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THE INHIBITIVE EFFECT OF *THYMUS SERPYLLUM* EXTRACT ON CORROSION OF STEEL

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Abstract: The study examined the inhibitive effect of thyme extract as a green inhibitor on the corrosion of two steel types, steel 1 - DC01 and steel 2 - X5 CrNi 18-10, in a 3% NaCl solution. Four test solutions were used: 1) blank 3% NaCl, 2) 3% NaCl + 0.5 g/L thyme extract, 3) 3% NaCl + 1.0 g/L thyme extract, and 4) 3% NaCl + 1.5 g/L thyme extract. Steel samples (3x3x0.2 cm) underwent chemical treatment before being exposed to the non-inhibited and inhibited solutions. Weight loss and electrochemical techniques, i.e. electrochemical impedance spectroscopy, were employed to investigate the corrosion rate and the inhibitive effect of thyme extract. All experiments were obtained on room temperature. After chemical treatment samples were immersed in blank and inhibited solutions for 2h, 4h, 6h, 8h, 24h, 48h и 168h. Based on the weight loss in steel samples for the time spent in prepared solutions, negative mass index of corrosion, K_m^- (g/m^2h), depth corrosion indicator, π (mm/year), and degree of efficiency, protection factor, z (%), were calculated. The results of the gravimetric and electrochemical measurements showed that thyme extract had an inhibitive effect on the corrosion of the tested steels, but not sufficient to be recommended for commercial application. The average corrosion inhibition efficiency of thyme extract was below 60% for both steel types. For steel 1, the protection factor was above 80% only in solution 4 after 48h and 168h, while for steel 2, the protection factor was greater than 80% for all three inhibited solutions only after 168h. These findings suggest a very slow adsorption of phytochemicals from thyme extract on the surface of the tested steels.

Keywords: corrosion, green inhibitors, thyme extract, weight loss, electrochemical techniques.

1. INTRODUCTION

The term corrosion refers to the spontaneous destruction of materials under the influence of physical and chemical factors of the external environment. A wide variety of construction materials, even those that are very stable, underlay to corrosion in greater or lesser extent. Corrosion of a metal means its destruction due to the chemical or electrochemical action of the external environment, whereby the metal/alloy component changes to an oxide (ionic) state. As a result of this process, there is a gradual and often sudden loss of the basic function of system elements or the system as a whole. Corrosion is a diffusion – controlled process. One of the common methods of corrosion protection is the use of corrosion inhibitors, which when added in small amounts slow down the corrosion process. Corrosion inhibitors are used in various industries that require the protection of metals, concrete, wood and glass. According to their composition, corrosion inhibitors can be various inorganic and organic compounds: sulphites, sulphates, sulfonates, molybdates, phosphates, petroleum derivatives, organic acids, lactones, esters, alcohols, amines, quaternary amines, alkyl-thiodiazoles, rubbers, surfactants and solvents [1-10]. The application of corrosion inhibitors in industry is wide: protection of engine parts, tanks, reservoirs, pipelines, protection of equipment from moisture, from radiation, in heat exchangers, in cooling towers, during the preparation of metal surfaces. However, this commercially used corrosion inhibitors possess some serious disadvantages, like toxicity, price and environmental risks. Since environmental protection regulative are very strict nowadays, researchers started to examine the way to produce more environmental friendly corrosion inhibitors. Among the various green sources being investigated for corrosion inhibition, plant extracts have garnered significant attention due to their easy availability, cost-effectiveness, and environmentally friendly nature. Plant extracts contain diverse phytochemicals that have the potential to replace synthetic organic and inorganic inhibitors. The mode of action of plant extract-based inhibitors depends on the structure of their active ingredients, which can vary from one plant to another and even within different parts of the same plant. Although the structures of these active components may be closely related, the mechanism of corrosion inhibition may or may not vary across different plant extracts. This provides a vast opportunity for the utilization of various plant bio-resources to achieve different levels of ecofriendly corrosion inhibition. The emergence of "green" chemistry has driven the use of plant extracts and fruit wastes as effective corrosion inhibitors that are biodegradable, non-toxic, and widely available. The main functional groups present in plant-based extracts, such as polysaccharides, tannins, alkaloids, amino acids and others organic compounds, have been found to be instrumental in mitigating corrosion [11-16]. The aim of this paper is to examine the utilization of thyme extract as corrosion inhibitor of two different types of steel, i.e. steel 1 - DC01 and steel 2 - X5 CrNi 18-10, in 3% NaCl. Different methods were applied in order to examine the possible protective effect of mentioned extract on corrosion of steel. The weight loss, as well as electrochemical impedance spectroscopy were used in order to examine the corrosion inhibition effect of the thyme extract. The influence of steel composition on the corrosion process was also examined, since two types of steel (S1 and S2) were used and were exposed to the effect of a corrosive environment under the same conditions. The influence of the content of alloying elements in the steel samples on the corrosion process was monitored through the change in the value of corrosion indicators, as well as the influence of thyme extract as a corrosion inhibitor.

