption isotherm parameters for the adsorption of chitosan molecules onto the carbon steel surface

Medium	Temperature, T (K)	R ²	K _{ads} (L/mol)	ΔG [°] _{ads} (kJ/mol)
NaCl	303.15	0.99	81653.64445	-38.63
	323.15	0.99	81404.88423	-41.17
	343.15	0.99	80705.40248	-43.69
HCl	303.15	0.97	364256.83429	-42.40
	323.15	0.98	405832.44445	-45.49
	343.15	0.99	457914.05771	-48.65

$$\Delta G^{\circ}_{ads} = -RT \ln (55.5 K_{ads}) \quad (3)$$

Where, R is the gas constant ($8.314 \text{ J/mol}\cdot\text{K}$), T is the temperature in Kelvin, and K_{ads} is the adsorption constant obtained from experimental data. The value 55.5 originates from calculating the molar concentration of water in an aqueous solution at 25°C . Water has a molar mass of about 18 g/mol , and at this temperature, the density of water is approximately 1 g/mL . This results in a molar water concentration in a solution of about 55.5 mol/L . This value is used in calculating the standard free energy of adsorption in the Langmuir model, as water is considered the main solvent in aqueous solutions, and this concentration of water is treated as constant even when inhibitor molecules are adsorbed.

The results show that ΔG°_{ads} decreases from -38.63 kJ/mol at 303.15 K to -43.69 kJ/mol at 343.15 K in saturated NaCl media and from -42.40 kJ/mol to -48.65 kJ/mol in 1 M HCl . Thus, the negative ΔG°_{ads} values indicate that the chitosan adsorption process on the carbon steel surface is spontaneous. The increasingly negative ΔG°_{ads} values indicate improved stability and efficiency of adsorption [28].

Adsorption is generally categorized into two main types: physical adsorption (physisorption) and chemical adsorption (chemisorption). Physical adsorption occurs with adsorption energy greater than -20 kJ/mol , whereas chemical adsorption typically involves adsorption energy less than -40 kJ/mol . Adsorption with energies in this range can be categorized as a mix of physical and chemical adsorption [29].

In the context of this study, the ΔG°_{ads} values for chitosan in saturated NaCl solution range from -38.63 kJ/mol to -43.69 kJ/mol , and in 1 M HCl , it ranges from -42.40 kJ/mol to -48.65 kJ/mol . The ΔG°_{ads} values in this range indicate that chitosan adsorption on carbon steel is characterized as chemical adsorption and a mix of physical and chemical adsorption. This indicates that the interaction between chitosan and carbon steel involves both physical interactions, such as van der Waals forces, and stronger chemical bonding [8].

The results of this study are compared with previous research on the effect of temperature on K_{ads} and ΔG°_{ads} . Another study investigating the adsorption of inhibitors on X70 steel in $3.5\% \text{ NaCl}$ solution saturated with CO_2 using quaternary ammonium salt, and thiourea shows that K_{ads} decreases with increasing temperature [11]. The study explains that increasing temperature raises the kinetic energy of molecules, potentially reducing inhibitor adsorption, which aligns with the observed decrease in K_{ads} in NaCl media in this study.

In contrast, another study explored the adsorption of Terazosin on carbon steel in 1 M HCl solution and found that K_{ads} increases with higher temperatures [12]. This result shows that Terazosin adsorption becomes more efficient at higher temperatures, which aligns with the findings in this study, where K_{ads} also increases in 1 M HCl at higher temperatures. The study suggests that acidic conditions generally promote increased adsorption efficiency with temperature. However, in this study, it

was observed that higher temperatures did not improve the inhibition efficiency of chitosan in 1 M HCl . Instead, the inhibition efficiency decreased with higher temperatures, suggesting that elevated temperatures might interfere with forming the protective layer on the metal surface, reducing the inhibitor's effectiveness. Therefore, temperature does not enhance the efficiency of chitosan as a corrosion inhibitor in this case.

This analysis shows that the effect of temperature on K_{ads} and ΔG°_{ads} varies depending on the corrosion medium. In saturated NaCl, higher temperatures decrease K_{ads} , while in HCl, higher temperatures increase K_{ads} . Additionally, the ΔG°_{ads} value tends to become more negative as the temperature increases, even though K_{ads} increases in HCl. In contrast, in NaCl, K_{ads} decreases at higher temperatures, and although ΔG°_{ads} remains negative, it is not as pronounced as in HCl. These findings emphasize the importance of selecting appropriate experimental conditions to optimize corrosion inhibitor effectiveness and demonstrate that chitosan as an inhibitor has greater potential in acidic media at higher temperatures compared to saturated salt media. Although higher temperatures increase K_{ads} in HCl, the %IE value decreases due to the increased corrosion rate at higher temperatures, which reduces the inhibitor's overall effectiveness.

