

Modeling and Optimization of Structural Steel Corrosion Inhibition using Barely Grass Extract as Green Inhibitor

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Abstract The work deals with studying the corrosion inhibition of structural steel in acidic medium (0.1M HCl) using barley grass extract as inhibitor. The effect of the concentration of inhibitor (432-768) ppm, time (15.3-176.7) h, and temperature (24-44)°C on corrosion rate, inhibition efficiency and degree of surface coverage of the metal alloy was investigated using Response Surface Methodology (RSM). Fitting of degree of surface coverage with Freundlich adsorption isotherm was conducted. The kinetics parameters of corrosion and inhibition processes including the activation energy and frequency factor were estimated as well as the thermodynamic parameters including the standard free energy of adsorption ΔG°_{ads} , the entropy of activation (ΔS°) and enthalpy of activation (ΔH°). The corrosion rate was found to increase with increasing time and temperature, while the inhibition efficiency was found to increase with increasing the inhibitor concentration and decrease with time and temperature. The RSM analysis results revealed that maximum corrosion rate of about 2.11 mg/h resulted at 42°C and 164 h without using inhibitor compared to 0.26 mg/h at 43°C and 72 h with using the green inhibitor respectively. The value and the negative sign of ΔG°_{ads} indicated that the inhibitor molecules adsorbed spontaneously onto the metal surface via physisorption. The positive shift of enthalpy of activation in presence of inhibitor reflected that the process of adsorption of the inhibitor on the alloy surface is an endothermic process and the negative values of entropy of activation represented association rather than dissociation of the inhibitor indicating the decrease of system disorder due the adsorption process. According to the estimated results, barely grass extract could be recommended as low cost green inhibitor for acid corrosion inhibition of structural steel used in manufacturing industrial equipment and vessels.

Keywords Barley grass extract, Inhibitor, Corrosion, Optimization, Modeling

1. Introduction

Steel is an important engineering material because of its outstanding structural and mechanical properties that recommended its use in various fields including oil and chemical industries. However, there are some challenges for applications of the alloy in a large industrial scale. The most important one is its moderate corrosion resistance. When steel structure exposed to an aggressive environment such as oil-well stimulation and other industrial processes including acid pickling, this may result in decrease the mechanical stability and the attractive appearance of the structure, therefore, the steel structure needs to be protected with a high performance treatment and may need to be designed with maintenance in mind if extended life is required.

The corrosion of structural steel is an electrochemical

process that requires the simultaneous presence of moisture and oxygen. Essentially, the iron in the steel is oxidized to produce rust, which occupies approximately 6 times the volume of the original material consumed in the process. The rate at which the alloy corrosion process progresses depends on the environment surrounding the structure, the most significant factors affected the process are time of wetness and the atmospheric pollution level.

To protect steel alloys from being corroded, several techniques are used including conversion surface treatments such as chromating, phosphating, etc., anodizing, electroplating and adding corrosion inhibitors. The key to success protection lies in identifying the corrosivity of the environment to which the structure will be exposed as well as defining the appropriate protection technique. A great number of scientific studies have been devoted to the corrosion techniques (Telegdi et al., 2000; Eliyan et al., 2013), however, adding corrosion inhibitors has been little involved.

Corrosion Inhibitors are chemicals that react with a metallic surface, or the environment the surface is exposed to resulted in giving the surface a certain level of protection.

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For the metals widely employed in the industry such as iron, copper, zinc and aluminum, adding corrosion inhibitors is an effective and convenient method to decrease the corrosion rate (Roberge, 1999).

Inhibitors slow corrosion processes by either increasing the anodic or cathodic polarization behavior (Hughes *et al.*, 2016), reducing the movement or diffusion of ions to the metallic surface, or increasing the electrical resistance of the metallic surface (Odewunmi *et al.*, 2015).

The addition of corrosion inhibitors is a standard practice in chemical, petrochemical and oil industries to control the internal corrosion of steel structures. Inorganic inhibitor including chromate (Cr_2O_4^-), nitrate (NO_2^-), molybdate (MoO_3^-), phosphate (H_2PO_3^-) and silicates have been the most widely used. Organic inhibitors belonging to different chemical families were tested and industrially applied as corrosion inhibitors for steel. These include hydroxyethyl, aminoethyl, and amidoethyl imidazolines (Villamizar *et al.*, 2007), N,N-di (poly oxy ethylene) (Migahed, 2005), and nicotinamide derivatives (Chakravarthy and Mohana, 2008). The inhibition of metal corrosion by organic compounds has been confirmed to be a result of adsorption of organic molecules at the metal surface due to the electrostatic attraction between the electrical charge of the metal surface and the ionic charge or dipole of the inhibitor molecules. Adsorption allows the collection of a thin film that does not react with the metal nor corrosive species, but rather acts as barrier that prevents corrosion of the base material. This phenomenon is influenced by the nature of the metal, the metal surface condition, mode of adsorption, type of aggressive electrolyte and by the chemical structure of inhibitors (Abd El-Lateef *et al.*, 2012; Abbasov *et al.*, 2013).

