Study of Anti-Corrosion Properties of Sodium Dodecyl Sulphate and Cetyl Pyridinium Chloride

Chandradip Kumar Yadav[1], Tulasi Prasad Niraula[2], Shova Neupane[1], Amar Prasad Yadav[1*], Ajaya Bhattarai[2*]

[1]Central Department of Chemistry, Tribhuvan University, Kirtipur, Nepal

[2]Mahendra Morang Adarsh Multiple Campus, Tribhuvan University, Biratnagar, Nepal

*Email correspondence author: bkajaya@yahoo.com

Abstract

Surfactant is a surface-active agent. Surfactants have both hydrophilic (water-attracting) and hydrophobic (water-repelling) portions in their molecular structure, effective inhibitors for the protection of mild steel in an acidic medium, the weight loss methods were used at lab temperature to evaluate the effect of surfactant cetyl pyridinium chloride (CPC) and sodium dodecyl sulfate (SDS) on the corrosion protection behavior of mild steel in 0.5 M H_2SO_4 solution. Inhibition efficiency, weight loss, corrosion rate, and surface coverage area of mild steel in different concentrations of surfactant were studied. The results showed that the inhibition efficiency of cetyl pyridinium chloride is 99.86%, which is slightly greater than that of sodium dodecyl sulfate (99.85%) in the presence 0.5 M H_2SO_4.

Keywords: Corrosion inhibition, Surfactants, Mild steel, Weight loss, Acid, Protection behavior, Hydrophilic, Hydrophobic

1. Introduction

Refined metal is naturally transformed into a more stable chemical form, like oxide, hydroxide, or sulfide, by the process of corrosion. Corrosion inhibition breaks the corrosion process on the metal. Mild steel (MS) is widely used as a structural material in many industries due to its good mechanical properties and low cost. The corrosion of mild steel is a fundamental academic and industrial concern that has received a

considerable amount of attention. Acid pickling baths are employed to remove undesirable scales from the surface of the metals. Once the scale is removed, the acid is then free for further attack on the metal surface. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media.

A survey of the literature reveals that the applicability of organic compounds as corrosion inhibitors for mild steel in acidic media has been recognized for a long time. These compounds can adsorb on the mild steel surface and block the active sites, decreasing the corrosion rate. But no more work has been done on how surfactant acts as corrosion inhibitors for mild steel.

Corrosion control has been a problem in recent decades due to industrialization. Corrosion is thought to account for the loss of 3–4.5% of the Gross National Products (GNP) of an industrialized country. Consequently, corrosion control has grown to be a global issue (Karki et al., 2021). Many techniques, including organic, inorganic, and polymer coatings, are used to stop corrosion. However, using green inhibitors has been more popular recently due to their non-hazardous nature, low cost, easy availability, eco-friendliness, and biodegradability (Gupta, Awasthi, et al., 2020).

The molecules are typically thought to bind to the metal surface as the initial step in the action mechanism of surfactants as corrosion inhibitors in aggressive environments. The type of metal and its surface charge, the surfactant's chemical makeup, and the characteristics of the aggressive electrolyte all have an impact on the adsorption process. One way to illustrate the surfactant molecules' adsorption on a metal surface (Bockris & Swinkels, 1964). If, for every surfactant molecule adsorbed, n is the number of water molecules removed from the metal surface. The cross-sectional area of the surfactant molecule about the water molecule determines the value of n. Because their interactions with the metal surface have a larger interaction energy than their interactions with water molecules, the surfactant molecules stick to it (Mirzaee & Sartaj, 2022). As a result, the inhibitory activity of the surfactant molecules is linked to their adsorption on the metal surface by their functional groups. The reactive metal is thus protected from the harsh environment because the adsorption rate is often rapid (Aslam et al., 2021). The ability of the surfactant to adsorb on the corroding surface is dependent on its ability to aggregate into clusters (micelles) and bind to the surface, both of which are necessary for corrosion inhibition. The critical micelle concentration, or CMC, is a crucial component of a corrosion inhibitor's effectiveness. Surface tension is lowered under CMC because molecules tend to congregate at the interface as surfactant concentration rises. Above CMC, surfactant molecules cover the metal surface in a monolayer. As additional molecules are added, micelles or several layers of surfactant are produced (Malik et al., 2011). This does not affect the surface tension or corrosion rate. The adsorption of surfactant on the surface of mild steel is described in Figure 1. There are two different types of interactions: chemisorption and