2. MATERIALS AND METHODS

Two types of steel sheet DC01 (S1) and X5 CrNi 18 - 10 (S2) were used. Dimensions of steel samples for weight loss method were 3x3x0.2 cm. The inhibitory effect of thyme extract on the corrosion process of steel samples was tested by weight loss and electrochemical methods in 3% NaCl solutions. Thyme extract was obtained by Soxhlet extraction with 96% ethyl alcohol as a solvent. The obtained extract has dark yellow colour. All steel samples were subjected to chemical preparation before experiments. The first operation is degreasing with detergent. After degreasing with detergent, the samples were washed with running and distilled water. The washed samples were immersed in a solution for chemical degreasing at a temperature of 85^{o}C for 20 minutes. The samples were washed again with running and distilled water and immersed in an etching solution (20% H_2SO_4) for τ= 1 minute at a temperature of 65^{o}C. After etching, the samples were rinsed with running and distilled water. The next in the series of operations is drying, but in order to make the drying faster and homogenous, the samples were previously immersed in alcohol (96% ethanol). The sample was dried for 5 minutes, after which the mass of the sample was measured. The measured mass represented the initial mass of the sample before corrosion. All experiments were performed at room temperature.

Before the immersion in inhibited and blank solutions, the surface of the samples were activated in 20% H_2SO_4 at a temperature of 65^{o}C for 2 seconds in order to remove formed oxide layer. After that, the samples were washed with running and distilled water and immersed as such in uninhibited and inhibited solutions for a time interval of 2, 4, 6, 24, 48 and 168 hours. The corrosion behaviour of steel samples were examined in blank 3%NaCl (solution 1) and 3%NaCl with different concentration of extract, i.e 0.5 g/L (solution 2); 1g/L (solution 3) and 1.5g/L (solution 4) thyme extract. Based on the weight loss of the steel samples during the time spent in the prepared solutions, the depth indicator of corrosion π and the degree of inhibitor protection z were calculated. The efficiency of thyme extract as a corrosion inhibitor was also investigated by electrochemical impedance spectroscopy. Corrosion measurements were performed using a potentiostat/galvanostat/ZRA Gamry Series GTM 750, in a three-electrode cell. The saturated calomel electrode was used as a reference electrode, a Pt electrode was used as a counter electrode and a tested steel sample with a surface area of 1 cm^2 was working electrode. The open circuit potential was recorded until a stable value was established before electrochemical tests. Electrochemical impedance spectroscopy frequency range was 100 kHz – 10 mHz, with a 7 mV sinusoidal voltage amplitude, at open circuit potential.

3. RESULTS AND DISCUSSION

3.1. Weight loss method

Figure 1 shows the dependence of the depth corrosion indicator of steel 1 on exposure time in blank and inhibited solutions.

The depth indicator of corrosion decreases linearly with an increase in concentration of added extract after 168 hours in blank and inhibited 3% NaCl solutions. The highest depth corrosion indicator value is obtained after 168 hours in solution 1, and the lowest in solution 2 and solution 4 after 2 hours. It is obvious that the highest values of depth corrosion indicator are obtained in blank solution, suggesting the active corrosion process of steel. The obtained values are lower in inhibited solutions for all test period. Also, it can be seen from the Figure 1 that thyme extract suppressed corrosion of steel after 7 days almost equal as after 2 hour in highest used concentration, i.e. 1.5 g/L. This phenomenon is most likely due to uniform passive layer formed on the steel surface, which is made of different phytochemicals from extract adsorbed on the metal surface. The average depth indicator is the smallest in solution 4 and amounts to 0.0699 mm/year, and average depth indicator of steel in pure NaCl is 0.1904 mm/year which is almost three times higher.

