Comparison Of Various Adsorption Isotherm Models For Allium Cepa As Corrosion Inhibitor On Austenitic Stainless Steel In Sea Water.

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ABSTRACT: The corrosion inhibition study was carried out using weight loss method at room temperature. The values of inhibition efficiency increased with increasing concentration of the allium cepa extract. The values of the Gibbs free energy of adsorption obtained were negative indicating a spontaneous adsorption process. The mechanism of adsorption for the study was physisorption. The El-Awady isotherm model showed that Allium cepa extract occupies more than one active site having 1/y value of 1.4051 greater than one. The adsorption process was an easy one obtained from the Freundlich isotherm parameter 1/n which equals 0.2866 satisfying the condition for easy adsorption. The sorption data of the extract obeyed Langmuir, Freundlich, Temkin, El-Awady and Adejo Ekwenchi isotherm of which Langmuir Isotherm gave the best model fit.

Keywords: Allium cepa, Adsorption isotherm, Austenitic Stainless Steel, Corrosion Inhibitor, physisorption, Langmuir, Freundlich, Temkin, El-Awady , weight loss.

1. INTRODUCTION

Corrosion is often referred to as metallic deterioration by chemical attack or reaction of a metal with its environment [8]. Metallic deterioration progresses very fast after the destruction or penetration of the passive barrier which is followed by a number of reactions that alter the constituents and behavior of both the superficial metal surface and the immediate environment. The speed and extent of the metallic deterioration depends on several factors such as temperature and concentration of the particular (aggressive) medium. Austenitic stainless steel is a specific type of stainless steel alloy. They are non-magnetic stainless steel; contain high levels of chromium and nickel and low levels of carbon. Stainless steel depends on passive films for corrosion resistance unfortunately; they can suffer dangerous localized corrosion in the form of pitting and crevice corrosion when local breakdown or crack of the protective film occurs under particular structural and environmental conditions [2]. Inhibitors have been widely used to mitigate and control corrosion of austenitic stainless steel utilized in saline environments. It is one of the most practical methods of curbing the corrosion menace on metals. The hazardous effects of most synthetic corrosion inhibitors has motivated scientists to use naturally occurring materials as corrosion inhibitors, as they are inexpensive, readily available, biodegradable, environmentally friendly and ecologically acceptable [1]. Saps of certain plants are very useful corrosion inhibitors. It is agreed that the inhibition performance of plant extracts is normally ascribed to the presence, in their composition, of complex organic species such as tannins, alkaloids and nitrogen bases, carbohydrates, amino acids and proteins as well as hydrolysis products [7]. Recent studies have shown that the efficiency of inhibitors is related to the amount of adsorbed inhibitor on the metal surface. In this study, the corrosion inhibition and adsorption models of Allium cepa extract in sea water was investigated.

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2. MATERIALS AND METHODS

2.1 Materials collection and preparation

Fresh Allium cepa used in this study was collected from Amassoma market in Bayelsa State, Nigeria. It was dried, pulverized and soaked in 1000ml of methanol for 5days. Maceration extraction method was used to separate the liquid solution containing the methanol and onion organic matter leaving behind the solution of onion organic matter. From the stock solution, different concentrations of the inhibitor were formed by dissolving (0.1-0.6g) of the extract in 500ml of sea water. Corrosion tests were performed on austenitic stainless steel. The stainless steel sheet was mechanically cut into coupons of different rectangular dimensions, polished and cleaned with abrasive paper, degreased with acetone, washed in distilled water and air dried

2.2 weight loss experiment

Weight loss measurements were performed on the austenitic steel samples in 500ml of sea water solution with and without addition of different concentrations of onion extract. The experiment was conducted at room temperature. Samples for weight loss measurements were removed every 4 days, rinsed in water, sun dried for 2 hours, weighed to get their new weights before re-immersing them in their respective solutions. This process was repeated continuously for a duration of 28 days in order to obtain the inhibition efficiency (η %) and the corrosion rate (CR). The corrosion rate (CR) for austenitic stainless steel was calculated using the relation

$$CR\left(\frac{mm}{yr}\right) = \frac{87.6W}{DAT}$$

Where w is weight loss in grams, D is density of coupon (g/cm^3), A is the area of coupon (cm^2) and t is exposure time (hr). The surface coverage (θ) and inhibition efficiency (η %) were determined by the following equations:

$$\theta = \frac{R_o - R_i}{R_o}$$

$$\eta\,\% = \theta \times 100\%$$

Where R_o and R_i represents corrosion rates of austenitic stainless steel in absence and presence of inhibitor respectively.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Weight loss measurement