physisorption. The amount of valence electrons in the mild steel (MS) and surfactant ions determines which form of adsorption occurs.
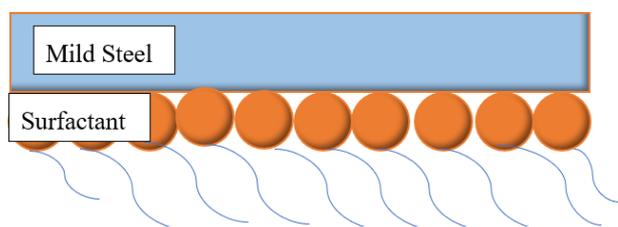

Figure 1: Surfactant absorbed on mild steel plate

Figure 2 shows a schematic representation of the possible mechanism of surfactant blocks the reaction on mild steel (MS) plate. Surfactant adsorbed on the mild steel. It forms one layer or bilayer on the mild steel surface and it minimizes the contact of moisture water with the MS layer.
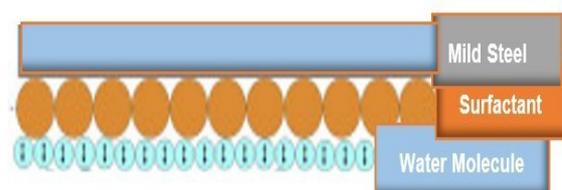

Figure 2: Mechanism of surfactant block the reaction on mild steel plate

In this paper, the comparative study the inhibition efficiency capacity of CPC and SDS. As a result of the data analysis, CPC has a higher inhibitory efficiency capacity than SDS. CPC-Fe interactions were greater than those between SDS-Fe. The CPC molecule on mild steel is highest due to the pyridinium ring present. Multilayers of surfactant on mild steel were also formed in more stable CPC than SDS (Choi et al., 2022)(Vankar, 2017).

Corrosion inhibition relies on the creation of single- or multi-layered protective layers on the metal surface, and its mechanism is intricate.

There are many factors that affect the protective properties of the surface layer, including the interaction between inhibitors and substrate, the incorporation of inhibitors into the surface layer, chemical reactions, electrode potentials, inhibitor concentrations, temperature, and surface properties. Adsorption of the surfactant molecules onto the metal surface is the initial step in the action mechanism of surfactants as corrosion inhibitors in aggressive environments (Shrestha et al., 2018). The adsorption process is influenced by the nature and the surface charge of the metal, the chemical structure of the surfactant, and the nature of the aggressive electrolyte. The type of aggressive electrolyte, the chemical makeup of the surfactant, and the composition of the metal all have an impact on the adsorption process. The surfactant molecules' adsorption on the metal surface can be represented by the following equation:

molecule adsorbed,

$$\text{surfactant (sol.)} + n H_2O \text{ (ads.)} = \text{surfactant (ads.)} + n H_2O \text{ (sol)}$$
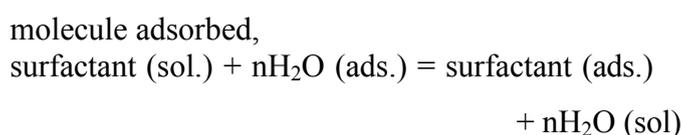
where n is the number of water molecules removed from the metal surface for each surfactant molecule adsorbed. The value of n is influenced by the surfactant molecule's cross-sectional area relative to the water molecule. Because the contact energy between the surfactant molecules and the metal surface is greater than that between the water molecules and the metal surface, adsorption of the surfactant molecules takes place. Therefore, the adsorption of the surfactant molecules onto the metal surface

via their functional groups is responsible for the inhibitory effect caused by surfactants (Malik et al., 2011).

Materials and Methods

Surfactants: Cetyl pyridinium chloride (CPC): Himedia laboratories pvt. ltd. Lot No: 0000197909. Ref No 23 Vadhani Ind. Est. L.B.S. Marg, Mumbai, India and sodium dodecyl sulfate (SDS): Fisher Scientific, Cas No: 151-21-3. prod No: 27815. Lot No: 2475741217 was used as the inhibitor. Figure 3 shows the molecular structure of the CPC and Figure 4 shows the molecular structure of SDS.
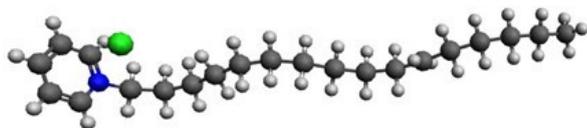

Figure 3: Cetyl pyridinium chloride (CPC)

The cationic surfactant cetyl pyridinium chloride (CPC) and anionic surfactants sodium dodecyl sulfate (SDS) were purchased from Lab Glassware, Kirtipur, Kathmandu, Nepal.

