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Application of a new inhibitor for the corrosion of iron in acidic solution: Electrochemical effect of a scorpion venom

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Abstract: In this study, the venom of the species *Leiurus abdullahbayrami*, known as the yellow scorpion from the Buthidae family, was applied for the first time as a natural corrosion inhibitor for iron in hydrochloric acid solution. The effectiveness of scorpion venom as an eco-friendly and natural inhibitor was determined by electrochemical methods such as electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (Tafel extrapolation method) and linear polarization resistance (LPR) after an hour of immersion. Four different concentrations were determined for the green and natural inhibitor scorpion venom in 1.0 M HCl, and it was observed that the corrosion of iron in these solutions was significantly inhibited. In general, the inhibition efficiency was above 80%. According to the potentiodynamic polarization data, it has been determined that the *Leiurus abdullahbayrami* venom acts as a cathodic-type inhibitor on the Fe surface. Finally, the surface images of the iron electrodes in 1.0 M HCl solutions without and with *Leiurus abdullahbayrami* venom after 1 h immersion were examined by field emission scanning electron microscope (FE-SEM), it was concluded that the surface containing scorpion venom had a flatter compared to the uninhibited surface.

Keywords: Scorpion venom, *Leiurus abdullahbayrami*, Acidic corrosion, Green inhibitor, Adsorption, EIS

1. Introduction

One of the most important problems experienced today is corrosion and its consequences. Corrosion is an inevitable natural disaster and an important phenomenon that must be struggled. In the industrial field, when considered in terms of production costs of metallic materials, it causes significant losses (Fang et al. 2019). All technical metals actually exist in nature as their oxides and sulphides, called ores. In this state, they are in their most stable state in nature, with minimum energy and maximum disorder. Since everything in nature is stable with the lowest energy and highest disorder, all metals spontaneously try to return to their stable state in nature when left uncontrolled. In fact, this rotation phenomenon is another expression of corrosion (Erbil 2012). The most commonly used metal in industry and architecture is iron, and the alloy is steel. They are highly preferred due to both their physical and chemical properties and cost. However, the biggest problem that limits the use of these materials is corrosion.

One of the methods of preventing corrosion, and the most preferred especially in cleaning processes with acidic solutions, is inhibitor applications. By means of various inhibitor compounds added to the corrosive solution, the interaction between the metal and the solution is interrupted, and these substances are physically and/or chemically adsorbed to the metal surface by the effect of the electric field formed at the interface (Doğru Mert 2017). The effectiveness of inhibitor substances is related to their chemical structures, and it is known that heteroatomic organic substances containing functional groups such as -OH, -COOH, -CN, -SN, double/triple bonds or unshared electron pairs will easily interact with the metal surface (Özkır 2019a). Unfortunately, chemicals known as corrosion inhibitors harm the environment due to their ecological side effects. However, in recent years, new and non-toxic inhibitors that cover the metallic surface strongly, are both highly efficient and environmentally safe, have attracted the attention of researchers (Srivastava et al. 2017; Nazlıgül et al. 2022).

Scorpions are predatory and living fossils that have existed on Earth for 430 million years by adapting very effectively to their natural habitat (Gomes and Gomes 2015). There are many harmful scorpions belonging to the Buthidae family in Türkiye, and one of the most poisonous Turkish scorpion species is known as *Leiurus abdullahbayrami* (Fig. 1). Scorpion venoms are the main sources that provide promising bioactive peptide molecules, especially in the discovery and development of new drugs in the field of medicine. Scorpion venoms consist of a complex mixture of small organic molecules and ions, bioactive peptides and proteins for the development of defense mechanisms (Numanoğlu Çevik and Kanat 2022). Scorpion venom incorporates both non-proteinaceous components consisting of water, mucosa, nucleotides, mucopolysaccharide, lipids, metals and inorganic compounds, and proteinaceous components consisting of enzymes and peptides (Tobassum et al. 2020).

