A New Inhibitor Approach to the Corrosion of Mild Steel in Acidic Solution with Long-Term Impedance Tests: A New Application Area for *Hypnum cupressiforme* (Bryophyta)

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Abstract

The most important aspect of this study is that the effect of *Hypnum cupressiforme* Hedw. which is a bryophyte species as a "green inhibitor" on the corrosion behavior of mild steel in 1.0 M HCl solution at 298 K is being examined for the first time. The inhibitory effect of moss extract was investigated applying the electrochemical impedance spectroscopy (EIS) technique. Nyquist diagrams were performed by EIS to examine the variation of the different concentrations of the extract with some immersion-time parameters. Also, the surface charge of the metal in terms of the inhibition mechanism was determined by the EIS technique and as a result, it was found that the protonated inhibitor molecules were adsorbed directly onto the metal surface. The surface morphology studies of working electrodes were performed using field emission scanning electron microscope (FESEM) and optical metal microscopy techniques. Electrochemical tests and surface analysis studies support each other.

Keywords: Bryophyte, *Hypnum cupressiforme*, Green inhibitor, Acidic corrosion, EIS.

Uzun Süreli İmpedans Testleri ile Asidik Çözeltideki Yumuşak Çeliğin Korozyonuna Yeni Bir İnhibitör Yaklaşımı: *Hypnum cupressiforme* (Bryophyta) için Yeni Bir Uygulama Alanı

Öz

Bu çalışmanın en önemli yönü, 298 K'de 1,0 M HCl çözeltisindeki yumuşak çeliğin korozyon davranışına, bir briyofit türü olan *Hypnum cupressiforme* Hedw.'nin "yeşil inhibitor" olarak etkisinin ilk kez inceleniyor olmasıdır. Karayosunu ekstraktının inhibitor etkisi, elektrokimyasal impedans spektroskopisi (EIS) tekniği uygulanarak araştırılmıştır. Ekstrakt'ın farklı derişimlerinin bazı zaman parametreleriyle değişimini incelemek amacıyla, EIS ile Nyquist diyagramları oluşturulmuştur. Ayrıca, EIS tekniği ile metalin inhibisyon mekanizması açısından yüzey yükü belirlenmiş ve bunun sonucunda, protonlanmış inhibitor moleküllerinin doğrudan metal yüzeyine adsorplandığı bulunmuştur. Çalışma elektrotlarının yüzey morfoloji incelemeleri alan emisyonlu taramalı elektron mikroskobu (FESEM) ve optik metal mikroskobu teknikleri kullanılarak gerçekleştirilmiştir. Elektrokimyasal deneylerle, yüzey analizi çalışmaları birbirini destekler niteliktedir.

Anahtar kelimeler: Briyofit, *Hypnum cupressiforme*, Yeşil inhibitor, Asidik korozyon, EIS.

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1. Introduction

Metallic materials undergo structural degradation called "corrosion" as a result of their interaction both electrochemically and chemically with their environment (Allaoui et al., 2017; Fang et al., 2019). Corrosion is a phenomenon that harms life from industry until it reaches homes (Xu et al., 2013). Since corrosion cannot be virtually eliminated in industrial and many areas, inhibiting and deceleration of corrosion have been their central focuses. In acidic solutions, the application of inhibitors is one of the most common and most influential methods used to protect metals against corrosion. Different organic compounds containing heteroatoms in their structure were synthesized and used as inhibitors on various metal surfaces (Emregül and Hayvali, 2006; Özkır and Çifcibaşı, 2017; Özkır, 2018, 2019). Also, synthetic organic and inorganic inhibitors are also used to prevent corrosion, but their utilization is restricted due to their toxic effects on the environment. For this reason, the trend towards environmentally friendly corrosion inhibitors called "green" is the majority instead of using toxic and harmful chemicals in recent years (Abakedi et al., 2016; Dar, 2011; Oguzie, 2008; Singh et al., 2016).

