

INVESTIGATION OF CORROSION INHIBITION POTENTIAL OF *HYPHAENE THEBAICA* SHELLS EXTRACT ON TANNERY MACHINES PARTS IN ACIDIC MEDIUM

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ABSTRACT

Corrosion inhibition potential of ternary machine part was investigated by using ethanoic extract of *hyphaene thebaica* shells as inhibitor at different temperature of 313K and 333K. The Tannery machines part which are majorly made up of mild steels are subjected to harsh conditions, which include exposure to moisture, air, acid, base, salt and other environmental components that causes corrosion on machines' parts. The aim of this research was to generate measurable and testable data towards the control of corrosion using plant (*hyphaene thebaica* shells ethanolic extracts) as inhibitor. This was accomplished through the determination of inhibitor's performance by weight loss techniques, determination of metal-inhibitor interaction mechanism using kinetic parameters and adsorption isotherms (Langmuir and Temkin), the corrosion process through the use of exposure time, phytochemicals of the shell extracts, inhibitor concentration, media concentration, temperature, initial weight of metal and the weight of the metals in every 2 hours for a total of 6 hours. A weight loss technique was adopted and the weights of the mild steel were recorded every 2 hrs for 6 hrs. The highest inhibition efficiency (78.44%) was attained at 333 K for 0.1 g/dm³ concentration of the plant inhibitor. Inhibition efficiency decreased with further increase in the temperature. The green inhibitor was found to be effective because it is ecofriendly, inexpensive and biodegradable.

Keywords; Corrosion inhibitor, Mild steel, Tannery machines, Langmuir, Temkin

INTRODUCTION

Corrosion is a natural phenomenon, which can be chemical or electrochemical in nature that causes metals, ceramics and alloys to undergo degradation, and then make them useless for their expected utility [1-2]. Corrosion inhibitors are chemical compounds used in small concentrations in industry to reduce the corrosion rate of metals and alloys in contact with aggressive environment, and therefore, retard the corrosion process and

keeps its rate to a minimum and thus prevents economic losses due to metallic corrosion [3].

Inorganic chemicals are widely used as inhibitors to protect metals against corrosion, but, most of them are not environmental friendly due to their toxicity levels, bioaccumulation and non biodegradability [4], hence, the research of new corrosion inhibitors which are non-toxic, eco-friendly and natural are desired [5].

Plant extract is a rich source of phytochemical compounds which are readily available at low-cost, eco-friendly, and can be obtained through simple extraction process and biodegradable [6]. Most plant extract are less toxic and are complex natural polymers consisting of surface-active units such as amino ($-NH_2$), hydroxyl ($-OH$) and carboxyl ($-COOH$), indicating that they are electrochemically active and can therefore interact with metallic surfaces through these units and inhibit corrosion [7]. *Sida acuta* leaves extracts has been used to inhibit corrosion of tannery machines parts in acidic environment and was found to be very efficient [3]. Seeds extracts of *Cola nitida* was used as a green inhibitor in the corrosion of mild steel in acidic environment using gravimetric and electrochemical (potentiodynamic polarization) methods. The inhibition efficiency increased with increase in the extracts concentration but decreased with increase in temperature [8]. The effect of *Citrus sinensis* seed extract on the corrosion of aluminium in 2 M HCl solution was studied using weight loss, thermometric and hydrogen evolution methods [9]. *C. sinensis* seed extract appreciably inhibited the corrosion of aluminium in HCl solution. The inhibition efficiency increases with increase in extract concentration and temperature. The experimental data conformed to the Langmuir adsorption isotherm. The spontaneity of the adsorption process was revealed by the

negative values of standard free energy obtained. Chemisorption process has been proposed for the adsorption of *C. sinensis* seed extract onto aluminium surface.

