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Article

Effect of Cetyl Pyridinium Chloride on Corrosion Inhibition Properties of Mild Steel in Acidic Medium

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Abstract: The corrosion inhibition behavior of cetyl pyridinium chloride (CPC) on mild steel in 0.5 M H₂SO₄ solution was examined using measurement techniques such as Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM), and Atomic Force Microscopy (AFM). The studies were carried out within a 25°C temperature range. The surface morphology of the corroded steel samples was investigated using FESEM and AFM. The results show that cetyl pyridinium chloride (CPC), a mild steel corrosion inhibitor, effectively prevents corrosion in 0.5 M H₂SO₄ and, when present, increases corrosion resistance. CPC has a stronger inhibitory effect on mild steel. The FESEM and AFM images clearly show how surface morphology changes when additives are present. The weight loss results were confirmed by energy dispersive X-ray (EDX) spectroscopy analysis, and a value of 98.54% was obtained from potentiodynamic polarization studies at 0.0077M CPC. CPC acts as an important corrosion inhibitor.

Keywords: FTIR; FESEM; EDX; inhibitor; mild steel; cetyl pyridinium chloride

1. Introduction

Mild steel is widely used in the building, transportation, and maritime industries due to its high mechanical and thermal stability, low cost, and availability. However, mild steel is prone to rust, especially in marine environments [1]. As a result, many methods have been employed to prevent steel from corroding, including electroplating, thermal spraying, micro-arc oxidation, and the application of organic coatings. Organic coatings are the most widely used method of preventing corrosion. Since organic adsorption isolates the steel substrate from corrosive media, it can effectively offer steel long-lasting protection. However, during the curing process, the solvent evaporation of pure organic adsorption might give rise to micropores, which inevitably affects the adsorption's barrier qualities [2]. A fundamental, scholarly, and industrial problem that has received a lot of attention recently is mild steel corrosion. One of the most practical and affordable ways to prevent corrosion on metallic surfaces in very acidic environments is to use inhibitors [3]. In a variety of sectors, pickling steel at temperatures as high as 60°C is a common usage for mineral acids. This technique is effective not only at cleaning industrial equipment but also at acidizing oil wells and eliminating corrosion scales from steel surfaces without destroying the metal [4].

The most potent pickling inhibitors are organic compounds containing heteroatoms, such as oxygen, phosphorus, nitrogen, sulfur, and many linkages or aromatic rings. The amount of loosely bound p-electrons and lone pairs of electrons in these functional groups are important structural elements that affect these compounds' inhibitory effect. These compounds reduce the amount of

active corrosion sites on the metal surface by adsorption, protective layer deposition, or the creation of an insoluble mixture [5].

Unfortunately, the majority of organic compounds used as corrosion inhibitors are dangerous to humans and the environment, thus safer, more environmentally friendly alternatives must be used in their place. Thus, the primary focus of current research trends is the creation of ecologically benign, cost-effective, and nontoxic green chemicals for corrosion inhibition.

Because they are completely soluble in aqueous solutions, biodegradable, nontoxic, and easily manufactured in high purity at a low cost, amino acids are frequently used as corrosion inhibitors [6]. It has been discovered that the sulfur-containing amino acid L-methionine is a potent corrosion inhibitor. Using Tafel polarization measurements, nineteen naturally occurring amino acids—including methionine—were examined for their ability to suppress the corrosion of mild steel in H₂SO₄ [7].

The current study examined the corrosion inhibition activity of CPC at low concentrations on mild steel in a 0.5 M H₂SO₄ solution. Weight loss, potentiodynamic polarization measures, FTIR, FESEM, and AFM were the characterization techniques used in the present study. Depending on the surfactant concentration, the adsorbed molecules form monolayers, bilayers, or micelles, which block acid from reaching the surface and hence reduce corrosion attacks [8]. The surfactant can boost their effectiveness as inhibitors. Surfactants interact with mild steel surfaces, increasing corrosion resistance [9]. One of the most practical ways to prevent metal from corroding is to utilize organic compounds, such as cetyl pyridinium chloride (CPC), as a corrosion inhibitor. This technique is gaining popularity. Based on available data, organic inhibitors function through adsorption and create a protective coating around the metal. Corrosion can be effectively inhibited by organic compounds like cetyl pyridinium chloride (CPC), which include heteroatoms with high electron density, such as phosphorus, sulfur, nitrogen, and oxygen, or by compounding numerous bonds that act as adsorption centres [10]. Among the inhibitors that work well in acidic solutions are those that contain nitrogen, such as mercapto functional compounds and derivatives of amines like pyridazine, quinoline, and pyridine, as well as pyrazole, pyrazine, acridine, benzimidazole, and triazole. The majority of these compounds have demonstrated mixed-type corrosion inhibition in acidic solutions, protecting mild steel. Benzothiazoles have been employed as corrosion inhibitors for copper and steel in literature reviews [11], although the focus of this paper's studies is on the inhibitory properties of cationic surfactant on mild steel in acidic environments. Surface analytical approaches are needed to characterize corrosion inhibitor films to have a comprehensive understanding of the adsorption mechanism for corrosion inhibitors. According to [12], weight loss and potentiodynamic measurement, FTIR, and Raman spectroscopy have proven to be effective methods for examining corrosion processes and inhibitor performance in various settings.

The capacity of surfactant molecules to assemble at surfaces and in solution is linked to their ability to suppress corrosion. Based on the surfactant inhibitor's micellar characteristics in a given media, its efficacy can be investigated [13].