As a "green" word, it is a branch of technology and science that uses environmentally friendly chemicals and reduces the application of environmentally hazardous materials. Recently, scientists working in the field of corrosion science have drawn attention to the green synthesis of organic inhibitors using techniques such as the ultrasound and microwave method (Aljuhani et al., 2018; Ameta et al., 2015). Besides, different plant extracts (Abdel-Gaber et al., 2006; Alibakhshi et al., 2018) attract researchers for the development of green corrosion inhibitors. Plants are unique assets that turn solar energy into a source of life through photosynthesis. Photosynthesis is a phenomenon that cleans the water, soil and air in the environment (Sheldon, 2016). It is also the raw material of many fruits and vegetables that we use in our daily lives. The use of corrosion inhibitors obtained from plant extracts among all green compounds is important because it is harmless to human health and is of interest for to low environmental toxicity. If we compare the synthetic corrosion inhibitors with the corrosion inhibitors obtained from the plant extract, those obtained from the plant extract are less costly and obtaining is shorter and easier than the inhibitors obtained by synthesizing (Mo et al., 2016; Fang et al., 2019).

To use plant-derived compounds as corrosion inhibitors, it is first necessary to understand the mechanisms to reduce the corrosion rate. Aromatic compounds generally found in their structure have high inhibitory properties and electrochemical activity. The mechanisms of action of plants as corrosion inhibitors are generally as follows: They perform their functions either by adsorbing molecules and ions on the metallic material or by reducing the reaction rate in the cathodic/anodic region or by increasing the electrical resistance of the metal surface (Dar, 2011; Houbairi et al., 2013; Al-Senani, 2016).

Bryophytes, the ancestors of land plants, are spread all over the world from the equator to the poles. The first bryophytes which are probably liverworts most likely appeared in the Ordovician period, about 450 million years ago (Delwiche and Cooper, 2015) and today they have could been still able to survive. Despite its primitive structures, bryophytes have many adaptive features for adaptation to terrestrial life. One of these adaptive features is the biosynthesis of secondary metabolites which are enormously diverse in the bryophytes against environmental stress (biotic or abiotic). The secondary metabolites of the bryophytes such as terpenoids, phenolic compounds, alkaloids are a defense against the competition, microbial attack and, insect or animal predation. Moreover, these metabolites are also important in UV protection, drought tolerance, and freezing survival (Xie and Lou, 2009).

Several studies have reported the successful use of plant extracts containing secondary metabolites as green corrosion inhibitors to inhibit the corrosion of metals in an acidic and alkaline environment (Rani and Basu, 2012; El Ouariachi et al., 2010; Abiola et al., 2007; Okafor et al., 2005; El-Etre, 2003; Ebenso and Ekpe, 1996). In these studies, higher vascular plants were used as plant material. In this context, no published studies on bryophytes which are non-vascular earliest land plants have been encountered as plant material. Therefore, the present study aimed to indicate the usability of bryophytes as green inhibitors against corrosion and revealing their anti-corrosion effects.

The present study is especially important for the first time by testing a corrosion inhibitor of cosmopolitan moss species *Hypnum cupressiforme* in Turkey. For this purpose, it was aimed to investigate the effect of moss extract as an inhibitor on the corrosion of mild steel in 1.0 M HCl solution. It is focused to find out by

calculating some thermodynamic parameters with which the adsorption isotherm that this green inhibitor is adsorbed on the mild steel surface by electrochemical tests at different concentrations. As a result of all these studies, it has been discussed that the environmentally friendly extract, which is not harmful and toxic, is an application-oriented and highly effective inhibitor.

2. Materials and Methods
2.1. Plant material
The plant material was collected from Adana-Aladağ, Başpınar highplateau, 1014 m, 37°33' N, 35°24' E, on rock in July 2019 and identified using relevant literature (Smith, 2004; Cortini Pedrotti, 2006).