Table 1 shows the results obtained from weight loss measurements for austenitic stainless steel in sea water in the absence and presence of inhibitor concentration of methanolic extract of Allium cepa at room temperature (303K). It was observed that the weights of the coupons decreased with time. The rate of corrosion was highest in the control solution due to the absence of the inhibitor, also the inhibition efficiency of the extract increases as the inhibitor concentration increases having its highest inhibitive efficiency of 76.43% at 0.6g/l inhibitor concentration. Table 1: Calculated values of corrosion rate, inhibition efficiency, and surface coverage for the coupons in sea water containing varying concentrations of Allium cepa extract.

Conc. (g/l)	Blank	0.1	0.2	0.3	0.4	0.5	0.6
CR(mm/yr.)	4.03	2.21	1.98	1.91	1.46	1.28	1.95
I.E (η %)	____	45.16	50.87	52.61	63.77	68.24	76.43
θ	____	0.45	0.51	0.53	0.64	0.68	0.76

3.2 ADSORPTION ISOTHERM CONSIDERATIONS

In this study, several adsorption isotherms were used to describe the adsorption behavior of the inhibitor. The experimental data were fitted into the following isotherms: Langmuir, Temkin, Freundlich, El-Awady and Adejo Ekwenchi to ascertain the best fit for the process.

3.2.1 LANGMUIR ADSORPTION ISOTHERM

The Langmuir isotherm describes gas-solid phase adsorption, quantifies and contrasts the adsorptive capacity of various adsorbents [4]. Langmuir isotherm describes the relationship between the surface coverage and inhibition concentration of a material and it is expressed as:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$

Where C_{inh} is inhibitor concentration (g/l), θ is surface coverage and K_{ads} is the adsorption constant (l/g). The Langmuir adsorption constant was determined to be 6.228l/g obtained from the reciprocal of the intercept. The R^2 value from the Langmuir plot is 0.9544, which is close to unity, a monolayer coating is formed i.e. the adsorbent surface saturated with adsorbate; this implies that the experimental data fit well into the model.

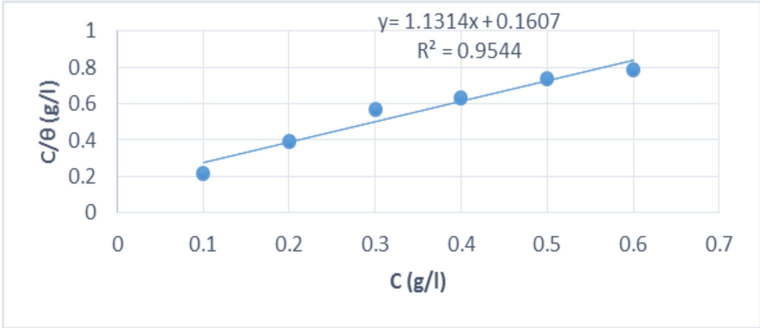

***Figure 1:** Langmuir isotherm plot of corrosion on austenitic stainless steel in the presence of allium cepa extract.*

3.2.2 TEMKIN ADSORPTION ISOTHERM

This model has been used to describe the nature of interactions taking place in the adsorbed layer. Temkin isotherm is expressed as:

$$\theta = \frac{1}{f * \ln(K_{ads}\,C)}$$

Where f determines the adsorbent-adsorbate interaction.

