Assessment of Langmuir and Freundlich Isotherms Fit for Mildsteel Pipe Corrosion inhibition Study by Extracts of Castor and Rubber Seeds: A Comparative Analysis

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ABSTRACT
The present study is concerned with the Comparative Assessment of Langmuir and Freundlich Isotherms Fit for Mildsteel Pipe Corrosion Inhibition Study by Extracts of Castor and Rubber Seeds. A flow system (locally designed, but with standard equipment) was used for the corrosion inhibition assessment at 60°C (temperature), 60% stroke (dosage) and 20g/L (inhibitor concentration in acid medium). The highest corrosion rate was recorded at 32hours, while the least was recorded at 4hours, which shows that loss of integrity of the material (via corrosion) increases with time. The empirical constant of the Langmuir model, $b$ was found to have all-negative values, affirming a continuous heat energy demand for the corrosion process with time; the model, in this regard, made a good fit for the data (for both samples). On the contrary, the Freundlich model does not fit the data, as the Freundlich intensity factor, $K_f$ (for both samples) have extremely wide values. The Langmuir model is, thus, preferred to the Freundlich model for data fit in corrosion inhibition assessment study.

Keywords: Comparative Assessment, Langmuir Isotherm, Freundlich Isotherm, Corrosion Inhibition, Castor Seed Oil, Rubber Seed Oil.

INTRODUCTION
Mildsteel has been extensively used (under varying conditions) in chemical and allied industries for handling alkaline, acid and salt solutions (including oil-derived compounds). And one way of protecting mildsteel from losing its integrity is the use of corrosion inhibitors. Undiandeye et al. (2014) reported that the known hazardous effects of
most synthetic corrosion inhibitors are the motivation for the use of some natural products. According to the report, most of these natural products are non-toxic, biodegradable and readily available in plenty. However, most oil flow pipes are made of mildsteel, and they are corrodbile, except in certain specific environmental conditions (such as in the presence of tetraoxosulphate (vi) acid and that of caustic alkalis). In the oil and gas industries, corrosion constitutes a major case of interest, which concentrates more on the remaining life predictions for the cracked structures. In other words, if cracks are discovered in pipelines, there will, inevitably, be questions relating to how long the structure may be operated safely if slow stress corrosion crack growth continues. Moreover, in relation to high pressure gas pipelines, where a major method of control currently involves hydrostatic re-testing, the period between such re-test need to be related to stress corrosion crack growth rates [Amadi, 2006].

However, corrosion process occurs sequentially, through systematic adsorption of the corrosion media by the corrodbile material. In other words, the principles of adsorption are very prominent in the study of corrosion. The quantity of a given corrosion medium that can be taken up by the metallic material, at given time, is a function of both the characteristics and concentration of the medium and the reaction temperature [Dobbs and Cohen, 1980]. Also, the amount of material adsorbed is determined as a function of the concentration at constant temperature, and the resulting function is the Adsorption Isotherm [Metcalf and Eddy, 2003].

**THEORY PRINCIPLES**

The assumptions of the Langmuir isotherm relates with the provisions of equation i, as contained in Offurum et al [2011].

\[
\frac{x}{m} = \frac{abC_e}{1 + bC_e}
\]

(1)

Where:
\[ \frac{x}{m} = \text{mass of adsorbate per unit mass of adsorbent} \]
\[ a, b = \text{empirical constants} \]
\[ C_e = \text{concentration of adsorbate in solution after adsorption.} \]

Equation 1 could be rearranged to another form as stated in equation 1(b)

\[ \frac{x}{m} = \frac{1}{ab} + \frac{1}{a} C_e \]

On the other hand, the empirical model of Freundlich Isotherm, as reported in Offurum et al (2011) is given by equation 2.

\[ \frac{x}{m} = K_f C_e^{1/n} \]

Where:
\[ x/m = \text{mass of adsorbate per unit mass of adsorbent} \]
\[ K_f = \text{Freundlich Capacity Factor} \]
\[ C_e = \text{Concentration of adsorbate in solution after adsorption} \]
\[ 1/n = \text{Freundlich Intensity Parameter} \]

Taking logarithm of both sides of equation 2 gives a linear form, as presented equation 3.

\[ \log \left( \frac{x}{m} \right) = \log K_f + \frac{1}{n} \log C_e \]  

**MATERIALS AND METHOD**

**Corrosion Inhibition Assessment**

A flow system, as presented in Figure 1, was used for the corrosion inhibition assessment. Though with standard equipment, the system is locally designed to reflect the dynamics of a flowline. The dosing pump, B (of model: JM-15774-C07) was firmly fixed on the wooden platform, G by means of screws. The inlet hose was then cut at the middle, and the ends of steel pipe, C firmly connected to each of the points (of the cut) using clips. The lower end of the pipe was passed through a sizeable opening made on the plastic reservoir, D (containing a given concentration of the inhibitor-in-acid), while the other end is connected to the pump inlet. Another hose connects the outlet of pump to the reservoir, which serves as a recycle stream (from the reservoir, through
the steel pipe, and back to the reservoir. The reservoir is already securely placed in the thermostat water bath, A [of model: TT-6], which contains about 4-litres of water, and both the pump and water bath are connected to a source of electric power, E. These gave rise to the composite flow system.