2.2. Preparation of extract solutions
Distilled water and HCl with analytical grade were used in all test solutions prepared for application in electrochemical experiments. The moss specimens were firstly cleaned from the grounded parts of its roots. Later, *H. cupressiforme* specimens were dried to prepare the stock solution of moss extract in an oven for approximately 2 h at 80 $^{\circ}$C and the moss specimens were powdered in a pestle. Powdered 7 g of the moss specimens were weighed and 250 mL distilled water was added and refluxed for 24 h. The refluxed solution was filtered and the extracted one was light yellow colored (Figure 1).
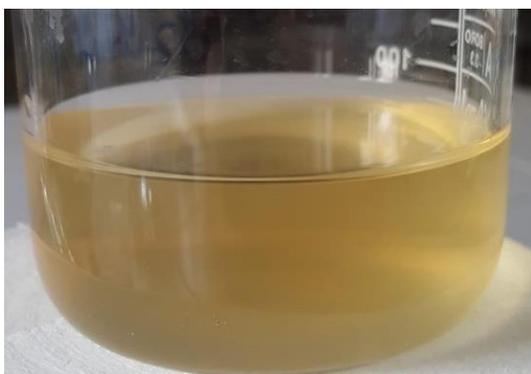

Figure 1. Filtered and evaporated moss extract

The concentration of the stock moss solution studied was 0.202% (w/v). Other concentrations were prepared by dilution of the stock solution. The concentration of the stock solution was determined by evaporation of 50 mL of the moss solution and weighed the residue. Electrochemical measurements were performed in 1.0 M HCl solution to provide electrolyte medium.

2.3. Electrodes and electrochemical tests
Mild steel with the following percentage composition (wt.%) such as 0.08400% C, 0.01100% P, 0.06030% Cr, 0.00222% Nb, 0.07890% Ni, 0.01100% V, 0.01040% Mo, 0.21700% Cu, 0.01900% S, 0.40900% Mn, 0.01620% Sn, 0.10200% Si, 0.00198% Co and 98.977% Fe was used as the working electrode. The electrodes were inserted in a cylindrical mold containing polyester and the surface area 0.5024 cm^2 of electrodes were exposed to the aggressive medium. The surfaces of the working electrodes were polished with 150 and 600 grids of abrasive paper before each electrochemical test. The electrodes' surfaces were cleaned with acetone and distilled water and allowed to dry at ambient temperature. Three conventional electrode techniques were used for all electrochemical experiments. The first of them is mild steel was used as the working electrode mentioned above. The second one, the counter electrode is a platinum plate with a surface area of 1.0 cm^2, and the third one is Ag/AgCl as the reference electrode. All potentials granted in this study are given by a reference electrode.

Electrochemical impedance spectroscopy tests were performed using a computer-controlled CHI 660B model electrochemical analyser. These tests were realized in 1.0 M HCl solution in without and with different moss extract concentrations. Before all electrochemical measurements, the working electrodes were immersed in the working solution for 1 h in order to stabilize the system for the open circuit potential (E_{corr}). EIS measurements were conducted on the E_{corr} at a frequency range of 10^5 to 5×10^{-3} Hz with 5 mV amplitude applied to the system. One, 48 and 120 h measurements were realized to examine long-term EIS experiments. Surface images were taken 120 h of duration in aggressive solution (1.0 M HCl) with and without moss extract using metal microscope (digital camera integrated OLYMPUS BX-51 model) and FE-SEM (Zeiss GeminiSEM 500 with computer controlled) techniques. The surface analyses were only performed in a 1.0 M HCl solution containing without and with 0.05% (w/v) moss extract for each surface measurement. The potential of zero charge (E_{pzc}) of mild steel was found by using EIS method. The values of the polarization resistance (R_p) at open circuit potential were enrolled at $\pm$ 0.200 V (Ag/AgCl) ranges and the R_p values recorded against their potential values were plotted as a graph. The all electrochemical experiments were conducted at 298 K.