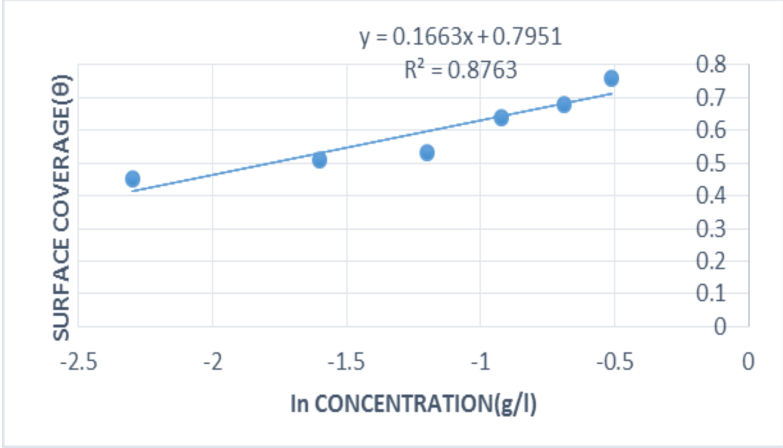

***Fig 2:** Temkin isotherm plot of corrosion on austenitic stainless steel in the presence of allium cepa extract.*

3.2.3 FREUNDLICH ADSORPTION ISOTHERM

The freundlich isotherm model relates the surface coverage to inhibitor concentration. The linearized form of the freundlich isotherm is expressed as:

$$\mathrm{Log}\theta = \mathrm{Log}K + \frac{1}{n}\mathrm{Log}C$$

The value of 1/n is used to describe the ease of adsorption. When 0<1/n <1, adsorption is believed to be easy, and moderate or difficult when 1/n =1 or 1/n >1 [3]. From the freundlich model plot, the freundlich isotherm constant which is also referred to as the adsorption constant gave a value of 0.6455l/g. The parameter $1/n$ from Table 3 is 0.2866, which depicts an easy adsorption process. Its correlation coefficient 'R^2' value of 0.9158 makes it favorable.

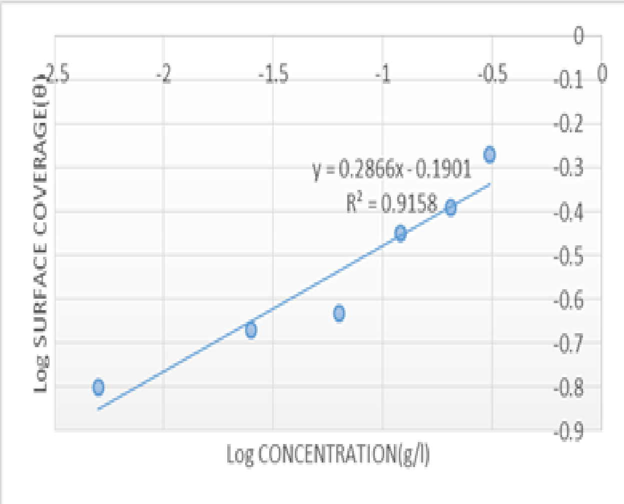

***Fig 3:** Freundlich isotherm plot of corrosion on austenitic stainless steel in the presence of allium cepa extract*.

3.2.4 El-Awady Adsorption Isotherm

The experimental data were fitted into the El-Awady's thermodynamic model. The characteristic of the model is expressed by the relation below:

$$\mathrm{Log}\left(\frac{\theta}{1-\theta}\right) = \mathrm{LogK} + \mathrm{yLogC} \qquad (7)$$

In this model, y represents the number of active sites. Values of 1/y less than one indicates multilayer adsorption while 1/y greater than one implies the given inhibitor occupies more than one active site [5]. The plot gave straight line with 'R^2' value of 0.8586 showing the data also fit into the isotherm. The values of 1/y and K are presented in Table 3. From Table 3 the value of 1/y is greater than one, proves that the onion extract occupies more than one active site.

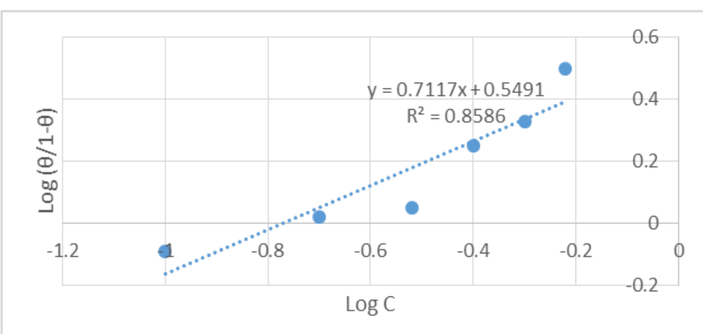

***Fig 4:** El-Awady isotherm plot of corrosion on austenitic stainless steel in the presence of allium cepa extract.*

3.2.5 ADEJO EKWENCHI ISOTHERM

The Adejo Ekwenchi isotherm establishes an inverse relationship between the amount of adsorbate uptake from the bulk concentration with the difference between the total available surface on the adsorbent surface and the fraction that is covered by the adsorbate at a given temperature, prior to the attainment of maximum value of surface cover [9]. It is given by the equation