Depending on the surfactant concentration, the adsorbed molecules form a monolayer, bilayer, or micelle hemimicelles, which lessen corrosion attacks by preventing acid from attacking the surface. To increase other drugs' effectiveness as inhibitors, the surfactant can be employed either by itself or in combination with them [14]. Acids and surfactants are likely to interact to create complex structures that aid in adhesion to the surface and provide increased corrosion resistance [15]. The goal of this investigation is to learn more about how CPC inhibits corrosion on mild steel in a 0.1 M H₂SO₄ solution. Measurements of weight loss, potentiodynamic polarization, FESEM, EDX, FTIR, Raman spectroscopy, and AFM are among the methods employed.

2. Materials and Methods

2.1. Materials

The mild steel used in corrosion inhibition studies had the following composition (wt%): 0.20 C, 0.53 Mn, 0.036 Si, 0.11 S, 0.098 P, and Fe for the remainder. The examples, which measured 15.92, 13.38, and 1.31 cm, were press-cut from mild steel sheets, machined, and abraded with emery sheets.

This was followed by a rinse with acetone and double distilled water before air drying. Before any experiment, the substrates were produced as directed and used immediately without further storage. The inhibitor CPC (molecular mass: 358 g/mol) was used exactly as received. A stock solution of 0.00192M and 0.0077M CPC was prepared in 0.5 M H₂SO₄ (AR grade), and the required concentration was obtained through appropriate dilutions. The concentrations of CPC used in the study ranged from low to high. All solutions were prepared using double-distilled water. The experiment was carried out at 25°C, with temperatures maintained using a thermostated water bath. Figure 1 shows the molecular structure of the CPC.

The surface morphology of the steel sample that has corroded both with and without the inhibitors was studied using FTIR (Model no: Bruker company limited, America), FESEM (model: JSM IT800, JEOL Field emission scanning electron microscopy, Made in Japan), EDX (Model no: Elect Super Company EDAX, Made in America) and AFM (model: Jp 02069 JPK Nanowizard, Bruker). The surface morphology of mild steel was studied by looking for surface imperfections, such as pits or obvious abnormalities like cracks, under an optical microscope before any corrosion response began [16][17]. Solely the specimens possessing a smooth, pit-free surface were submerged. The samples were submerged at 25 °C for six hours. Following the test, the specimens underwent a comprehensive cleaning process in double-distilled water, followed by drying and examination with an FTIR, FESEM, and AFM.



Figure 1. Cetyl pyridinium chloride.

2.2. Weight Loss Measurements

The recently built mild steel specimens were suspended in 50 mL beakers containing 25 mL of the test solution and maintained at 25°C in a thermostated water bath equipped with glass rods and hooks. The weight loss was computed by subtracting the specimens' original weight from their weight at a specific moment in time [8]. Both the uncontrolled solution and the solution containing CPC surfactant mixes were subjected to the measurements. Weight loss experimentation took six hours. The average corrosion rate was determined after the specimens were dipped three times. Less than 5% separated the three identical measurements from one another. The following formula was used to determine the corrosion rates.

$$\text{Corrosion Rate (CR)} = \frac{\text{Weight loss (W)}}{\text{Area (A)} \times \text{Time (T)} \times \text{Density (d)}} \times 8.76 \times 10^4$$

where W is the weight loss of the MS (g) after immersion time, t (hours), A is the MS's area (cm²), and d is the MS's density (g cm⁻³).

$$\text{Inhibition Efficiency (IE) \%} = \frac{(W_o - W_i)}{W_o} \times 100$$

where W_o is the MS weight loss in the absence of an inhibitor and W_i is the MS weight loss in the presence of an inhibitor.

$$\text{Inhibition Efficiency (IE) \%} = (W_o - W_i / W_o) \times 100$$

where W_o is the MS weight loss in the absence of an inhibitor and W_i is the MS weight loss in the presence of an inhibitor.

2.3. Potentiodynamic Polarization Measurements

Three electrode systems were used for potentiodynamic polarization measurements, and each device was Gamry controlled by a PC running AUTOLAB's general-purpose electrochemical system

(GPES) software. The experiments were conducted using. The working electrode is a mild steel sample, the counter electrode is platinum wire, and the reference electrode is a saturated calomel electrode (SCE+ 0.241V) [18].

Potentiodynamic polarization was recorded from -0.3 V to +0.3 V vs. OCP at a scan rate of 0.5 mV/s, examining the potential from cathodic to anodic limits. greater energy than the constant open circuit voltage [4]. All measurements were conducted at room temperature, 25°C. Before starting the measurements, the specimen was submerged in the solution for thirty minutes to create a steady state, as shown by a constant potential. From the measured I_{corr} values, the IE was calculated using the following relationship [17]:

$$\text{Corrosion inhibition efficiency} = \frac{I_{Corr} - I^*_{Corr}}{I_{Corr}} \times 100 \%$$

where I^*_{corr} = corrosion current when an inhibitor is present, and I_{corr} = corrosion current when an inhibitor is not present.

3. Results and Discussion

3.1. Weight Loss Measurements

The corrosion behavior of mild steel in 0.5 M H₂SO₄ with and without varying CPC concentrations was investigated at 25°C using a weight loss approach. Table 1 presents the results of the six-hour immersion. With the temperature at 25°C and the inhibitor concentration, CPC reduces the rate of mild steel corrosion proportionately when compared to a free acid solution [4].