3. Results and Discussion
3.1. EIS test results

EIS is one of the most common and practical techniques used to investigate the protective effect of inhibitor molecules on metal (Sürme and Gürten, 2009; Sürme et al., 2011). The most important reason for choosing this method is that it does not disrupt the metal / solution interface in time-based tests. Inhibitor concentrations studied in 1.0 M HCl solution are 0.001%, 0.005%, 0.01%, 0.025% and 0.05% (w/v), respectively. The experimental data of the Nyquist diagrams obtained from the electrochemical analyser were enrolled as "txt" files and the equivalent circuit of the system was formed from these data by using Zview2 software. Proposed equivalent electrical circuits (Figure 2) and Nyquist diagrams formed of the mild steel electrodes in hydrochloric acid solution and all concentrations of the moss extract have been indicated for 1 h, 48 h and 120 h exposure times in Figure 3. Figure 2 shows two types of equivalent circuit models. The first is the equivalent circuit used for the 1.0 M HCl solution in Figure 2a. The other is the circuit model valid for all inhibitor solutions (Figure 2b).
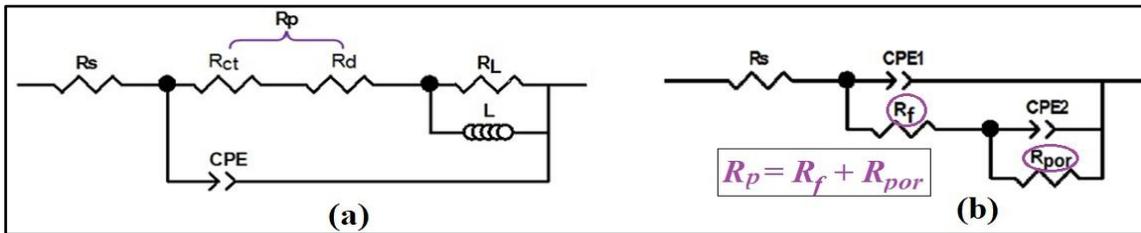

Figure 2. Proposed equivalent circuits for blank (a) and inhibited (b) solutions

The main difference between the two is the presence of film resistance (R_f) caused by adsorption in inhibited solutions. On the other hand, only for the blank solution are inductive resistance (R_L) and inductance (L). All these equivalent circuits describe the corrosion process, and especially the adsorption process in inhibited solutions. The polarization resistance (R_p) in the equivalent circuit valid for the 1.0 M HCl solution is responsible for the charge transfer resistance (R_{ct}) together with the diffuse layer resistance (R_d). However, during the adsorption process of the moss extract to the metal surface, the polarization resistance includes the sum of the film resistance (R_f) and the pore resistance (R_{por}). When pore resistance is referred to here, all types should come to mind from the resistance of the accumulated species (R_a) originating from corrosion products on the metal surface to the charge transfer (R_{ct}) and diffuse layer resistance (R_d). While the inhibitor adsorbs to a mild steel surface, the contribution of these species is inevitable.
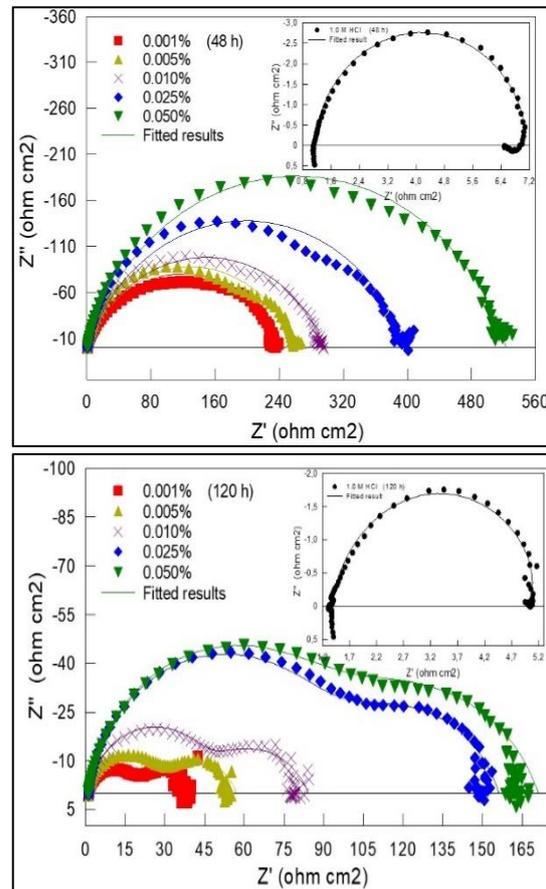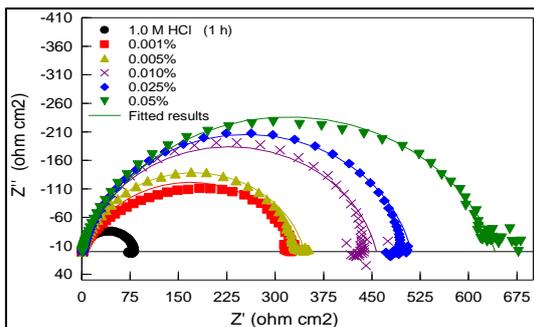