The most important idea in this study emerged from the fact that scorpion venoms can play a role as an effective inhibitor in preventing metallic corrosion, as they have a molecular structure suitable for corrosion inhibitors, as they are known to contain molecules such as bioactive peptides and proteins. In the light of this idea, in this study, the effect of venom from the *Leiurus abdullahbayrami* species as an environmentally friendly green inhibitor on the corrosion of iron (mild steel) electrodes kept in 1.0 M HCl solution for one hour was investigated by some electrochemical methods. This study is also noteworthy because there is no previous study in the literature showing that scorpion venom has been used as an inhibitor to prevent metallic corrosion.

Fig. 1 Photograph of the yellow scorpion *Leiurus abdullahbayrami*, whose venom was used in the study (original)

2. Materials and Method

2.1. Leiurus abdullahbayrami venom

Leiurus abdullahbayrami venom was obtained from Niğde Ömer Halisdemir University Arachnology Museum (NOHUAM).

2.2. Determination of concentration of stock Leiurus abdullahbayrami venom solution and preparation of working solutions

The mass of scorpion venom obtained from NOHUAM was 0.1733 g. For this reason, the actual concentration of the stock scorpion venom solution was calculated as 0.3466% (w/v). After the stock solution concentration, the working concentrations for electrochemical experiments were determined as 0.160% (w/v); 0.100% (w/v); 0.050% (w/v); 0.020% (w/v) and 0.010% (w/v), respectively, from the most concentrated solution to the most dilute. Electrochemical experiments were carried out in 1.0 M HCl solution.

2.3. Electrochemical experimental processes

Iron (mild steel) was tapped as the working electrode with the following percentage composition (wt.%) such as 0.06030% Cr, 0.00222% Nb, 0.07890% Ni, 0.01100% V, 0.01100% P, 0.01040% Mo, 0.08400% C, 0.21700% Cu, 0.40900% Mn, 0.01900% S, 0.01620% Sn, 0.00198% Co, 0.10200% Si and 98.977% Fe. The electrode surfaces were added in a cylindrical mould including mixture of polyester and surface area of Fe electrode was 0.5024 cm^2 exposed to the HCl solution. The Fe electrode' surfaces were smoothed with 150, 600 grids of emery paper. The Fe electrodes' surfaces were polished with acetone and distilled water. The conventional three-electrode technique was applied utilizing the computer-integrated CHI-660B electrochemical analyzer device in experiments. The working test electrode is iron was utilized. The Pt plate is a counter electrode with a surface area of 2.0 cm^2, and the reference electrode is Ag/AgCl. All potentials are given by reference electrode.

Electrochemical experiments were conducted by LPR, EIS and Tafel extrapolation methods. These methods were performed in 1.0 M HCl solution without and with four different *Leiurus abdullahbayrami* venom concentrations. Before starting all electrochemical experiments, the Fe electrodes were immersed in the hydrochloride acid solution for one-hour in order to balance the system at 298 K for the open circuit potential (E_{corr}). EIS experiments were carried out on the E_{corr} at a frequency range of 10^5 to $5x10^{-3}$ Hz with 5 mV amplitude practised to the corrosion system. The Tafel extrapolation measurements were conducted with ±0.350 V anodic/cathodic potential from E_{corr}, respectively. It is practised at a scan rate of 1.0 mV s^{-1}. LPR method as the third experiment was conducted at a scan rate of 0.1 mV s^{-1} ±10 mV from E_{corr} and polarization resistance (R_p) was calculated from the potential slope versus current.

2.4. Surface examinations of iron electrodes

The images of Fe surfaces were examined by FE-SEM (Zeiss GeminiSEM 500 with computer controlled) technique in aggressive blank solution with and without 0.160% (w/v) *Leiurus abdullahbayrami* venom after 1 hour of duration at 298 K.

3. Results and Discussion

3.1. Evaluation of electrochemical data for Leiurus abdullahbayrami venom

It is important that the method to be applied to determine the corrosion rate does not essentially change the natural structure of the metal surface. For this reason, alternative current impedance, which is an electrochemical method and is thought to change the nature of the metal at a minimum level, is one of the most preferred methods (Erbil, 2012). Therefore, measurements were made and evaluated with EIS, LPR and Tafel extrapolation methods end of an hour of immersion in 1.0 M HCl solutions with and without four different concentrations of scorpion venom as inhibitor, in order to determine the electrochemical corrosion behavior of iron. The two types of equivalent circuits of the corrosion process were composed from the EIS data by using Zview2 software. Two types of electrical equivalent circuit models in Figure 2 and 3 for blank and all inhibited solutions, respectively were indicated in process.

