Research on the steel corrosion inhibition of green tea leaf extract in a simulated sea water environment

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ABSTRACT

In this paper, the effect of polyphenol compounds extracted from green tea leaves to inhibit CT3 steel corrosion in a simulated sea water environment was studied. The corrosion inhibitor is evaluated through some specifications: electrochemical corrossion and salt spray corrosion test by the B117-16 standard. A scanning electron microscope (SEM) and the salt-sprayed steel plate surface observation were used to evaluate the level of corrosion. The CT3 steel soaked in polyphenol solutions with various concentrations and times showed different corrosion resistance in marine conditions. At the polyphenol concentration of 1.5 mg in 1 liter solution, the corrosion rate of CT3 steel is reduced from 0.057 mm/year compared to 0.113 mm/year in the 3.5% NaCl solution without polyphenol, and soaking CT3 steel for 45 minutes in polyphenol : water : ethanol solution (1 g : 90 ml : 910 ml) gives the best resistance to salt spray corrosion.

Keywords: Green tea leaf; Polyphenol; Corrosion inhibitor; Electrochemical corrosion; Marine corrosion; CT3 steel.

1. INTRODUCTION

Corrosion of metals and alloys is a major problem worldwide, affecting the economy accounting for 4% of global GDP and nearly 15% of steel produced is lost due to corrosion. Our country has a coastline of over 3,260 km stretching from North to South, with a hot and humid climate all year round, so the loss caused by corrosion is statistically 20-30%, especially structures built near coastal areas are very susceptible to corrosion. Steel corrosion in structures and equipment in a marine climate is an electrochemical process that causes the dissolution of iron to form a series of solid products. Nowadays, metal protection can be achieved by using various methods, such as corrosion inhibitors, anti-corrosion coatings or cathodic protection. Among the corrosion protection methods for metals, the use of corrosion inhibitors is an effective and cost-effective solution [1]. Corrosion inhibitors are compounds that are capable of reducing the rate of corrosion of metals when added to a corrosive environment. Inorganic corrosion inhibitors are usually nitrite, phosphate, molybdate, silicate ions and organic ones such as amines, amides, imidazolines, benzoates,… has been widely studied and applied over the years and has shown to be highly effective in protecting metals from corrosion [2]. However, the potential environmental risks of inorganic and organic corrosion inhibitors produced from industrial raw materials have prompted a reduction in the use of these inhibitors and their replacement with less toxic, more environmentally friendly alternatives. Recently, scientists have shown increasing interest in "green" corrosion inhibitors extracted from plants, the extracts containing polyphenols that can combine with metal ions to form stable complexes, thereby preventing the oxidation of metals [3-5]. Natural polyphenol compounds are found in plants, trees, fruits, etc. [6-8]. In this article, the authors studied the ability to inhibit steel corrosion in seawater environments of polyphenol compounds extracted from tea leaves.

2. EXPERIMENTS

2.1. Chemicals and sample preparation

Chemicals preparation: C_2H_5OH 96% (Xilong); NaCl 99,5% (Xilong); distilled water; 20% VĐ Varnish (TCVN/QS 576 : 2018), etc.

Figure 1. *Image of green tea leaves studied.*

Green tea leaves collected from Thai Nguyen province, Vietnam were washed with water, freeze-dried to 70% humidity, then ground into powder, dissolved in a water : ethanol solution (ratio 50 : 50 by volume) at a ratio of 50 g/l. Then ultrasonicated for 30 minutes on an ultrasonic machine, stirred and heated the resulting solution at 60 °C for 2 hours, the solution was filtered with a vacuum filter to obtain a solution containing polyphenol and the polyphenol content was determined to be 15 g/l (TCVN 9745-1-2013) [8]. Ethanol was added to adjust the composition according to the ratio of polyphenols: water: ethanol (1 g : 90 ml : 910 ml) to be used as a research solution.

CT3 steel plate has composition and properties according to TCVN 1765 : 1975 standard. The scanning electron microscopy (SEM) and electrochemical corrosion samples have dimensions of 10 × 10 × 2 mm. The salt spray corrosion test sample has dimensions of 120 × 40 × 2 mm and is immersed in a solution containing polyphenol at the ratio of polyphenol: water: ethanol of 1 g : 90 ml : 910 ml with the time varying from 30 ÷ 60 minutes. The sample is taken out, dried and covered with a layer of 20% VĐ Varnish (TCVN/QS 576 : 2018), after 24 hours of salt spray test.