The IE increases with rising CPC concentrations. As inhibitor concentration rises, more CPC molecules are adsorbed on the steel surface at higher concentrations because of the increased IE, which enhances surface coverage and results in the formation of a protective layer. The relatively low IE at lower CPC concentrations may be due to the solubility of adsorbed intermediates generated on the surface as well as the limited surface coverage brought on by the tiny molecular area [19]. At 25°C, individual tests of mild steel corrosion in 0.5 M H₂SO₄ with and without different CPC concentrations were conducted to examine the impact of CPC on its corrosion-inhibitory behavior. The results are presented in Table 1.

S.N.	Concentration	Corrosion rate (Acm ⁻¹)	% of Inhibition efficiency
1	0.5 M H ₂ SO ₄	1.20949×10 ⁻⁰⁴	
2	0.00192 M CPC	8.23565×10 ⁻⁰⁵	99.66
3	0.0077 M CPC	6.63607×10 ⁻⁰⁷	99.99

Figure 1. weight loss measurement of mild steel in 0.5 M H₂SO₄ in the absence of and presence of CPC.

It has been found that IE is more affected by higher surfactant concentrations. The kind and concentration of surfactant molecules determine how they adsorb on surfaces. Although the adsorption of cationic surfactants on like-charged surfaces is less well understood, hydrogen bonding or attractive dispersion forces may play a role, just like in the case of nonionic surfactants. At low surfactant concentrations, the adsorption behavior is typically explained by a simple electrical double-layer model [12]. Catalytic surfactant monomers adsorb as separate ions apart from each other. Tail-tail interactions may cause head groups to face the surface at higher concentrations of adsorbed surfactants. Surfactant monomer head groups form a bilayer on the surface, with one facing the surface and the other the bulk liquid [20]. The surfactant molecules' adsorption on the

steel surface slows down the corrosion process by lowering the quantity of electrons accessible for reactions. Micelle-like aggregates spontaneously form at far lower concentrations than bulk CMC, and cationic surfactants adsorb to surfaces with opposing charges to form a complete bilayer [21].

3.2. Potentiodynamic Measurement

A potentiodynamic study of a surfactant on mild steel employs electrochemical methods to explore how the presence of the surfactant influences the corrosion tendencies of mild steel. This investigation typically entails immersing mild steel samples in an electrolyte solution containing the surfactant and subjecting them to controlled changes in electrode potential while monitoring resulting currents [22]. Through analyzing parameters such as corrosion potential, corrosion current density, and polarization resistance, researchers gain insights into how the surfactant either inhibits or exacerbates corrosion processes on the mild steel surface. Such studies are crucial for understanding the effectiveness of surfactants in protecting mild steel against corrosion, informing potential industrial applications where mild steel components are exposed to corrosive environments [23].

Using the potentiodynamic polarization methodology, the Tafel polarization approach calculated the corrosion protection potential of CPC as a function of inhibitor concentration and immersion time in a corrosive solution. A thorough description of the results is provided below. The concentration of the inhibitor and length of immersion determine CPC in a corrosive solution [24]. Figure 2 depicts the Tafel polarization behavior of a mild steel electrode immersed in a 0.5M H₂SO₄ solution blank and exposed to various CPC concentrations [25].

The shape of the anodic and cathodic Tafel slopes provides information on the processes (reactions) taking place on the surface of the mild steel electrode. At the cathodic site, where cathodic currents are produced, electrons released from the breakdown of Fe atoms into Fe²⁺ ions transform H⁺ ions into H₂ gas, which is the main source of anodic currents [26]. Figure 2 illustrates how the formation of stable corrosive compounds (such as FeCl₂) is implied by the falling slope of the anodic branch and comparatively steady current response following around 160 mV of overpotential at the anodic site [27].

Cathodic currents are created at the cathodic site when H⁺ ions are transformed into H₂ gas. The anodic branch slope in Figure 2 decreases following approximately 160 mV of overpotential at the anodic site, signifying the generation of stable corrosive chemicals (such as FeCl₂) [28].

The current response then becomes rather steady. The inhibitory efficiency (IE) of CPC at each concentration was determined using Tafel polarization data, and the findings are shown in Table 2. As CPC concentrations rise from 0.00192M to 0.0077M, Figure 2 shows how cathodic and anodic current densities decrease and stable corrosive products (such as FeCl₂) form [29].

The anodic current was almost equally reduced by both CPC concentrations, while the cathodic zone shows a stronger tendency [30]. The greatest IE (98.54%) was reached with a CPC concentration of 0.0077 M and an icorr of 0.00025Acm⁻². The following formula is used to get IE: Since the effects of the two dosages on anodic sites are almost comparable, the mechanism of concentration-dependent anodic CPC inhibition is most likely at play.

Cl ions may be preferentially adsorbed at anodic sites due to electrostatic contact, covering reactive (anodic) sites, at CPC concentrations of 0.00192M and 0.0077M, respectively. Furthermore, the lower values of α (Table 2) show that the rate of increase in anodic current density is noticeably slower in the presence of both inhibitor dosages than in the absence of them due to the slow rate of Fe dissolution [31].

As concentration increases, anomalous current responses are observed at the cathodic site, where CPC molecules attempt to arrange themselves into different geometrical groups inside the adsorbed layer. Lower CPC concentrations (0.00192 M) appear less effective than higher concentrations, with an IE value of 94.42%. Under the same circumstances, the structure and coatings produce higher IE values in 0.0077 M CPC. At a CPC concentration of 0.0077M, the adsorbed surfactant layer was stable on the mild steel surface.

