CORROSION INHIBITION OF REINFORCED STEEL BY THYMUS VULGARIZE (THYME) EXTRACT IN SIMULATED CHLORIDE CONTAMINATED CONCRETE PORE SOLUTION

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ABSTRACT

Thymus Vulgarize extract (TVE) was reported to be good corrosion inhibitor for copper and brass in acid media. This paper presents experimental study to investigate the efficiency of Thyme leaves extract as corrosion inhibitor for concrete reinforcing steel samples exposed to alkaline solution consisting of 2% KOH and 3% NaCl which is a simulation to the chloride contaminated concrete pore solution (SCP) using open circuit potential and potentiodynamic polarization technique. Various concentration (100 ml/L, 150 ml/L, 250 ml/L) of TVE were used in this experiment. Open circuit potential (OCP) measurements indicated a shifting in potential toward noble direction for steel samples immersed in SCP solution containing TVE compared with control sample.

Potentiodynamic polarization measurements was done after zero hr. immersion in test solutions and after 30 day. Data from these measurements showed that the corrosion parameters values of the reinforced steel were decreased and inhibition efficiency increased higher than that values of zero hour immersion, maximum efficiency of 89.71% and lower corrosion current density of 0.56 µA/ cm² was achieved at TVE concentration of 250 ml/L. This is an indication that TVE inhibitor maintained stable protective film on the steel surface even in the presence of chloride ions. The results of this experimental work showed that thyme extract worked effectively as green corrosion inhibitor, gave good corrosion inhibition for concrete reinforced steel samples immersed in simulated chloride contaminated concrete pore solutions during the time of this research.

Keywords: Thymus Vulgarize Extract (TVE), Concrete Reinforced Steel, Corrosion Inhibitor, PotentioDynamic Polarization, Simulated Concrete Pore Solution (SCP).
1. INTRODUCTION

Corrosion inhibitors have been proved to be effective and practical way to reduce or stop the corrosion process of reinforcing steel in most corrosive environments enhancing the surface life of concrete structures [1-10]. There are two types of corrosion inhibitors, the first one inhibit corrosion by enhancing the formation of protective oxide film through oxidizing process and the second one inhibit corrosion by adsorbing on the metal surface creating a barrier have ability to prevent the aggressive ions to access to the metal surface [11]. Several studies indicated that most syntheses organic and inorganic inhibitors are toxic cause severe hazards to both human beings and environment during its applications [12-15]. Thus many researchers focus their efforts to replace these toxic inhibitors with nontoxic one, so there is a great interest toward the using of green corrosion inhibitors to protect concrete rebar from corrosion because these inhibitors are not only nontoxic and environmental friendly, but also readily available and renewable[16-19].

Green inhibitors are reported to be low cost, safe, easily applicable, ecofriendly, preserve the environment and are easily available, they can be extracted by simple procedures with low cost from natural products such as plant extracts [20]. Extracts from plant leaves, seeds, stems, peels, barks, roots and flowers have been widely studied and reported to be efficient inhibitor to metallic corrosion in acidic media [12, 15, 21, 22, 23, 24]. These extracts are organic in nature, its inhibition efficiency is related to the presence of complex organic compounds such as alkaloids, tannins, amino acids and saponins in their composition [25]. Most of these organic compounds contain electronegative atoms such as phosphorous, nitrogen, sulfur, oxygen and multiple bond in their molecules which strongly adsorbed to metal surface through the coordination of their electrons with the ions of the corroding metal, so protective barrier film is formed on the metal surface block the active sites and then reducing the corrosion rate[26, 27, 28, 29, 30].

In recent time several investigations have been reported about using plant extract as corrosion inhibitor for concrete reinforcing steel such as Vernoniamygdalina leaves extract [31], BambusaArundinacea (Indian Bamboo) leaves extract [32], Extracts of kola plant and tobacco [33], pawpaw (carica papaya) leaves extract[34], ChamaeropsHumilis L. leaves extract [35] which have been found to be efficient corrosion inhibitors.