2.2. Sample analysis

Scanning electron microscopy (SEM) was used to analyze the microstructure of the sample surface layer. CT3 steel samples were soaked for different times from 15 ÷ 75 minutes in a solution containing polyphenol at the ratio of polyphenol : water : ethanol of 1 g : 90 ml : 910 ml before analysis.

All electrochemical measurements were performed on an Autolab PGSTAT12/30/302 at room temperature in a three-electrode system consisting of Ag/AgCl reference electrode (RE), Pt auxiliary electrode (CE) and a steel reinforcement sample as the working electrode (WE) (Fig. 2). Polarization curve measurements were performed in a constant volume (500 ml) 3.5% NaCl solution with the addition of different concentrations of polyphenols. The open circuit potential (OCP) was stabilized for 45 mins before electrochemical testing. Polarization curves were obtained at a scan rate of 0.1 mV/s in a potential range of ± 100 mV versus OCP to determine the kinetic parameters and corrosion inhibition efficiency [9]. Electrochemical impedance spectroscopy (EIS) analysis was performed at OCP in the frequency range: 100 kHz ÷ 0.1 Hz. EIS spectra were obtained using Nova 2.1.5 software. The rebar samples used in the EIS method were coated with a varnish solution containing different concentrations of extractants before measurement. The experiments were repeated three times for each extractant concentration.

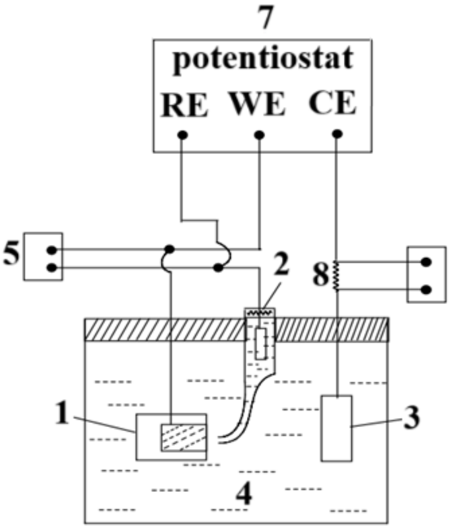


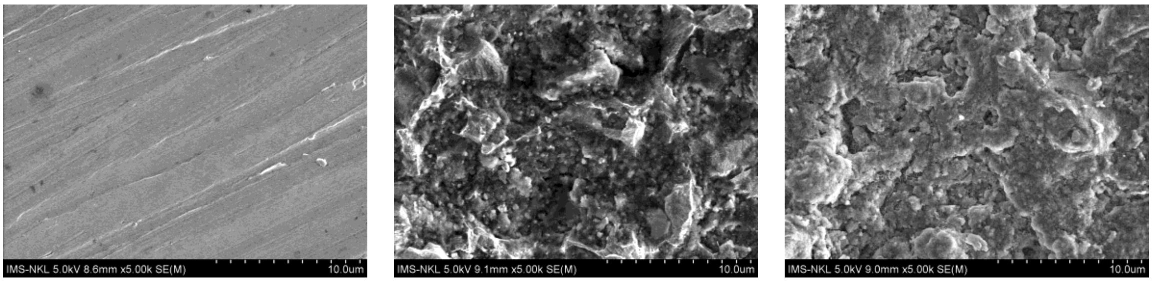
Figure 2. *Schematic diagram of electrochemical measurement method.*
1. Working electrode (WE); 2. Reference electrode (RE) - Ag/AgCl electrode;
3. Auxiliary electrode (CE) made of Pt; 4. Electrolyte solution (3.5% NaCl solution);
5, 6. Cacmilivol; 7. Potentiometer; 8. Sample resistance with known value.

Corrosion assessment by salt spray method according to B117-16 standard on ERICHSEN salt spray equipment, Germany. Anti-corrosion coated samples were put into the salt spray equipment with different spray times. After a certain time, the samples were taken out, washed with continuously running distilled water to clean the salt water on the surface. The surface was dried, and the surface was photographed with a digital camera.