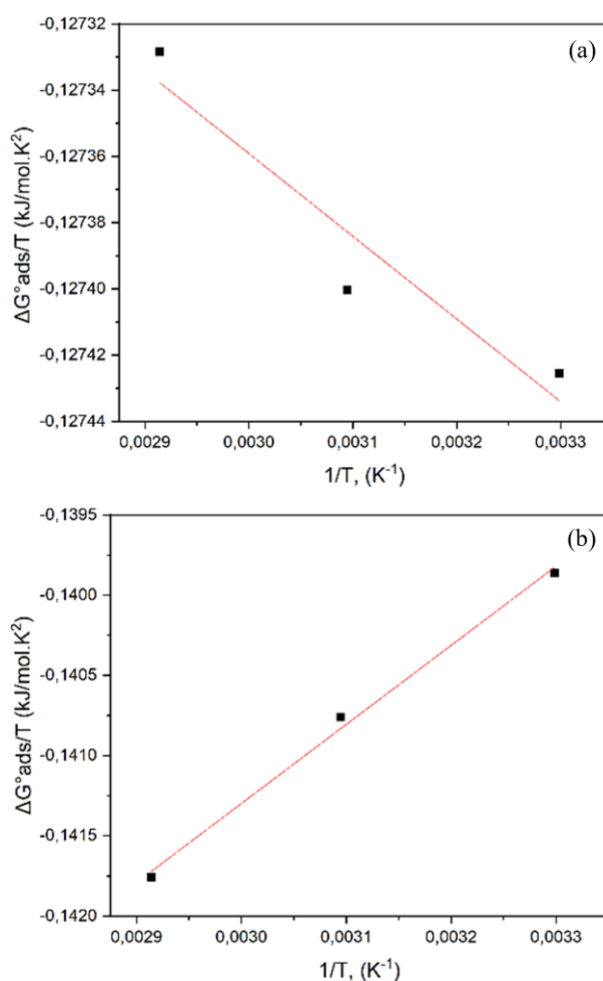


Figure 2. Van't Hoff and Gibbs-Helmholtz relations. The relationships between $\frac{\Delta G^{\circ}_{ads}}{T}$ and $\frac{1}{T}$. (a) saturated NaCl solution, (b) 1 M HCl solution

Table 3. The thermodynamic parameters for the adsorption of chitosan molecules onto the carbon steel surface

Medium	ΔH°_{ads} (kJ/mol)	ΔS°_{ads} (kJ/K mol)
NaCl	-0.24976	-0.12661
HCl	4.93560	-0.15610

To gain a deeper understanding of the thermodynamics of chitosan adsorption on carbon steel, it is crucial to analyze the changes in enthalpy (ΔH°_{ads}) and entropy (ΔS°_{ads}) during the adsorption process. The changes in enthalpy and entropy can be calculated using the Van't Hoff equation with the Gibbs-Helmholtz in Equation (4).

$$\frac{\Delta G^{\circ}_{ads}}{T} = \frac{\Delta H^{\circ}_{ads}}{T} - \Delta S^{\circ}_{ads} \quad (4)$$

By plotting $\frac{\Delta G^{\circ}_{ads}}{T}$ against $\frac{1}{T}$, the slope of the resulting line represents ΔH°_{ads} , and the intercept represents $-\Delta S^{\circ}_{ads}$ [30].

The Van't Hoff plots for chitosan adsorption on carbon steel in saturated NaCl and 1 M HCl media are presented in Figure 2. Based on the slope and intercept of the linear regression lines in these plots, the ΔH°_{ads} and ΔS°_{ads} values were calculated for both media.

In saturated NaCl media, ΔH°_{ads} was found to be -0.24976 kJ/mol, and ΔS°_{ads} was -0.12661 kJ/mol. The negative ΔH°_{ads} value indicates that the adsorption process is exothermic, meaning that heat is released during the adsorption process. The negative ΔH°_{ads} value suggests a decrease in disorder (entropy) at the interface between chitosan and the carbon steel surface during the adsorption process, indicating that the adsorption layer becomes more ordered.

Conversely, in 1 M HCl media, ΔH°_{ads} was 4.93560 kJ/mol, while ΔS°_{ads} was -0.15610 kJ/mol. The positive ΔH°_{ads} value indicates an endothermic process, requiring energy absorption during adsorption. The more negative ΔS°_{ads} compared to saturated NaCl media suggests a greater decrease in disorder at the interface in HCl, likely due to stronger interactions between chitosan and the carbon steel surface under acidic conditions [26].