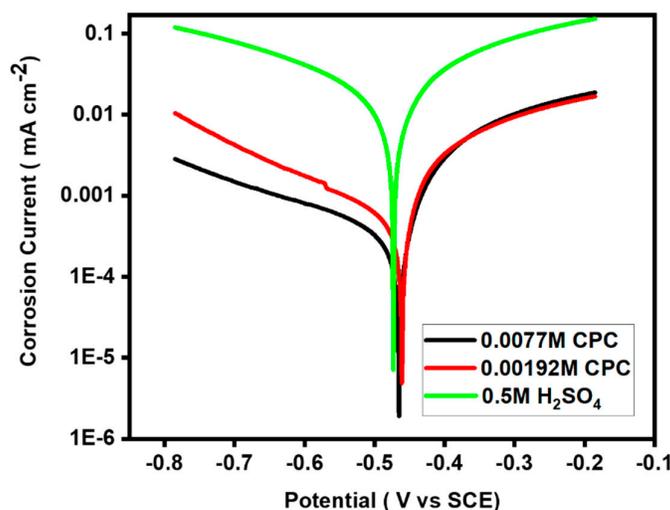


Figure 2. Potentiodynamic curves for mild steel in 0.5 M H₂SO₄ in the absence of and presence of various concentrations of CPC.

Table 2. Potentiodynamic measurement.

S.N.	Concentration	Corrosion rate (Acm ⁻¹)	% of Inhibition efficiency
1	0.5 M H ₂ SO ₄	0.01721	
2	0.00192 M CPC	0.00096	99.66
3	0.0077 M CPC	0.00025	99.99

The discovered differences in E_{corr} and I_{corr} between samples shed light on the adsorption's corrosion processes. The evolution of E_{corr} values in surfactant-containing samples points to a significant reliance on CPC levels in the CPC-Fe layer. The best balance in this composition of the sample is shown by sample CPC's peak performance, which shows the highest positive E_{corr} and the lowest i_{corr} . Additionally, it is shown that samples with higher CPC concentrations have the best corrosion inhibition capabilities.

The sample with the lowest corrosion inhibition characteristics is the one with a lower concentration of CPC. There appears to be a correlation between the molecule's adsorption on mild steel and the thickness of the surfactant layer; samples with lower surfactant concentrations have thinner mild steel layers. It correlates with the strongest corrosion inhibition qualities at greater surfactant concentrations[32].

3.3. Fourier Transform Infrared Spectroscopy (FTIR) of Analysis of CPC

Fourier Transform Infrared Spectroscopy (FTIR) is a technique for determining the functional groups in a sample by analyzing infrared light absorption. It has to do with cetylpyridinium chloride (CPC) precipitation, and the infrared spectra of the precipitate are typically used to identify the functional groups[33]. Moreover, using Fourier Transform Infrared Spectroscopy (FTIR) technology, the Functional Group Identification technique assessed CPC adsorption as a function of inhibitor concentration and immersion time in corrosive solutions [34].

A thorough description of the results is provided below. Figure 3 illustrates the adsorption behavior of a mild steel electrode immersed in a 0.5 M H₂SO₄ solution blank and exposed to two CPC concentrations. The mild steel functional group provides information on the adsorption process occurring on the surface of the electrode. Figure 3(b) shows the functional group of the CPC molecule. Figures 3(a) and 3(c), respectively, depict the mild steel functional groups before and following immersion in a CPC solution. When CPC molecules come into contact with mild steel, adsorption takes place [35].

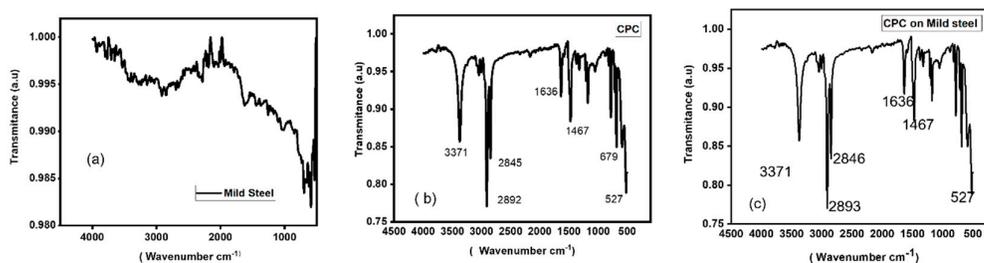


Figure 3. Fourier Transform Infrared Spectroscopy (FTIR) of Mild steel.

Functional Groups in CPC: Quaternary ammonium groups (which have a positive charge on nitrogen atoms) and aromatic rings are two of the functional groups found in cetylpyridinium chloride. Additional functional groups from the interacting chemicals may be present in the precipitate [36]. Aromatic: Usually observed between 1342 and 1266 cm⁻¹ (C-N stretching). Aromatic: Usually detectable between 1690 and 1640 cm⁻¹ (C=N stretching). It is common to detect aliphatic C-H stretching in the range of 3000-2500 cm⁻¹. It is common to see aromatic C-H stretching in the range of 2000-1650 cm⁻¹. The C-H stretching vibrations of the alkyl chain are observable in the 2800-3000 cm⁻¹ range. Figures 3(a), (b), and (c) show the mild steel's adsorbed layer of CPC. This explains why mild steel submerged in CPC solution corrodes at a low pace, which is further corroborated by electrochemical tests.

