Corrosion inhibition of iota-carrageenan natural polymer on aluminum in presence of zwitterion mediator in HCl media

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**ABSTRACT**

t-Carrageenan a natural polymer has been used as corrosion inhibitor of aluminum in presence of pefloxacin mesylate, acting as zwitterionic mediator, in acidic medium. Considerable improvement in inhibition efficiency occurred in the presence of the mediator. Activation energy of corrosion and other thermodynamic parameters such as standard free energy, standard enthalpy, and standard entropy of the adsorption process revealed better and well-ordered physical adsorption layers in presence of pefloxacin. Adsorption isotherms in absence or presence of pefloxacin mediator appropriately fit in the Langmuir isotherms. The scanning electron microscope (SEM) images demonstrated smooth, glossy, and relatively coherent adsorption layers of the inhibitor on the metal surface in aqueous solution. After the exposure to 2.0 M HCl for 2 h, a smaller but consistent regular shaped fractured layer is obtained.

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1. Introduction

The use of environmentally-friendly compounds in various applications gained wide interest in the recent years due to the global awareness of the impact of the human activities on the ecology of our planet. This had diverted the attention of researchers to re-consider using natural products, natural polymers, plants and plant extracts as green corrosion inhibitors. Such green compounds are less harmful to the environment and to humans and can act effectively as successful corrosion inhibitors. They have many advantages over chemical inhibitors such as being natural, cheap, readily available and in general nontoxic with optimal biodegradability profile. Many green inhibitors have been studied such as plant seeds [1,2], leaves [3–5], plants aqueous extract, peels, fruits [6–11], pectin [12], lignin [13], oil extracts [14–16] and plant alka-loids extracts [17,18]. Carrageenan is a gel-forming polysaccharide obtained by extraction of *Rhodophyceae* red seaweeds, in particular from *Chondrus crispus*, *Euchema*, *Gigartina stellata* and *Iridaea*. The major constituents of such compound are the so-called carrageenans, co-polysaccharides with a linear backbone of β-D-galactose and 3,6-anhydro-α-D-galactose partially sulfated (Fig. 1). Various degrees of sulfation (between 15% and 40%) identified by a Greek prefix: the three commercially available carrageenans are called Iota t-(mono-sulfate), Kappa κ-(di-sulfate), and Lambda λ-carrageenan (three-sulfate). The first two are gel-forming systems, whereas λ-carrageenan is a thickening agent [19].

On the other hand, pefloxacin mesylate is a fluoroquinolone antibiotic that offers a broad spectrum of antibacterial activity against some microorganisms [20]. Pefloxacin contains three tertiary amine groups and a carboxylic acid group within its structure (Fig. 2). These acidic and basic groups allow pefloxacin to exist in a zwitterionic form at some pH values and to undergo the protolytic equilibria summarized in Fig. 2. At low pH value, the amine groups are protonated and pefloxacin is positively charged. At higher pH value the carboxylic acid groups are deprotonated and pefloxacin is negatively charged. The interesting acid–base properties of pefloxacin could be of great importance in corrosion studies as it could act as mediator in the adsorption of polymeric molecules to metallic surfaces, which in some cases are weakly or cannot be adsorbed at all due to configurational or steric factors.

Aluminum and its alloys numerously used as vessels, pipes, machinery and chemical batteries could form passive oxide layer against corrosion. Upon pickling using hydrochloric acid, this passive layer readily dissolves leaving the aluminum surface unprotected [21,22]. In this report, t-carrageenan is studied as green corrosion inhibitor mediated by pefloxacin mesylate on the aluminum surface. The formation of well-oriented synergistic adsorption layers at the solid/liquid interface at different temperatures and in acidic media was investigated via the kinetic and thermodynamic parameters. Morphology of the adsorption layers also checked and investigated by scanning electron microscopic technique (SEM).
2. Experimental

2.1. Materials and methods

\( \text{\textalpha{-}Carrageenan} \) purchased from FMC Corporation Gelcarin GP-379NF and used as received. Pefloxacin mesylate was obtained for a Jordanian pharmaceutical company and used without any further purification. 99.7\% Aluminum sheets (Aldrich) abraded with emery paper up to 1200 grade were cut into 30 x 10 x 1.5 mm dimensions. The sheets were washed with acetone, and dried between filter paper prior use.

