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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 corrodible, 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 corrodible 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 1*, as contained in Offurum et al (2011).

$$\frac{\mathrm{x}}{\mathrm{m}} = \frac{\mathrm{ab}C_e}{1 + \mathrm{b}C_e} \qquad (1)$$

Where:

x/m = mass of adsorbate per unit mass of adsorbent
a,b = empirical constants
C_e = concentration of adsorbate in solution after adsorption.
Equation 1 could be rearranged to another form as stated in *equation 1(b)*

$$\frac{C_e}{(\frac{x}{m})} = \frac{1}{ab} + \frac{1}{a} C_e \qquad 1(b)$$

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

$$\frac{x}{m} = \boldsymbol{K_f} {C_e}^{1/n} \qquad (2)$$

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

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

$$\mathrm{Log}\left(\frac{x}{m}\right) = \mathrm{Log}\boldsymbol{K_f} + \frac{1}{n}\mathrm{Log}C_e \qquad (3)$$

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 dozing 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-9101-1SA*) for 5minutes. Haven 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 *Tables1.* 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.

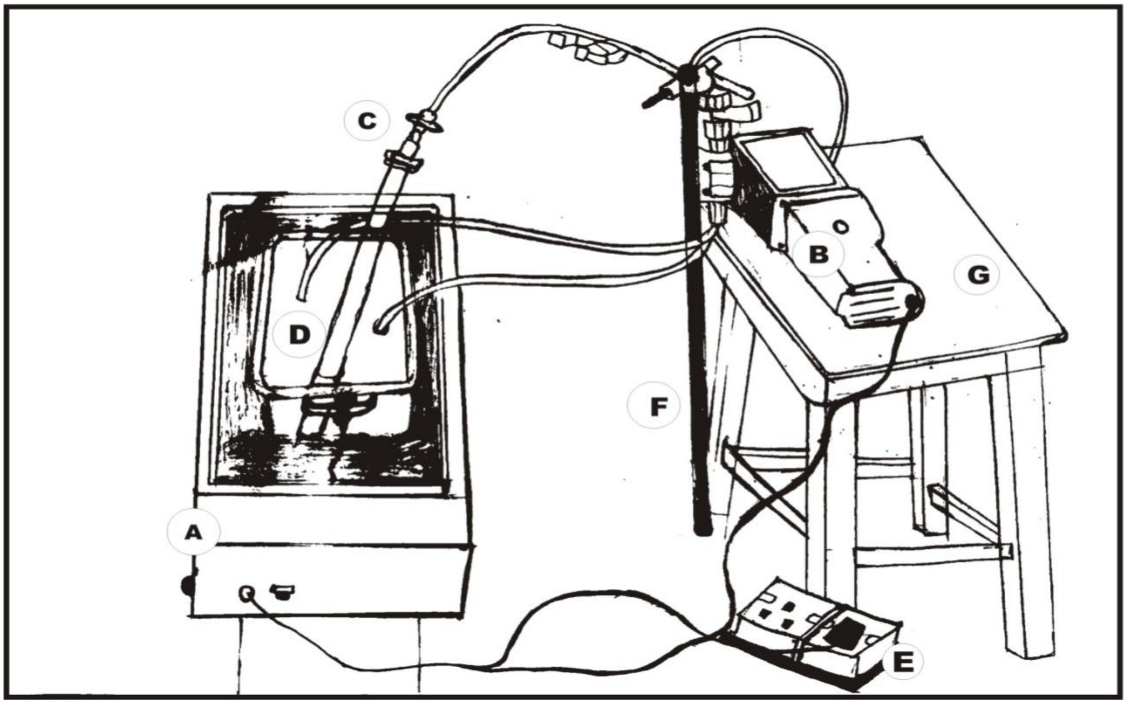


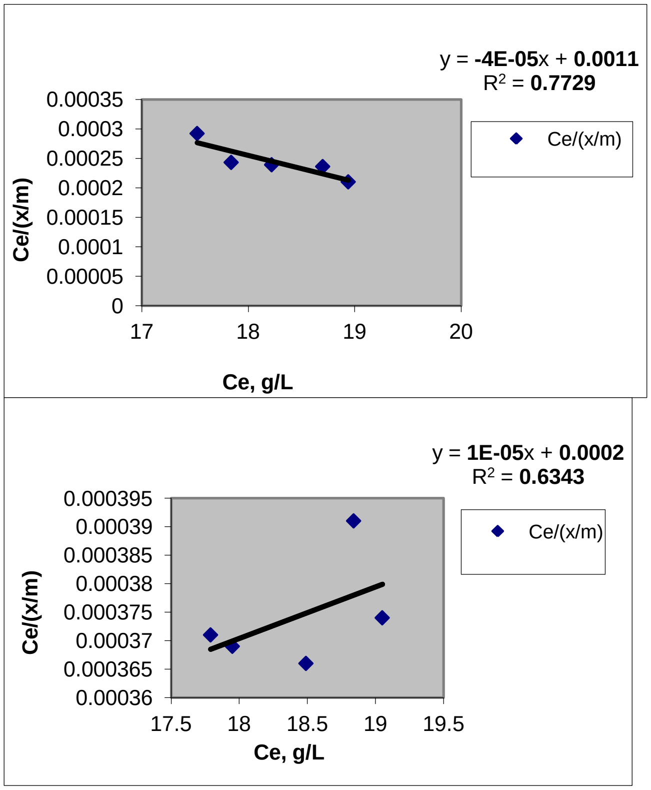
Fig. 1: Flow System Setup for the Study

Table 1: *Weight* Loss (in gram) at the given conditions (*20g/l at 60°C, 60% Stroke*)

Time, hr	Sample A (CSO)		Sample B (RSO)	
	With Inhibitor	*Without Inhibitor*	*With Inhibitor*	*Without Inhibitor*
4.00	7.4317	11.8126	5.2178	6.8827
8.00	10.3484	15.2115	6.7234	7.8726
16.00	11.8996	19.0473	10.0388	15.3102
24.00	18.6218	26.4816	19.6624	22.0182
32.00	26.1153	29.0887	24.1285	25.5783

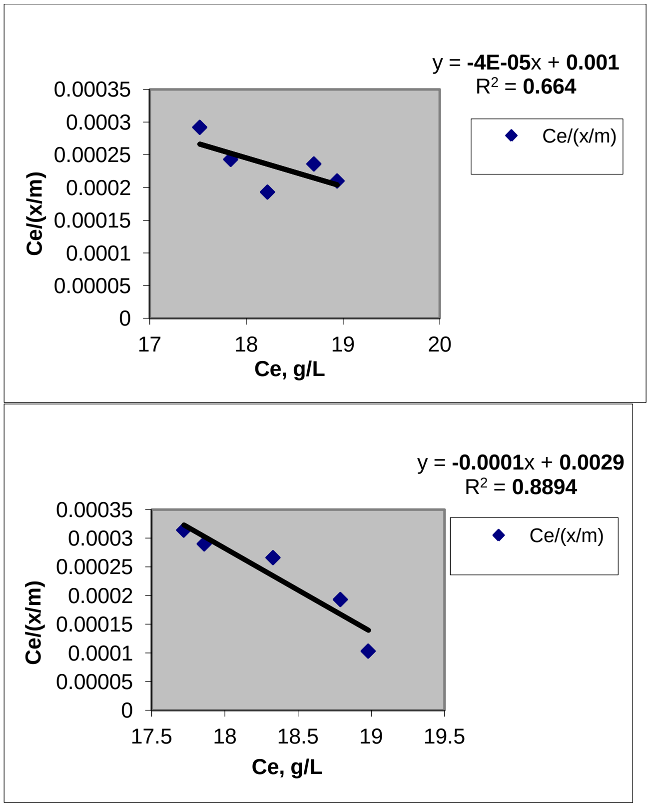
Isotherm Study

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 '**1/a**', from which '**a**' was evaluated. Also, the intercept is equivalent to '**1/ab**', and '**b**' was evaluated, haven 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 '**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*.



