Application of Stabilized Cefixime-Agnps-Go Thin Films As Corrosion Inhibitors for Mild Steel Alloy

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Abstract

In this work, the corrosion inhibition of mild steel at ambient conditions by an antibiotic in a solution that contains silver nanoparticles (AgNPs) and graphene oxide (GO) was studied. GO and AgNPs were prepared by one-step simple and ecofriendly method and characterized by different techniques. Different concentrations of the inhibitor were prepared and their inhibition efficiency in acidic media was investigated. The adsorption characteristics of the inhibitor were studied and it was found that the antibiotic (Cefixime) alone and with GO combined with AgNPs inhibit the corrosion of mild steel by being adsorbed on the surface of mild steel by a physical adsorption mechanism. The adsorption of Cefixime and GO with AgNPs on the mild steel surface was found to be spontaneous. Incorporating AgNPs and GO with Cefixime showed an additional inhibition efficiency when compared with using only Cefixime. This indicates the strong inhibition efficiency offered by incorporating the antibiotic with AgNPs and GO.

Keywords: Mild steel, Corrosion, Antibiotic, Silver nanoparticles, Graphene oxide, Inhibition efficiency

Introduction

Mild steel is known as plain carbon steel and considered a common form of steel due to its relatively low price. Its unique properties make it applicable for many applications [1]. However, its low corrosion resistance especially in acidic environments is considered a significant challenge [2]. Corrosion inhibition in mild steel drew a great attention of scientific and industrial communalities [3]. The high anticorrosion materials for iron are called self-assembled materials (SAMs) [4]. The immersion of a particular piece of metal in suitable acid solution to remove undesirable scales such as rust is known as acid pickling. This process utilizes some of the most frequently used acids such as hydrochloric, sulfuric and phosphoric acids. The acidic solution attacks and dissolves the rust and scales it from the metal surface. After dissolving the rust, the acid then starts to attack the metal surface. Corrosion inhibitors are added to the pickling solution to reduce the metal dissolution and the consumptions of acid [5]. The use of many inorganic inhibitors, particularly those containing phosphate, chromate, and other heavy metals is being gradually restricted or banned by various environmental regulations because of their toxicity and the difficulties faced during their disposal especially in the marine industry, where aquatic life is at threat [6]. The efficiency of an organic compound as an inhibitor is mainly determined by its ability to get adsorbed on a metal surface by replacing a water molecule at the corroding interface. However, only a few non-toxic and eco-friendly compounds have been investigated as corrosion inhibitors. The inhibitive effect of four antibacterial drugs, namely ampicillin, cloxacillin, flucloxacillin, and amoxicillin towards the corrosion of aluminum was investigated [7]. The self-assembly technique has been investigated to enhance the iron resistance against environmental corrosion [8-9].

Cefixime is a third generation of the semi-synthetic cephalosporin antibiotic. Cephalosporins are derivatives of 7-aminocephalosporic acid and are closely related to penicillins in structure. Cephalosporins have a six-membered sulfur that contains ring adjoining a ß lactam ring. The molecular formula of Cefixime is $C_{16}H_{15}N_5O_7S_2$ and the molecular weight is 453.44g. As a result of the rapid advancement of nanotechnology, thin films with thickness starts from few nanometers becoming more popular in scientific and technological applications [10].

Nanoparticles have a high tendency to interact with each other to form agglomeration [11]. Their unique properties are mainly due to the higher surface area to volume ratio compared to the microparticles [12]. On the other hand, graphene processes superior corrosion protection property due to its impermeability and chemical inertness. Graphene-based coatings showed an excellent corrosion inhibition capability [13].

The present paper describes a study of corrosion protection activity of antibiotic alone and antibiotic combined with GO and AgNPs on mild steel. Different concentrations of the inhibitors were prepared and their inhibition efficiency in acidic media was investigated. Adsorption characteristics of the inhibitors were also studied and it was found that the only antibiotic (Cefixime) and when it combines with GO and AgNPs inhibits the corrosion of mild steel by being adsorbed on the surface of mild steel by a physical adsorption mechanism.

Mechanism of Inhibition

An elucidation of inhibition mechanism requires elaborated knowledge of the fundamental interaction amongst the protective compounds and the metal surface. Many of the organic corrosion inhibitors have at least one polar unit with atoms of nitrogen (N), sulphur (S), oxygen (O) and in some cases phosphorous (P). It has been reported that the inhibition efficiency decreases in the order of O < N < S < P.