Scanning Electron Microscope (SEM); Polaroid films were used for the micrographs. The samples mounted on the specimen stabs, and coated with gold ion by sputtering method with DSM 950 (ZEISS) model, Polaron (E6100) model. Semi-micron balance (Saratorius 2024 MPb) was used for weight measurements in Eqs. (1) and (2) with triplicate replications and a precision of ±0.01 mg.

2.2. Adsorption layers formation

White powder (1.0 g) \( \text{\textalpha{-}carrageenan} \) dissolved in 200 mL of distilled water and stirred magnetically at elevated temperatures up to 40 °C until complete dissolution and homogeneity took place. Four different solutions that contain different \( \text{\textalpha{-}carrageenan} \) concentrations namely; 0, 400, 800, 1200 and 1600 ppm, by weight, in 200 mL of 1.0 M HCl solution were prepared. Therein, aluminum sheets were immersed in the sequent solution tubes. The tubes were transferred to a fixed temperature thermostat, and kept there for 2 h. After time completion, the sheets were removed from the acidic solution, rinsed and washed thoroughly with distilled water, cleaned with a soft cloth and then dried to constant weight. The same procedure was repeated in the presence of 400 ppm pefloxacin mediator using 1.5 and 2.0 M HCl solution at different temperatures; 10, 20, 30 and 40 °C. The mediator was dissolved in HCl solution prior to the addition of different \( \text{\textalpha{-}carrageenan} \) concentration solutions. The inhibition efficiency was calculated as follows;

\[
\text{Inhibition efficiency} \left( \% \right) = \frac{W_0 - W_i}{W_0} \times 100
\]

where \( W_0 \) and \( W_i \) were the weight loss of aluminum in the absence and in the presence of inhibitors, respectively. The corrosion rate (i.e. \( R_c \)) of aluminum was determined from the following relation;

\[
R_c = \frac{W}{St}
\]

where \( W \) was the weight loss of aluminum. \( S \) was the surface area of the aluminum sheet and \( t \) was the exposure time.

3. Results and discussions

3.1. Adsorption layers at solid/liquid interfaces

Formation of adsorption layers on the surface of aluminum was primarily checked by weight loss measurement and the results are summarized in Figs. 3 and 4. In Fig. 3 the normalized weight loss was monitored with respect to changes of inhibitor concentration in the absence and presence of mediator, HCl concentration, and temperature. The weight loss was directly proportional to temper-
ature and inversely proportional to the concentration of \(\kappa\)-carrageenan inhibitor. In addition, similar exponential decay curves in the absence or presence of mediator, as well as larger weight loss in the absence than in the presence of the mediator were observed. The inhibition efficiency (Fig. 4) was directly proportional to inhibitor concentration and inversely proportional to temperature. Moreover, increase of corrosiveness of HCl with concentration always led to increase in weight loss and decrease in inhibition efficiency. Table 1 summarizes the weight loss, corrosion rate and inhibition efficiency values at different temperatures, and pefloxacin and \(\kappa\)-carrageenan concentrations in 2.0 M HCl solution.

It has been proposed that the aluminum oxide layer on the aluminum surface interacts with water to produce aluminum hydroxide layer (Al–OH). Such hydroxylated layer could, depend on pH value, form either positive (Al–OH\(_2^+\)) or negative site layers (Al–O\(^-)\) [22]. The pH for the potential for zero charge of aluminum lies between 6 and 9 [23–25], and therefore in acidic solution (1.0–2.0 M HCl solution) the positive charge of Al–OH\(_2^+\) species dominates forming oriented surface sites. Such positive surface sites could hook and attract electrostatically negative sulfated and partially negative charge oxygen heteroatoms of \(\kappa\)-carrageenan leading to the formation of adsorption layers. Along with that, the prior addition of pefloxacin mediator in the acidic medium (i.e. 1.0 M HCl), can mediate the adsorption \(\kappa\)-carrageenan to the metal surface through a protonated tertiary amine group (i.e. \(\text{R'}_2\text{HN} –\text{R}–\text{COOH}\)). Such a compound may interact with the metallic surface through the carboxylate group and with the \(\kappa\)-carrageenan through the positively charged protonated amine group. Furthermore, the formation of a positively charged metallic surface by the adsorption of pefloxacin can contribute to the inhibition of corrosion repelling the corrosive protons and creating a protective layer that shields the metal from corrosion. In addition, the protonated tertiary amine groups of the adsorbed pefloxacin molecules will repel each other causing a decrease in entropy and consequently a tighter adsorption to the metallic surface as shown in Fig. 5. The fluorine atom may also contribute to the adsorption through hydrogen bonding to the hydroxyl group of surface (Al–OH) and/or to the hydroxyl group of \(\kappa\)-carrageenan. All of the above simultaneous electrostatic interactions may lead to a tight and well-ordered adsorption protective layer that contributes to the inhibition of corrosion.