Figure 4: Sodium Dodecyl Sulfate (SDS)

Tests were performed on a mild steel of the following composition, presented in Table 1.

Table 1. Chemical composition (wt. %) of mild steel (Attari et al., 2015)

Elements	wt.%
C	0.21
Si	0.38
P	0.09
S	0.05
Mn	0.05
Al	0.01
Fe	Balance

Preparation of inhibitor solution:
0.5 M H_2SO_4 was prepared from original extra pure H_2SO_4 in double distilled water. The resulting solutions were stored with an airtight cork of a volumetric flask. Various concentrations of CPC, 0.00175M, 0.00198M, 0.00230M, and 0.00283M were prepared on 0.5 M H_2SO_4 and used as a solvent. The same concentration of SDS was also prepared and used.

Corrosion test by weight loss method:
The weight loss was determined from the difference of sample weighed before and after immersion in acid and inhibitor solutions. The effect of immersion time and inhibitor concentration in the corrosion rate was studied by weight loss. The MS samples were immersed in 0.00175 M, 0.00198 M, 0.00230 M, 0.00283 M of CPC different concentration of surfactant solutions for time intervals 3 hour to study. There are relations to determine the corrosion rate (CR), surface coverage (θ), and inhibition efficiency (IE%).

Preparation of mild steel sample

Mild steel (MS) sheet purchased from the local vendor of Kathmandu valley was mechanically cut into samples of a dimension of 3 cm x 3 cm x 0.1 cm. MS samples were polished with silicon carbide (SiC) paper of #100 to #2000 grits. Abraded samples were ultrasonicated in ethanol, dried, and stored in desiccators.

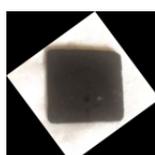
Figure 5

Figure 6

Figure 7

Figure 5 shows silicon carbide (SiC) paper, Figure 6 shows mild steel pieces before immersion, and Figure 7 shows mild steel pieces after immersion.

Preparation of inhibitor solution

0.5 M H_2SO_4 solution was prepared in double distilled water. 0.00175 M, 0.00198 M, 0.00230 M, 0.00283 M of CPC were prepared using 0.5 M as a solvent. The same concentration of SDS was prepared. Measurements were performed at room temperature.

Figure 8

Figure 9

Figure 8 represents the MS going to be immersion in a surfactant solution. Figure 9 represents the MS immersion time on surfactant solution.

Corrosion test by weight loss method

Weight loss is conventional, easy to be done in a research lab, less expensive and it gives the idea about corrosion. The weight loss was determined from the difference of sample weighed before and after immersion 0.00175 M, 0.00198 M, 0.00230 M, 0.00283 M of CPC inhibitor solutions. The effect of inhibitor concentration in the corrosion rate was studied by weight loss. The MS samples were immersed in inhibitor solutions for different concentrations to study. The following relations determine the corrosion rate (CR), surface coverage (θ), and inhibition efficiency (IE%) using the literature (Gupta, Kafle, et al., 2020):

Corrosion Rate (CR) =

$$\frac{Weight\ Loss\ (W)}{Area\ (A) \times Time(T) \times Density\ (D)} \times 8.76 \times 10^4$$

where, W is the weight loss of the MS (g) after immersion time, t (hours), A is the area of the MS (cm^2), and d is the density of the MS (g cm^{-3}).

Surface Coverage (θ) = $\frac{W_0 - W_1}{W_0}$

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

Inhibition Efficiency (*IE*) % =

$$\frac{(Corrosion\ Rate\ without\ Inhibitor - Corrosion\ Rate\ with\ Inhibitor)}{Corrosion\ Rate\ without\ Inhibitor} \times 100$$

3.   Results and Discussion

This paper explained the effect of concentration of inhibitors CPC and SDS on mild steel. Table 2 shows the weight loss, corrosion rate, surface coverage, and inhibition efficiency for CPC.