The polar unit is considered as the reaction centre for the chemisorption process. Moreover, the size, orientation, shape and electric charge on the molecule determine the degree of adsorption and therefore, the effectiveness of inhibition. The Increase in the inhibition efficiencies with the increase of the concentration of Cefixime shows that the inhibition action is due to adsorption on the mild steel surface. The physisorption and chemisorption mechanism of corrosion inhibition is given in the **Schemetic 1**. Following are the types of adsorption that may take place at metal / solution interface:

(a) Electrostatic attraction between the charged molecules and the charged metal.

(b) Interaction of unshared electron pairs in the molecule with the metal.

(c) Interaction of p-electrons with the metal.

(d) Combination of (a) and (c)

In the HCl solution the following mechanism is proposed for the corrosion of iron and steel

According to this mechanism anodic dissolution of iron follows:

$$Fe + Cl^- \leftrightarrow (FeCl^-)_{Ads}$$

$$(FeCl^-)_{Ads} \leftrightarrow (FeCl)_{ads} + e^-$$

$$(FeCl)_{Ads} \leftrightarrow (FeCl)^+ + e^-$$

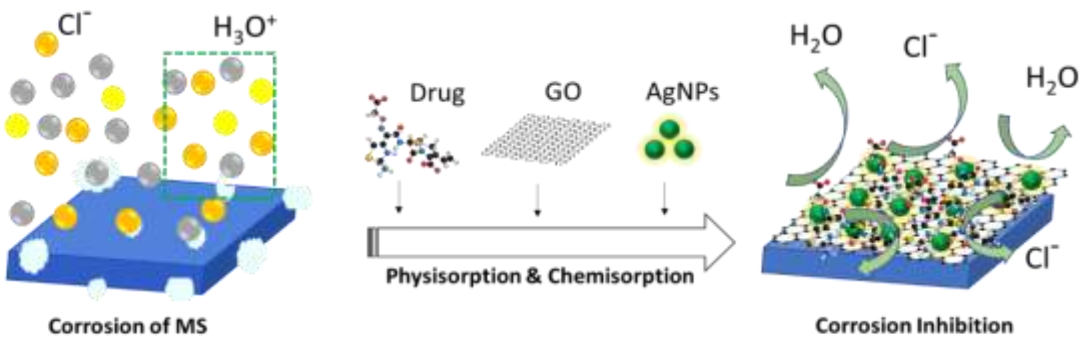
$$(FeCl^+) \leftrightarrow Fe^{2+} + Cl^-$$

The cathodic hydrogen evolution mechanism is:

$$Fe + H^+ \leftrightarrow (FeH^+)_{ads}$$

$$(FeH^+)_{ads} + e^- \leftrightarrow (FeH)_{ads}$$

$$(FeH^+)_{ads} + H^+ + e^- \leftrightarrow Fe + H^+$$



Scheme 1. Mechanism of corrosion inhibition

Materials and Methodology

Materials

All reagents used in this study were analytical grade chemicals. Silver nanoparticles were derived from *Bryophyllum Pinnatum* and graphene oxide were synthesized by modified Hummer method.

Synthesis of AgNPs

The *Bryophyllum Pinnatum* leaf broth was prepared using 10mg of fresh leaves that were collected from local market. The leaves were thoroughly washed three times with deionized water and chopped into small pieces. The chopped leaves were boiled and stirred in 100 ml of deionized water for 20 minutes at 60°C. After boiling, the mixture was cooled and filtered yielding 75 ml of transparent yellow colored leaf broth that was stored in the refrigerator. The leaf broth was added to 0.01M of an aqueous solution of silver nitrate ($AgNO_3$) and was stirred at ambient condition. After 10 minutes of stirring time, the color of the mixture changed from transparent yellow to dark brown indicates the formation of AgNPs in the reaction mixture. The synthesized liquid sample solutions were centrifuged at 2000 rpm for 1 hr. The pellets were washed with 2 ml of deionized water and dried at 90°C to form a thin film of AgNPs from which the AgNPs powder was obtained [14].