Other plant extract used as inhibitors include: *Abelmoschus esculentus* seed extract – chloride ions [10] *Microdesmis puberula* root extract [11] *Piliostigma thoningii* extract [12] and *Chromolaena odorata* leaf extract [13]. Literatures reveal that addition of halide ions to some plant extracts has the potential to increase (synergistic effect) their corrosion inhibitive properties. Synergistic effect of plant extracts – halide mixtures mild steel in acidic medium are: *Sida acuta* leaves extract – iodide ions [14] *Chicoriumintybus* extract – iodide ions [15] coconut coir dust extract – iodide ions [16] (and rice husk extract – iodide ions [17]. Because of their prospect in acting as green corrosion inhibitor, some natural gums of plant origin have also been studied and utilized as inhibitors for several corrosive systems. For instance [18] investigated the anti-corrosive effect of *Pachylobus edulis* exudate gum in combination with halides ions (Cl^- , Br^- and I^-) for aluminium corrosion in HCl at temperature range of 30 °C to 60 °C, using weight loss method. Results obtained showed that the naturally occurring exudate gum acted as an inhibitor for aluminium corrosion in acidic environment. Inhibition efficiency (%IE) was found to increases with increase in concentration of the exudate gum and

synergistically increased to a considerable extent on the addition of the halide ions.

In spite of the broad spectrum of information available for some plant extract and their corrosion inhibition potentials, a survey of literature reveals that *hyphaene thebaica* shells has not been used as a corrosion inhibitor for mild steel in solutions of HCl. Therefore, the present study is aimed at investigating the chemical constituents of *hyphaene thebaica* shells and its corrosion inhibition potential for mild steel in solutions of HCl.

MATERIALS AND METHODS

Materials

Ethanol, acetone, hydrochloric acid, distilled water, Digital Analytical balance, Volumetric flasks (1000 cm³), Water bath, Thermometer, Oven, Measuring cylinder (100 cm³) Different sets of beakers (Pyrex), Press knife, Desiccator, mild steel (2 × 4 cm² coupons) and *hyphaene thebaica* plant.

Materials preparation

The machine was used to press and cut mild steel sheets into 2.0 cm x 4.0 cm area coupons and was polished with emery papers. The mild steel was decreased in detergent, dried in acetone and stored in moisture free desiccators before corrosion studies started.

Extraction of plants extracts

The shells of *Hyphaene thebaica* was cut separately into pieces, oven dried at 105 °C for two hours, cooled and trimmed uniformly. The

shell was pulverized and soaked in 98% ethanol for five days in order to extract the juice by leaching. The extract was filtered at the end of the extraction period and the solution was distilled at 78 °C to remove the ethanol from the juice extracts and concentrate the inhibiting chemical(s). The juice extracts was kept in a clean bottle and preserved properly.

Phytochemicals screening

2.2.5 Test for alkaloids, tannins, anthraquinones, flavonoids, saponins, phenols, glucosides and steroids

Tests for the above named phytochemicals were carried out following the methods reported by [3].

Preparation of inhibitor concentrations

A 1 g/L of the plant inhibitor (*Hyphaene thebaica shell*) was prepared and used as stock solution to attain 0.1 g/L, 0.3 g/L and 0.5 g/L through serial dilution, using 0.2 M HCl as blank to make it up to mark.

Weight loss experiment

The mild steel coupon which have been pre-weighed were fully immersed in each of the test media contained in a 250 cm³ beaker for 24 hours. Experiments were performed with hydrochloric acid test medium in which some had the solution extracts added. The specimens were taken out of the test media every 2 hours, washed with distilled water, rinsed with ethanol, dried in acetone, and re-weighed. Graphs of weight loss versus the exposure time and of calculated corrosion rate versus time of exposure were made. All the experiments were performed at 313 K and 333 K temperature(s) [19].

Determination of corrosion rate

Equation 1 below was used for the calculation of corrosion rate (CR) expressed in millimeter per year

$$\text{Corrosion rate (mpy)} C_R = \frac{87.63 W \times 1000}{DAT} \quad (1)$$

Where:

W = Weight loss = Initial weight, (W_1) – Final weight (W_2) in milligrams.

A = Total surface area of specimen in cm^2 , T = Total time sample was immersed in hours,

D = Density of the specimen in g/cm^3 , CR = Corrosion rate in millimeters per year.

