CORROSION BEHAVIOUR OF LOW CARBON STEEL IN SULPHIDE MEDIUM USING THEVETIA PERUVIANA AS INHIBITOR

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ABSTRACT

Corrosion cannot be completely stopped; however, the rate of corrosion can be retarded, hence the need for corrosion inhibitors. Corrosion process can be mitigated by the use of various chemical inhibitors; using green inhibitors is one of the methods used to control corrosion and still preserved the environment. The present study presents the extraction of Thevetia peruviana (TP) extract using soaking method in Ethanol, and bio inhibitive properties of TP fruit extract on low carbon steel corrosion in sulphide solution. Low carbon steel samples were subjected to six sodium sulphide solution environments; five of the environments have TP extract ranging from 10 ml to 50 ml while the 6th which served as control has no TP extract. Weight loss experiment was carried out for 28 days and readings were taken at 4 days interval. The results revealed that TP extract displayed inhibitive property at concentrations (10 ml, 20 ml, 30 ml, 40 ml and 50 ml), but the effect was more pronounced at higher concentrations (40 ml and 50 ml). The inhibitor with 50 ml of TP extract showed the lowest corrosion rate of 0.0028 mm/yr on the 28th day and highest inhibition efficiency of 90% on the 8th day. Hence TP extract was successfully used as inhibitor of low carbon steel in sulphide environment.

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1.0 INTRODUCTION

Corrosion direct and indirect losses have made its study of principal importance (Komalasari et al. 2018). The degradation of more than a quarter of steel produced in the world are traced to corrosion problem (Lgaz et al., 2018). Corrosion products of electrical contacts can lead to fire disaster, while medical implants corrosion products may poison patients’ blood and eventually leads to death. Some of the methods used in corrosion prevention and control are: corrosion inhibitors, environmental modification, cathodic prevention, metal selection, plating and coating (Singh et al. 2013). Corrosion inhibitors can be obtained from diverse plant extracts also known as green inhibitors, most of the plant extracts contain tannin as an active ingredient to shield ferrous products from corrosion, tobacco leaves extracts can protect aluminium and steel in strong pickling acids and saline solutions (Davis et al. 2001). Researchers have worked on a number of natural products with proven efficacy as good corrosion inhibitors for metals (Souza et al. 2015; Desai, 2015; Yamuna and Anthony, 2014; Gupta, 2014; Singh et al. 2013; Okafor et al. 2013;
Corrosion inhibitors contain elements like oxygen, Sulphur and some hydrocarbon, the inhibitors are absorbed on the metal surface either physically or chemically, and the inhibitor change the interfacial energy of the metal (Singh and Pani, 2016). Corrosion inhibitor can either be inorganic or organic. Inorganic inhibitor has active groups, they are negative anions which have ability to decrease rate of corrosion of metal (Wiston, 2000), examples of inorganic inhibitor are Zinc, Phosphate, Sodium Nitrite and Chromate. The demerit of use of Sodium Nitrite is that, high concentration (300-500 mg/l) is needed, chromate and Zinc have weakness of toxicity and phosphate increases phosphorous content in water (Marcus and Mansfield, 2006), thus make such inhibitors harmful to the marine environment. A popular way for inhibiting corrosion involves formation of a passivation layer, which shield the metal from corrosive substance. Chrome plating, one of the permanent treatments cannot be considered as an inhibitor; however, additives to the fluids that surround the metal or related object are referred to as corrosion inhibitors.

Komalasari et al. (2018) reported that Organic inhibitors can be synthetic type or the one extracted nature. Compound used as organic inhibitors contains Oxygen, Sulphur or Nitrogen atoms having a pair of free electrons, that can interface with metal to form complex compound and prevents such metal from corrosion attacks, Organic inhibitors are friendly to the environment, cheap, renewable and biodegradable. Komalasari et al. (2018), also opined that organic compounds are more effective inhibitor for metal corrosion, because their carbon chain in the aromatic chain system has free pair of electrons that have affinity to bind to positive charge of metal by adsorption process between the inhibitor and the metal surface and by physisorption formed protecting layer on the metal surface. This finally prevent the corroder from direct contact with the metal (Zang et al. 2004). The common features in natural extracts, that is majorly linked to inhibitory are the presence of unsaturated bonds and/or heteroatoms, and a polyphenol compound called tannin; found with different qualitative and present in nearly every green flora is another corrosion inhibitive constituents in organic inhibitor (Rahim and Kasssim, 2008), this also can form undissolved complex compound with metal ions. Gusti, 2013, corroborated this fact that tannin complex compound formed with metal ions can protects the metal from direct contact with the corrosive media, there by lead to decrease in corrosion rate. Bell, (2016) supported this statement by reporting that inhibitors can work by adsorbing themselves on the metal's surface and forming a protective film. These chemicals can be used as a solution or as a protective coating through dispersion techniques (Bell, 2016 and Omotosho, 2016).