Synthesis of complex inhibitor

In this study, GO was obtained by modified Hummers method as described in many other literatures [15]. At first, Graphite (3.0 g) was stirred in 95% H_2SO_4 (75 mL). The required amount of $KMnO_4$ (6.0 g and 15 g) was gradually added to the solution keeping the temperature <10°C. The mixture was then stirred at 35°C for 2 h. The resulting mixture was diluted by water (75 mL) under vigorous stirring and cooling so that temperature does not exceed 50°C. The suspension was further treated by adding 30% aq. H_2O_2 (7.5 mL). The resulting graphite oxide suspension was purified by centrifugation with water until neutralization. Several GOs were analyzed by CHNS elemental analysis to evaluate the oxygen content. 50 ml of GO solution was prepared with ultra-pure water. Then, centrifugation was done for 15 min prior to sonication for 30 min in ultra-sonic bath at 30°C.After preparation of GO, centrifugation and sonication were done to make nanosheet. Antibiotic mixed solution was prepared at different concentration. Antibiotic solution with three different molar concentrations (1M, 2M and 3M) were prepared by dissolving the specified amount of Cefixime in acidic solution. The solution of Cefixime and AgNPs was prepared with three different molar (1M, 2M and 3M) concentrations at 1:10 ratio of AgNPs to Cefixime in acidic solution.

Corrosion test

Mild steel (MS) coupons with dimensions of 6.5cm × 3cm × 0.1cm were cut from a steel sheet. These coupons were used for weight loss experiments. Prior to their use, the samples were polished successively by the use of SiC papers and then thoroughly cleansed with distilled water. The specimens were dried and kept in a desiccator till their use. The corrosive solution of hydrochloric acid was used for all studies. Double distilled water was used to prepare the acid solutions. A medical grade of Cefixime was purchased from a pharmacy. Cefixime with a chemical structure shown in **Figure 1,** is a third-generation cephalosporin antibiotic that is stable to hydrolysis by beta-lactamases. All the experiments were performed at room temperature. The inhibition efficiency (%) and corrosion rate were calculated from weight loss measurement technique.

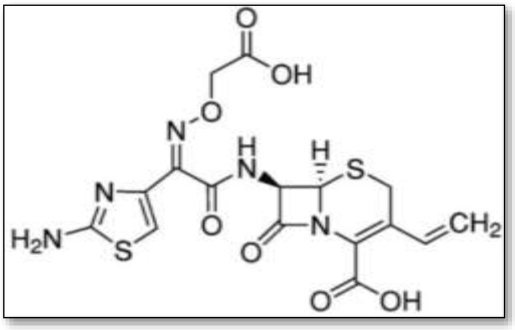


Figure1. Molecular structure of Cefixime

Results and discussion

Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) was performed to identify the surface morphology of the prepared sample. In Fig 1(a) the presence of GO was clearly observed as form of nanosheet which indicated that GO had a flaky, smooth and paper like structure [16]. When AgNPs were doped in GO the crystal AgNPs were homogenously distributed in GO nanosheet in Fig 1(b). The SEM image of **Figure 1(a) and 1(b)** ensure the accessibility of GO-AgNPs in the drug. The AgNPs were uniformly spread on GO with an average size of around 100 nm.