Figure 2 shows the dependence of the corrosion protection factor of steel 1 in blank and inhibited solutions depending on time.

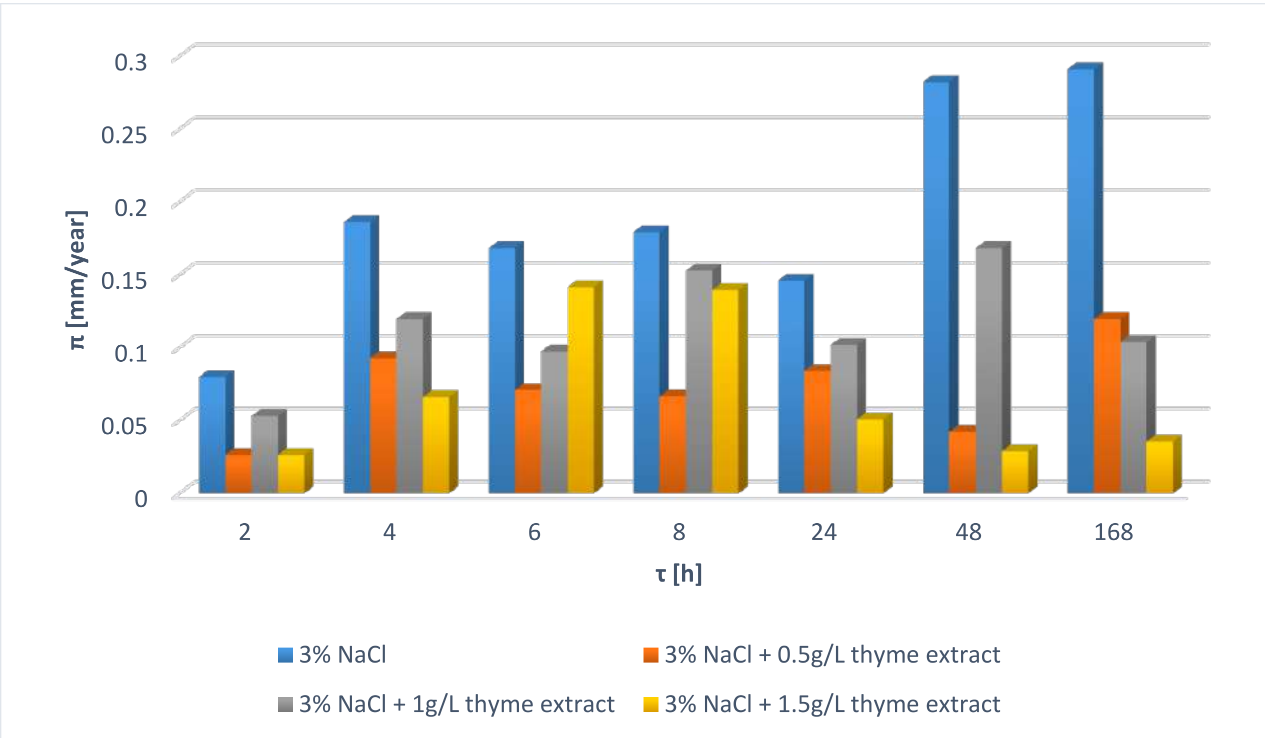

Figure 1. *Graphic representation of the depth indicator of corrosion of steel 1 in solutions 1–4 depending on time*