Surface coverage

The degree of surface coverage (Θ) was calculated using equation

$$\Theta = \frac{CR_0 - CR_1}{CR_0} \quad (2)$$

2.2.10 Determination of percentage inhibition efficiency (%IE)

The percentage inhibitor efficiency was calculated from equation 3:

$$IE (\%) = \frac{CR_0 - CR_1}{CR_0} \times 100 \quad (3)$$

where CR_0 = corrosion rates in the absence predetermined concentration of inhibitor,

CR_1 = corrosion rates in the presence of predetermined concentration of inhibitor,

The percentage inhibitor efficiency was calculated for all the inhibitors throughout the exposure period. The area and density of the specimen used are 8 cm^2 and 7.86 g/cm^3

Adsorption isotherms

The relationship between surface coverage and concentration was studied using the following isotherms.

Langmuir isotherm:

$$\log (\theta/1) \text{ vs } \log C \quad (4)$$

$$\text{Temkim: } \log \theta \text{ vs } \log C \quad (5)$$

The correlation co-efficient (R^2) values were used to determine and to select the best fit isotherm.

RESULTS AND DISCUSSION

Phytochemical screening of plant material

The result obtained from this investigation revealed that the plant (*Hyphaene thebaica*) extract is rich in the following phytochemicals; Tannins, flavonoids, saponins and phenols. These phytochemicals are known to contain functional groups which carry heteroatoms such as nitrogen and oxygen, OH groups and aromatic rings. These functional groups enhance the process of corrosion inhibitor adsorption on the mild steel. This corroborates the findings of [3,20]. These active constituents had been reported to promote the corrosion inhibition of mild steel in aggressive acid media and they are responsible for the inhibition efficiency of the extract, especially that of alkaloid, due to the presence of heterocyclic atoms of nitrogen.

Weight loss studies

From the mass values, the corrosion rate, surface coverage (θ) and inhibition efficiency (IE %), were calculated using equations 1, 2 and 3. The results obtained from mass loss measurements are presented in Figure 2 and 3

which shows the variation of the mass of the mild steel coupons with time in 0.2 M hydrochloric acid for an immersion period of 2

to 6 h and Table 4 shows the inhibition efficiency (IE %), surface coverage (θ) and corrosion rate.

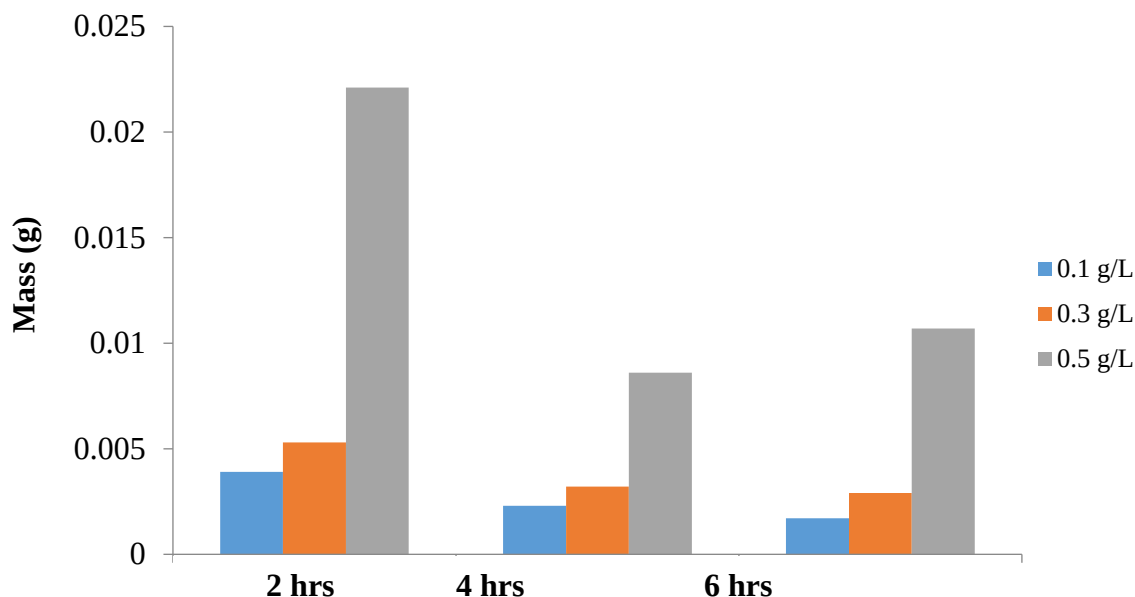


Fig. 1: Variation of weight loss with time (hrs) for mild steel in 0.2M HCl for plant inhibitor at 313K