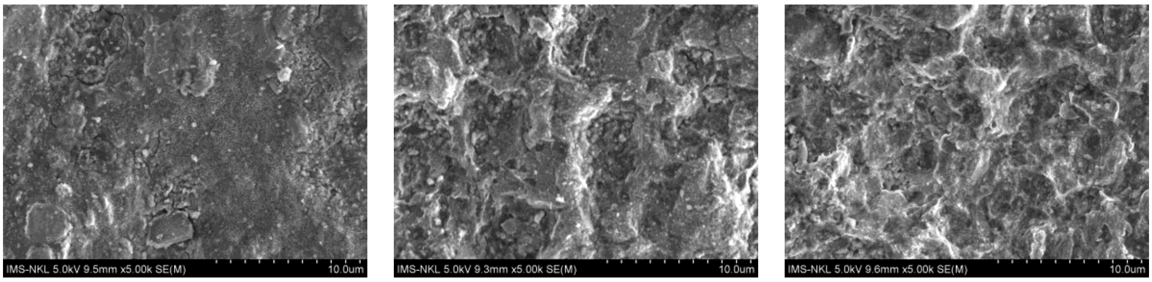
3. RESULTS AND DISCUSSION

3.1. Structure of the oxide film on the surface

Observing the surface of CT3 steel sample before and after soaking in a solution containing polyphenol corrosion inhibitor extracted from green tea leaves for different times (figure 3), it can be seen that an oxide film has formed on the surface of the steel sample. At different soaking times, the Reddish brown iron (III) oxide film Fe_2O_3 has formed with different structural morphologies [3]. After 15 and 30 minutes, an oxide film has formed, however, this film is still thin and not tight (figures 3b, c). After 45 minutes, the film has tightened and covered evenly over the entire surface of the sample (figure 3d). However, when the soaking time was increased to 60 and 75 minutes respectively, the oxide layer tended to become rougher and less durable (figure 3e, f). The reason was that when soaked in a solution containing polyphenol with a ratio of polyphenol : water : ethanol (1 g : 90 ml : 910 ml) with pH = 5, it caused a reaction on the surface of the CT3 steel sample, creating an iron oxide layer, with a suitable time of 45 minutes for the tightest oxide layer. When the soaking time was increased, the steel continued to be deeply corroded and the oxide layer became rough, blistering on the surface (figure 3e, f).



a) CT3 steel. *b) After soaking for 15 min.* *c) After soaking for 30 min.*



d) After soaking for 45 min. *e) After soaking for 60 min.* *f) After soaking for 75 min.*

Figure 3. *Surface structure of CT3 steel after immersion in solution containing polyphenol corrosion inhibitor for different times.*

3.2. Electrochemical corrosion

Polarization measurements were performed to determine the kinetics of the cathodic and anodic reaction of steel in simulated seawater without and with different concentrations of polyphenols added. The addition of polyphenol concentrations from 0.5 mg/l to 2.5 mg/l reduced the corrosion current density, corrosion rate and became more positive corrosion potential. As shown in the figure of the conversion of the cathodic and anodic Tafel slopes, the adsorption of polyphenols modifies the anodic dissolution as well as the hydrogen evolution at the cathode. It is clear that both the cathodic and anodic reactions are inhibited here.

Table 1. *Corrosion parameters of CT3 steel in 3.5% NaCl solution containing polyphenol corrosion inhibitor with different concentrations.*

C (mg/l)	E_{corr} (V)	J_{corr} ($A.cm^{-2}$)	V_{corr} (mm/year)
0.000	-0.655	9.710E-06	0.113
0.500	-0.594	9.330E-06	0.108
1.000	-0.584	7.860E-06	0.091
1.500	-0.541	4.920E-06	0.057
2.000	-0.558	5.920E-06	0.069
2.500	-0.629	9.510E-06	0.110

Observing the diagram in figure 4 and table 1 shows that with a polyphenol concentration of 1.5 mg/l in a 3.5% NaCl solution, the corrosion level is the smallest as the most positive corrosion potential (E_{corr}), the smallest corrosion current density (J_{corr}); the least corrosion rate (V_{corr}). When the polyphenol concentration increases to greater than 1.5 mg/l, the corrosion level increases. This is because polyphenol is acidic. Increasing the concentration will reduce the pH, increase the acidity of the electrolyte solution, causing the newly formed passive layer to break down and corrosion to occur continuously.