3.4. Emission Scanning Electron Microscopy (FESEM) study

FESEM analysis was used to examine the morphology of mild steel specimens before and following corrosion (Figure 4), with and without inhibitors. Figure 4(a, b) shows the presence and absence of CPC in an acid solution containing 0.05 M H₂SO₄[37].

The surfaces of the polished steel samples were uniformly smooth. On mild steel surfaces, however, 0.05 M H₂SO₄ has a detrimental effect that leads to significant corrosion after 6 hours (Figure 4(a)). The mild steel surface corrodes far less in the presence of inhibitors (CPC) than it does in the blank solution, as seen in Figure 4(b) [38].

It is thought that the inhibitor molecules form an adsorbed layer on the mild steel surface, shielding it from the corrosive species in the solution. Electrochemical tests reveal that the adsorbed CPC layer acts as a barrier between the mild steel surface and the corrosive environment, resulting in a very slow rate of corrosion [39].

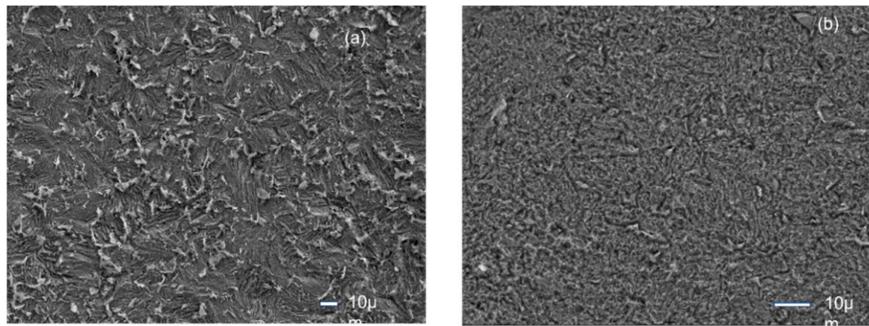


Figure 4. FESEM photomicrograph of the surface of mild steel after immersion in 0.5 M H₂SO₄, CPC inhibited 0.5 M H₂SO₄ solution for 6 h at 25 °C.

3.5. X-ray Energy Dispersive Spectroscopy (EDX)

An examination of mild steel Energy dispersive X-ray (EDX) analysis and compositional analysis using electron microscopy are the same. Cetyl pyridinium chloride's effects on mild steel were investigated using energy-dispersive X-ray analysis [37].

The components that are present and distributed on the surface of mild steel both before and after Cetyl Pyridinium Chloride treatment are depicted in Figure 5. The surface composition was determined by EDX analysis, which indicated the presence of mild steel constituents and cetyl pyridinium chloride adsorbed on the mild steel (Figure 5(b)) [40].

According to this investigation, corrosion products were not formed on the mild steel surface after cetyl pyridinium chloride treatment [40]. This illustrates the inhibitory effect of cetyl pyridinium chloride, which forms a layer of protection against corrosion on the mild steel surface. FESEM studies, which demonstrate that the degree of corrosion attack on mild steel reduces as the inhibitor ratio increases, corroborate this conclusion. The EDX experiment additionally demonstrated the physical and spontaneous adsorption of cetyl pyridinium chloride on the mild steel surface.

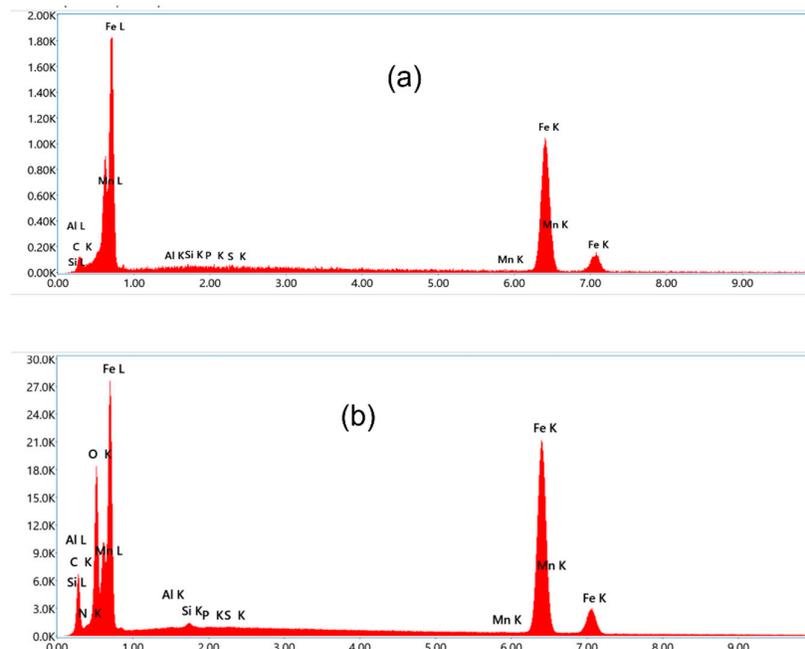


Figure 5. EDX data of mild steel after immersion in 0.5 M H₂SO₄, CPC inhibited 0.5 M H₂SO₄ solution for 6 h at 25 °C.