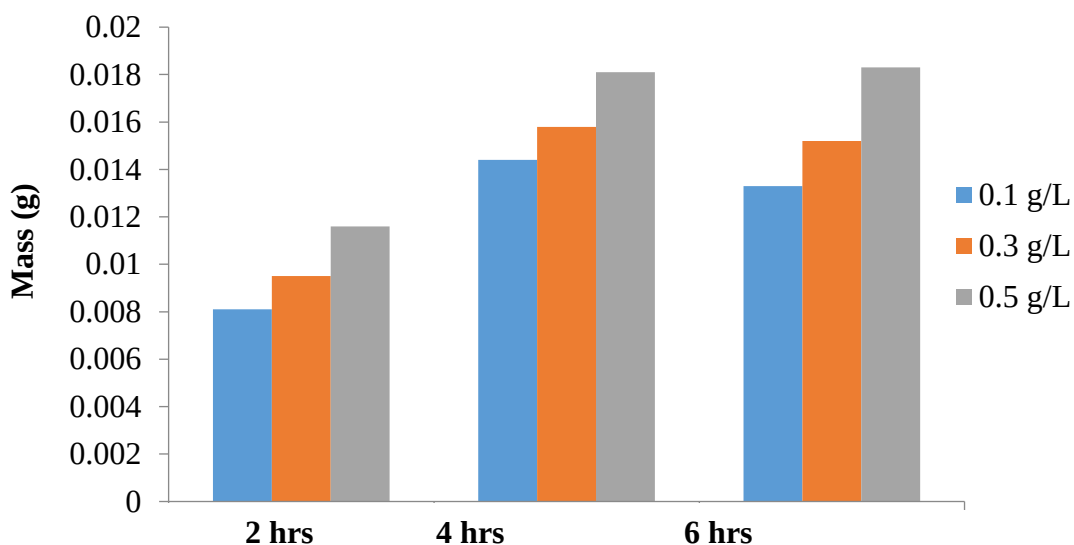


Fig. 2: Variation of weight loss with time (hrs) for mild steel in 0.2M HCl for plant inhibitor at 333K

Effect of temperature and inhibitors concentration on corrosion behaviour of mild steel in 0.2 M HCl acid with inhibitor

The effect of temperature on corrosion inhibition of mild steel in 0.2 M hydrochloric acid with 0.1 g/dm³, 0.3 g/dm³ and 0.5 g/dm³ of plant inhibitor between the temperature of 313 K and 333 K was

studied. The data were calculated and shown in the table 4, 5 and 6. There was much mass loss at higher temperature (333 K). From table 5, it was observed that the rates of corrosion of mild steel in 0.2 M hydrochloric acid containing the plant inhibitor, decreased compared to the blank.

Table 4: Calculated values of corrosion rate, Inhibition Efficiency and surface coverage of plant inhibitor

Temp. K	Conc (g/dm ³)	CR (mpy)	IE %	Log I%	Surface coverage
313	Blank	41.4135			
	0.1	26.83984	35.19062	1.546427	0.351906158
	0.3	10.44446	74.78006	1.873786	0.747800587
	0.5	10.29485	75.6217	1.836461	0.686217009
333	Blank	65.33861			
	0.1	14.08788	78.43866	1.89453	0.784386617
	0.3	21.98195	66.35688	1.821886	0.663568773
	0.5	22.22484	65.98513	1.819446	0.659851301

Table 5: The values of the rate constant (K) and half-life for mild steel in 0.2 M HCl in different concentration of the plant inhibitor at different temperature