Figure 3. Nyquist plots for mild steel in 1.0 M HCl in the absence and presence of different moss extract concentrations after 1, 48 and 120 h immersion times

It is clear that from Figure 3 by adding moss extract to 1.0 M HCl solution leads to increase resistance owing to the adsorption of bryophyte molecules to the mild steel surface (Özkır et al., 2012). It is indicated that the charge transfer process occurring at the metal/solution interface is delayed with the contribution of the moss and that it is caused by the protective feature of this inhibitor. The impedance parameters related to the adsorption process are also presented in Table 1.

Table 1. The related impedance parameters obtained from fitting results for mild steel 1.0 M HCl solution with and without containing the moss extract at different exposure time.

Time / C (w/v %)	R_s (Ω cm^2)	R_p (Ω cm^2)	CPE (μF cm^{-2})	n	R_L (Ω cm^2)	L (H)	η (%)
1 h							
Blank	1.2	72	110	0.94	8	4	-
0.001	1.2	334	101	0.80	-	-	78.4
0.005	1.2	344	91	0.86	-	-	79.1
0.010	1.0	456	80	0.86	-	-	84.2
0.025	1.2	510	69	0.86	-	-	85.9
0.050	1.0	640	55	0.81	-	-	88.8
48 h							
Blank	1.1	5	10123	0.94	0.7	1	-
0.001	0.8	240	1037	0.74	-	-	97.9
0.005	0.9	258	523	0.76	-	-	98.1
0.010	1.1	296	301	0.75	-	-	98.3
0.025	1.1	396	107	0.77	-	-	98.7
0.050	1.1	522	67	0.79	-	-	99.0
120 h							
Blank	1.4	4	36520	0.89	0.4	0.3	-
0.001	1.2	40	5681	0.74	-	-	90.0
0.005	1.0	56	3395	0.74	-	-	92.9
0.010	1.2	83	1713	0.72	-	-	95.2
0.025	1.2	155	514	0.77	-	-	97.4
0.050	1.1	170	211	0.75	-	-	97.7

The protective effect of this moss extract is determined by calculating the percent inhibition efficiency (η%) values for each concentration of the inhibitor at each immersion time. The η% values were calculated with the following equation (Özkır, 2019b):

$$\eta\,(\%) = \left(\frac{R'_p - R_p}{R'_p} \right) \times 100 \qquad (1)$$

where η% is the percent inhibition efficiency value, R'_p and R_p are in inhibited and uninhibited polarization resistance values, respectively. Depending on immersion times in acidic solutions with and without inhibitor, deviations from the semicircles are observed in the EIS curves. The frequency scattering becomes more evident as the immersion times increase (especially at the end of 120 h). Frequency dispersion is also caused by the increment in surface roughness due to prolonged exposure to an acidic solution. In Figure 3, as the concentration rises at each immersion time, R_p values enhanced accordingly. The inhibitor protects the mild steel surface at the highest concentration (0.05%) with an 89% effect after a 1-hour immersion time. This is a very good and high result for green inhibitors. As a result, Nyquist diagrams in the moss extract solutions progress in depressed cycles at low and high frequencies. The high frequency loop is responsible for R_{ct} and R_d, the low one is control of R_f and R_a (Figure 2). According to EIS diagrams of Figure 3, the resistance values of both hydrochloric acid solution and solutions containing the moss extract decrease as the immersion times increase. In other words, the capacitive loop diameters of Nyquist curves are getting smaller.