Although much inorganic, organic and macromolecular compounds have been showed good performances as corrosion inhibitors for different metals and alloys, many of these compounds are toxic and do not satisfy completely the requirements obeyed by the environmental protection standards. The new generation of environmental regulations requires the replacement of toxic chemicals with the so-called "Green chemicals". Therefore, the development of non-toxic and environmental friendly inhibitors is considered more important and attractive.

On another hand, plant extracts and products are organic in nature, and some of the constituents including tannins, amino acids, alkaloids, and pigments are known to exhibit inhibiting action (Al-Turkustani *et al.*, 2012; Buchweishaija and Mhinzi, 2008; Gadow *et al.*, 2017; Raja and Sethuraman, 2008; Zarrok *et al.*, 2013). Different extracts from agro sources were produced by simple procedures, they have been investigated and showed anticorrosive activities (Abdel-Gaber *et al.*, 2006; Benali *et al.*, 2013; De Gisi *et al.*, 2016 Ngobiri *et al.*, 2015; Pehlivan *et al.*, 2012; Singh *et al.*, 2013; Umoren *et al.*, 2015).

To the best of our knowledge, the present work is the first one that describes the using of barely grass extract as corrosion inhibitor. Barley grass is an agricultural

by-product; it is the leaf portion of the barley plant that remains after the seeds have been removed from agricultural, household and industrial sectors treatment. Barley grass has been recognized for its high concentrations of amino acids and other constituents. Because of the nontoxicity and eas to produce barely grass extract in high purity. The present work aims to use the discarded barley grass as eco-friendly source to produce green corrosion inhibitor for structural steel in acidic medium. Using this agriculture waste will provide two advantage to environment. The volume of agro waste could be reduced and the low-cost inhibitor could be easily produced for reducing the pollution problems arising from structural steel corrosion.

2. Experimental

2.1. Methodology

Response Surface Methodology (RSM) is a statistical tool used to investigate the interaction between several illustrative variables and one or more response variables. The process of RSM includes designing of a series of experiments for sufficient and reliable measurement of the response and developing a mathematical model of the second order response surface with the best fittings. The Software portable statgraphics plus for Windows software (5.1 version) was used to analyze the data. The mathematical empirical model is defined as:

$$Y = \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_{11}X_1^2 + \beta_{22}X_2^2 + \beta_{12}X_1X_2 \quad (1)$$

Where: Y: is the response or dependent variable; X_1 and X_2 are the independent variables; $\beta_0, \beta_1, \beta_2, \beta_{11}, \beta_{22}, \beta_{12}$ are the regression coefficients.

The analyses of variance (ANOVA) are used to determine significant differences between the effects of independent variables ($p < 0.05$). Pareto chart is used to identify the impact level of the independent variables on each considered response. The vertical line (significant front) in Pareto chart determines the effects that are statistically significant at 95% as confidence level. Main Trends and Surface Response, as well as the empirical regression model can be used to optimize the dependent parameter (responses). Theory and applications of RSM are highlighted in the literature (Raymond *et al.*, 2016).

2.2. Experimental Design

A central composite design of 16 experiments include 2-operating parameter (with $2 \times 2 = 4$ factorial points, 2×2 star-points and 8 repetitions of central point) was adopted for the experiments used for studying the effect of temperature and immersion time on corrosion parameters of structural steel without using inhibitor, while another central composite design of 18 experiment include 3-operating parameter was established for the experiments used for studying the effect of temperature, time, and inhibitor concentration on corrosion parameters. The

analysis for each sample was replicated three times. The experimental design for the experiments without inhibitor and with inhibitor are shown in Table 1 and Table 2 respectively.

Table 1. Independent Variables, the Coded and Natural Levels Employed in a Central Composite Design for Optimization the Corrosion Parameters in the Absence of the Inhibitor

| Coded level | $-\alpha$ | -1 | 0 | 1 | $+\alpha$ |
|----------------|-----------|----|----|-----|-----------|
| Temperature °C | 26 | 28 | 34 | 40 | 42 |
| Time (hour) | 28 | 48 | 96 | 144 | 146 |

| Exp. No. | Temperature (°C) | Time (h) |
|-------------------|------------------|----------|
| 1 | 34 | 164 |
| 8* Central Points | 34 | 96 |
| 10 | 40 | 144 |
| 11 | 34 | 28 |
| 12 | 42 | 96 |
| 13 | 28 | 144 |
| 14 | 40 | 48 |
| 15 | 26 | 96 |
| 16 | 28 | 48 |
| Extra exp. | 30 | 96 |

α (axial distance) = $\sqrt[N]{N}$, where: N = number of experiments of orthogonal design. In this case there are 2 parameters, so: $\alpha = 1.4142$.