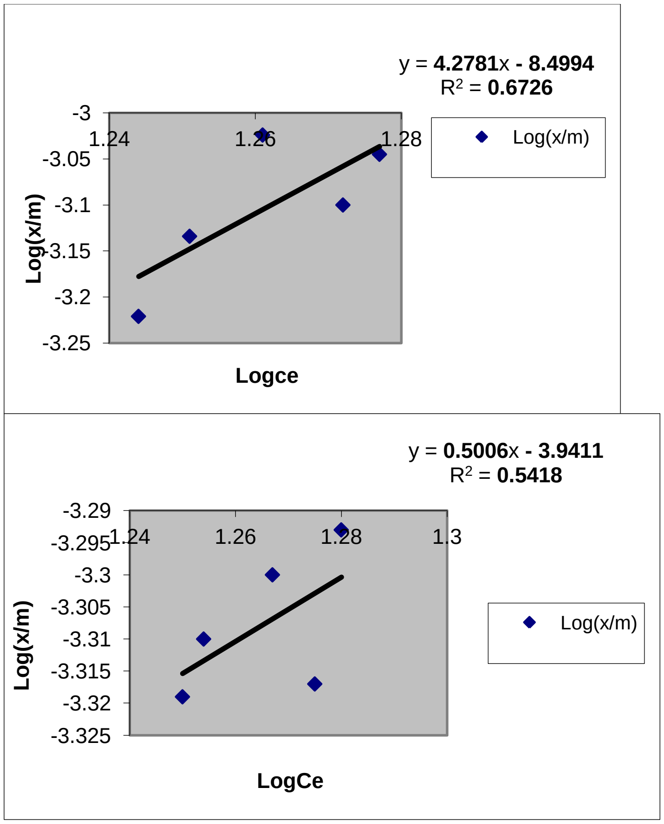
(a) With Inhibitor (b) Without Inhibitor

Fig 1: Langmuir Plot for CSO at 20g/L, 600C, 60% Stroke



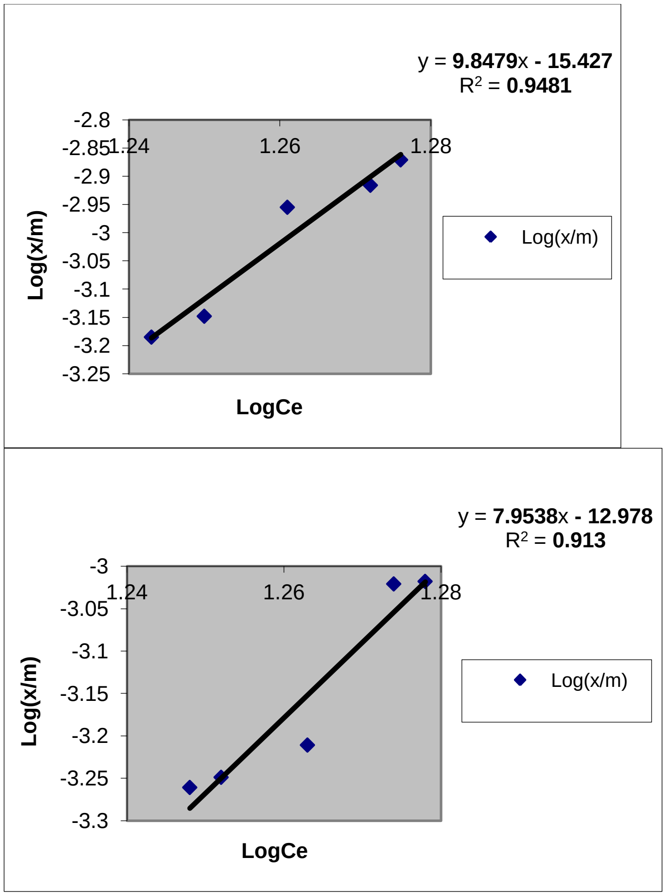
(a) With Inhibitor (b) Without Inhibitor

Fig 2: Langmuir Plot for RSO at 20g/L, 600C, 60% Stroke



(a) With Inhibitor (b) Without Inhibitor

Fig 3: Freundlich Plot for CSO at 20g/L, 600C, 60% Stroke



(a) With Inhibitor (b) Without Inhibitor

Fig 4: Freundlich Plot for RSO at 20g/L, 600C, 60% Stroke

Table 2: Langmuir and Freundlich Parameters

SAMPLE	State of the Medium	LANGMUIR PARAMETERS			FREUNDLICH PARAMETERS		
		a ($X10^4$)	b	R²	K_f	1/n	R²
A (CSO)	*With Inhibitor*	-2.50	-0.036	0.7229	$3.2X10^{-9}$	4.274	0.6726
	At Blank	-10.00	-0.050	0.6343	$1.2X10^{-4}$	0.501	0.5418
B (RSO)	*With Inhibitor*	-2.50	-0.040	0.6640	$3.7X10^{-16}$	9.804	0.9481
	At Blank	-1.00	-0.034	0.8894	$1.1X10^{-13}$	7.937	0.9130

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 to 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 $1.2X10^{-4}$ - $3.7X10^{-16}$). 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.

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