Several remarks could further be deduced from Figs. 3 and 4; temperature increase from 10 to 40 °C induced large decline in inhibition efficiency values. The inhibition efficiency decreased from 91.8 at 10 °C to 33.5% at 40 °C using [\(\kappa\)-carrageenan] = 1600 ppm (Fig. 4). This reflects that at elevated temperatures, the surface gains larger kinetic energy enough to prohibit and expel the adsorbed molecules away from metal surface, and therefore minimum coverage of the surface took place. In addition, the presence of pefloxacin mediator had induced larger increase in inhibition efficiency values. In some cases, the increase reached 50% (e.g. 40 °C). This may be attributed to the ability of pefloxacin to mediate the adsorption of \(\kappa\)-carrageenan to the aluminum surface and to form more effective protective layers at the metal surface.

3.2. Activation energy of corrosion process

The minimum energy required for corrosion process to occur in the absence or presence of inhibitors (i.e. activation energy \(E_a\)) is
a measure of the resistivity of the metal to corrosion. This is a crucial parameter that could be determined by the equation [26,27]:

\[ R_c = \frac{Ae^{E_a/R}}{C_0} \]

where \( A \) is pre-exponential factor, \( R \) is gas constant and \( E_a \) is the activation energy. Eq. (3) shows the corrosion rate (\( R_c \)) calculated using Eq. (2), varies linearly with reciprocal temperature (1/T) (Fig. 6).

The calculated values of activation energy and the correlation coefficients, \( r^2 \), of the curve fitting at the various experimental conditions are summarized in Table 2. It could be seen that the addition of \( i \)-carrageenan to the corrosive solution produces two to threefold increase in the activation energy values depending on the concentration of \( i \)-carrageenan. On the other hand, the presence of \( i \)-carrageenan and pefloxacin in the reaction mixture further increased the activation energy by 4.3–7.8 kJ/mol. These findings clearly demonstrate that the presence of pefloxacin in HCl solution enhances the effectiveness of \( i \)-carrageenan as a corrosion inhibitor for aluminum. The observed increase in the effectiveness of \( i \)-carrageenan can be attributed to the synergistic adsorption of \( i \)-carrageenan and pefloxacin on the surface of aluminum.

3.3. Adsorption isotherms & thermodynamic parameters

Adsorption isotherm describes the relation of the amount of substance attached to surface with its solution concentration through an equation. Langmuir isotherm relates the fraction of the covered surface \( \theta \) to the concentration of solution (C) (in g L\(^{-1}\)) through the relation [28]:

\[ \frac{C}{\theta} = \frac{1}{K} + \frac{C}{C_0} \]

where \( K \) is the equilibrium constants of the adsorption process. Plot of \( C/\theta \) versus \( C \) can be used to determine the adsorption equilibrium constants (\( K \)). Fig. 7 shows a plot of \( C/\theta \) versus \( C \) for the data obtained herein and the linear relationship observed confirms that the adsorption of \( i \)-carrageenan on the surface of aluminum fits the Langmuir isotherm.