Thyme herb (Thymus Vulgarize) is an aromatic plant, literatures show that it has a number of medical applications [36]. Thymus Vulgarize extract (TVE) is known to contain essential oil, tannins, flavonoids, saponins and triterpenic acid, these compounds having polar functions with S, O or N atoms in their molecule, heterocyclic compounds and pi electron Thyme constituents such as saponins and tannins can be strongly adsorb onto the metal surface enhancing its corrosion resistance in corrosive environments [37]. TVE was found to be good corrosion inhibitor for copper and brass in acid media [37]. However, no study till date according to our knowledge has been reported about TVE inhibition effect on reinforcing steel in concrete exposed to corrosive environment containing chloride ions.

In the present paper experimental study was done to investigate the efficiency of Thyme leaves extract as corrosion inhibitor for reinforcing steel in concrete exposed to simulated chloride contaminated concrete pore solution consisting of 2% KOH and 3% NaCL using open circuit potential and potentiodynamic polarization technique.

2. EXPERIMENTAL WORKS

2.1. Inhibitor preparation

Thyme herb was purchased from local food supermarket. Digitally weighed 6 gram from crushed thyme leaves herb boiled for one minute in 500 ml distilled water, cooled and filtrated by filter paper. This filtrate solution was used in this experiment as a corrosion inhibitor.
2.2 Reinforced steel samples preparation

Steel bar which is already used as concrete reinforcement was purchased from local market. For open circuit test four specimens of 0.095 cm diameter and 4.5 cm length were cut from the rebar. For electrical connection one end of the specimen was soldered to copper wire. All specimens were grinded by grinding machine in order to remove any rust stains or mill scales. 2.5 cm of the sample length was defined as the exposing length and the remaining was painted with epoxy paint. For potentiodynamic polarization tests 12 disc of 1 cm diameter were cut from rebar and then braded with different grades grinding papers. For optical images tests 4 discs of 20 mm diameter were cut from steel bar, braded with abrasive grinder machine and then polished by polishing machine till mirror surface. The samples were immediately decreased by acetone and air dried and then immersed in the tests solutions.

2.3 Solutions preparation

Analytical grade chemicals purchased from local supplier were used to prepare the test solutions. Simulated concrete pore solution (SCP) was prepared by dissolving appropriate amount of solid KOH in the required deionized water to obtain 2% KOH solution. The aggressive environment in this experiment consist of 2% NaCl was made by adding appropriate amount of solid NaCl to SCP solution to simulate the chloride contaminated SCP solution (control solution). 100 ml, 150 ml and 250 ml of TVE was added to each liter of the control solution to form three thyme inhibitor solutions so in this experiment four solutions were prepared one as a control solution (PH = 12.85) and the others as thyme extract inhibitor solutions (PH = 13.04).

2.4. Electrochemical Measurements

Experimental work was carried out using potentiodynamic polarization and open circuit potential technique to evaluate the inhibition effect of TVE inhibitor in SCP solution contaminated with corrosive NaCl. All tests were carried out in aerated solution at room temperature and atmospheric pressure.

2.4.1 Polarization measurements

The potentiodynamic polarization measurements of concrete reinforced steel were carried out using three electrode cell, consisting of Ag/AgCl electrode as reference electrode, platinum wire as counter electrode and working electrode. The working electrode was rebar steel disk axially embedded in a Teflon holder to offer a flat disc shaped exposed surface area of 0.785 cm². Before each test disc was abraded with different types of silicon carbide paper, degreased with acetone and rinsed with distilled water. Steel disc represent control specimen was immersed in SCP solution and the other three discs immersed in SCP solution containing thyme extract inhibitor at concentrations of 100ml/L, 150 ml/L and 250 ml/L respectively.

The experiments were performed in SCP solution with and without thyme inhibitor after zero hour of immersion as (Initial), after one day of immersion, and after 30 days of immersion (final) to verify the stability of the passive film even in the presence of aggressive chloride ions. Polarization curves were conducted by changing the electrode potential automatically 200 mV more negative to open circuit potential (OCP) toward 200 mV more positive to OCP at a scan rate of 1 mV/s. Wenking M Lab Potentiostat Galvanostat instrument (GERMAN origin) under potentiodynamic conditions was used to carry out the tests. The programs of this instrument was used to evaluate the corrosion parameters such as corrosion current (Icorr), corrosion potential (Ecorr), anodic Tafel slope (ba) and cathodic Tafel slope (bc) from the conducted polarization curves. Corrosion inhibition efficiency (IE %) was calculated according to the measured corrosion parameters by using the following equation [38]:

\[ IE\% = \left(1 - \frac{I_{corr}}{I_{corr_{o}}}ight) \times 100 \]
IE % = \left(\frac{I_0 - I}{I_0}\right) \times 100

Where \( I_0 \) and \( I \) are the corrosion current density without and with the inhibitor respectively.