Concentration (g/dm ³)	Rate constant (K)		Half. life (hrs)	
	313	333	313	333
0.1	0.1883	0.0346	3.6803	2.0029
0.3	0.1432	0.0248	4.8394	27.9435
0.5	0.1997	0.039	3.4702	17.7692s

The corrosion rate (CR) was also found to significantly decrease with increasing inhibitor's concentration from 0.1 g/dm³ to 0.5 g/dm³ at 313K but slightly decreased at higher temperature of 333K (Table 5). The percentage inhibition efficiency (IE%) of the inhibitor was found to increase with increase in inhibitor's concentration at 313K but decreased at higher temperature.

This signifies that the dissolution of the metals increased at higher temperatures and the observation is attributed to the general rule guiding the rate of chemical reaction, which says that chemical reactions increase with increasing temperatures. Also, an increased temperature favours the formation of activated molecules, whose formation rate doubles with 10 °C rise in temperature, thereby increasing the reaction rate. This is because the reactant molecules gain more energy and are able to overcome the energy barrier more rapidly [21]. An increase in temperature may also increase the solubility of the protective films on the metals, thus increasing the susceptibility of the metal to corrosion [22].

For solids, solubility generally increases with increasing temperature. This explains why the protective film which is solid becomes more soluble as the temperature is increased. The highest inhibition efficiency (78.44%) was attained at 323 K for 0.1 g/dm³ concentration of the plant inhibitor. Inhibition efficiency decreased with further increase in the temperature.

The least inhibition efficiency (35.19 %) was attained at 313 K for 0.1 g/dm³ green inhibitor. This is may be due to the desorption at metal surface [23].

Adsorption mechanism and isotherm for the plant inhibitor

The inhibition of metal corrosion by organic compounds is attributed to either the adsorption of inhibitor molecule or the formation of a layer of insoluble complex of the metal on the surface which acts as a barrier between the metal surface and the corrosive medium [24].

Since no insoluble material was observed on the metal surface, the inhibitive action of the extract may be due to its adsorption on the metal surface. Investigations of the shell of *Hyphaene thebaica* revealed the presence of the essential chemical compounds: saponins, flavonoids, alkaloids, glycosides. This makes it difficult to assign the observed inhibiting effect to a particular constituent. The net adsorption of these organic matters on the corroding mild steel surface creates a barrier that isolates the metal from the corrodent.

The relationship between inhibition efficiency and the bulk concentration of the inhibitor at constant temperature, which is known as isotherm [25-26], gives an insight into the adsorption process. Two adsorption isotherms were attempted to fit surface coverage values to classical isotherms of Langmuir and Temkin. The value of the correlation (R^2) was used to determine the best fit isotherm which was obtained for Langmuir and Freundlich isotherms.

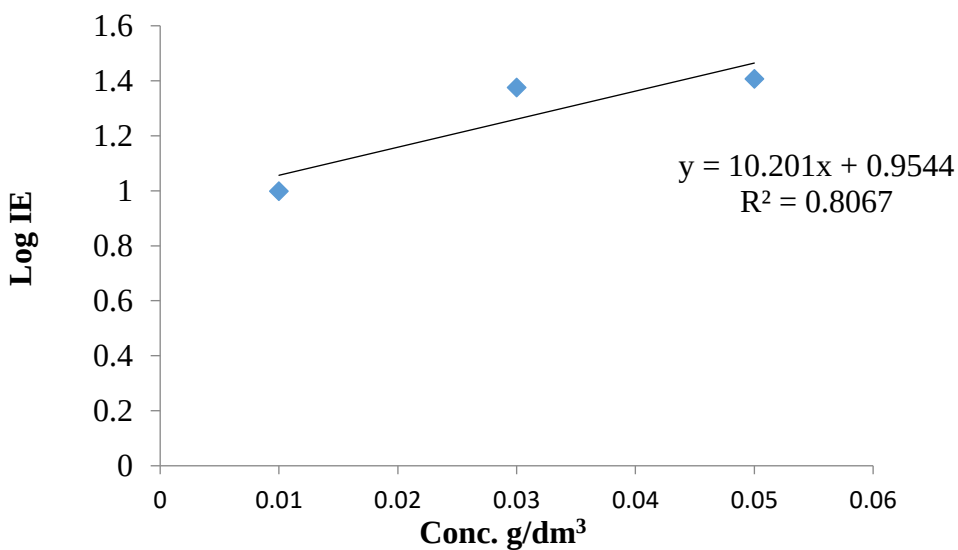


Fig. 3: Langmuir adsorption isotherm plotted as Log IE against Concentration for plant Inhibitor at 313 K