Table 2: Weight Loss, corrosion rate, surface coverage, and inhibition efficiency of the CPC in 0.5 M H_2SO_4 solution

Concentration (M liter)	Weight loss (gm) ($\times 10^{-5}$)	Corrosion rate (mm/Year) ($\times 10^{-5}$)	Surface coverage (θ cm^2)	Inhibition Efficiency (%)
0.00175	8.4717	4.3625	0.998359	99.836
0.00198	8.2373	4.3406	0.998405	99.84
0.00230	8.1953	4.3565	0.998413	99.841
0.00283	7.3201	4.3447	0.99852	99.858

Table 3 includes the weight loss, corrosion rate, surface coverage and inhibition efficiency of the SDS in 0.5M H_2SO_4 at different concentrations for 3 hours.

Table 3: Weight loss, corrosion rate, surface coverage, and inhibition efficiency of the SDS in 0.5M H_2SO_4 at different concentrations for 3 hours

Concentration (M/ liter)	Weight loss (gm) ($\times 10^{-5}$)	Corrosion rate (mm/Year) ($\times 10^{-5}$)	Surface coverage (θ)	Inhibition Efficiency (%)
0.00175	11.2745	10.5274	0.9978	99.782
0.00198	11.1774	7.8834	0.9978	99.784
0.00230	9.8981	7.3052	0.9981	99.808
0.00283	7.5286	5.8159	0.9985	99.854
0.5 M H_2SO_4	57.7312	29.001		

Weight loss Methods :

The weight loss method is one of the simplest and oldest conventional techniques for measuring the corrosion rate of a material (Abdulelah et al., 2020). It involves monitoring the mass loss of a material over a specified period as it corrodes in a particular environment.

Variation of weight loss of mild steel

The fully polished mild steel and the shining-like mirror were immersed in the solution of CPC and SDS. It was kept for 3 hours. The four different concentrations of SDS and CPC were used. The inhibitor solution was prepared in 0.5 M sulphuric acid.
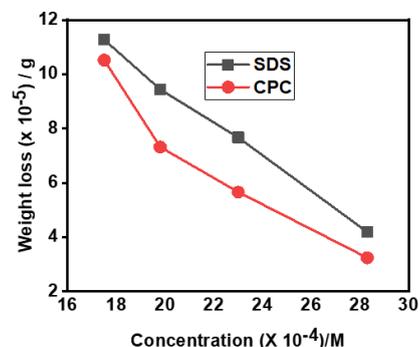

Figure 10: Representation of the variation of weight loss of mild steel of immersion time 3 hours in different concentrations

Figure 10 represents the variation of weight loss of mild steel of immersion time 3 hours in different concentrations. From Figure 10, the weight loss of the mild steed decreases from lower concentration to higher concentration. The adsorption of the surfactant molecule on the mild steel is directly proportional to the concentration of surfactant. It minimises the reaction between acid and mild steel surfaces. So higher the concentration lower the weight loss.

Corrosion rate:

Corrosion rate refers to the speed at which a material deteriorates due to chemical reactions with its environment, typically with substances like water, oxygen, acids, or other chemicals. It is commonly expressed in units of mass loss per unit of surface area over a specified period (e.g., millimetres per year or inches per year). Corrosion rates can vary significantly depending on factors such as the type of material, environmental conditions, temperature, and the presence of corrosive agents.