Based on the ΔH°_{ads} and ΔS°_{ads} values, it can be concluded that the adsorption of chitosan on carbon steel in saturated NaCl media is an exothermic process with a decrease in entropy, indicating that the adsorption layer formed is more ordered. Conversely, in 1 M HCl media, the adsorption of chitosan is an endothermic process with a greater decrease in entropy, indicating that the interactions between chitosan and the carbon steel surface are stronger under acidic conditions.

The differences in enthalpy and entropy between the two media indicate that the adsorption process is influenced by both thermal effects and the structure of the solution. The more ordered adsorption process and stronger interactions in HCl media suggest that chitosan has greater potential as a corrosion inhibitor under acidic

conditions. Therefore, thermodynamic analysis using the Van't Hoff equation enhances our understanding of the adsorption mechanism of chitosan as a corrosion inhibitor on carbon steel, providing additional insights into the stability and thermodynamic properties of the interaction between chitosan and the metal surface under various corrosion conditions.

3.3. Thermodynamic Activation Parameters of The Corrosion Process

After discussing the enthalpy and entropy of adsorption, the next step is to analyze the activation energy (E_a) of the corrosion process using the Arrhenius equation. Activation energy provides information on how much energy is required to initiate corrosion and the inhibitor's impact on the corrosion rate.

The activation energy E_a for the corrosion process is calculated using the Arrhenius equation in Equation (5).

$$C_R = A \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

Where, C_R is the corrosion reaction rate (mpy or mg/cm²h), A is a constant depends on a metal type and electrolyte (mpy or mg/cm²h), E_a is the activation energy for the corrosion process (J/mol K), R is the ideal gas constant (8.314 J/mol·K), T is the temperature in Kelvin [26].

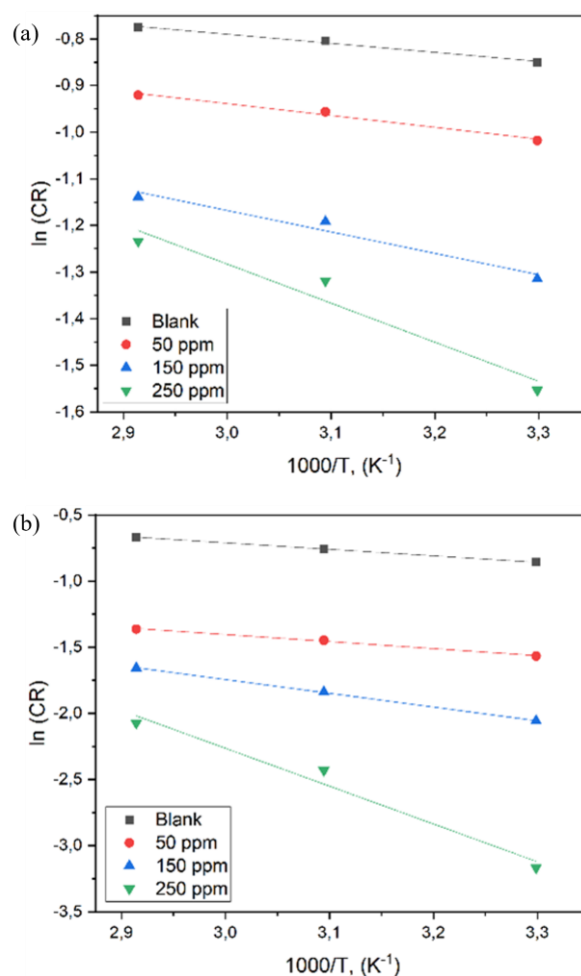


Figure 3. Plotting Arrhenius equation $\ln C_R$ versus $\frac{1}{T}$ for various concentrations of chitosan. (a) Saturated NaCl solution, (b) 1 M HCl solution

Table 4. Activation parameters as a function of chitosan concentration

Media	Inhibitor Concentration, C (mg/L)	R ²	Activation Energy, E _a (kJ/mol)
NaCl	Blank	0.99	1.61
	50	0.99	2.11
	150	0.96	3.82
	250	0.95	6.96
HCl	Blank	0.99	4.10
	50	0.99	4.42
	150	0.99	8.65
	250	0.97	23.79

To determine E_a, the Arrhenius equation can be reformulated in a logarithmic form (Equation (6)).

$$\ln C_R = \ln A - \frac{E_a}{RT} \tag{6}$$

From Equation (6), a plot of ln C_R versus $\frac{1}{T}$ will yield a straight line with a slope of $-\frac{E_a}{R}$, where E_a can be calculated from the slope of the line [26].