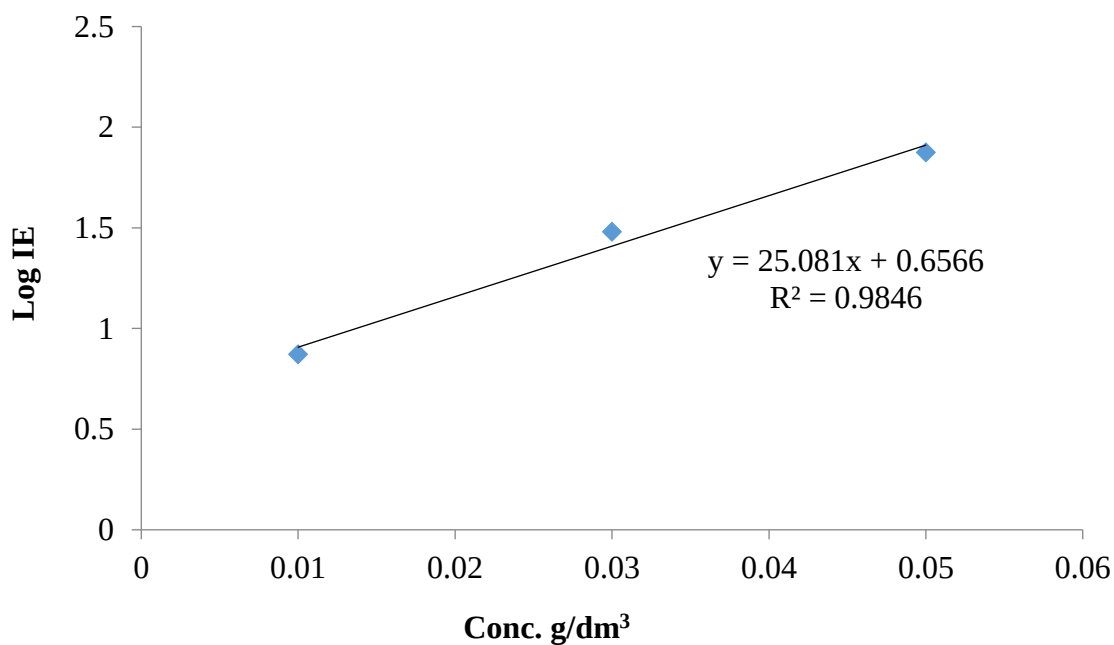


Fig. 4: Langmuir adsorption isotherm plotted as Log IE against Concentration for plant Inhibitor at 323 K