2.4.2 Open circuit potential measurements

The potential of an electrode that measured with respect to a reference electrode when there is no current flowing (zero current) into it or from it is called open circuit potential (OCP). Open circuit voltage method does not give any information about the corrosion rate, it only indicates the corrosion activity at the time of measurement [39, 40]. To indicate the corrosion inhibition of TVE, open circuit voltage tests were performed for reinforced steel specimens immersed in four SCP solutions, control solution was the first one and the other three solutions were the control solution with TVE inhibitor at concentrations of 100 ml/L, 150 ml/L and 250 ml/L respectively. High impedance digital voltmeter was used to measure the open circuit voltage at interval of 2 days for a period of 7 days using Ag/AgCl electrode as reference electrode. The more negative reading of the voltmeter means the high corrosion activity on the reinforced steel at the time of experiments.

2.5 Digital optical microscope image

Digital optical microscope was used to examine the microstructure of the specimens surface after six days immersion in both inhibited and uninhibited solution.

3. RESULTS AND DISCUSSION

3.1 potentiodynamic polarization

Figure 1 shows the polarization curves of concrete reinforced steel samples immersed in test solutions for zero hour. Corrosion parameters such as corrosion potential (Ecor), corrosion current (Icor), cathodic Tafel slope (bc) and anodic Tafel slope (ba) were measured from Tafel plots, inhibition efficiency (IF%) was calculated from the measured values and all these parameters were tabulated in table 1.

From the table it was apparent that in the case of control sample, the passivity that formed due to the high alkalinity of the solution is destroyed by the chloride ions as indicated by the corrosion potential of \(-492\) mV and corrosion current of \(11.4\ \mu\text{A/cm}^2\). In the case of TVE inhibitor samples the corrosion potential in 100 ml/L concentration shifted to more noble side \((-403\) mV), and the corrosion current density decreased to \((5.91\ \mu\text{A/cm}^2)\) with IF% of 47.9 and in 150 ml/L concentration shifted to \((-371\) mV) and current density decreased to \((3.45\ \mu\text{A/cm}^2)\) with IF% of 69.73, and in 250 ml/L concentration to \((-387.5\) mV) and corrosion current to \((2.71\ \mu\text{A/cm}^2)\) with IF% of 76.2.

From figure and table it can be observed that the increasing in the inhibitor concentration not only decreased corrosion current density (Icor) but also increased inhibition efficiency IF% and changed anodic and cathodic Tafel slope (ba and bc) with more clear change in cathodic branch compared with anodic branch which mean that TVE is a mixed type inhibitor with predominantly cathodic action [41]. This results indicate that the TVE blocking the cathodic and anodic sites due to the adsorption of tannins, alkaloid and saponins molecules on steel surface forming a barrier film prevent the diffusion of ions from or to the corroded surface then stopping hydrogen evolution and steel dissolution providing protection to the passive film that formed due to the solution alkalinity [42].
Figure 1: Electrochemical parameters of concrete reinforced steel samples without and with thyme extract at various concentrations studied after zero hr. immersion in the SCP solution.