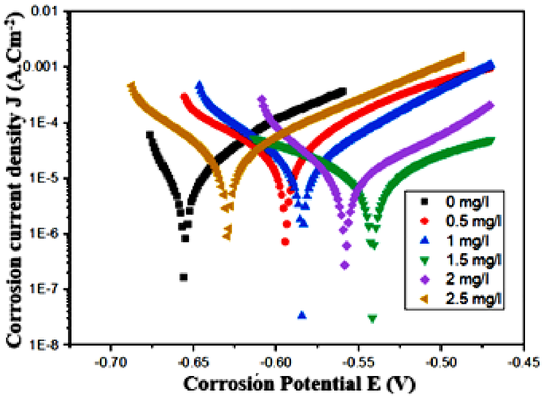


Figure 4. *Polarization curve diagram of CT3 steel sample in 3.5% NaCl solution containing different concentrations of polyphenol.*

The effect of polyphenol concentration on the impedance of steel in 3.5% NaCl solution is presented as a Nyquist plot. The diameter of the semicircle of the Nyquist plot increases with increasing corrosion resistance.

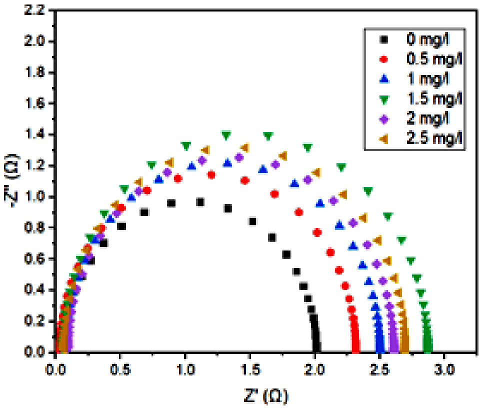


Figure 5. *EIS spectrum of CT3 steel sample in 3.5% NaCl solution containing different concentrations of polyphenol.*

From this diagram, it can be seen that the impedance response of the metal increases with inhibitor concentration from 0.5 mg/l to 2.5 mg/l. These results are consistent with the polarization measurement results. Combining the above methods, steel samples immersed for 45 minutes in 3.5% NaCl solution containing 1.5 mg/l polyphenol concentration gave the best corrosion inhibition in this case.

3.3. Salt spray corrosion

After different spraying times, the surface corrosion level of the samples is different, shown in figure 6. Observing the surface images of salt spray samples in figure 6, the CT3 steel sample after 45 minutes was soaked in a solution containing at a ratio of polyphenol : water : ethanol (1 g : 90 ml : 910 ml) and covered with a layer of varnish (sample M6.1) has the best ability to resist salt water corrosion. After 1 day of salt spray, the surface of the test sample was not corroded; after 2 days of salt spray, only a small corrosion spot appeared; after 4 days of salt spray, the surface appeared more corroded, especially on the outer edge of the test sample. However, the corrosion level of sample M6.1 was less than that of samples M5.1, M7.1 and M8.1 under the same test conditions. The reason is that when soaked in a solution containing polyphenol corrosion inhibitor, a tight oxide film was formed on the surface of CT3 steel, which has the ability to protect the steel. Then the sample was covered with a protective varnish layer, which will increase the ability to prevent salt water and salt vapor from penetrating the steel substrate. This is also consistent with the surface morphology analysis in figure 3.