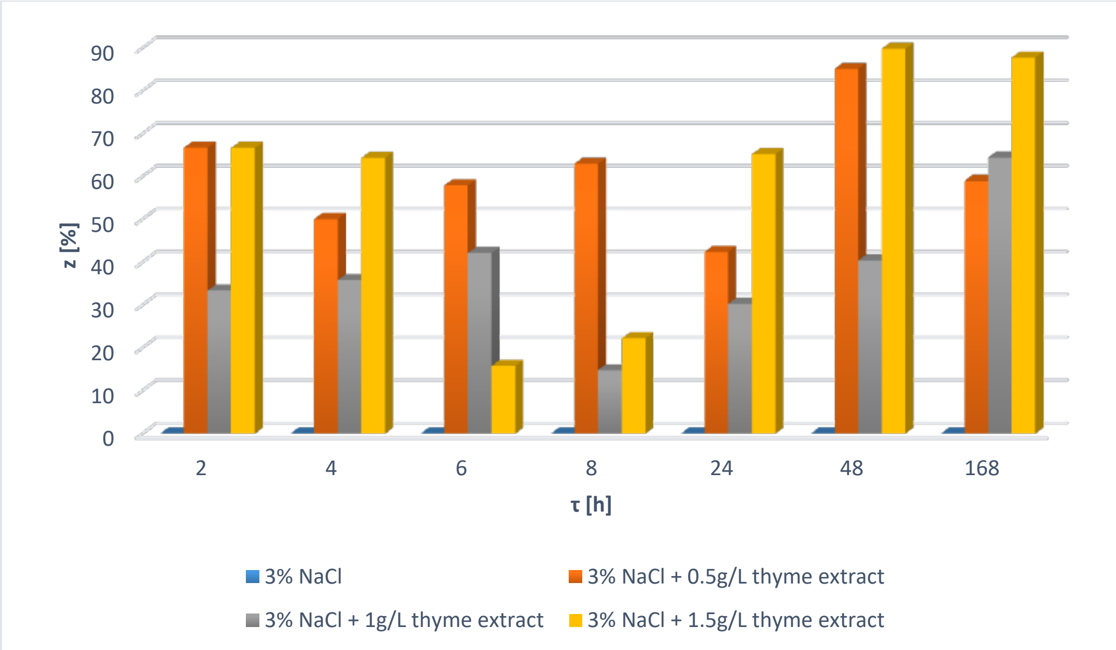

Figure 2. *Graphic representation of the corrosion protection factor of steel 1 in solutions 1–4 as a function of time*

It can be seen from Figure 2 that the linear dependence occurs only when the sample is exposed to solutions for 168 hours. The highest protection factor is obtained when the highest concentration of thyme extract (1.5 g/L) were used after 48 and 168 hours in examined solutions and it amounts 89.80% and 87.74%, respectively. The protective factor of thyme extract in all other solutions and for shorter times of exposure to the corrosion solutions was significantly lower than 80%. Although there is some inhibitive effect of the used extract on the steel corrosion, the obtained results implies that thyme extract cannot be recommended as a corrosion inhibitor for the protection of steel 1 in NaCl solutions, since protection is not enough. Figure 3 shows the dependence of the depth corrosion indicator of steel 2 on exposure time in blank and inhibited solutions.