<table>
<thead>
<tr>
<th>System</th>
<th>Ecor (mV)</th>
<th>Icor (µA/cm²)</th>
<th>ba (mV/dec)</th>
<th>-bc (mV/dec)</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-492</td>
<td>11.4</td>
<td>214.3</td>
<td>371.5</td>
<td></td>
</tr>
<tr>
<td>Control + 100 ml/l thyme</td>
<td>-403.5</td>
<td>5.91</td>
<td>177</td>
<td>156.3</td>
<td>47.9</td>
</tr>
<tr>
<td>Control + 150 ml/l thyme</td>
<td>-371</td>
<td>3.45</td>
<td>112.1</td>
<td>131.9</td>
<td>69.73</td>
</tr>
<tr>
<td>Control + 250 ml/l thyme</td>
<td>-387.5</td>
<td>2.71</td>
<td>102.1</td>
<td>129.9</td>
<td>76.22</td>
</tr>
</tbody>
</table>

Figure 2 shows the polarization curve of concrete rebar samples immersed in SCP solution without and with thyme extract immersed for one day. The corrosion parameters that measured and calculated from the polarization curves were reported in table 2. The results show that Ecor also shifted to more positive direction, Icor decreased and IE% increased more than that for zero hour immersion with increasing in TVE concentrations. For 250 ml/L TVE inhibitor the IE% is 84.43% which is more than that of zero hour immersion (76.22%) and the same thing is for other concentration the IE% is more than that of zero hr. immersion. This an indication that TVE inhibitor build up more protective film on the steel surface.
After 30 days immersion in SCP solution containing different concentrations of TVE inhibitor the corrosion parameters values of the reinforced steel were decreased higher than that values of zero hour and one day immersion as shown in figure 3 and table 3. This is an indication that TVE inhibitor maintained stable protective film on the steel surface even in the presence of chloride ions. It is observed from table 3 that the maximum efficiency is 89.71% and lower corrosion current density of 0.56µA/ cm$^2$ was achieved at TVE concentration of 250 ml/L.

According to the data in table 4 [43] which represent the proposed relationship between the corrosion current density and the remaining service life, the reinforced steel samples immersed in SCP solution without inhibitor (control solution) having corrosion current density of 11.4 µA/ cm$^2$ for zero hr immersion and 13.3 µA/ cm$^2$ for one day immersion and 5.44 µA/ cm$^2$ for 30 day immersion which is more than 2.7 µA/ cm$^2$, that means that the expected corrosion damage is within 2-10 years but when TVE inhibitor was added to the control solution the corrosion current density of the steel sample decreased after 30 days immersion to 0.56 µA/ cm$^2$ at inhibitor concentration of 250 ml/L which means that the expected corrosion damaged became 10-15 year instead of 2-10 years due to the action of the inhibitor. Since the corrosion rate decrease with increasing TVE inhibitor so

### Table 2: Electrochemical parameters of concrete reinforced steel samples without and with thyme extract at various concentration studied after one day immersion in the SCP solution

<table>
<thead>
<tr>
<th>System</th>
<th>Ecorr</th>
<th>Icorr</th>
<th>Bas</th>
<th>-bc</th>
<th>IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-384.2</td>
<td>13.3</td>
<td>325.5</td>
<td>196.4</td>
<td></td>
</tr>
<tr>
<td>Control + 100ml/l thyme</td>
<td>-375.9</td>
<td>3.26</td>
<td>169.1</td>
<td>136</td>
<td>75.5</td>
</tr>
<tr>
<td>Control + 150 ml/l thyme</td>
<td>-338.4</td>
<td>2.1</td>
<td>235.4</td>
<td>120.7</td>
<td>84.21</td>
</tr>
<tr>
<td>Control + 250 ml/l thyme</td>
<td>-367.6</td>
<td>2.07</td>
<td>126.6</td>
<td>88.9</td>
<td>84.43</td>
</tr>
</tbody>
</table>

### Figure 2: Electrochemical parameters of concrete reinforced steel samples without and with thyme extract at various concentration studied after one day immersion in the SCP solution
it can expect that the inhibitor concentration more than 250 ml/L may decrease the corrosion current density to less than 0.5 µA/cm² and then make the reinforced steel in the no corrosion damage state or in a passive state. This results reveal that TVE has ability to be a good green corrosion inhibitor for reinforced steel in concrete.