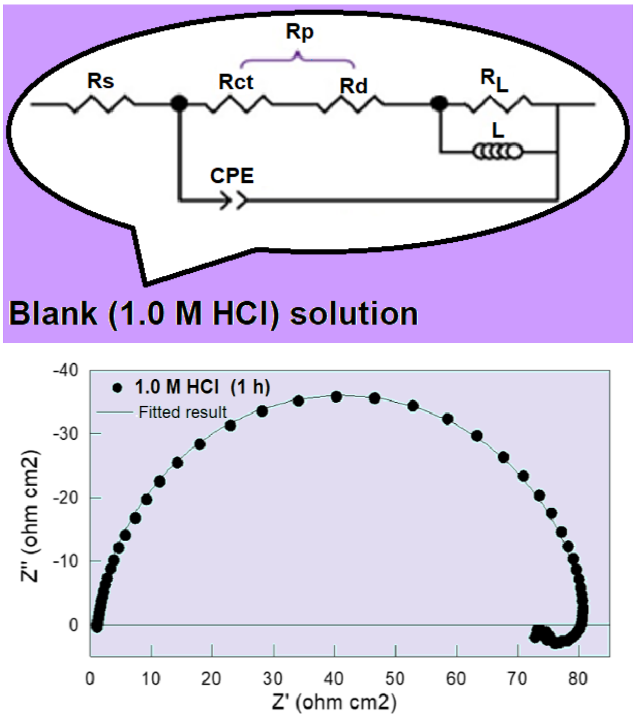

Fig. 2 Electrical equivalent circuit proposed and impedance diagram for blank solution after 1 h immersion

It will be seen that in Fig. 2 and 3, the two circuits proposed are dissimilar from each other. The most logical separation for solutions containing the scorpion venom is the inhibitor film composed on the Fe electrode surface and the resistance (R_{film}) it forms (Fig. 3). Film resistance results from the adsorption of complex organic molecules such as peptides and proteins in the scorpion venom, directed to the Fe electrode surface in the acidic solution. When four different concentrations of scorpion venom are added to the aggressive 1.0 M HCl electrolyte, it can be followed that the corrosion of Fe electrodes declines more plainly in the impedance diagram in Figure 3 (Özkır 2019b; Özkır 2021a). *Leiurus abdullahbayrami* venom adsorbed on the surface of iron in fact hinders the corrosion by forming a protective film layer on the Fe surface. In addition, this situation is clearly understood from the increasing radius as the inhibitor is added to the solution.

Impedance diagrams generally consist of two parts: High and low frequency regions. While the corrosion process consists of the total of these two frequency regions, charge transfer (R_{ct}) and diffuse layer (R_d) processes occur in the high frequency region. The low frequency region is basically the important part affected by the inhibitor. In other words, surface protection occurs with the film layer (R_f) formed due to total adsorption from the scorpion venom, as well as the products (R_a) accumulated on the surface due to corrosion.