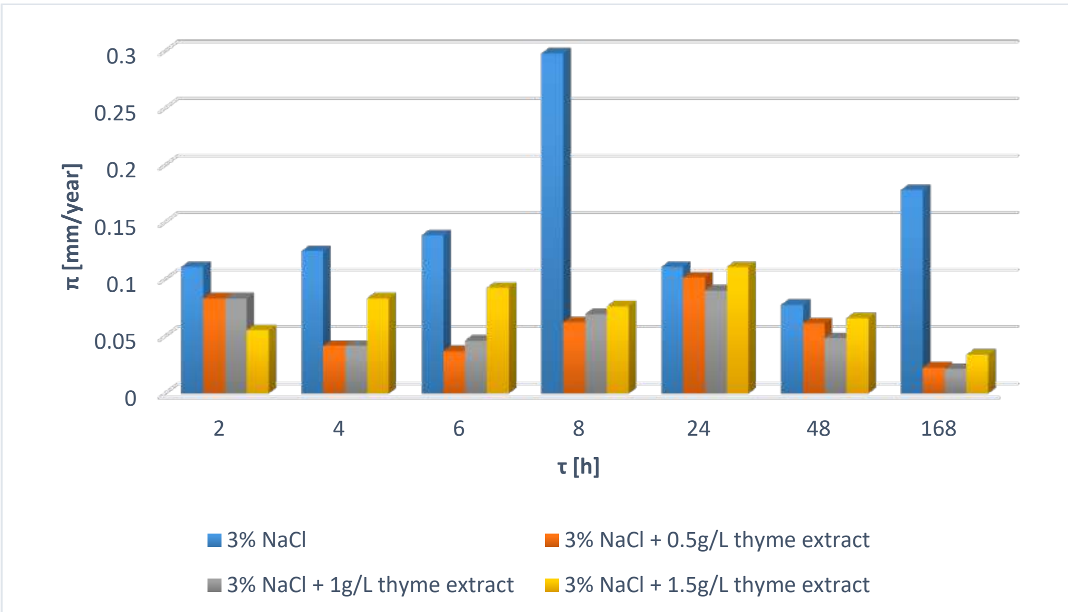

Figure 3. *Graphic representation of the depth indicator of corrosion of steel 2 in solutions 1–4 depending on time*

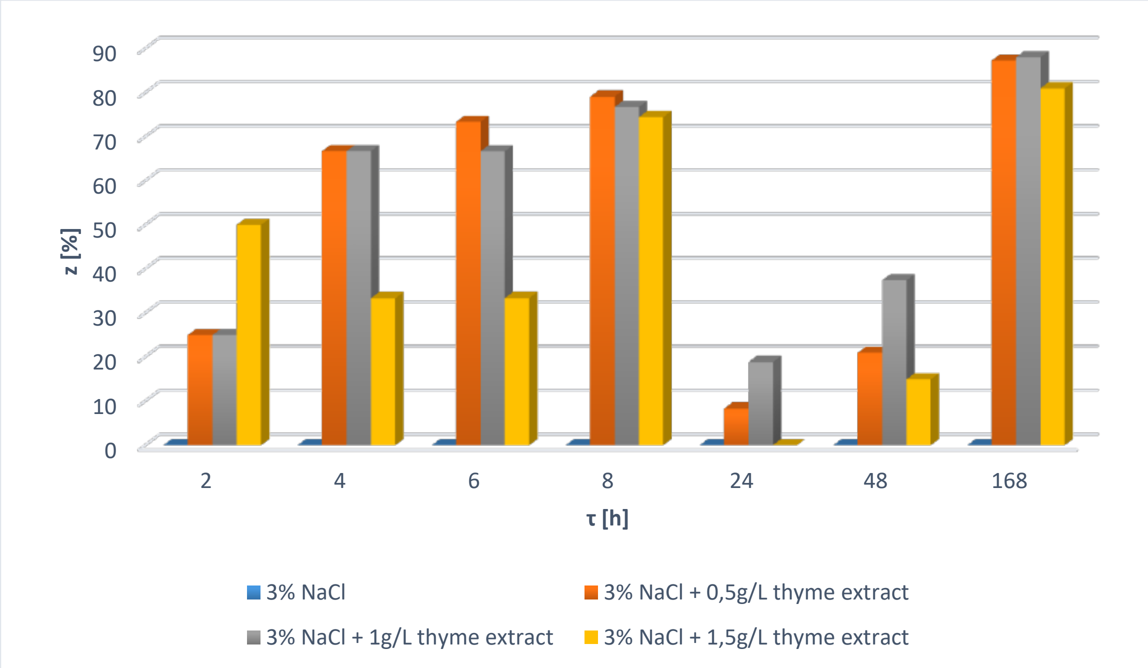

Figure 4. *Graphic representation of the corrosion protection factor of steel 2 in solutions 1–4 as a function of time*

The depth indicator of corrosion decreases linearly with an increase in the amount of added extract in NaCl solutions for a time period of exposure of 2 hours. The highest corrosion depth indicator value is obtained for steel after 8 hours in blank 3%NaCl (0.2687 mm/year), and the lowest after 168 hours in solution 3 (0.0214 mm/year). The obtained results pointed that depth indicator was 12 times lower in inhibited solution, which implies that added extract suppress the corrosion process of steel 2 in chloride rich environment. Figure 4 shows the dependence of the corrosion protection factor of steel 2 in blank and inhibited solutions depending on time.