Several methods can be used to measure corrosion rates, including weight loss measurements, and electrochemical techniques. Literature reported that the weight loss of carbon steel decreases with increasing inhibitor concentration and increases with increasing immersion time (Migahed & Al-Sabagh, 2009) such as polarization resistance and electrochemical impedance spectroscopy (Nallakukkala, 2018). This paper discusses a weight loss method, but future works will use another approach. The choice of method depends on the specific application the accuracy required, instrument available in the lab. The results indicated that these compounds function via adsorption on reactive sites on the corroding surface, reducing the corrosion rate of the metal. When referring to corrosion, surface coverage is the extent to which a material's surface is covered in the products or byproducts of the corrosive process. When metals come into contact with air, water, or chemicals in the environment, they corrode and produce corrosion products on their surface. The surface coverage of these corrosion products may provide important information about the kind and extent of corrosion. Migahed et al. (2004) reported on the effectiveness of the synthetic anionic surfactant [p-myristyloxy carbonyl methoxy-p′-sodium carboxylate- azobenzene] in inhibiting mild steel corrosion in 1 M sulfuric acid solution by chemical and electrochemical approaches. When the studied inhibitor was present, the corrosion rate significantly decreased. The findings that have been seen suggest that the prevention of mild steel corrosion is caused by the inhibitor molecules adhering to the surface and obstructing the active sites. The decrease in the corrosion rate is attributed to the adsorption of surfactant. The inhibition efficiency of different concentrations of surfactant CPC and SDS at 3 hours is shown in Figure 11.
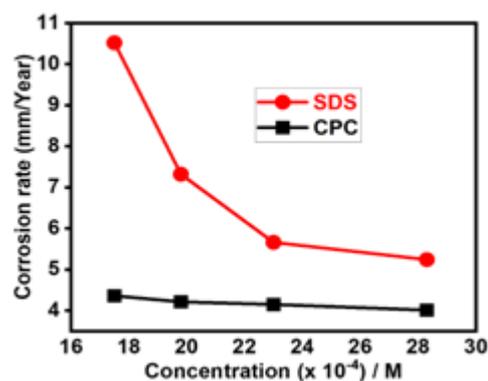

Figure 11: Variation of corrosion rate with concentration of surfactants

A notable impact of the surfactant CPC and SDS in 0.5M H_2SO_4 solution on the mild steel sample was explained by variations in their corrosion rates. As the surfactant content increased, the rate of corrosion decreased. The adsorption of surfactant is responsible for the reduction in the rate of corrosion. Thus, the surfactant reduces the pace at which mild steel corrodes**.**

Surface Coverage :

Surface coverage, as used in the context of corrosion, describes how much of a material's surface is coated in products or byproducts of the corrosive process. Metals corrode when they react with environmental elements such as water, oxygen, or chemicals, creating corrosion products on the metal's surface. These corrosion products' surface coverage might reveal crucial details on the degree and coarse of corrosion. The variation of surface coverage with different concentrations of surfactant (CPC and SDS) in 0.5 M H_2SO_4 for 3 hours by weight loss method (Figure 12).
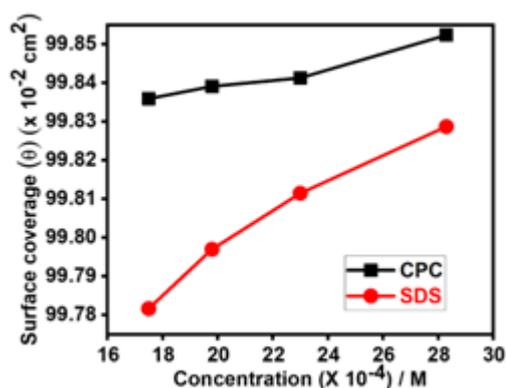

Figure 12: Variation of surface coverage with different concentrations CPC and SDS in 0.5 M H_2SO_4 solution at 3 hours immersion

Here's how surface coverage is relevant in the process of corrosion:

Corrosion Product Formation: When a metal corrodes, it undergoes chemical reactions with the corrosive agents in its environment. These reactions produce various corrosion products, which can include oxides, hydroxides, salts, and other compounds. These products may form a layer on the metal's surface (Shrestha et al., 2019).

Surface Protection: In some cases, the corrosion products can act as a protective layer, preventing further corrosion of the underlying metal. For example, in the case of iron, the formation of rust (iron oxide) can create a barrier that slows down the corrosion process. The extent of this protective layer's surface coverage is crucial in determining the level of protection it provides.

Assessing Corrosion Severity: The surface coverage of corrosion products can be used to assess the severity of corrosion on a metal surface. A higher surface coverage typically indicates more advanced or severe corrosion. Monitoring changes in surface coverage over time can help predict the remaining service life of a corroding component.

Corrosion Inhibitors: Surface coverage can also be relevant when using corrosion inhibitors. Corrosion inhibitors are chemicals that are added to the environment to reduce or control corrosion. They can form a protective layer on the metal surface, and the effectiveness of the inhibitor is often related to the degree of surface coverage it achieves (Elkacimi et al., 2011).

The surface coverage of every concentration was acquired in a method that increased the surfactant concentration before increasing the surface coverage value. The value of surface covering is directly correlated with surfactant concentration.