In this study, the activation energy for the corrosion process was measured at various chitosan concentrations in two different media: saturated NaCl and 1 M HCl. The results of the activation energy analysis are shown in Table 4. In saturated NaCl media, the activation energy E_a was calculated at different chitosan concentrations, showing increased activation energy with higher chitosan concentrations. Specifically, E_a increased from 1.61 kJ/mol at 0 mg/L chitosan to 6.96 kJ/mol at 250 mg/L chitosan. The increase in E_a with higher chitosan concentrations indicates that chitosan raises the energy barrier for the corrosion process. This means that chitosan inhibits the corrosion rate by increasing the energy required for the corrosion reaction to occur on the carbon steel surface.

In 1 M HCl media, E_a increased from 4.10 kJ/mol at 0 mg/L to 23.79 kJ/mol at 250 mg/L. The increase in E_a in 1 M HCl media shows that chitosan is more effective at inhibiting corrosion at higher concentrations. The larger increase in E_a in HCl compared to NaCl indicates that chitosan significantly hinders the corrosion process at higher concentrations.

These findings indicate that chitosan acts as a corrosion inhibitor by increasing the activation energy for the corrosion process in both media. At higher concentrations, chitosan raises the energy barrier for the corrosion reaction, thereby reducing the corrosion rate [12]. The differences in E_a values between saturated NaCl and 1 M HCl media show that chitosan is a more effective corrosion inhibitor in acidic conditions. This aligns with the observation that higher chitosan concentrations enhance the energy barrier for corrosion, demonstrating greater potential as a corrosion inhibitor under acidic conditions.

3.4. SEM Analysis

Scanning Electron Microscope (SEM), analysis provides a deep understanding of the changes in carbon steel surfaces after exposure to various corrosive media, both with and without inhibitors [25]. This evaluation compares the condition of the metal surface before and after contact with corrosive media and assesses the differences arising from using inhibitors. The images below offer a clear visualization of the metal surface conditions before and after exposure to corrosive media and the effects of inhibitor use.

3.4.1. Carbon Steel Blank

The SEM image shows that the surface of carbon steel before exposure to corrosive media is very smooth and clean, without significant scratches or defects. This surface indicates an optimal condition of the metal, free from contamination or degradation, providing a clear baseline for comparison with conditions after exposure to corrosive media. The image was captured at a magnification of 500×, allowing detailed visualization of the surface morphology.

3.4.2. Carbon Steel in Saturated NaCl without Inhibitor

The carbon steel surface exposed to saturated NaCl without an inhibitor shows significant damage with many pits, cracks, and corrosion deposits. This indicates an aggressive chemical reaction between the metal and chloride ions, leading to the formation of corrosion compounds and extensive material degradation. The metal experiences severe corrosion attacks without an inhibitor, highlighting the importance of protection to prevent such damage. The image is taken at a magnification of 1000×, providing a detailed view of the corrosion effects on the metal surface.

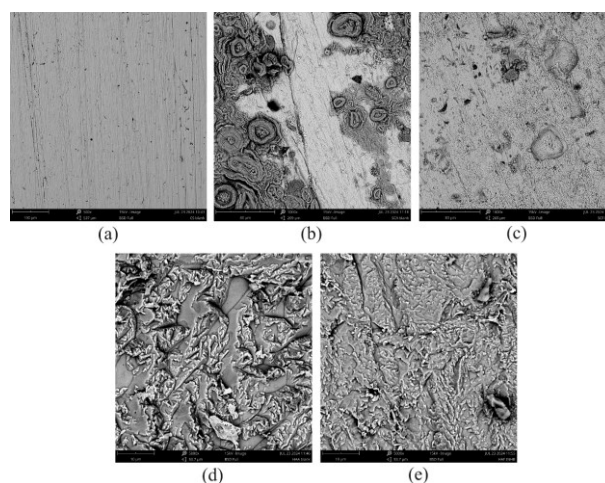


Figure 4. Micrographs of carbon steel under various conditions: (a) Carbon steel blank, (b) Carbon steel in saturated NaCl without inhibitor, (c) Carbon steel in saturated NaCl + chitosan 250 ppm, (d) Carbon steel in HCl 1 M without inhibitor, and (e) Carbon steel in HCl 1 M + chitosan 250 ppm

3.4.3. Carbon Steel in Saturated NaCl + Chitosan 250 ppm

On the surface of carbon steel exposed to saturated NaCl with added chitosan, corrosion damage appears much less compared to the condition without an inhibitor. There are signs of corrosion, such as scratches and deposits, but the amount and depth of damage are significantly reduced. This shows that chitosan effectively forms a protective layer that reduces the corrosion rate, indicating its effectiveness in extending the lifespan of the metal. The image is taken at a magnification of 1000×, providing a detailed view of the corrosion reduction with chitosan.