It can be seemed clearly from both Figure 3 and Table 1 that the surfaces of mild steels immersed for 48 h in acidic solutions containing moss extract, have reached a more stable state than the first hour measurements. This means that the inhibitor molecules are adsorbed tightly on the mild steel surface and have a protective effect. It can also be easily understood from the fact that the inhibition efficiency values in Table 1 are above

98% at the end of 48 h. Also, at the end of this period, it can be said that the best inhibition of the mild steel surface is achieved at an optimum concentration as 99.0%. Even at the end of the 120-hour exposure period, the protection effect is still above 90%. The durability of the inhibitor is quite good even after this time. This high inhibition effect results from secondary metabolites known to contain molecules such as phenolic compounds, nitrogenous compounds and terpenes, the main source of which is bryophyte. It can be said that this high effect is caused primarily by the aromatic ring and the π-electrons in this ring, which are particularly present in phenolic and nitrogenous compounds. There is also an orientation towards the Fe surface from heteroatoms such as oxygen and nitrogen in phenolic compounds and nitrogenous compounds, and unshared electron pairs in these heteroatoms. In this case, it can be interpreted that it closes the surface like a cover and performs corrosion inhibition. As a result, considering all the immersion times of the inhibitor, extremely successful results were achieved with EIS completely.

CPE is the **C**onstant **P**hase **E**lement value. CPE values progressively attenuated as concentration increased during all immersion times. This diminish in CPE values is due to the reduction in local dielectric constant or increase of double layer thickness (Obot and Obi-Egbedi, 2011). "n" value is the roughness coefficient of the metal surface. As seen in Table 1 in particular, as the

inhibitor was added to the acidic solution, the "n" values were smaller than the uninhibited solution. As the inhibitor molecules are added to the hydrochloride acid solution, the "n" values will gradually get smaller, since the adsorption of these molecules on the mild steel surface will increase (Charitha and Rao, 2018).

In general, adsorption of an inhibitor molecule of organic origin on a metal surface can be explained as follows in the corrosion process; when these molecules begin to move towards the metal in the acidic solution, they gradually undergo a replacement process with other ions and water molecules previously adsorbed in the medium. In this process, the more adsorption and the more inhibition efficiency will be.