TP plant is from Apocyanaceae family, it is an ever-green ornamental dicotyledonous shrub that is common in the sub-tropics and tropics regions, but it is native to South and Central America. The plants' height is between 3 – 7 meters having linear leaves of length 13-15 centimeters, spirally arranged. The plant has two varieties; namely: yellow oleander (yellow flowers), and nerium oleander (purple flowers), the flowers are funnel-like spirally twisted with petals. The two varieties produce seeds round the year and the rainfall pattern and age determines its fruiting, usually between 400–800 fruits per annum. The fruits are to some extent globular, with mesocarp that is fleshy and have a diameter of 4 – 5 cm. The fruits are usually green in colour and turned black on ripening. Each fruit contains a nut which is divided transversely and longitudinally. The fruit contains between 1 to 4 seeds in its kernel, and all
the plants organs produces milky juice (Owa et al. 2018).

Singh et al. (2012) described the plants' parts as toxic, and contain cardiac glycosides. Ingestion of oleander may lead to abdominal pain, vomiting, nausea, diarrhea, disrhythmias and hyperkailema in most cases. Administration of activated charcoal and supportive care are the clinical management of poisoning by TP. The presence of cardiac glycoside in the seed makes it not edible, despite the fact that the seed contains high level of oil and protein (Owa et al. 2018).

2.0 MATERIALS AND METHOD

2.1. Materials

The materials used for this research are TP fruits, which were picked from Oke-Ayedu, Ekiti state, Nigeria, Sodium Sulphide salt, FeCl, and Ethanol were purchased from Pascals Scientific Ltd, Akure, Ondo state, Nigeria and low carbon rod was purchased from Scrap dealer in Akure, Ondo state.

The elemental analysis of the low carbon steel was done using the Mass Spectrometer and the result is shown in Table 2.

2.2 Methods

78.1 g of Na, S was dissolved in 1 litre of distilled water to produce 1M of Na, S solution used as the main corroden for this work.

The TP fruits (about 50 fruits) obtained, were washed with water, peeled, mashed/milled and soaked in 600 ml (60 cl) of Ethanol for 24 hours, after that, the extract was sieved with Whatmann filter paper to obtain the extract. Finally, the TP fruits extract was evaporated by rotary evaporator at ±50 °C for 4 hours and stored in the refrigerator at 4°C prior its use as bio inhibitor.

Qualitative analysis test was carried out to identify the presence of tannin in the extract, using Harborne, (1987) method. This was done by adding 1% FeCl, solution to 5 ml of TP extract in test tube at room temperature, the colour of the mixture changed to greenish black. This confirmed that tannin in extract react with ion Fe³⁺ to form complex compound (Harborne, 1987).

The low carbon steel was cut into 18 cylindrical shape samples (15mm diameter and 10mm length). The samples were polished with silicon carbide (SiC) grit papers of various grades and emery paper from 60-1,200 grade to remove any mill scale.

The nomenclature adopted for the corrosive environments used for this research are stated in Table 1, for example the corrosive environment Na, S is named B0.

Weight loss method was used for the corrosion test, the test consisted of 1M of Sodium sulphide solutions with and without TPF extract as inhibitor of various concentrations (10 ml; 20 ml; 30 ml; 40 ml and 50 ml) of TP extract, respectively. While the control did not have any addition of inhibitor. The samples were pre-weighed, labeled and suspended in the test solutions. The samples were removed after every

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>B0</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>B4</th>
<th>B5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medium</td>
<td>Na₂S</td>
<td>Na₂S + 10ml TP extract</td>
<td>Na₂S + 20ml TP extract</td>
<td>Na₂S + 30ml TP extract</td>
<td>Na₂S + 40ml TP extract</td>
<td>Na₂S + 50ml TP extract</td>
</tr>
</tbody>
</table>

Table 1: Adopted Nomenclature Designation
4 days for 28 days, carefully dried and re-weighed.

The corrosion rate was calculated using equation 1;

\[
C.R = \frac{3.65 \times 10^5}{A.D.T} \cdot W \quad \text{mm/yr} \quad (1)
\]

\( C.R \) = corrosion rate (mm/yr)
\( W \) = Weight loss/gain

\( D \) = metal density (7.85 g/cm³)
\( T \) = exposed time (days)
\( A \) = coupon total surface area (mm²)

While the Inhibitor efficiency (%) was calculated using equation 2;

\[
\text{IE} (%) = \frac{CRA - CRP}{CRA} \times 100 \quad (2)
\]

\( \text{IE} \) = Inhibition Efficiency
\( CRA \) = Corrosion rate without inhibitor
\( CRP \) = Corrosion rate with inhibitor