3.6. Atomic Force Microscopy (AFM) Study

Studies of mild steel's surface using atomic force microscopy (AFM) in an acidic solution:

The morphological alterations on the mild steel surface, both with and without inhibitors, were also examined using AFM. Figure 6 shows AFM images of mild steel that has been immersed in acid, and different concentrations of surfactant solution [39]. Figure 6a shows pictures of 0.05M H₂SO₄ acid solution, Figure 6b shows the mild steel in the CPC solution, and Figure 6c shows the 3D picture of mild steel in the CPC solution. Even with the occasional imperfection on the mild steel surface, polished steel retains its homogeneity and smoothness as compared to steel treated with 0.5M H₂SO₄.

Conversely, inhibitors significantly lessen surface roughness and strengthen the mild steel surface's defence against SO₄²⁻ ion attack (Figure 6(b)), which results in fewer crest peaks and shallow valleys [41]. The surface roughness of the steel coupons can also be computed using the height profiles obtained from AFM analysis (Figure 6(c)). The root mean square (RMS) roughness of the polished steel coupons is displayed [42].

However, after six hours of exposure to 0.5 M H₂SO₄, the surface has significantly deteriorated and is now displaying RMS roughness. The presence of CPC causes the RMS to drop to 108 nm, indicating the efficacy of the inhibitors.

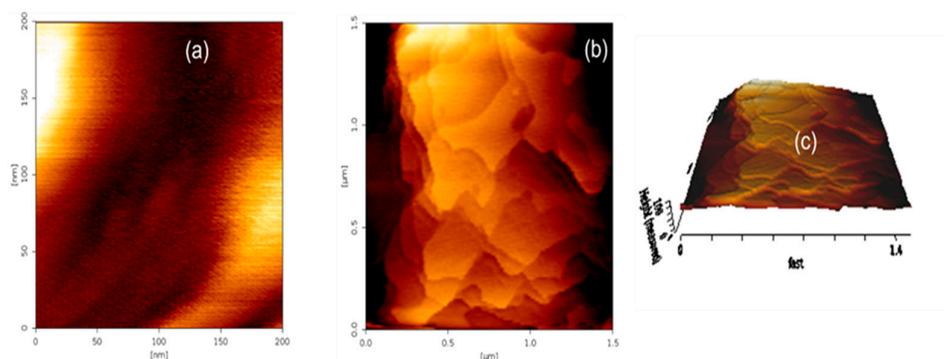


Figure 6. AFM photograph of the surface of mild steel after immersion in 0.5 M H₂SO₄, CPC inhibited 0.5 M H₂SO₄ solution for 6 h at 25 °C.

The morphologies of mild steel specimens with and without CPC after immersion in 0.5M H₂SO₄ solutions are shown in Figure 6. Because of the corrosion attack, the surface showed a very uneven topography when the inhibitor was absent (Figure 6). The average roughness of mild steel in 0.5M H₂SO₄ solution without inhibitor was found to be 46 nm using atomic force microscopy (Figure 6(a)) [39]. A protective inhibitor layer formed on the mild steel surface when CPC was present, reducing corrosion damage and producing a smoother surface with a Ra value of 108 nm (Figs. b and c). Without an inhibitor, it is clear that the mild steel surface was extensively corroded with regions of uniform corrosion (Figure 6 a). Inhibitors, on the other hand, caused the specimen surface to become smoother (Figure 6 (b, c)). This is because inhibitor molecules demonstrate a consistently good inhibitory effect by binding with the reaction sites on the mild steel surface, hence limiting the amount of interaction between the mild steel and the aggressive medium.

3.7. Surface Morphological Studies

To find out if the inhibitor adsorption produced a protective layer that prevented corrosion, surface photos of the mild steel specimens were taken using an AFM and a FESEM. Other than polishing scratches, the material's surface appeared to be devoid of apparent defects, pits, and cracks according to the results of the FESEM inspections performed on it before it was submerged in the solutions. [5]. The 0.5 M H₂SO₄ concentration has no restrictions, which results in a rough and damaged surface.

The addition of inhibitor CPC significantly reduces surface heterogeneity. Figure 4 displays a typical FESEM photomicrograph of the mild steel surface following immersion in a 0.5 mm H₂SO₄

solution that CPC had occluded [43]. The AFM results of steel specimens produced at 25 °C in the range of and in uncontrolled and inhibited acid solutions, respectively, provide additional support for the FESEM results. The specimen's rough surface and the steel's quick degradation in an uncontrolled acid solution are both visible in the AFM image. The steel surface corrodes less and is noticeably smoother after being coated with CPC [44]. The adsorbed inhibitor creates a more rounded and visually pleasing protective layer. Because some metal areas are not fully covered, they are susceptible to acid attack due to the thin inhibitor coating.

3.8. Interaction of Surfactant, acid, and water with Mild Steel

3.8.1. Surfactant -Acidic Water Interaction

Surfactants are molecules that possess both hydrophilic (water-attracting) and hydrophobic (water-repelling) regions within their structure. the interaction between surfactants and acidic water is complex and can involve various molecular processes such as ionization, hydrophobic interaction, and changes in surface tension and solubility. The specific behavior observed will depend on the properties of the surfactant and the characteristics of the acidic water[45].

When surfactants are introduced into acidic water, several interactions can occur depending on the specific properties of the surfactant and the acidity of the water.

Ionization: In acidic water, the surfactant molecules may undergo ionization. This process involves the dissociation of the surfactant molecule into ions, usually a negatively charged hydrophilic headgroup and a hydrophobic tail. The degree of ionization can vary depending on the pH of the water and the pKa (acid dissociation constant) of the surfactant, which is shown in Figure 7a.