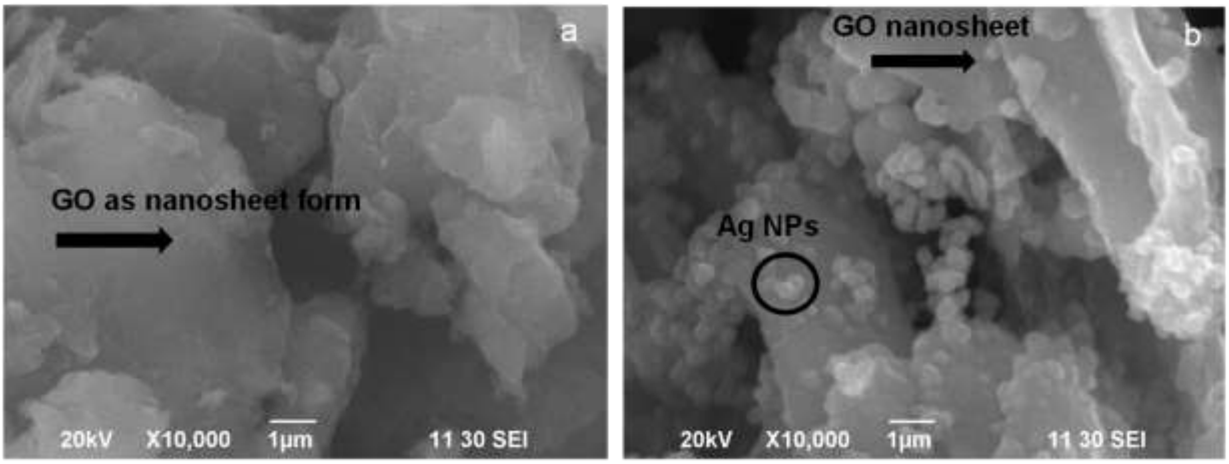


Figure 2. The scanning electron microscopy of (a) GO (b) AgNPs doped in GO

Weight loss measurements

Inhibition efficiency of Cefixime drugs that are commercially available and also environmentally safe was tested in 1N solution of hydrochloric acid solution against MS at room temperature by weight loss technique. Inhibition efficiency results for Cefixime, Cefixime with AgNPs and Cefixime along with AgNPs and GO are obtained using weight loss measurements. From the overall experiment, it is clear that the corrosion of mild steel significantly decreased by introducing the antibiotic and the antibiotic with AgNPs along with GO into the corrosive medium. The increase of inhibition efficiency seems to be proportional to the inhibitors concentration. It may be suggested that the inhibition caused by the adsorption and coverage of the inhibitor molecules on the steel surface [16]. It is appeared that the adsorption and coverage of Cefixime, Cefixime along with AgNPs and Cefixime along with AgNPs and GO molecules inhibit corrosion. It has been observed the weight loss of the mild steel in the corrosive medium was reduced with addition of different concentration of inhibitor.

Effect of Cefixime in corrosive medium

The weight loss measurements of MS in the presence of Cefixime in 1.0 M HCl at different concentrations of Cefixime drug under study are summarized in **Table 1**. It has been observed that the corrosion rate of MS decreased in 1.0 M HCl solution with the increasing concentration of Cefixime.

Table 1. Weight loss values and the calculated inhibition efficiency for the mild steel corroded by 1N HCl in the absence and presence of different concentrations of Cefixime drugs in days.

Inhibitor concentration	1 Day		2 Days		3 Days	
	Weight loss	IE%	Weight loss	IE%	Weight loss	IE%
Blank	.8092	_	1.8095	_	2.2973	_
1×10^{-3} M	.2606	67.80	.2646	85.34	.2686	88.31
2×10^{-3} M	.2326	71.26	.2366	86.92	.2416	89.48
3×10^{-3} M	.2056	74.60	.2096	88.42	.2226	90.31

The corrosion inhibition efficiency increased with a corresponding increase in the concentration of the inhibitor. This may be due to the sufficient adsorption and the wider coverage of the inhibitor molecules. The calculated values of the corrosion rates indicate that the corrosion rates of the mild steel in the corroding medium were reduced by the addition of different concentrations of the inhibitor. It has also been observed that the weight loss increase as the time of exposure increased.

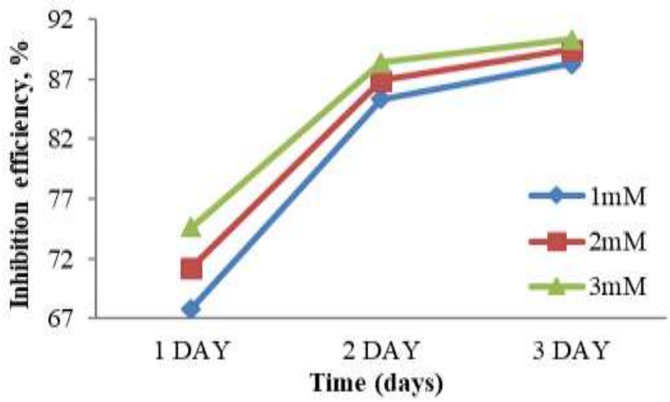


Figure 3. The variation of weight loss with respect to days for the corrosion of mild steel in 1N HCl solution in absence and presence of different concentrations of Cefixime.

Effect of Cefixime with AgNPs in corrosive medium

In **Table 2**, it has been observed that the weight loss measurements of MS in the presence of AgNPs with Cefixime in 1.0 M HCl at different concentrations the corrosion rates of mild steel in 1.0 M HCl solution with the addition of AgNPs and Cefixime decreased as the concentration of the inhibitor increased.