Inhibition Efficiency: Inhibition efficiency in the context of corrosion refers to the effectiveness of a corrosion inhibitor in slowing down or preventing the corrosion of a material. Corrosion inhibitors are chemicals or compounds that are added to a corrosive

environment to reduce the rate of corrosion of a metal or other materials. Inhibition efficiency is a measure to corrosion inhibitor performs in protecting the material from corrosion.

The variation of inhibition efficiency with different concentrations of surfactant (CPC and SDS) in 0.5 M H_2SO_4 for 3 hours by weight loss method (Figure 13).
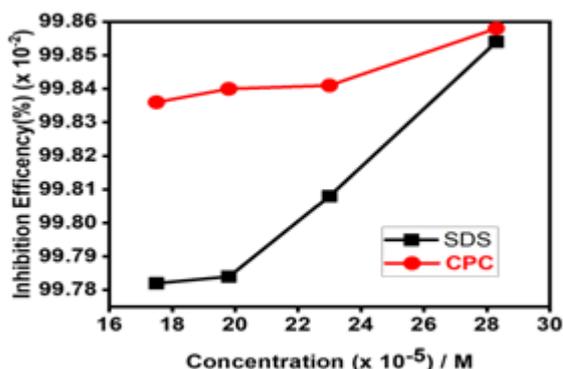

Figure 13: Variation of inhibition efficiency with different concentrations of CPC and SDS in 0.5M H_2SO_4

A higher inhibition efficiency percentage indicates that the corrosion inhibitor is more effective at reducing corrosion. For example, an inhibition efficiency of 90% means that the corrosion rate is reduced to 10% of what it would be without the inhibitor (Bammou et al., 2014). Corrosion inhibitors can be categorized into various types, including organic inhibitors, inorganic inhibitors, and mixed inhibitors. But surfactant is conventional organic inhibitor. Inhibitor forming a protective film or barrier on the metal surface, reducing the access of corrosive agents to the metal. Figure 13 shows that the inhibition efficiency increases with an increase in the concentration of the surfactant CPC and SDS. Similar observations have been reported for EDTA, when the gravimetric method was reported (Y. Musa et al., 2009). The results suggest that an increase in surfactants concentration increases the number of inhibitor molecules available for the adsorption onto the MS surface. It results in decreasing the surface area available for the direct acid attack on the metal surface inhibiton efficency of surfatant CPC (0. 00283M) is 99.86% and SDS (0.00283M) is 99.85%. Both surfactants work well as mild steel inhibitors. CPC and SDS, two surfactants, both displayed increased efficiency. Because it has a pyridinium ring on it, CPC is more efficient than SDS when it comes to surfactants which demonstrate that mild steel and CPC have a stronger interaction than does the SDS molecule (Table 4).

Table 4: Comparative study of different surfactants and their inhibition efficiency

SN	Inhibitor	Media	Samples	Inhibition efficiency(%)	References
1.	CTAB	HCl	Carbon steel	87.000	(D'Souza et al., 2015)
2.	SDS	HCl	Mild steel	83.000	(D'Souza et al., 2015)
3.	DTAB	H_2SO_4	Mild steel	98.850	(Shahi et al., 2023)
4.	CPC	H_2SO_4	Mild steel	98.080	(Shahi et al., 2023)
5.	CPC	H_2SO_4	Mild steel	99.858	This work
6.	SDS	H_2SO_4	Mild steel	99.854	This work

DTAB = Dodecyl trimethylammonium bromide

CTAB = Cetyltrimethylammonium bromide

Conclusions: The anti-corrosion behavior of CPC and SDS were studied for mild steel in 0.5 M H2SO4 on varying different surfactant concentrations.The weight loss of mild steel was measured and the corrosion parameters such as surface coverage, corrosion rate, inhibition efficiency for CPC and SDS of different concentrations were calculated. It is found that the corrosion rate for CPC is 4.3447×10^{-5} mm/year which is lesser than the results of the calculated values that of SDS (5.8159×10^{-5} mm/year) at lab temperature. The inhibition efficiency of both CPC and SDS varied proportionally with increase of their concentrations in acidic medium. Finally, the inhibition efficiency is found to be 99.86 %for CPC that is a bit more than that of SDS (99.85 %). This paper reports that CPC and SDS can be used as an effective non-toxic inhibitor for mild steel in acidic medium.

Acknowledgments

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