The values of the \( K \) and the correlation coefficients of the fitting curve are summarized in Table 2. The equilibrium constant values can further be utilized to calculate the standard Gibbs free energy (\( \Delta G_{\text{ads}} \)) of the adsorption process using the following relation [29]:

\[ \Delta G_{\text{ads}} = -RT \ln(55.5K) \]

where 55.5 mol L\(^{-1}\) was the molar concentration of water substituted with 1000 g L\(^{-1}\) to meet the unit requirement of \( K \) (in L g\(^{-1}\)). Furthermore, \( \Delta G_{\text{ads}} \) could also be calculated from the thermodynamic relation:

\[ \Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}} \]

where \( \Delta H_{\text{ads}} \) and \( \Delta S_{\text{ads}} \) were the standard enthalpy and entropy of adsorption, respectively. Moreover, Van’t Hoff equation used to calculate the standard enthalpy of adsorption (\( \Delta H_{\text{ads}} \)) from the slope value of \( \ln K \) versus 1/T plot as follows [30]:

Fig. 4. Inhibition efficiency (%) versus \( i \)-carrageenan concentration in the absence of pefloxacin denoted as continuous line (———), and in the presence of 400 ppm pefloxacin denoted as dashed line (———) using different HCl concentrations at (A) 10 °C, (B) 20 °C, (C) 30 °C, and (D) 40 °C.
Table 1
Weight loss, corrosion rate and inhibition efficiency values at different temperatures, and pefloxacin and \( \alpha \)-carrageenan concentrations in 2.0 M HCl solution for 2 h.

<table>
<thead>
<tr>
<th>Pefloxacin (ppm)</th>
<th>( \alpha )-Carrageenan (ppm)</th>
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<th>Wt loss (mg)</th>
<th>( R_c ) (mg cm(^{-2}) h(^{-1}))</th>
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Fig. 5. Schematic representation of adsorption layer formation using \( \alpha \)-carrageenan inhibitor in the absence and presence of pefloxacin mesylate mediator on the aluminum surface.
\[ \ln K = -\frac{\Delta H_{\text{ads}}}{RT} + I \]

where \( I \) is the constant of integration. However, from Eqs. (5) and (6)

\[ \ln(55.5K) = -\frac{\Delta G_{\text{ads}}}{RT} = -\frac{\Delta H_{\text{ads}}}{RT} + \frac{\Delta S_{\text{ads}}}{R} \]

This is re-arranged to be:

\[ \ln K = -\frac{\Delta G_{\text{ads}}}{RT} - \ln55.5 = -\frac{\Delta H_{\text{ads}}}{RT} + \frac{\Delta S_{\text{ads}}}{R} - \ln55.5 \]

Plot of \( \ln K \) versus reciprocal temperature \((1/T)\) in Eq. (9) yields slope value equals \( -\Delta H_{\text{ads}}/R \), and intercept value equals \( \Delta S_{\text{ads}}/R - \ln55.5 \), for which \( \Delta H_{\text{ads}} \) and \( \Delta S_{\text{ads}} \) could be determined, respectively [26,31].

The calculated values of the adsorption equilibrium constants and other thermodynamic parameters in the absence and the presence of pefloxacin at various temperatures investigated are summarized in Table 2. The equilibrium constant values decreased as temperature increased due to larger surface energy that could sufficiently release and desorb the adsorbed molecules and/or hinder or impede the adsorption of inhibitor and mediator on the metal surface as follows:

\[ \text{Adsorption} \frac{\text{high } T}{\text{low } T} = \text{Desorption} \]

The higher equilibrium constant values determined in presence of pefloxacin add another proof that demonstrates the ability of pefloxacin to enhance the adsorption of \( \iota \)-carrageenan on the aluminum surface. The calculated values of the standard free energy of adsorption \( (\Delta G_{\text{ads}}) \), the standard enthalpy of adsorption \( (\Delta H_{\text{ads}}) \) and the standard entropy of adsorption \( (\Delta S_{\text{ads}}) \) summarized in Table 3. It has been proposed that the absolute standard free energy value of the adsorption process up to 20 kJ mol\(^{-1}\) or less attributed to physisorption, while 40 kJ mol\(^{-1}\) or higher consistent with chemisorption process [32,33]. The absolute \( \Delta G_{\text{ads}} \) values (Table 3) in the absence or presence of mediator confirm that adsorption is physisorption type. Furthermore, the absolute standard enthalpy value for physisorption and chemisorption approaches 40 and 100 kJ mol\(^{-1}\), respectively [34]. Accordingly, the absolute \( \Delta H_{\text{ads}} \) values in absence or presence of mediator lies in the physisorption adsorption range. This unambiguously provides another evidence that adsorption process lies in the physisorption range process. On the other hand, negative sign (i.e. less entropic) standard entropy of adsorption demonstrates that adsorbed inhibitor’s molecules on the metal surface were less entropic than free inhibitor’s molecules in the solution. Moreover, in the presence of mediator smaller \( \Delta S_{\text{ads}} \) value was observed, which indicated that better and more assembled adsorption layers with less entropic state occurred on the metal surface.