The lowest protection factor of 8.3% is obtained when steel is exposed to solution 2 in a 24 – hour time interval. The highest protective factor is obtained after 168 hours in solution 3, which was 87.99%, as well as in solutions 2 and 4, where the protective factor was 87.24% and 80.96%, respectively. Since highest values of protective factor are obtained after 7 days in inhibited solutions it can be concluded that adsorption of active compounds from the extract on the steel 2 surface is very slow process. The thyme extract is mainly composed of thymol. However, this cultivar contains carvacrol, the isomer of thymol that possess the same biological activity. Also, this extract possesses linalool. Both carvacrol and linalool are natural effective antimicrobials, which means that effective adsorption of this compounds on the steel surface can supress microbial corrosion, along with passive effect [17,18]. The S1 is composed of 0.12 wt.% C, 0.60 wt.% Mn, 0.045 wt.% P, 0.045 wt.% S and Fe up to 100% and S2 is composed of 0.07 wt.% C, 17 wt.% Cr, 8 wt.% Ni, 2 wt.% Mn, 0.045 wt.% P, 0.015 wt.% S and Fe up to 100%. The weight loss results showed the superior corrosion behaviour of S2 in sodium rich environment, which is consequence of the presence of Cr and Ni. This pointed the importance of right choice of material for the certain purpose.

3.2. Electrochemical impedance spectroscopy

Figures 5 and 6 showed the Nyquist plots for steel 1 and 2 in blank and inhibited solutions.

As shown at Figures 5 and 6 the Nyquist plots depict the depressed semicircle when steel is immersed in blank and also in inhibited solutions. The radius of the semicircle however increase with addition of the thyme extract suggesting the increase in corrosion resistance to aggressive influence of chloride ions. The Z_{real} impedance values was about 600 Ω cm^2 for steel 1 in blank NaCl solution, but when extract is added the Z_{real} value increased to the more than 2500 Ω cm^2. Also, the Nyquist semicircle of steel 1 in inhibited solutions