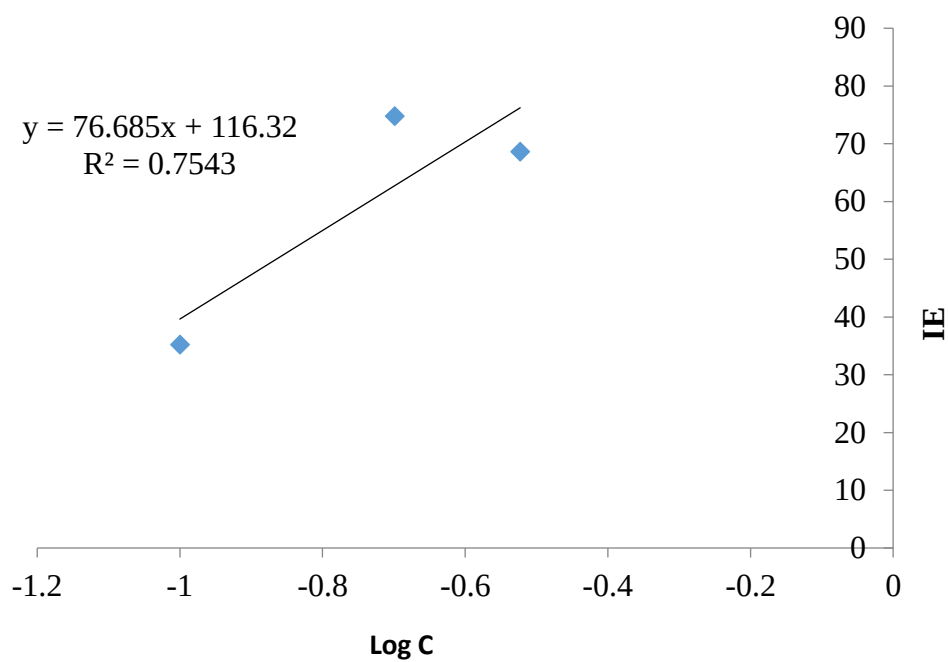


Fig. 5: Temkim adsorption isotherm plotted as IE against Log Concentration (C) for Plant Inhibitor at 313 K

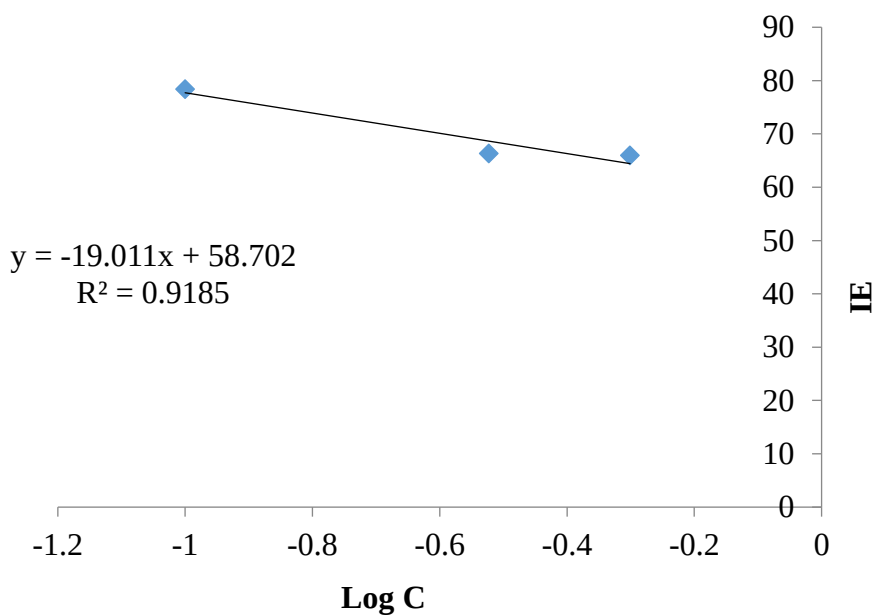


Fig. 6: Temkim adsorption isotherm plotted as IE against Log Concentration (C) for Plant Inhibitor at 323 K

The R^2 value for the Langmuir and Temkin adsorption isotherm at 313K is 0.8067 and 0.7543 respectively (Figure 3 and 5) while the value at 333k is 0.9846 and 0.9185 respectively (Figure 4 and 6). The result obtained from the adsorption isotherm showed that Langmuir isotherm described the adsorption process of the green inhibitor unto the surface of the coupon better than temkin isotherm at both temperature.

CONCLUSION

Ethanollic extracts of *hyphaene thebaica* shells has proven to be an effective green inhibitor for corrosion of mild steel in 0.2 M hydrochloric acid because it is ecofriendly, inexpensive, and biodegradable. The inhibition efficiency increased with increase in extract concentration but

decreased with increase in temperature. The inhibitive action was realized through adsorption of extract phytochemical compounds onto mild steel surface as demonstrated by fitting to Langmuir adsorption isotherm. The presence of the extract increases the activation energy of the corrosion reaction.

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