Table 2. Independent Variables, the Coded and Natural Levels Employed in Central Composite Design to Optimize the Corrosion Parameters in Presence of Inhibitor

| Coded level | $-\alpha$ | -1 | 0 | 1 | $+\alpha$ |
|-------------------------------|-----------|-----|-----|-----|-----------|
| Temperature °C | 24 | 28 | 34 | 40 | 44 |
| Inhibitor concentration (ppm) | 432 | 500 | 600 | 700 | 768 |
| Time (hour) | 15.3 | 48 | 96 | 144 | 176.7 |

| Exp. No. | Inhibitor Concentration (ppm) | Temperature (°C) | Time (h) |
|-------------------|-------------------------------|------------------|----------|
| 1 | 431.8 | 34 | 96 |
| 2 | 500 | 28 | 48 |
| 3 | 700 | 40 | 48 |
| 4 *Central Points | 600 | 34 | 96 |
| 8 | 500 | 40 | 48 |
| 9 | 700 | 28 | 48 |
| 10 | 700 | 40 | 144 |
| 11 | 500 | 40 | 144 |
| 12 | 700 | 28 | 144 |
| 13 | 500 | 28 | 144 |
| 14 | 600 | 44.1 | 96 |
| 15 | 600 | 24 | 96 |
| 16 | 768.2 | 34 | 96 |
| 17 | 600 | 34 | 176.7 |
| 18 | 600 | 34 | 15.3 |
| Extra exp. | 600 | 30 | 96 |

2.3. Preparation of Barley Grass- acid Solutions

About 100 g of the grass powder was refluxed with 0.1M HCl for about 5 h and was kept overnight to completely extract the basic components. The solution was filtered off and the filtrate was concentrated by rotary evaporator. The resultant gummy material was dried and powdered and weighed accurately by digital micro-balance. The extracted mass was used in preparation of the acid solutions of different concentrations of the inhibitor according to the experimental design.

2.4. Weight Loss Measurements

The present study employed weight loss as measurement techniques for corrosion to monitor the effect of temperature, time, and concentration of inhibitor on structural steel grade A500A corrosion in 0.1M hydrochloric acid solution in order to determine its viability in process industries. The acid used was of AR grade and used as such. Distilled water was used in the preparation of the test solutions.

The structural steel bars were cut to specimens of 2.5 cm \times 2.0 cm \times 0.6 cm. Each specimen was perforated to give a hole of same diameter, at about 0.5 cm from the length of the specimen. The specimens were abraded with emery papers (grades 320, 500, 800 and 1200) and then washed with distilled water and acetone. They have been weighed accurately. The pre-cleaned and weighed specimens were suspended in beakers containing the test solutions. Tests were conducted under total immersion conditions in (500-mL beakers containing 350 ml of the 0.1M HCl solution in absence and presence of the inhibitor at different temperature and time intervals according to the experimental designs.

After immersion time intervals, the specimens were carefully washed in double-distilled water, dried, and re-weighed accurately by analytic digital micro-balance. The weight loss was taken to be the difference between the weight of the specimen at a given time and its initial weight.

The corrosion rate (C_R) and the inhibition efficiency (η %) were calculated using the following equations:

$$C_R = \frac{W}{S t} \quad (2)$$

$$\eta \% = \frac{C_R - C_{R(inh)}}{C_R} \times 100 \quad (3)$$

where W is the average weight loss of three parallel structural steel specimens, S is the total area of the steel specimen, and t is immersion time, C_R and $C_{R(inh)}$ are the corrosion rates obtained in absence and presence of inhibitors, respectively. The degree of surface coverage θ for different concentrations of the inhibitor at different time and temperature was evaluated from the weight loss using the equation:

$$\theta = 1 - \frac{C_{R(inh)}}{C_R} \quad (4)$$

The efficiency of a corrosion inhibitor mainly depends on its adsorption ability on the metal surface. So, it is necessary to know the mechanism of adsorption and the adsorption isotherm that can give valuable information on the interaction of inhibitor and metal surface. The degree of surface coverage (θ) as function of concentration (C) of the inhibitor was studied graphically by fitting it to the Freundlich adsorption isotherm. The logarithmic adsorption isotherm relationship of Freundlich is represented by the following equation:

$$\log \theta = \log K_{ads} + n \log C \quad (5)$$

Where, K_{ads} and C represent the equilibrium constant of adsorption process, and inhibitor concentrations respectively.

The adsorption coefficient K_{ads} is related to the standard free energy of adsorption, ΔG_{ads}^0 by:

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^0}{RT}\right) \quad (6)$$

where, the constant value 55.5 is the concentration of water in the solution in mole /l, R is the gas constant and T is the absolute temperature.

The dependence of corrosion rate on temperature was discussed using Arrhenius equation and transition state equation to calculate thermodynamic parameters such as frequency factor (A), activation energy (E_a), entropy of activation (ΔS^*) and enthalpy of activation (ΔH^*).