With the electric power supply (to the Pump and Water Bath), the temperature of the water bath was set at 60°C and the pump set at 60% stroke (dosage); the inhibitor concentration was 20g/L. The fluid mixture in the reservoir was then transmitted in a continuous flow pattern, through the steel pipe, under the set conditions for a period of 4 hours. At the elapse of the time, the steel sample was removed, washed gently with distilled water and placed in an oven dryer [of model: DHG-9101-15A] for 5 minutes. Having taken the initial weight of the steel pipe \( W_1 \), the final weight \( W_2 \) was then measured, and the weight difference \( W_1 - W_2 \) was obtained and recorded. The same procedure was followed for the blank condition (without inhibitor in the reservoir). This procedure was repeated at various time intervals of 8, 16, 24 and 32hrs for both samples, and their results duly presented in Tables. The result shows that the highest corrosion rate was observed at 32hours, while the least was observed at 4hours, indicating that material degradation (via corrosion) increases with increase in time.
Table 1: Weight Loss (in gram) at the given conditions (20g/l at 60°C, 60% Stroke)

<table>
<thead>
<tr>
<th>Time, hr</th>
<th>Sample A (CSO)</th>
<th>Sample B (RSO)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>With Inhibitor</td>
<td>Without Inhibitor</td>
</tr>
<tr>
<td>4.00</td>
<td>7.4317</td>
<td>11.8126</td>
</tr>
<tr>
<td>8.00</td>
<td>10.3484</td>
<td>15.2115</td>
</tr>
<tr>
<td>16.00</td>
<td>11.8996</td>
<td>19.0473</td>
</tr>
<tr>
<td>24.00</td>
<td>18.6218</td>
<td>26.4816</td>
</tr>
<tr>
<td>32.00</td>
<td>26.1153</td>
<td>29.0887</td>
</tr>
</tbody>
</table>

**Isotherm Study**

The constants of Langmuir Isotherm were determined by plotting $C_e/(x/m)$ against $C_e$ as contained in equation 1/b, while those of the Freundlich Isotherm were then determined by plotting $\log (x/m)$ against $\log C_e$ as contained in equation 3. The results of the Langmuir plots are
presented in *Figures 1 and 2* for **Samples A** (Castor Seed Oil, CSO) and **B** (Rubber Seed Oil, RSO) respectively. The slope of the plot is equivalent to ‘\( \frac{1}{a} \)', from which ‘\( a \)' was evaluated. Also, the intercept is equivalent to ‘\( \frac{1}{ab} \)', and ‘\( b \)' was evaluated, having known ‘\( a \)’. Similarly, the plots of Freundlich isotherm are presented in *Figures 3 and 4* for **Samples A** and **B** respectively. The slope of the Freundlich plot is equivalent to ‘\( \frac{1}{n} \)', while the intercept is equivalent to ‘\( \log K_f \)’. With the known values of the slope and intercept, the Freundlich factors were successively evaluated. The Langmuir and Freundlich constants generated are presented in *Tables 2*.

(a) With Inhibitor (b) Without Inhibitor

**Fig 1: Langmuir Plot for CSO at 20g/L, 60°C, 60% Stroke**
(a) With Inhibitor (b) Without Inhibitor

Fig 2: Langmuir Plot for RSO at 20g/L, 60°C, 60% Stroke
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(a) With Inhibitor  (b) Without Inhibitor

Fig 3: Freundlich Plot for CSO at 20g/L, 60°C, 60% Stroke
The data presented in Table 2 indicate all-negative values for the empirical constant of the Langmuir model, $b$ for both study samples, which demonstrates the heat loss during the adsorption process of a given concentration of the medium at constant temperature. This
suggests that the number of available active sites increases with continuous increase in energy demand, which results in reduced competition for adsorption sites, and the adsorption process readily increases; a similar observation was reported by Offurum et al (2011). However, the Langmuir model [by these features] fits the research data (Metcalf and Eddy, 2003).

On the other hand, it can be observed that the Freundlich Intensity Factor, \( K_f \), for both study samples (CSO and RSO), as presented also in Tables 2, are extremely wide (between \( 1.2 \times 10^{-4} \) - \( 3.7 \times 10^{-16} \)). This wide variation in the Freundlich capacity factor demonstrates that the model does not fit the data for both study samples (Metcalf and Eddy, 2003). Generally, the coefficient of determination \( (R^2) \) values, for all conditions studied, fall between 0.5418 and 0.9481, which fairly indicates a good fit of the data points.

**CONCLUSION**

During the corrosion reaction, heat loss increases with time, which justifies the continuous heat energy demand during the process. The Langmuir model fits the data as shown by the ‘all-negative values’ of the empirical constant of the model, \( b \), for both study samples. The Freundlich model, on the contrary, does not fit the data for the samples, as there exist extremely wide variations in the values of the Freundlich capacity factor, \( K_f \). However, the values of the coefficient of determination \( (R^2) \) fairly indicate a good fit of the data points.

**REFERENCES**