Table 2. Weight loss values and calculated inhibition efficiency for MS corrosion in 1N HCl in the absence and presence of different concentrations of Cefixime along with AgNPs in days

Inhibitor concentration	1 Day		2 Days		3 Days	
	Weight loss	IE%	Weight loss	IE%	Weight loss	IE%
Blank	.8095	_	1.8092	_	2.2973	_
1×10^{-3}M	.1775	78.07	.2096	88.42	.2388	89.60
2×10^{-3}M	.1505	81.40	.1796	90.07	.2138	90.69
3×10^{-3}M	.1215	84.99	.186	91.78	.1868	91.86

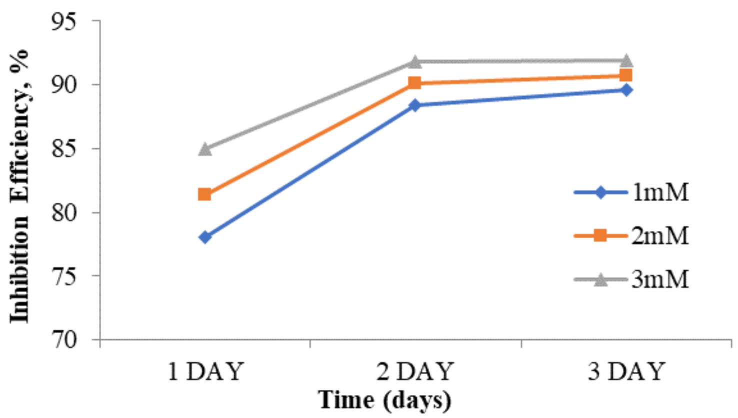


Figure 4. The variation of weight loss with respect to days for the corrosion of MS in 1N HCl solution in the absence and presence of different concentrations of Cefixime along with AgNPs

Figure 4 represents the weight loss variations with the change of concentration using 1N HCl solution with Cefixime and AgNPs. When AgNPs is added to prepare solution the weight loss of MS decreases than the previous observation is studied.

Effect of GO with Cefixime and AgNPs in the corrosive medium

In the presence of GO with AgNPs and Cefixime in 1.0 M HCl at different concentrations the weight loss measurements of MS are summarized in Table 3.

Table 3. Weight loss values and the calculated inhibition efficiency for MS corrosion in 1N HCl in the absence and presence of different concentrations of the inhibitors (Cefixime along with AgNPs and GO) in days

Inhibitor concentration	1 Day		2 Days		3 Days	
	Weight loss	IE%	Weight loss	IE%	Weight loss	IE%
Blank	.8092	_	1.8095	-	2.2973	-
1×10^{-3}M	.1350	83.32	.1369	92.43	.1604	93.01
2×10^{-3}M	.1310	83.81	.1348	92.55	.1597	93.05
3×10^{-3}M	.1289	84.07	.1320	92.70	.1401	93.90

The weight loss of MS decrease with the increase of the concentration of inhibitors shown in Figure 5, in which GO is used along with 1N solution of HCl, Cefixime and AgNPs.

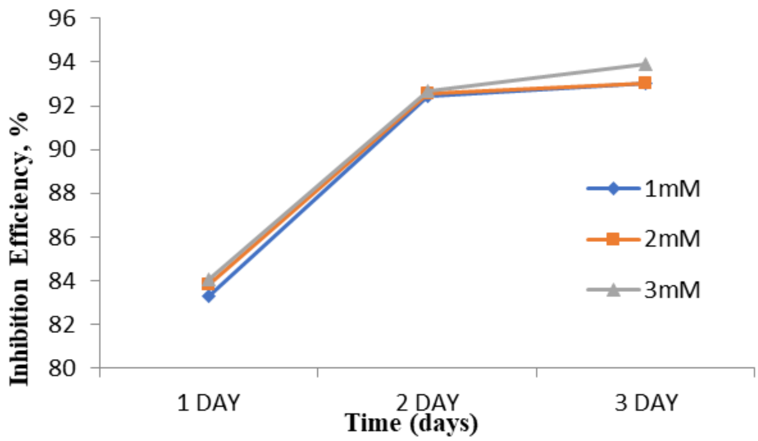


Figure 5. The variation of weight loss with respect to days for corrosion of MS in 1N HCl solution in the absence and presence of different concentrations of Cefixime along with AgNPs and GO

Now the overall weight loss comparison and inhibition efficiency for inhibitors in an indication is given below: In order to measure the weight loss variation of MS the Fig 6 is plotted in which it is clear that when only Cefixime is used with solution the weight loss is smoothly increased but when AgNPs is used with Cefixime the weight loss degradation is significantly changed. However, when GO is used in solution along with Cefixime and AgNPs the value of weight loss is smaller than Cefixime and Cefixime with AgNPs.