The activation energy E_a , the enthalpy of activation ΔH^* and the entropy activation ΔS^* for corrosion of structural steel in 0.1 M HCl solutions in absence and presence of different concentrations of the green inhibitor at constant temperature range (24-42°C) were calculated from Arrhenius equation:

$$R_{corr} = A \exp\left(\frac{-E_a}{RT}\right) \quad (7)$$

And transition state equation:

$$R_{corr} = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \quad (8)$$

where, R_{corr} is the rate of corrosion from weight loss, N is the Boltzmann constant ($1.380658 \times 10^{-23} \text{ J.K}^{-1}$), h is Planck's constant ($6.6260755 \times 10^{-34} \text{ J.s}$), R is the gas constant, and T is the absolute temperature in Kelvin.

From the plot of $\log R_{corr}/T$ against $1/T$ in absence and presence of the green inhibitor, ΔH^* could be calculated from the slope of the relation [slope = $(-\Delta H^*/2.303R)$], and ΔS^* from the intercept [intercept = $\log (R/Nh) + \Delta S^*/2.303R$].

3. Results and Discussion

The RSM analysis results of the impact of temperature and immersion time on structural steel corrosion in 0.1M HCl in absence and presence of the inhibitor are shown in

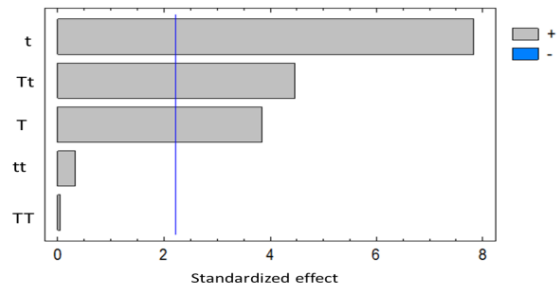
Figure 1 and Figure 2 respectively. A summary of the results is shown in Table 3.

The polynomial empirical models estimated from RSA are shown in the following equations:

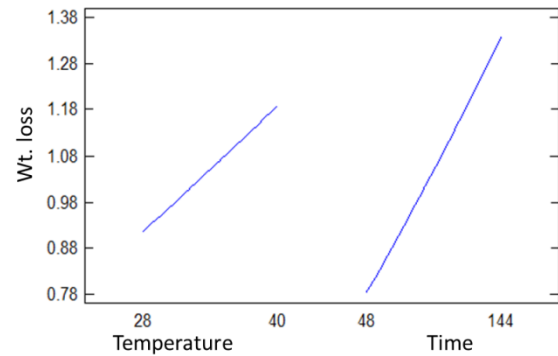
$$\text{Weight loss (in absence of inhibitor)} = 2.3579 - 0.0551*T - 0.0215*t + 0.00005*T^2 + 0.0008*T*t + 0.000005*T^2 \quad (9)$$

$$\text{Weight loss (in presence of inhibitor)} = 0.8483 - 0.0021*C + 0.0019*T - 0.00006*t + 0.000001*C^2 + 0.000004*C*T + 0.0000012*C*t - 0.00003*T^2 - 0.000009*T*t - 4.25E-7*t^2 \quad (10)$$

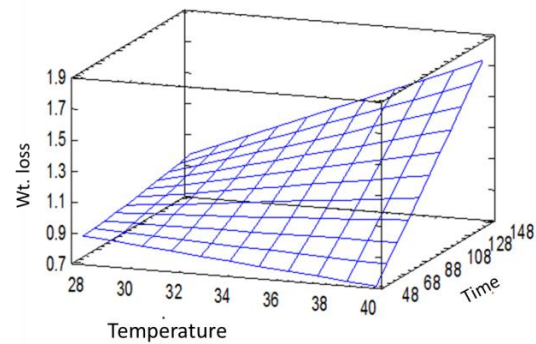
Where; T : Temperature, t : Time, C : Concentration of Inhibitor.



(A). Standardized Pareto Chart for weight loss

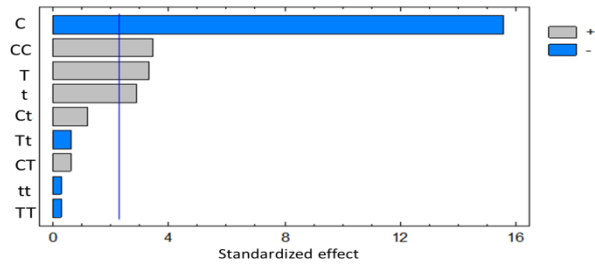


(B). General trends

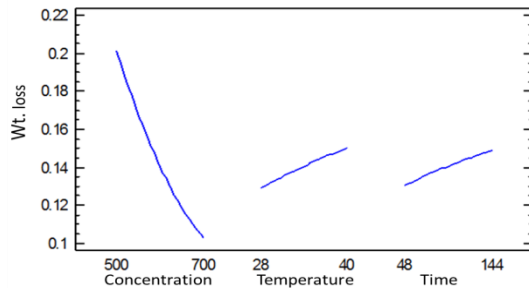


(C). Response Surface

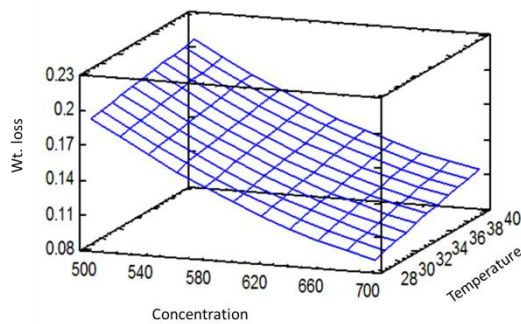
Figure 1. Pareto chart of the effect temperature and time (A), general trends (B), response surface (C) for corrosion process in absence of inhibitor