$$\mathrm{Log}\left(\frac{1}{1-\theta}\right) = \mathrm{LogK_{AE}} + \mathrm{bLogC}$$

Where 'b' parameter is used to determine the mode of adsorption of an inhibitor on the metal surface and K_{AE} represents the Adejo Ekwenchi adsorption constant which is obtained from the isotherm plot.

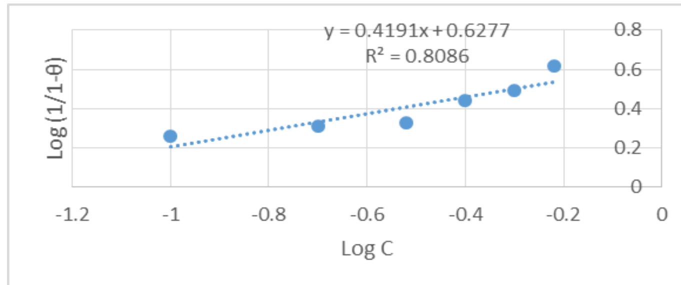

***Fig 5**: Adejo Ekwenchi isotherm plot of corrosion on austenitic stainless steel in the presence of allium cepa extract*.

To further describe the type of adsorption either physiosorption or chemisorption occurring on the metal surface, the Gibbs free energy of adsorption was considered. The values of the free energy of adsorption presented in Table 3 were calculated from the plot of the isotherms using Equation

$$\Delta G_{ads} = -\,RT\,In\,(55.5K) \qquad (9)$$

Where 'R' is the gas constant in $Jmol^{-1}k^{-1}$, 'T' is the absolute temperature in 'K' and '55.5' denote the value of the molar concentration of water in mol/L.

***Table 2:** Parameters for plotting Langmuir, Temkin, Freundlich, El-Awady and Adejo Ekwenchi isotherms of Allium cepa extract on austenitic stainless steel in sea water.*

Conc (g/l)	Θ	$\frac{C}{\theta}$	Log θ	Log C	Log $(\frac{\theta}{C})$	Log (1-θ)	Log $(\frac{\theta}{1-\theta})$	Log $(\frac{1}{1-\theta})$
0.1	0.45	0.22	-0.35	-1.00	0.65	-0.26	-0.09	0.26
0.2	0.51	0.39	-0.29	-0.70	0.41	-0.31	0.02	0.31
0.3	0.53	0.57	-0.28	-0.52	0.25	-0.33	0.05	0.33
0.4	0.64	0.63	-0.19	-0.40	0.20	-0.44	0.25	0.44
0.5	0.68	0.74	-0.17	-0.30	0.13	-0.49	0.33	0.49
0.6	0.76	0.79	-0.12	-0.22	0.10	-0.62	0.50	0.62

Table 3: Parameters of the various adsorption isotherms for adsorption of Allium cepa extract onto the austenitic stainless steel surface. The ΔG_{ads}, all were negative which indicates the adsorption of Allium cepa extract to be spontaneous and occur as physiosorption. This is due to the fact that values of ΔG_{ads} up to -20KJ/mol signifies physiosorption while value more than -40KJ/mol signifies chemisorption [6].

CONCLUSION

Corrosion studies of austenistic stainless steel were carried out at room temperature. Five adsorption isotherms were investigated and compared. From the results obtained from the adsorption isotherm plots, the Langmuir isotherm amongst others gave the best fit having the highest regression value as well as having the highest energy of adsorption. Allium cepa extract has been identified as a suitable corrosion inhibitor for austenitic stainless steel in sea water. The mechanism of adsorption proposed for the extract is physiosorption and the negative values of ΔG_{ads} indicates the spontaneity of the process.

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