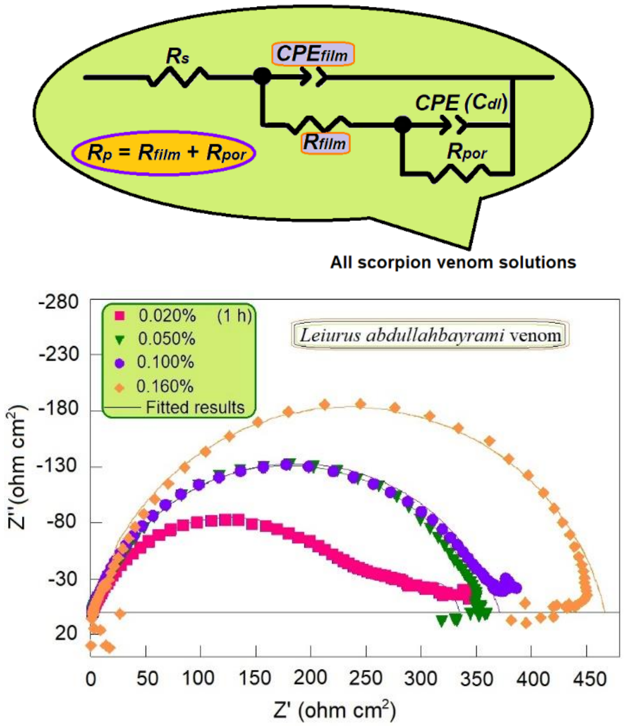

Fig. 3 Electrical equivalent circuit proposed and impedance diagrams in containing four different concentrations of *L. abdullahbayrami* venom

Looking at Fig. 3, the equivalent circuit proposed for the inhibited system consists of two constant phase elements: Double layer capacitance (CPE_{dl}), which refers to the double layer between the Fe metal and the solution, and film capacitance (CPE_{film}), which results from the adsorption of the scorpion venom on the surface of the Fe metal.

The polarization resistance (R_p) values obtained from the EIS, LPR and Potentiodynamic polarization experiments are indicated in Table 1.

Table 1 Electrochemical experiment data in solutions without and with *L. abdullahbayrami* venom

Scorpion venom	EIS				
C (w/v %)	**Blank**	**0.020**	**0.050**	**0.100**	**0.160**
E_{corr} (V/Ag/AgCl)	-0.474	-0.530	-0.522	-0.520	-0.514
R_s (Ω cm^2)	1.2	1.3	1.5	1.4	1.3
CPE (μF cm^{-2})	110	84	80	69	57
n	0.94	0.85	0.81	0.80	0.76
R_L (Ω cm^2)	8	-	-	-	-
L (H)	4	-	-	-	-
R_p (Ω cm^2)	72	335	356	370	466
η (%)	-	**78.5**	**79.8**	**80.5**	**84.5**
Scorpion venom	*LPR				
$^*E_{corr}$ (V/Ag/AgCl)	-0.475	-0.530	-0.529	-0.526	-0.523
$^*R_p$ (Ω cm^2)	71	351	355	392	435
$^*\eta$ (%)	-	**79.8**	**80.0**	**81.9**	**83.7**
Scorpion venom	**Potentiodynamic polarization				
$^{**}E_{corr}$ (V/Ag/AgCl)	-0.475	-0.531	-0.528	-0.530	-0.523
$-\beta_c$ (mV dec^{-1})	108	108	105	111	111
i_{corr} (μA cm^{-2})	265	62	55	51	41
$^{**}\eta$ (%)	-	**76.6**	**79.2**	**80.8**	**84.5**

At the end of the one-hour immersion period, the η% values calculated from the R_p values by the EIS method increased as scorpion venom was added to the solution medium. The distribution range of η% values was 78.5–84.5%. While the *CPE* value in blank solution was 110 $\mu F/cm^2$, it was monitored that it dominated when scorpion venom was added to the HCl solution. The distribution range of CPE values is 84–57 $\mu F/cm^2$. While the corrosion potential value (E_{corr}) was –0.474 V in HCl electrolyte, it shifted to more negative (cathodic) potentials in solutions containing *L. abdullahbayrami* venom (Table 1). According to the LPR method data, the $^{*}R_p$ value was 71 $\Omega\ cm^2$ in 1.0 M HCl solution without inhibitor, but it rised when scorpion venom was added to the acidic solution. $^{*}\eta$% values calculated from $^{*}R_p$ values increased as scorpion venom base was added to the HCl solution and the distribution range became 79.8–83.7%. The inhibitory efficiency results of the *L. abdullahbayrami* venom calculated by both electrochemical methods were highly consistent with each other (Özkır 2021b). The dissolution process parameters of iron electrode calculated by the Tafel extrapolation method, which is another electrochemical method, are shown in **Table 1. Potentiodynamic polarization curves of working electrodes in HCl solution for four different *L. abdullahbayrami* venom concentrations at 298 K are offered in Figure 4. While the corrosion current density (i_{corr}) value in the blank solution was 265 μA/cm^2, these values gradually dimunated as scorpion venom was added to the HCl solution.