![Graph showing electrochemical parameters](image)

**Figure 3:** Electrochemical parameters of concrete reinforced steel samples without and with thyme extract at various concentration studied after 30 days immersion in the SCP solution

**Table 3:** Electrochemical parameters of concrete reinforced steel samples without and with thyme extract at various concentration studied after 30 days immersion in the SCP solution

<table>
<thead>
<tr>
<th>System</th>
<th>Ecor mV</th>
<th>Icor µA/cm²</th>
<th>Ba mV/dec</th>
<th>-bc mV/dec</th>
<th>IE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-401.1</td>
<td>5.44</td>
<td>264.1</td>
<td>198.9</td>
<td></td>
</tr>
<tr>
<td>Control + 100 ml/l thyme</td>
<td>-327.1</td>
<td>1.34</td>
<td>181</td>
<td>114.8</td>
<td>75.36</td>
</tr>
<tr>
<td>Control + 150 ml/l thyme</td>
<td>-371.8</td>
<td>1.18</td>
<td>101.3</td>
<td>72.2</td>
<td>78.31</td>
</tr>
<tr>
<td>Control + 250 ml/l thyme</td>
<td>-322</td>
<td>0.56</td>
<td>108.5</td>
<td>76</td>
<td>89.71</td>
</tr>
</tbody>
</table>

**Table 4:** Proposed relationship between corrosion rate and remaining service life (43)

<table>
<thead>
<tr>
<th>Icor (µA/cm²)</th>
<th>Severity of damage</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.5</td>
<td>No corrosion damage expected</td>
</tr>
<tr>
<td>0.5 - 2.7</td>
<td>Corrosion damage possible in 10 to 15 year</td>
</tr>
<tr>
<td>2.7 – 27</td>
<td>Corrosion damage expected in 2 to 10 years</td>
</tr>
<tr>
<td>&gt; 27</td>
<td>Corrosion damage expected in 2 years or less</td>
</tr>
</tbody>
</table>

### 3.2 Open circuit potential

Plots of open circuit potential readings against time, obtained during 7 days of the experiment for concrete reinforced steel samples immersed in SCP solution with and without TVE inhibitor are presented in Figure 4. From the open circuit potential readings shown in the plots of Figure 4, The
potential of all specimens in pore solution containing TVE inhibitor were shifted to more positive direction compared with specimen immersed in control sample which indicates that the TVE inhibitor slow the corrosion process on reinforced steel surface due to the attack of the aggressive chloride ions.

Figure 4: Potential variation of reinforced steel samples with the exposure time in chloride contaminated simulated pore solutions with and without TVE inhibitor for week.

3.3 Optical microscope image

Digital optical microscope was used to examine the surface of reinforced steel discs immersed in control solution and in control solution with various concentration of TVE inhibitor for six days. The results were presented in Figure 4. From micrograph(a) which represent the image of steel specimen in control solution it can be visibly observed a large number of pitting due to the attack of the chloride ions. where micrographs (b), (c) and (d) showed a decreased in the number of pitting due to the inhibitive action of TVE inhibitor by forming barrier film on steel surface and the decrease in pitting area decreased with increasing inhibitor concentration. This resultsarein good agreementwith the results that obtained from open circuit and potentiodynamic polarization technique that studies.

Figure 4: Optical micrographs of reinforced steel surface after six days of immersion in (A) Control sample, (B) 100 ml/L thyme inhibitor sample, (C) 150 ml/L thyme inhibitor sample, (D) 250 ml/L thyme inhibitor sample
4 CONCLUSION

From the obtained results the following can be deduced:

a) Thyme (Thymus Vulgarize) can be used as good green corrosion inhibitor for reinforced steel.
b) The inhibition efficiency increases with increasing TVE concentration.
c) Maximum efficiency of 89.71% was obtained at TVE concentration of 250 ml/L after 30 day of immersion in corrosive solution.
d) TVE inhibitor can increase the expected service life of concrete reinforced steel five times than that without inhibitor.
e) Polarization results showed that TVE is mixed type inhibitor with predominantly cathodic action on the steel surface.
f) Optical microscope images of reinforced steel surfaces showed that the pitting area decreased with increasing TVE concentration due the formation of protective film on the steel surface.
g) Studies with actual concrete specimens are needed to know the effect of amoxicillin on the concrete mechanical properties.
h) In order to recommend the final TVE inhibitor dosage required to protect concrete steel from corrosion long term studies are needed.

REFERENCES