(A). Standardized Pareto Chart for weight loss



(B). General trends



(C). Response Surface

Figure 2. Pareto chart of the effect temperature, time and inhibitor concentration (A), general trends (B), response surface (C) for corrosion process in presence of inhibitor

Table 3. Summary of the RSM Analysis Results for Structural Steel Corrosion in 0.1M HCl in Absence and Presence of the Green Inhibitor

| Property | Optimum value | R-squared (adjusted for d.f.) % | Optimum conditions |
|-----------------------------------|---------------|---------------------------------|---|
| Wt. loss in absence of inhibitor | 2.10524 | 85.859 | Temp.= 42.5°C Time =163.9 h |
| Wt. loss in presence of inhibitor | 0.264643 | 94.406 | Inhibitor Concentration = 431.8 ppm Temp.= 44.1°C, Time =176.7 h |

In absence of Inhibitor, Pareto chart (Figure 1) demonstrate that both temperature and time are significant and have positive effect on increasing the weight loss from the corroded steel alloy. When temperature increases from 24-44°C, weight loss increases, the situation approves that

the corrosion reaction is an endothermic reaction. However, time seemed most significant regarding increasing the weight loss. The estimated polynomial empirical model is shown in equation (9).

The predicted regression coefficient ($R^2 = 85.859\%$) reflects that the model is capable to explain the experimental results. An optimum value of weight loss (2.16 mg/h) was estimated from the model analysis resulted at Temperature = 42.5°C and Time =163.9 h.

In presence of the inhibitor, the three parameters seemed to have significant effect on corrosion parameters such as the corrosion proceeds with much lower weight loss. The concentration of the inhibitor seemed the top most significant parameter followed by temperature and immersion time as shown in Pareto chart (Figure 2).

The predicted higher regression coefficient ($R^2 = 94.046\%$) reflects that the developed empirical model can adequately account for nearly all the variability in the system. An optimum value of weight loss (0.21 mg/h) was estimated from the model analysis resulted at Temperature = 44.1°C, Time =176.7 h, and inhibitor concentration = 431.8 ppm. The estimated polynomial empirical model is shown in equation 10.

The optimal operating conditions can be determined by navigating the response surfaces as described by the developed models (Figure 1(c), and Figure 2 (c)).

The reduction in wt. loss at optimum conditions of about more than 8 times (comparing of 2.1 by 0.26 mg/h) by adding the inhibitor confirmed the effective inhibition efficiency of the corrosion process by the green inhibitor.

In order to get more information about the mode of adsorption of the green inhibitor on the steel alloy surface, the thermodynamic properties of the corrosion processes in presence and absence of the green inhibitor were investigated.

The corrosion rates (CR), the inhibition efficiency ($\eta\%$), and the degree of surface coverage θ were calculated for all the experiments carried out in this work according to the experimental designs in absence and presence of inhibitor. Some θ values from the experiments run at identical conditions but with different concentration of inhibitor were tested graphically by fitting a suitable adsorption isotherm. In the present case, the plot of $\log \theta$ versus C (Figure 3) yields straight lines with the linear correlation coefficient (R^2) values close to unity, which suggests that the adsorption of inhibitor in 0.1 M HCl medium on the metal alloy surface obeys the Freundlich adsorption isotherm. The value of the slope of line (0.302) suggested that the adsorbed molecules form monolayer on the metal alloy surface and there is no interaction among the adsorbed inhibitor molecules (Chakravarthy and Mohana, 2014).

The correlation coefficient values ($R^2 = 0.9972$) also an indication that the inhibition of structural steel by the investigated inhibitor was attributed to the adsorption of the inhibitor molecules on the metal surface (El-Sayed et al., 2010).