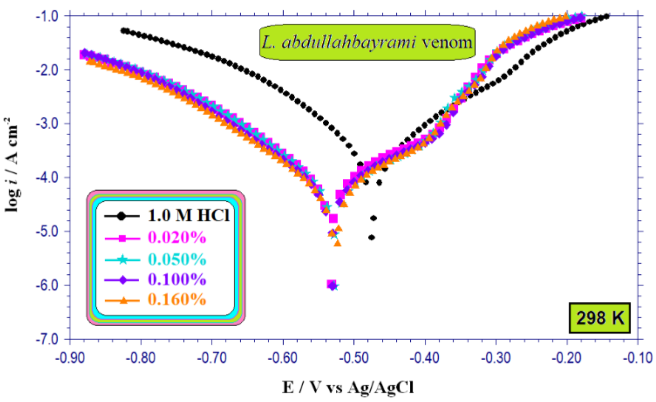

Fig. 4 Potentiodynamic polarization plots of Fe electrode in HCl solution for four concentrations of *L. abdullahbayrami* venom

In all experimental solutions, as the scorpion venom concentration enhanced, corrosion current density (i_{corr}) values decreased and inhibition efficiency values rised. While the cathodic Tafel constant ($-\beta_c$) was 108 mV/dec in the blank solution, it varied between 97 mV/dec and 102 mV/dec in the solutions with inhibitor. The fact that the cathodic Tafel constants calculated in solutions containing and without scorpion venom did not change much indicates that the hydrogen formation mechanism was not affected by the inhibitor scorpion venom studied. As can be seen from the semi-logarithmic current-potential curves and Table 1, the $^{**}E_{corr}$ values of Fe electrode read directly from the CHI device were -0.475 V at 298 K in an uninhibited solution, while the $^{**}E_{corr}$ values shifted to more negative (cathodic) potentials when scorpion venom solutions were added to the medium. The maximum potential change in solutions without and containing inhibitors is 56 mV. In the solution with scorpion venom, in contrast to the blank solution, the $^{**}E_{corr}$ values shift very slightly to negative values, and all of the shifts of the E_{corr} values are less than 85 mV (Wen et al. 2023). Looking at the cathodic curves in Figure 4, the contribution of scorpion venom significantly reduced the current density in 1.0 M HCl solution. For this reason, it was thought that the scorpion venom used acted as a cathodic inhibitor in 1.0 M HCl solution (Policarpi and Spinelli 2020; Akkoç et al. 2023). The results obtained with the three experimental methods applied were both supportive of each other and it was concluded that the adsorption of *L. abdullahbayrami venom* on the Fe surface is inevitable and it can also be used as a green inhibitor because it does not have an environmentally friendly effect.

A visual graphic summary of the electrochemical experiment data in Table 1 is presented in Figure 5.

3.2. Surface examinations by FE-SEM analysis

Since FE-SEM is a field emission scanning electron microscope, it provides the opportunity to perform much clearer surface analysis with high resolution (Singh et al. 2018). Detailed surface examinations were carried out by FE-SEM analysis to determine the surface morphologies of the Fe electrodes that were kept at 298 K for one hour in 1.0 M HCl solutions containing *L. abdullahbayrami* venom at the highest (0.160% w/v) concentration and without inhibitor. FE-SEM images were monitored in Figure 6.

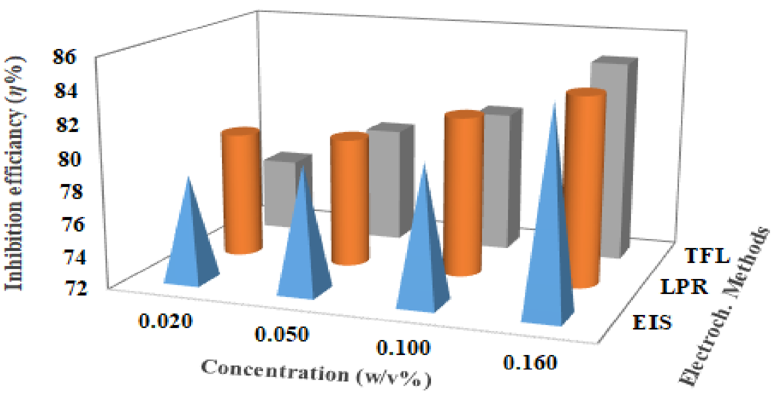

Fig. 5 Variation of inhibition efficiency values according to experimental methods and concentration