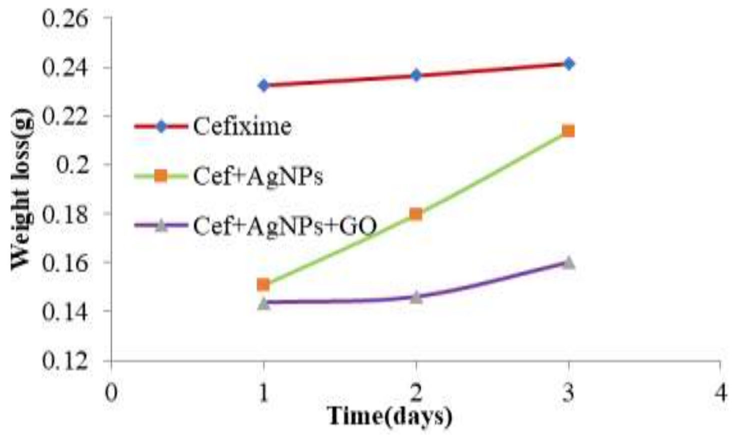


Figure 6. The variation of weight loss with respect to days for corrosion of mild steel in 1N HCl solution for Cefixime, Cefixime along with AgNPs and Cefixime along with AgNPs and GO

The corrosion inhibition efficiency (IE) of Cefixime, Cefixime and AgNPs and Cefixime, AgNPs, GO is graphically plotted in Fig 6 where the IE of Cefixime + AgNPs and GO is greater than others in which it is clear that the corrosion rates can be significantly reduced by using the Cefixime drug with various NPs where the inhibitor molecule inhibits the corrosion by absorption and coverage in the surface [17].

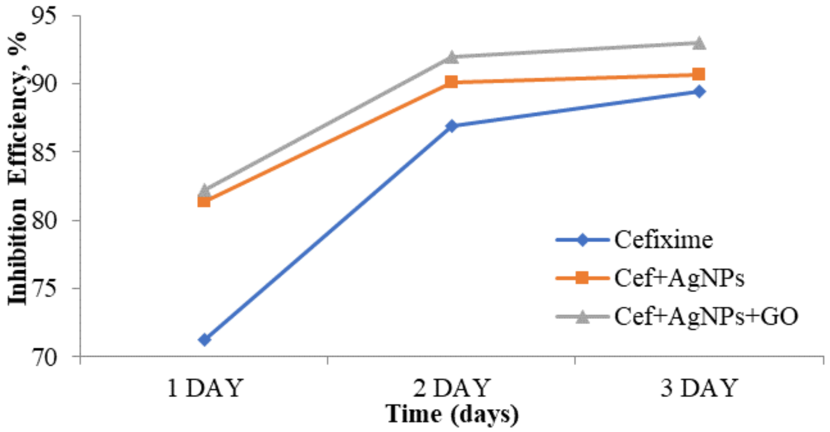


Figure 7. Comparison of corrosion inhibition efficiency among Cefixime, Cefixime along with AgNPs and Cefixime along with AgNPs and GO

Conclusion

Though organic, inorganic and mixed material inhibitors were used for a long time to combat corrosion, silver nanoparticles and graphene oxide are established elements that sufficiently inhibit corrosion. From the results obtained in this study, it is clear that the results obtained from weight loss methods revealed that the antibiotic (Cefixime), silver nanoparticles and graphene oxide are effective corrosion inhibitors for mild steel in HCl solution. Furthermore, it was observed that the inhibition efficiency increased with the increase of exposure time and the addition of the inhibitors. The results obtained from weight loss method and inhibition efficiency studies revealed that silver nanoparticles and graphene oxide are more effective inhibitors than organic compound.

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