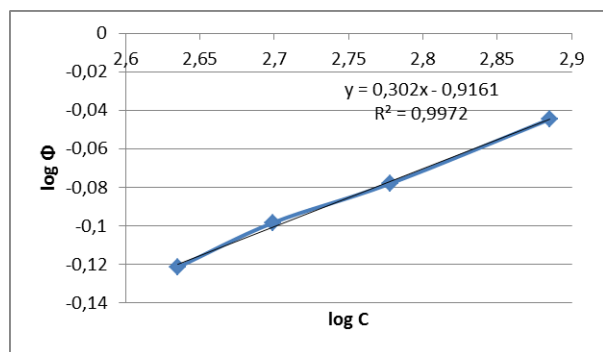


Figure 3. Freundlich isotherm for corrosion inhibition in presence of different concentrations of inhibitor

On another hand, the values of the standard Gibbs free energy of adsorption ΔG°_{ads} were calculated using Equation (6). The obtained value for ΔG°_{ads} was -4.6 kJ/mole. The negative value indicates the feasibility of the process and the spontaneous nature of the adsorption processes. On the other hand, it is usually accepted that the value of around -20 kJ/mol or lower indicates physisorption interaction between the metal surface and the inhibitor organic molecules whereas those around -40 kJ/mol or higher indicate chemisorption (Singh *et al.*, 2013).

Figure 4 shows the Arrhenius plots for the corrosion processes in absence and presence of the inhibitor. These plots represent the relation between the inverse of the absolute temperature on the x-axis and the corrosion rate constant on the y-axis. The activation energy, E_a , and the frequency factor, A , were calculated from the slopes and intercepts respectively using equation (7). Accordingly, the values of E_a and A were 15.5 kJ/mole and 836 hr $^{-1}$, and 15.19 kJ.mole and 112 h $^{-1}$ for the corrosion processes in absence and presence of the inhibitor respectively.

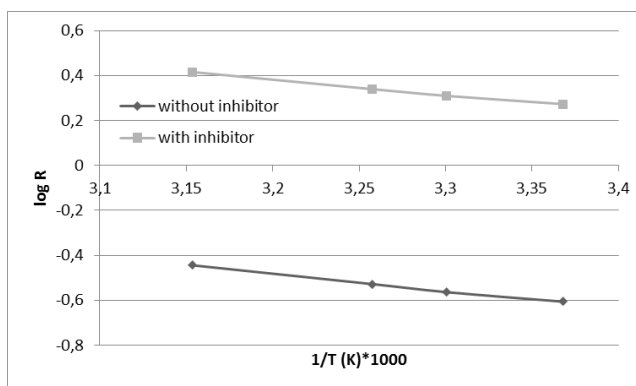


Figure 4. The Arrhenius plot for the corrosion process in absence and presence of the green inhibitor

Based on these values, the mechanism of the corrosion process may be discussed. It was reported that energies of activation below 42 kJ.mol $^{-1}$ generally indicate diffusion-controlled processes and higher values represent chemical reaction processes (Scheckel and Sparks, 2001). In terms of E_a , diffusion-controlled reactions are those governed by mass transfer or diffusion of the aqueous phase

from the solid reactant to the bulk solution. Accordingly, the obtained activation energy values obtained in the recent work indicate clearly a diffusion control mechanism for the corrosion process in absence as well as in presence of the green inhibitor, such as (the adsorption is more physisorption than chemisorption adsorption) (Li *et al.*, 2009).

It was reported that physical adsorptions (physisorption) occurs when the force of attraction existing between the adsorbate and adsorbent are vander Waals forces (weak forces) therefore this type of adsorption can easily reverse by heating or decreasing the pressure (Obi and Nsirim, 2016). However, under favorable conditions, physisorption and chemisorption can occur simultaneously or alternatively (Zaafarani, 2013).

To gain a deeper understanding of the corrosion process, the activation thermodynamic ΔH° and ΔS° parameters were calculated from the transition state theory using Eyring equation (8).

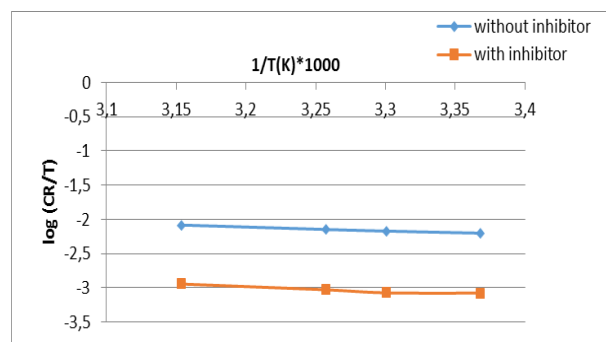


Figure 5. The Eyring plot for the corrosion process in absence and presence of the green inhibitor

Figure 5 shows the Eyring plot for the processes. From the values of the slope and the intercept the standard enthalpy of activation (ΔH°) and the standard entropy of activation (ΔS°) were calculated using equation (7). The values of ΔH° were $(12.60, 12.64$ kJ mol $^{-1})$, and the values of ΔS° were $(-197.57, -214.31$ kJ \cdot K $^{-1}$ \cdot mol $^{-1})$ in the absence and presence of inhibitor respectively. The positive values of ΔH° indicate that the corrosion reaction is an endothermic reaction in absence and presence of inhibitor. In another word, the corrosion rate increases with increasing temperature. However, the impact of temperature on the acid-metal reaction in presence of inhibitor is complicated, because temperature may induce different changes on the metal surface such as etching and desorption of inhibitor, moreover decomposition and/or rearrangement of the inhibitor molecules may take place at higher temperature (Singh *et al.*, 2010).