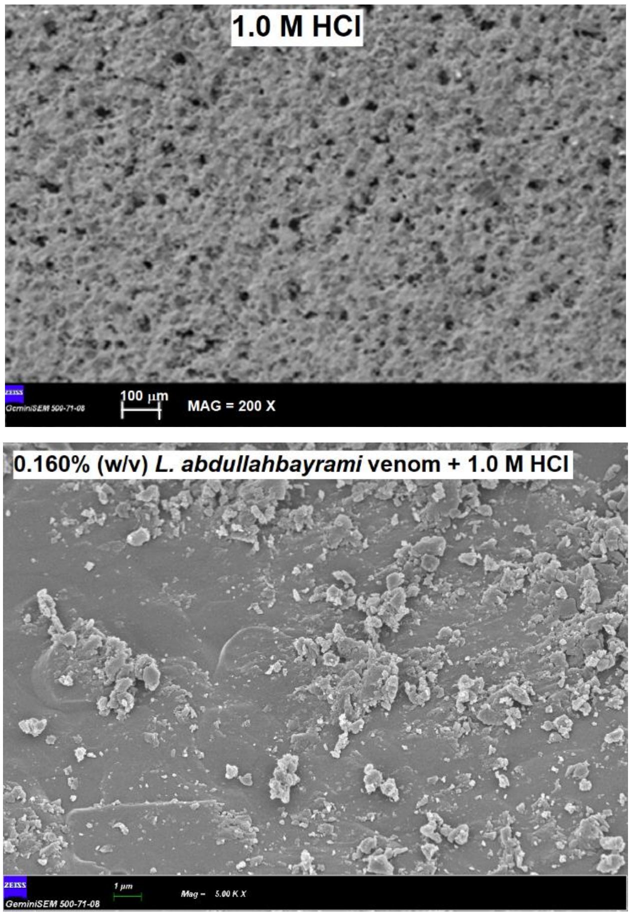

Fig. 6 FE-SEM images of the Fe electrodes for 1 h immersion at 298 K

It was observed that the surface of the Fe electrode, which was immersed in the solution without inhibitor, was indented and in the appearance of pits, the electrode kept in the solution with *L. abdullahbayrami* venom was flatter and the pits both diminuated in number and became smaller (Özkır and Kayakırılmaz 2020).

5. Conclusion

According to the results obtained with EIS, LPR and potentiodynamic polarization curves, it was observed that the inhibition efficiency values enhanced as the *Leiurus abdullahbayrami* venom concentration rised. Even in the solution containing the highest concentration of scorpion venom, Fe electrode is protected with approximately 85% inhibition after 1 hour of immersion time. Scorpion venom affected the corrosion of iron electrode in acidic solution as a cathodic-type inhibitor. In addition, FE-SEM micrographs clearly show that scorpion venom prevents corrosion of Fe surface by forming a protective inhibitor film on the metal surface.

This study stands out for the first application of *Leiurus abdullahbayrami* venom from the family Buthidae as an eco-friendly and green inhibitor for Fe electrode in 1.0 M HCl solution. The main sources of scorpion venom are bioactive peptide molecules. It has been reported that the main components in scorpion venom consist of a complex mixture of non-proteinaceous and proteinaceous components. Considering these main components and the results obtained, these properties are among the main reasons for the high inhibitory effectiveness in preventing metallic corrosion. The use of such compounds as corrosion inhibitors is a very important study in terms of both industrial processes and the development of a different application area, since they are biodegradable and do not contain harmful compounds.

Authors' contributions: DÖ, obtaining data & principle investigation & experimental measurements & editing & writing; OS, obtaining data & principle investigation & editing & writing.

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