Hydrophobic Interaction: The hydrophobic tails of the surfactant molecules tend to aggregate or associate with each other to minimize contact with water molecules. This can lead to the formation of micelles or other self-assembled structures, where the hydrophobic tails are shielded from the surrounding water molecules, which is shown in Figure 7c [46].

Effect on Surface Tension: Surfactants are known for their ability to reduce surface tension in water. In acidic conditions, the degree of surface tension reduction may vary depending on the specific surfactant and its interaction with the acidic environment. Some surfactants may exhibit enhanced surface activity in acidic water due to changes in their molecular conformation or ionization state.

Solubility: The solubility of surfactants in acidic water can be influenced by factors such as pH, temperature, and the chemical structure of the surfactant molecule. In some cases, the solubility of surfactants may decrease under acidic conditions, leading to phase separation or precipitation of the surfactant from the water [47]. Mild steel was immersed in a surfactant solution then one layer of surfactant was adsorbed on the mild steel surface shown in Figure 7b.i.e there is the origin of the formation of a double layer. These layers help to block the corrosion process of the mild steel.

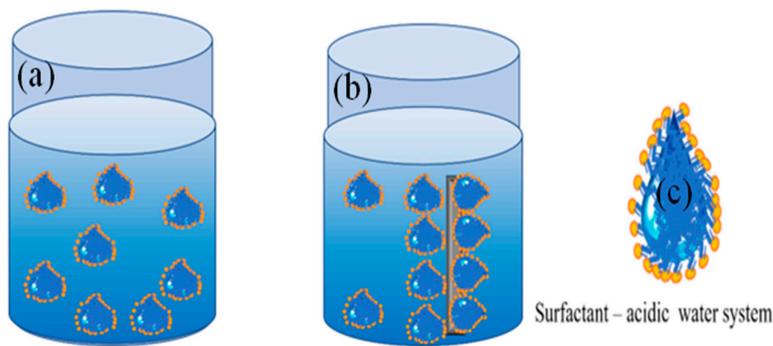


Figure 7. a): surfactant acidic water interaction. b) Micelle of surfactant attached to mild steel. c) structure of aggregation of the surfactant molecule.

3.8.2. Mild Steel - Surfactant -Acidic Water Interaction

When mild steel comes into contact with acidic water in the presence of surfactants, several interactions can occur, which may impact the steel's surface properties and its overall corrosion behavior. The interaction between mild steel, surfactants, and acidic water is multifaceted and can involve corrosion inhibition, surface cleaning, micelle formation, pH buffering, and surface modification processes [48]. The specific impact on corrosion behavior will depend on factors such as the type of surfactant Figure 8c, its concentration, the acidity of the water Figure 8b, and the characteristics of the steel surface Figure 8a.

Corrosion Inhibition: Surfactants act as corrosion inhibitors by forming a protective layer double layer on the surface of the mild steel. In acidic water, where corrosion rates tend to be higher due to increased hydrogen ion concentration, surfactants may adsorb onto the steel surface and hinder the access of corrosive species such as oxygen and ions to the metal surface, thereby reducing the corrosion rate, which is shown in figure 8c. This is clearly shown in the micelle of surfactant attached to the mild steel surface.[49].

Micelle Formation: Surfactants can form micelles in aqueous solutions, where the hydrophobic tails aggregate together while the hydrophilic heads face outward towards the surrounding water. In acidic water, micelle formation may be influenced by factors such as pH and surfactant concentration. [50]. the presence of micelles can affect the adsorption behavior of surfactants onto the steel surface and may influence corrosion inhibition properties [51].

pH Buffering: Some surfactants may exhibit pH buffering properties, which can help stabilize the pH of the acidic water. Fluctuations in pH can influence the corrosion behavior of mild steel, so maintaining a relatively stable pH environment through the addition of surfactants may help mitigate corrosion.

Surface Modification: Surfactants may interact with the surface of mild steel through adsorption processes, leading to modifications in surface properties such as surface charge, wettability, and surface energy. These surface modifications can affect the corrosion resistance of the steel by altering its interaction with corrosive species present in the acidic water [52].

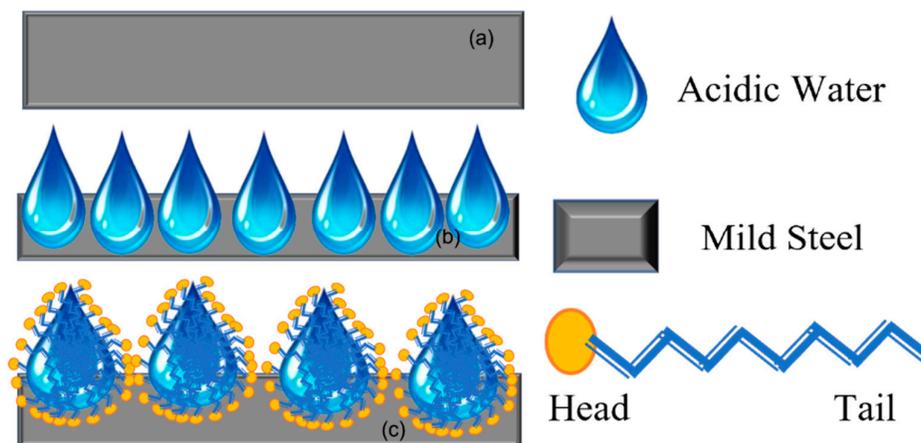


Figure 8. a): Polished mild steel. b) Acidic water on mild steel. c) Surfactant Mild steel, and Acidic water.