The sign and value of ΔS° gives information about the degree of order in the transition state. Large negative values of ΔS° , indicate unfavorable reactions, which means that the activated complex in the transition state has a more ordered or more rigid structure than the reactants in the ground state, while positive values of ΔS° , indicate favorable reactions (Noor and Al-Moubaraki, 2008).

A positive value for entropy of activation indicates that the transition state is highly disordered compared to the ground state in absence and presence of the inhibitor. In our case, the values obtained for ΔS^* were found to be negative represents association rather than dissociation indicating the decrease of system disorder due to the adsorption of inhibitor molecules on the metal alloy surface (Tang et al., 2006). The values of ΔS^* are higher for inhibited solutions than those for the uninhibited solution reflecting an increase in randomness on going from reactants to the activated complex.

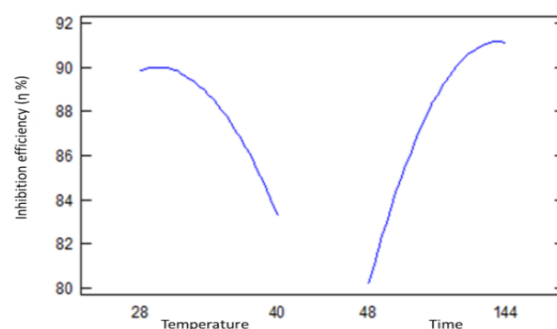
To optimize and modeling the inhibition efficiency ($\eta\%$) and degree of coverage of the metal surface θ in presence of the inhibitor, another 16 experiments were carried out at different temperatures and immersion time in absence and presence of a constant concentration of inhibitor (600) ppm according to an adopted experimental design. The inhibition efficiency and the degree of coverage were calculated for the 16 experiments using equations (3) and (4) respectively. The experimental design with the actual values of the dependent and independent variables is illustrated in Table 4.

Table 4. Actual Values of the Factors and Responses for Corrosion in Absence of Inhibitor, and in Presence of Inhibitor (600) ppm

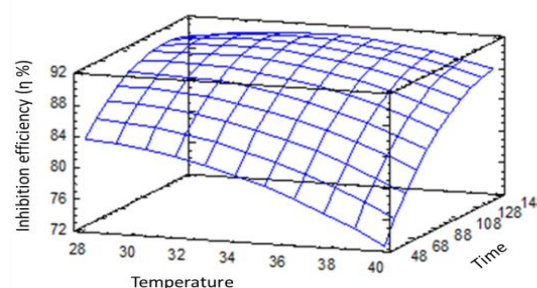
| Exp. No. | Temp. (°C) | Time (h) | Without inhibitor | | With inhibitor | | $(\eta \%)$ | θ |
|----------|------------|----------|-------------------|-------------------------|----------------|-------------------------|-------------|----------|
| | | | wt. loss (mg) | (CR) mg/h $\times 10^5$ | wt. loss (mg) | (CR) mg/h $\times 10^5$ | | |
| 1 | 34.0 | 164 | 1.64 | 200 | 0.169 | 19 | 90.458 | 0.905 |
| 8* | 34.0 | 96 | 1.05 | 219 | 0.138 | 29 | 86.905 | 0.869 |
| 10 | 40.0 | 144 | 1.58 | 219 | 0.109 | 15 | 93.117 | 0.931 |
| 11 | 34.0 | 28 | 0.55 | 391 | 0.118 | 154 | 60.672 | 0.607 |
| 12 | 42.5 | 96 | 1.25 | 260 | 0.173 | 36 | 86.200 | 0.862 |
| 13 | 28.0 | 144 | 0.84 | 117 | 0.096 | 13 | 88.542 | 0.885 |
| 14 | 40.0 | 48 | 0.8 | 333 | 0.098 | 41 | 87.813 | 0.878 |
| 15 | 25.5 | 96 | 0.9 | 188 | 0.119 | 25 | 86.806 | 0.868 |
| 16 | 28.0 | 48 | 0.95 | 396 | 0.074 | 31 | 92.237 | 0.922 |

* are central points

The RSM analysis for the experiments for corrosion without using inhibitor and in presence of constant concentration (600) ppm of the inhibitor showed no significance of the independent variables. However, the charts of the general trends and the response surface shown in Figures 6 and 7 respectively can clarify the effect of temperature and immersion time on inhibition efficiency ($\eta\%$) and degree of coverage of the metal surface θ . The summary of the results is shown in Table 5.