\[ 3.4. \text{ Micro-level SEM surface analysis} \]

The analysis of metallic surfaces after the exposure to acids and bases by scanning electron microscopy (SEM) is widely used to examine the nature and the topology of the interaction between the corrosion inhibitor and the metallic surface [35–40]. Fig. 8 compares the SEM images of aluminum surface that has been
subjected to different treatments. Fig. 8A, shows the severely damaged surface of unprotected aluminum after the exposure to 2.0 M HCl for 2 h. It can be seen that the acid has penetrated deep into the metal forming punctures, which is consistent with two-dimensional corrosive behavior of HCl. Fig. 8B and 8C show a SEM image of aluminum surface after been soaked in 400 ppm pefloxacin aqueous solution and 1600 ppm carrageenan and 400 ppm pefloxacin aqueous solution for 2 h, respectively. Both figures clearly show the formation of an adsorption layer at the surface of the aluminum surface, the cracks seen in Fig. 8C are most probably caused by defects in metal surface. Comparatively, Fig. 8D shows the aluminum surface after been exposed to 2.0 M HCl for 2 h in presence of inhibitor and mediator. All punctures appeared in Fig. 8A have totally been disappeared. Furthermore, Fig. 8D shows an adsorption layer similar to that in Fig. 8C was fractured into smaller and regular island layers with 100 μm² average surface area due to the corrosive action of HCl. These features provide strong evidence that the nature of corrosion is changed from pitting to general corrosion in presence of inhibitor and the thick fractured layer also shows the formation of oxide layer due to corrosion. Such adsorption layers play a dominant role in protecting aluminum surface against severe corrosive HCl molecules. Finally, these observations came in accordance with high inhibition efficiency = 91.8% upon the use of [1-carrageenan] = 1600 ppm and [pefloxacin] = 400 ppm values (Fig. 2), which adapts 1-carrageenan to be the next generation green and nontoxic alternative inhibitor for many chemical and toxic inhibitors.

4. Conclusions

1-Carrageenan natural polymer was studied as corrosion inhibitor of aluminum in presence of pefloxacin mesylate, which believed to act as zwitterion mediator, for the adsorption of 1-carrageenan on the aluminum surface. A significant increase in the inhibition efficiency values from 66.7% in the absence of mediator to 91.8% in the presence of mediator was observed. The enhancement of the inhibition efficiency attributed to the formation of a well-ordered and coherent physical adsorption layer on the surface of aluminum. This interpretation was confirmed by the higher activation energy, higher equilibrium constant, larger exothermic standard enthalpy and lower standard entropy of adsorption in presence of pefloxacin mediator. Smooth, glossy, and relatively coherent adsorption layers were formed on the metal surface in aqueous solution as revealed by SEM images. The exposure of aluminum surface to 2.0 M HCl for 2 h in presence of 1600 ppm 1-carrageenan and 400 ppm pefloxacin resulted with smaller but consistent regular shape fractured island layers.

### Table 3
Adsorption equilibrium constant and thermodynamic parameters in the absence and presence of pefloxacin mesylate mediator at different temperatures.

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<th>Pefloxacin (ppm)</th>
<th>Temperature (°C)</th>
<th>$K$ (L.g⁻¹)</th>
<th>$r^2$</th>
<th>$\Delta G_{ads}$ (kJ mol⁻¹)</th>
<th>$\Delta H_{ads}$ (kJ mol⁻¹)</th>
<th>$\Delta S_{ads}$ (J mol⁻¹ K⁻¹)</th>
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Calculated standard enthalpy and entropy of the adsorption process performed in the range of 10–30 °C.
Acknowledgment

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References

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