3.4.4. Carbon Steel in HCl 1 M without Inhibitor

The carbon steel surface exposed to HCl 1 M without an inhibitor shows severe damage with numerous pits and corrosion cavities. Hydrochloric acid is highly aggressive, causing significant degradation to the metal. The corrosion products formed erode the metal surface, illustrating the critical need for inhibitor protection in acidic environments. The image is taken at a magnification of 5000×, providing a detailed view of the extensive damage caused by the aggressive corrosion in the HCl solution.

3.4.5. Carbon Steel in HCl 1 M + Chitosan 250 ppm

Carbon steel exposed to HCl 1 M with added chitosan shows a much better surface condition than without an inhibitor. Corrosion damage is significantly reduced with a smoother surface and fewer corrosion deposits. This indicates that chitosan effectively forms a protective layer, reduces direct interaction between the metal and corrosive medium, and inhibits the corrosion process. The image is taken at a magnification of 5000×, providing a detailed view of the improved surface condition after treatment with chitosan.

The SEM analysis in this study reveals that using an inhibitor significantly reduces the corrosion rate of carbon steel exposed to various corrosive media compared to the conditions without an inhibitor. These results align with previous findings, though notable differences are worth addressing. Previous studies have shown that certain inhibitors form a more robust protective film on carbon steel than those used in this study. The SEM analysis in this study revealed significant differences in the surface morphology of zinc exposed to 1 M HNO₃, showing distinct corrosion products between untreated zinc and zinc treated with inhibitors C1 and C2, indicating the effectiveness of these compounds in reducing corrosion [15].

Additionally, other studies have reported that certain inhibitors significantly reduced damage to X65 steel; however, the effectiveness of the inhibitor in this study did not reach the same level, possibly due to differences in the type or concentration of the inhibitor [23]. Some studies have also observed that inhibitors maintain a smoother surface, though variations in smoothness can be attributed to different mechanisms of action [31, 32]. Significant reductions in corrosion were also reported with the use of inhibitors on stainless steel and mild steel,

while in this study, the reduction effects varied depending on the corrosive medium and the type of inhibitor [30, 33]. Other research has shown differences in surface morphology depending on the combination of inhibitors, which explains the differing results in this study [11]. Overall, these differences highlight the importance of considering various factors, such as the type and concentration of inhibitors and experimental conditions, when evaluating the effectiveness of inhibitors in protecting metals from corrosion.

4. Conclusion

This study demonstrates that chitosan is a highly effective corrosion inhibitor for carbon steel in chloride electrolyte solutions, particularly in saturated NaCl and 1 M HCl. The results revealed that chitosan achieved the highest inhibition efficiency of 90.07% in a 1 M hydrochloric acid solution at a concentration of 250 mg/L and 303.15 K, while the maximum inhibition efficiency in a saturated sodium chloride solution was 50.50% under the same concentration and temperature conditions. Thermodynamic analysis showed that chitosan adsorption is spontaneous and exothermic in both media. The standard free energy of adsorption was found to be -38.63 kJ/mol at 303.15 K, decreasing to -43.69 kJ/mol at 343.15 K in saturated NaCl, and -42.40 kJ/mol at 303.15 K, decreasing to -48.65 kJ/mol at 343.15 K in 1 M HCl. The enthalpy of adsorption was -0.24976 kJ/mol in NaCl and 4.93560 kJ/mol in HCl, while the entropy of adsorption was -0.12661 J/mol·K in NaCl and -0.15610 J/mol·K in HCl, indicating the formation of a stable, protective layer. Furthermore, the activation energy for corrosion increased significantly with chitosan concentration, from 1.61 kJ/mol at 0 mg/L to 6.96 kJ/mol at 250 mg/L in NaCl and from 4.10 kJ/mol at 0 mg/L to 23.79 kJ/mol at 250 mg/L in HCl, further supporting the inhibition mechanism. SEM analysis confirmed the formation of a chitosan film on the carbon steel surface, significantly reducing corrosion damage compared to the uninhibited surface. These findings indicate that chitosan is an environmentally friendly corrosion inhibitor and an effective solution with favorable thermodynamic properties for chloride-containing environments. Future research should focus on optimizing chitosan concentrations and exploring its potential in other aggressive corrosive media for industrial applications.

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