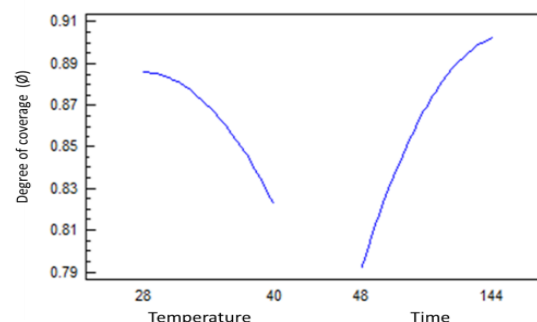


(A). General trends

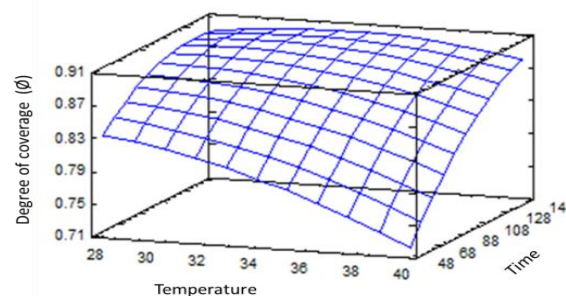


(B). Response Surface

Figure 6. General trends (A), response surface (B) for corrosion process in absence of inhibitor



(A). General trends



(B). Response Surface

Figure 7. General trends (A), response surface (B) for the inhibition efficiency ($\eta \%$) and degree of coverage of the metal surface θ in the presence of inhibitor (600) ppm

Table 5. Summary of the RSM Analysis Results for Structural Steel Corrosion in 0.1M HCl in Absence and Presence of (600 ppm) of the Inhibitor

| Property | Optimum value | Optimum conditions |
|-----------------------------------|---------------|-----------------------------------|
| Inhibition efficiency (η %) | 91.4136 | Temp.= 31.8 °C, Time =131.65 h |
| Degree of coverage (θ) | 0.903483 | Temp.= 33.5 °C, Time =152.3 h |

The polynomial empirical models estimated from RSA of the data of Table 4 regarding the experiments conducted in presence of constant concentration of inhibitor are shown in the following equations:

$$\text{Inhibition Efficiency } (\eta \%) = 39.8811 + 2.7936 \cdot T + 0.1083 \cdot t - 0.060 \cdot T^2 + 0.0078 \cdot T \cdot t - 0.0014 \cdot t^2 \quad (11)$$

$$\theta = 0.6287 + 0.016 \cdot T + 0.00009 \cdot t - 0.000436 \cdot T^2 + 0.00009 \cdot T \cdot t - 0.0000098 \cdot t^2 \quad (12)$$

Where; T: Temperature, t: Time.

The RSM analysis of the the experimental data of Table 4 revealed that as temperature increases (25.5-42.5)°C, degree of coverage θ and inhibition efficiency (η %) decrease, but time has opposite effect, θ and inhibition efficiency (η %) increase with immersion time (28-164) h.

The high experimental value of degree of coverage θ indicates the efficient coverage of the metal surface with the adsorbed inhibitor molecules. Conclusively, it reflects a good physical barrier shielding the metal alloy surface from corrosive medium and dumping the corrosion rate significantly.

The predicted optimum values of degree of coverage (0.9034) and Inhibition Efficiency (η %) (91.4136) estimated from RSA as well as those obtained experimentally are in line with the findings of other researchers who attributed the protection of the metal surface from corrosion in the acidic medium to the strong adsorption of the inhibitor molecules on the metal surface (Negm *et al.*, 2010; Aribo *Et al.*, 2016).

The effective performance of Barley grass extract as corrosion inhibitor may be related to Barley grass composition of (40%) proteins which are made up of one or more polypeptide molecules. Polypeptides are chains of amino acids. The highest inhibition efficiency of the investigated inhibitor may be attributed to the higher electron density on the functional groups carboxylic acid group (COOH), an amino group (NH₂) of barley grass amino acids. The higher electron density on the functional groups leads to greater adsorption, and consequently, higher inhibition. Also, the long length of the hydrocarbon chain in the organic molecule means a more bulk molecule, which screen the surface from attack (Migahed, 2005).

In view of the results cited above, barely grass extract could be considered as a promising low cost green inhibitor. It has the capacity for 0.1M HCl corrosion inhibition of structural steel used in manufacturing industrial equipment

and vessels such as pipes and scrubbers in oil, chemical and petrochemical facilities.

4. Conclusions

Barley grass extract has been prepared and tested for inhibition the corrosion of structural steel in acidic medium. The corrosion process was optimized and modeled in absence and presence of the new inhibitor throughout adopted experimental designs using Response Surface Methodology (RSM). The thermodynamics of the corrosion processes was studied. The green extract exhibited a very good performance as inhibitor for structural steel corrosion in 0.1 M HCl such as an optimum reduction in wt. loss of the metal alloy of more than 8 times by adding the inhibitor was predicted. The corrosion process in presence and absence of the green inhibitor seemed endothermic and the inhibition mechanism has been confirmed as physisorption. An optimum values of degree of coverage (0.9034) and Inhibition Efficiency % (91.4136) using 600 ppm of the green inhibitor was obtained which highly recommend using such low cost waste for corrosion inhibition of industrial steel equipment and vesseles.

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