3.2. The surface charge of mild steel

The adsorption of organic molecules to the metal surface primarily depends on the chemical structure of that molecule. It also depends on parameters such as the type and charge of the metal. The charge of the metal surface can be determined by comparing the open circuit potential (E_{corr}) of the metal with the zero-charge potential (E_{pzc}) (Prathibha et al., 2017). To determine the surface charge of the mild steel electrode, EIS measurements of different potentials were made in 1.0 M HCl solution containing 0.05% (w/v) moss extract and the R_p values measured were plotted against the potential in Figure 4. The measured potential range is ± 0.200 V (Ag/AgCl).
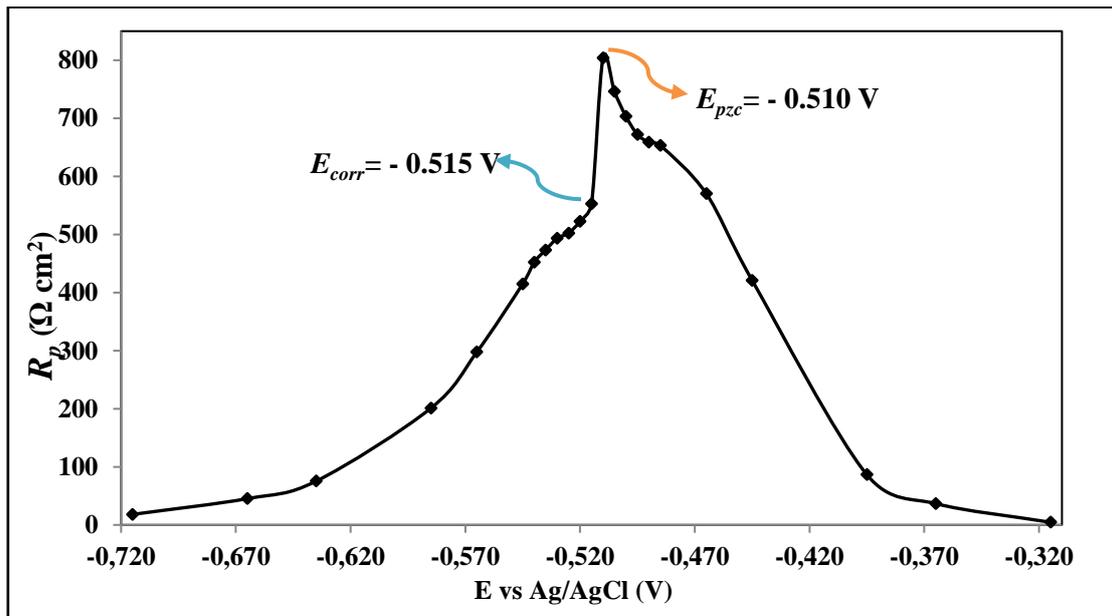

Figure 4. E-R_p graph in acidic solution containing 0.05% (w/v) moss extract of mild steel electrode at 298 K.

The surface charge of the metal can be interpreted by comparing the positions of E_{corr} and E_{pzc} against each other in Fig. 4. The maximum point in the curve obtained indicates E_{pzc}. Referring to Figure 4, the E_{corr} value (-0.515 V) of the mild steel electrode under measuring conditions is more negative than the E_{pzc} value (-0.510 V). This result shows that the surface of the mild steel electrode is negative under these conditions. According to this result, it can be interpreted that the protonated inhibitor molecules are adsorbed directly to the metal surface or adsorption of cations to the metal surface (Fitöz et al., 2018). Thus, the protective layer formed on the metal surface contributes to the inhibition mechanism by inhibiting the direct interaction of the metal with the chloride solution (Sin et al., 2017; Wang et al., 2018).

3.3. The surface morphologies of mild steel electrodes

FESEM and optical microscope surface analyzes were carried out in 1.0 M HCl with and without moss extract at an optimum concentration at 298 K and an immersion time of 120 h, providing a detailed understanding of corrosion morphology. Optical microscope (Özkır and Kayakırılmaz, 2020) and FESEM at 200 times magnification (Saraswat et al., 2020) images were evaluated in Figure 5 and Figure 6, respectively.
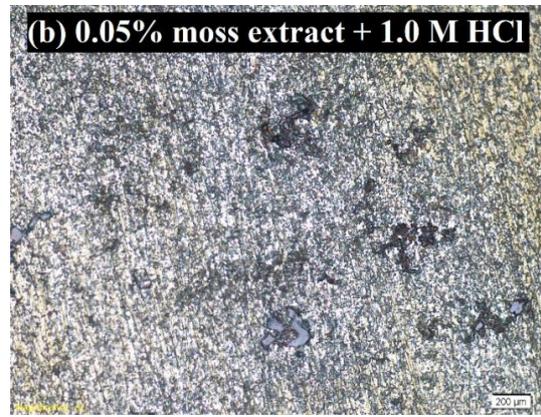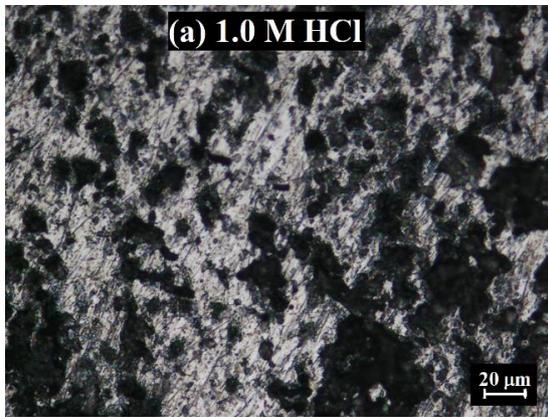