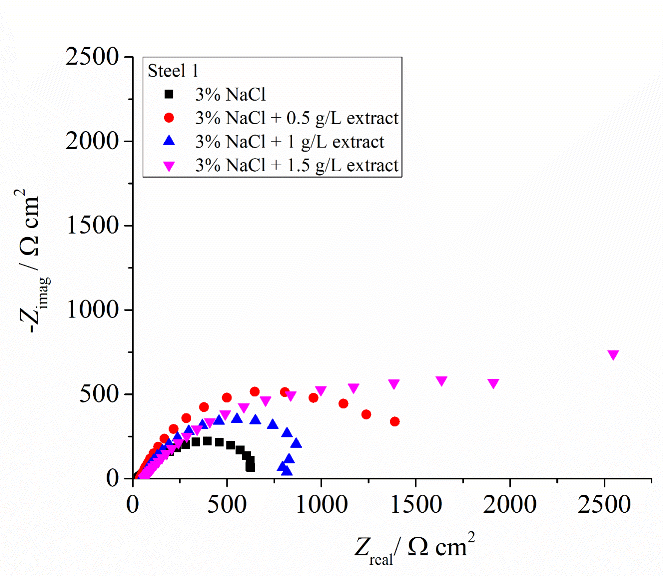

Figure 5. *Nyquist plot for steel 1 in solutions 1–4*

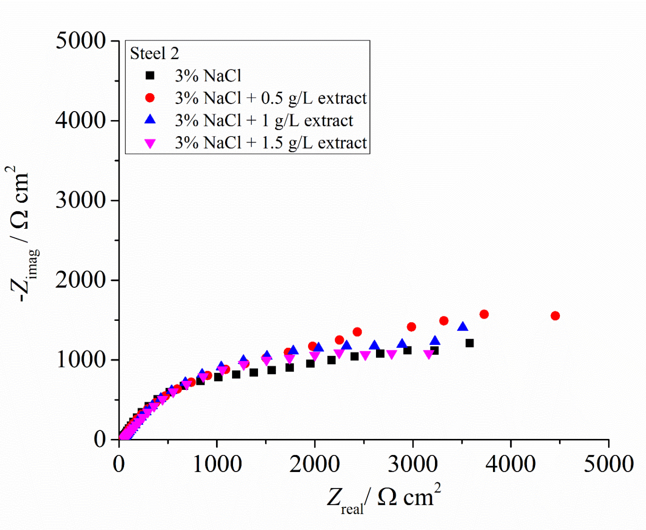

Figure 6. *Nyquist plot for steel 2 in solutions 1–4*

showed the diffusion path, suggesting the change in corrosion mechanism compared to blank solution. This diffusion path could be due to penetration of corrosion media throughout the formed inhibition film on steel surface. Figure 6 showed that steel is more resistant to the corrosion in chloride rich environment compered to steel 1. Also, the electrochemical impedance spectroscopy showed that increase in concentration of thyme extract had no influence of the corrosion process of steel 2 in inhibited NaCl solution. According to the Z_{real} values, the 0.5 g/L thyme extract is optimal, and those values reach 5000 Ω cm^2. The EIS results confirmed the results obtained by weight loss method, i.e. the steel 2 showed better resistance to corrosion compared to steel 1, due to presence of Cr and Ni in its composition.

4. CONCLUSION

Based on the obtained results, it can be concluded that thyme extract possess inhibitive effect on corrosion of steel in chloride rich environment, but it is not sufficient to be proposed for commercial utilization. The presence of thyme extract in all concentrations reduces the weight loss of steel 1 and 2, i.e. thyme had corrosion inhibitory effect in 3% NaCl. The weight loss results showed that adsorption process of active compounds from thyme extract is slow process, since high protection factor is obtained after 7 days in corrosion media. The electrochemical impedance spectroscopy showed the increase in semicircle radius with addition of thyme extract for steel 1, which indicates a decrease in the corrosion rate. The corrosion resistance of steel 2 was higher compared to steel 1, due to better composition for the utilization in sodium rich environment. This pointed the importance of wise and thorough choice of material for the certain application. The obtained results of gravimetric and electrochemical measurements showed that thyme extract possess an inhibitory effect on the corrosion process of both types of steel, but not enough to be recommended for commercial use.

ACKNOWLEDGMENT

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5. LITERATURE

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ЕКСТРАКТ МАЈЧИНЕ ДУШИЦЕ (THYMUS SERPYLLUM) КАО ИНХИБИТОР КОРОЗИЈЕ ЧЕЛИКА

Сажетак: Испитивано је инхибиторско дејство екстракта мајчине душице (ЕМД) као зеленог инхибитора на корозију двије врсте челика у 3% NaCl (челик 1 – DC01 и челик 2 – X5 CrNi 18–10). За испитивање корозије челика коришћена су четири раствора, један без инхибитора и три раствора са различитим концентрацијама ЕМД као инхибитора корозије: 1) 3% NaCl, 2) 3% NaCl + 0,5g/L ЕМД, 3) 3% NaCl + 1,0g/L ЕМД и 4) 3% NaCl + 1,5g/L ЕМД. Коришћени узорци челика димензија 3 x 3 x 0,2 cm подвргнути су хемијској припреми, а потом је извршено испитивање брзине корозије у неинхибираним и инхибираним растворима. За испитивање брзине корозије и дејства екстракта мајчине душице као инхибитора корозије коришћена је гравиметријска метода, а од електрохемијских метода коришћена је спектроскопија електрохемијске импедансе (СЕИ). Сви експерименти су рађени у лабораторијским условима на собној температури. При гравиметријским мјерењима узорци челика након хемијске припреме потапани су у четири припремљена раствора 2 h, 4 h, 6 h, 8 h, 24 h, 48 h и 168 h. На основу губитка масе након времена проведеног у растворима рачунат је масени показатељ корозије K_m^- (g/m²h), дубински показатељ корозије π (mm/год.) и заштитни фактор инхибитора z (%). Добијени резултати гравиметријских и електрохемијских мјерења показују да екстракт мајчине душице (ЕМД) има инхибиторско дејство на процес корозије кориђених челика, али не и довољно висок да би се могао препоручити за комерцијалну примјену. Средње вриједности заштитног фактора ЕМД као инхибитора корозије коришћених челика у 3% NaCl су испод 60%. За челик 1 заштитни фактор z је изнад 80% само у раствору 4, након 48 h и 168 h, док за челик 2 заштитни фактор z је већи од 80% за сва три инхибирана раствора тек након 168 h, што говори о веома спорој адсорпцији активних компонената ЕМД на површину коришћених челика.

Кључне ријечи: корозија, зелени инхибитори, екстракт мајчине душице, гравиметријска метода, електрохемијске методе.

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