3.8.3. Mechanism of CPC – Mild Steel

The protonated pyridinium group atom in the molecule is the mechanism underlying the increased adsorption of CPC in acidic liquids. Interaction between the CPC's pyridinium functional group and the corroding steel surface is conceivable shown in Figures 9b and 9c. Protonated pyridinium's functional group is adsorbed at anodic sites to prevent iron dissolution and at cathodic sites to halt the hydrogen evolution reaction Figure 9a. [15].

This implies that the anodic and cathodic partial responses are regulated by the CPC through a multimodal inhibitory mechanism [53]. The fact that the CPC molecules adhere to the steel surface implies that, depending on their concentration, they self-aggregate there to form a variety of stripes that are uniformly wide, regularly spaced, and well-organized. [54]. The surface is adequately covered by the molecules' long-range interactions, which lowers the rate of corrosion. On the surface of the steel, the CPC molecules are flat. When the pyridinium groups and side chains are near the steel surface, the ideal energy conditions are reached. [14].

The inertial axis of the molecule runs nearly parallel to the surface. This configuration of CPC molecules explains the high levels of IE on mild steel.

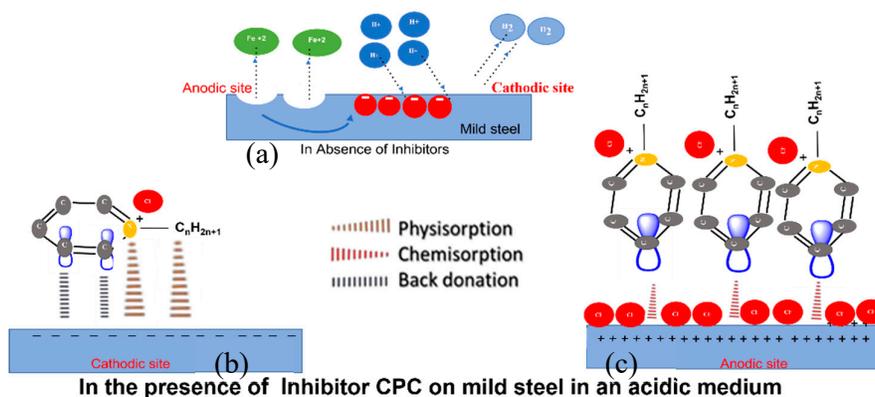


Figure 9.): Mechanism of CPC – Mild steel.

To predict the inhibition's adsorption mechanism onto the metal's surface, one must comprehend the corrosion mechanism of the metal [41]. This article describes the mechanism of mild steel corrosion in a solution of sulfuric acid.

The anodic dissolving mechanism of metals is the capacity of the free electron pairs on N and O to form a coordination with Fe shown in Figure 9b. Furthermore, the molecule's double bonds enable the interaction of metal d-electrons being donated in reverse to the p*-orbitals, which isn't feasible, for instance, with pyridinium. Furthermore, the p-electrons of the aromatic rings may interact with the metal surface [55]. Furthermore, after the basic functions of the inhibitor are protonated, electrostatic contact between the negatively charged iron surface (which may be caused by particular adsorption of Cl⁻ anions) and the positively charged inhibitor is feasible, especially in acidic environments shown in Figure 9c. Essentially, the same interactions can happen in the case of a CPC inhibitor; the only difference is that neither nitrogen nor oxygen atoms are present. Because of their capacity to form metallic complexes, heat of hydrogenation, molecular size, the presence of free electron pairs in the N atoms, and the p-electrons on the aromatic rings, these compounds primarily prevent corrosion [56]. It is well known that ligands with the letters N have a coordination affinity towards mild steel. Thus, the adsorption on mild steel is caused by coordination between the p-electrons and heteroatoms of aromatic rings shown in Figure 9c. [23]. Pyridinium under study has the potential to form a bond with mild steel due to unshared electron pairs on N. The double bonds in the molecule also allow for back donation. The high inhibitory efficiency in CPC is caused by the presence of another hetero-atom N, which has a large number of free lone pairs of electrons that can interact with steel. It is well known that CPC produces a thin polymeric layer with excellent inhibitory efficacy on mild steel like Figure 9c [46].

In the instance of CPC, an extra anchoring point for the inhibitor to bond with the metal surface is provided by the lone pair of electrons of the pyridinium group's "N" atom connected to the pyridinium ring. This increases the strength of adsorption and, consequently, the inhibition.

4. Conclusions

Based on the results and discussion, we concluded that CPC demonstrated good mild steel corrosion inhibitor performance in 0.5 M H₂SO₄, which is further strengthened in the presence of surfactants. CPC It implies that surfactants have an adsorption-based mechanism that affects the corrosion prevention activity of CPC. At every concentration under investigation, the weight loss measurement data point to an adsorption process that inhibits corrosion. FTIR measurement provides a comprehensive understanding of CPC adsorption on mild steel. As a combination inhibitor, CPC works. Research using FESM and AFM further supports the inhibitory nature of CPC. The high-resolution AFM micrographs showed that the corrosion of mild steel in 0.5 M H₂SO₄ solution was described by corrosion attack and the addition of inhibitor to the aggressive solutions diminished the corrosion of mild steel.

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