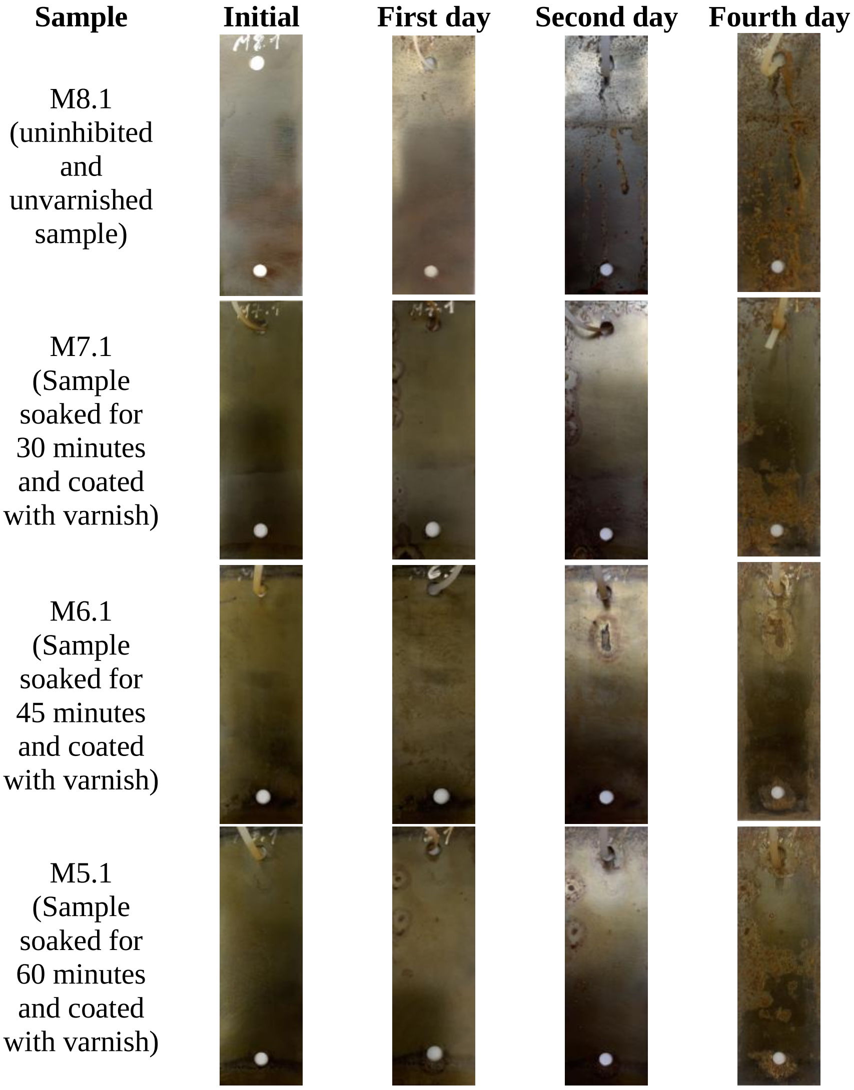


Figure 6. *Surface images of salt spray test specimens after different immersion times in corrosion inhibitor solutions.*

4. CONCLUSIONS

In this study, the polyphenol corrosion inhibitor for CT3 steel working in seawater environment was successfully extracted from green tea leaves. The results showed that green tea leaf extract has the ability to effectively inhibit corrosion, creating a tight oxide layer on the steel surface to prevent salt from penetrating and causing corrosion. The study showed that different times and concentrations of polyphenol give different anti-corrosion abilities in marine environments. At a polyphenol concentration of 1.5 mg in 1 liter of 3.5% NaCl solution, the best anti-corrosion ability for CT3 steel was achieved, the steel corrosion rate was reduced by 50% compared to when there was no polyphenol compound from green tea leaf extract and the time of 45 minutes of soaking CT3 steel in a solution with a ratio of polyphenol : water : ethanol (1 g : 90 ml : 910 ml) gave the best anti-corrosion ability for up to 4 days of salt spray testing according to standard B117-16.

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TÓM TẮT

Nghiên cứu khả năng ức chế ăn mòn thép của dịch chiết lá chè xanh trong môi trường nước biển mô phỏng

Trong bài báo này, nghiên cứu khả năng ức chế ăn mòn thép CT3 của hợp chất polyphenol từ dịch chiết lá chè xanh trong môi trường nước biển mô phỏng. Khả năng ức chế ăn mòn được đánh giá thông qua đặc trưng tính chất: ăn mòn điện hóa và ăn mòn phun muối thử nghiệm theo tiêu chuẩn B117-16. Thiết bị phân tích hiển vi điện tử quét (SEM) và quan sát bề mặt tấm thép phun muối được sử dụng để đánh giá mức độ ăn mòn. Thép CT3 được ngâm trong dung dịch chứa polyphenol với nồng độ và thời gian khác nhau cho khả năng chống ăn mòn môi trường nước biển khác nhau. Ở nồng độ polyphenol 1,5 mg trong 1 lít dung dịch 3,5% NaCl cho khả năng chống ăn mòn tốt nhất, tốc độ ăn mòn thép giảm từ 0,057 mm/năm so với 0,113 mm/năm khi không có polyphenol và thời gian 45 phút ngâm thép CT3 trong dung dịch polyphenol : nước : ethanol (1 g : 90 ml : 910 ml) cho khả năng chống ăn mòn phun muối tốt nhất.

Từ khóa: Lá chè; Polyphenol; Ức chế ăn mòn; Ăn mòn điện hóa; Ăn mòn nước biển; Thép CT3.