3.0 RESULTS AND DISCUSSION

Table 2: Chemical Composition of Mild Steel

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>F</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt %</td>
<td>0.2</td>
<td>0.4</td>
<td>0.17</td>
<td>0.03</td>
<td>0.03</td>
<td>0.006</td>
<td>0.007</td>
<td>99.157</td>
</tr>
</tbody>
</table>

Table 2: Chemical Composition of Mild Steel

<table>
<thead>
<tr>
<th>Samples</th>
<th>Corrosion Rate (mm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Day 4</td>
</tr>
<tr>
<td>B0</td>
<td>0.0453</td>
</tr>
<tr>
<td>B1</td>
<td>0.0324</td>
</tr>
<tr>
<td>B2</td>
<td>0.0219</td>
</tr>
<tr>
<td>B3</td>
<td>0.0194</td>
</tr>
<tr>
<td>B4</td>
<td>0.0135</td>
</tr>
<tr>
<td>B5</td>
<td>0.0106</td>
</tr>
</tbody>
</table>

Figure 1 shows plot of the corrosion rates of low carbon steel in 1 M Na₂S solutions with various concentrations (0 ml; 10 ml; 20 ml; 30 ml; 40 ml and 50 ml) of TP inhibitors respectively. It was observed that the rate of corrosion in the control (BO) was high throughout the 28 days, with highest value (0.0662 mm/yr) on the 8th day, while the least was recorded in 28th day. It was also observed that the addition of TP inhibitor reduces the corrosion rate drastically, even as small as 10 ml, the effect of the reduction is more pronounced as the concentration of the inhibitor increases from 10 ml to 50 ml, which is expected since more complex compound were observed, because of
the reaction of tannin compound present in the inhibitor; which increases with the increase in inhibitor concentration, and this complex compound are attracted to the surface of the low carbon steel shielding the metal to have direct contact with the corrosive environment. The steep positive gradient of the graphs shown from 0-8 days by all the corrosive medium is due to the gradual formation of the tannin complex compound and corrosion product settling on the metal surface, the average time for all the corrosive environments to form the complex compound was 8 days; with the exception of the corrosive environment with 10 ml of inhibitor (Na,S + 10 ml TP inhibitor), as shown in Figure.1 and Table 3.

It was also observed that exposure time influenced the corrosion rates, Fig. 1 shows that the longer exposure time the more the reduction in corrosion rate. This can probably be attributed to formation of tannin complex compound on the metal surface; thereby reducing the corrosion rate and Fe(OH), (corrosion product) also formed on the metal surface to develop passive layer in cathode side; thus reduction reaction in cathode is affected. If reaction in cathode was inhibited, steel oxidation in anode would be inhibited. The corrosion rate was observed to decrease with the inhibitor concentration; due to increase of the inhibitors’ adsorption on the steel surface (Li and Mu, 2005).

Generally, steel exposed to corrosive environment with 50 ml inhibitor exhibited the lowest value of corrosion rates, from 0.0028 – 0.0113 mm/yr for 28th day and 12th day, respectively.

Figure 2 showed the graph of inhibition efficiency of low carbon steel in sodium sulphide solutions with various concentrations of inhibitor. From fig.2, it was observed that corrosive environment with 50 ml of inhibitor shown highest efficiency of inhibition 90% on the 8th day, followed by that of concentration 40 ml 79.58% on 16th day, while the least was demonstrated by corrosive environments with 20 and 30 ml inhibition addition as 23.75% on 16th day, as shown in Figure. 2 and Table 4. The inhibition efficiency of the two concentrations were more stable as compared with the other three concentrations (30 ml, 20 ml and 10 ml), because more tannin complex compound was present, there by shielding the sample steels from corrosive environment aggression.

Generally, corrosive environments with 10 ml, 20 ml and 30 ml concentrations of TP inhibitor showed inhibitive behavior, but not as it was pronounced with 40 ml and 50 ml concentrations; throughout the period of the research (28 days).

4.0 CONCLUSION

With the results from above, the following conclusions were made:

- TP extract inhibitor has been successfully developed.
- The inhibition efficiency of *Thevetia peruviana* increases with increasing concentration and the maximum inhibition efficiency during this work was observed to be 90% on the 8th day for concentration of 50 ml inhibitor.
- The corrosion rate of low carbon steel decreases with increasing concentration of *Thevetia peruviana* inhibitor.
- Presence of tannin in *Thevetia peruviana*
extracts could be responsible for its inhibitory ability.

- *Thevetia peruviana* inhibitor can be used as green inhibitor for corrosion of low carbon steel in sodium sulphide solutions at concentrations of 40 ml and 50 ml for high inhibitive efficiency.

**REFERENCE**


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Zhang, D; Gao, L and Zhou, G (2004): Inhibition of Copper Corrosion by Bis-(1-Benzotriazolymethylene)-disulfide in Chloride Media. Applied Surface Science 225(1-4), pp.287-293