Figure 5. Surface images of the mild steels by optical microscopy after 120 h at 298 K

When Figures 5(a) and 6(a) are examined, it is observed that the mild steel electrodes, which are kept in an acidic solution for 120 h, are highly affected by corrosion and deep pits are formed on the surface of the electrode.
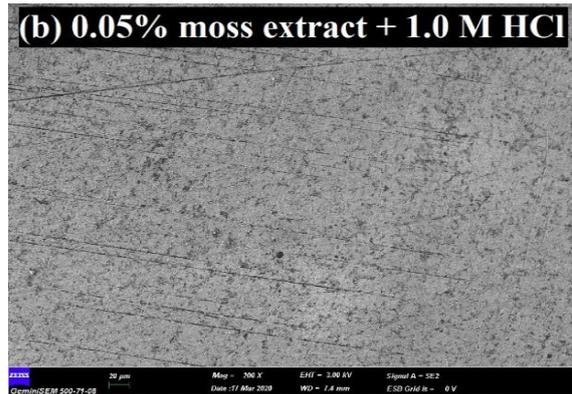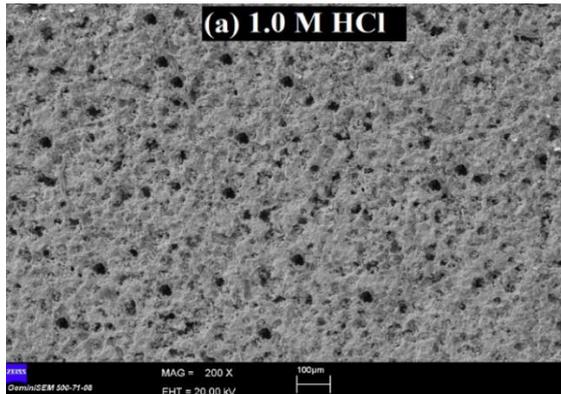

Figure 6. Surface images of the mild steels by FESEM after 120 h at 298 K

When the images in the inhibited solutions in Figure 5(b) and 6(b) are examined, it is seen that it is extremely smooth and more uniform compared to the images in the uninhibited ones. It is clearly observed that the pits are reduced in number and the deep cavities are filled to a considerable extent. It can be concluded that the surface images are another distinguishing indicator that the inhibitor studied is very well protected in the acidic solution of the mild steel electrode.

4. Conclusions

This study is quite important for a moss species *Hypnum cupressiforme* the first application of green inhibitor in Turkey. In the long term, EIS moss extract tests provided a good inhibition by adsorbing the mild steel surface very well with decreasing CPE values in response to increasing R_p values. It even showed 98% inhibition at the highest concentration after 120 h of immersion. It is concluded that protonated inhibitor molecules are adsorbed directly to mild steel because the surface charge of the metal is negative. Finally, the optical microscope and FESEM images are highly compatible with electrochemical measurements. Surface morphologies clearly showed that the pits in the acidic solution are closed as the inhibitor is added to the medium during the corrosion process.

The anti-corrosion effect of organic substances such as tannins, alkaloids, amino acids and organic dyes of plant origin is important for industry and the environment, as they are biodegradable and free of toxic compounds. Although several studies have been conducted on green corrosion inhibitor using the plant extracts, there is need for more study on this subject. In particular, further studies should be conducted on the use of bryophytes, which form an extremely rich source of bioactive molecules such as terpenoids and aromatic compounds, as a new green inhibitor to protect metals against corrosion.

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