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Assessment of the Inhibitive Action of Velvet Tamarind on Low Carbon Steel Corrosion in Acetic Acid

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Abstract:
Different concentrations (0.05 - 0.25 g/500ml) of African Black velvet tamarind (VT) has been tested as a non-toxic corrosion inhibitor of low carbon steel in acetic acid medium at different temperatures (30, 40 and 50^{o}C). The technique employed was weight loss methods of corrosion test. The corrosion inhibition efficiency (%) was found to be directly proportional to the inhibitor concentration but inversely proportional to the temperatures studied. 99.46% was obtained as the highest inhibition efficiency with 0.25g/500ml of VT at 30^{o}C. This ability of VT to be an excellent inhibitor of mild steel corrosion in the medium studied is as a result of the high content of some electron rich organic compounds (Vitamin C, histidine and the amino acid) in it. The inhibition is due to the adsorption of VT on the low carbon steel surface which obeyed the Langmuir adsorption isotherm. Therefore, African Black velvet tamarind can be recommended as a cheap, readily available and environmentally friendly inhibitor for low carbon steel corrosion in acetic acid.

Keywords: *Metals, Corrosion, Organic compounds, Adsorption.*

1. Introduction

Low carbon steel has a very wide application in constructions, chemical and allied industries. It is used to handle acid, alkali and salt solutions during industrial acid pickling, cleaning, descaling and oil well acidizing. Therefore, steel must be protected so as to increase their life span during usage [1]. No matter how useful a metal is, corrosion is its Achilles's heel.

The development of a country can be greatly affected by metal corrosion just as natural disasters such as earthquakes, flood, etc. do on the economy [2]. The estimated cost of corrosion in the United States of America was $276 billion annually. This is much higher than the normal losses as a result of natural disasters ($17 billion per annum) [3]. The study further revealed that economic losses due to corrosion of metals were greater than 4% of the Gross National Profit [4]. This means that approximately 25-30% of the yearly expenses on corrosion can be economized if corrosion of metals is properly controlled [2].

Corrosion does not only affect the economy of a country; it also impairs human health (when used as metallic implant in the body). It affects safety (when it causes failures of automobiles, aircrafts, ships, etc.) andit slows down the development of new technologies in construction and engineering [4].

In acid environment, the commonly used method for preventing corrosion of metal is by using inhibitors [5]. Corrosion inhibitors have been applied in refinery, petroleum, chemical and petrochemical industries [6].As a result of the toxic nature of organic inhibitors, frantic efforts have been directed towards the use of plant extracts as inhibitors of metal corrosion. This is because plant extracts are biodegradable, cheap and safe to the environment. They have many organic compounds that are electron rich which enables them prevent corrosion by being adsorbed on the metal surface [7].

Black Velvet Tamarind is a fruit with the botanical name *dialium guianeense*. It is popularly called **Icheku** in Igbo**, Awin** in Yoruba and **Tsamiyar Kurm** in Hausa. The fruits are dietary supplement for rural dwellers in Nigeria during the dry season when fruits are scarce [8]. They are usually circular and flattened, black in colour with stalk 6mm long, a little collar is seen near the apex and a bristle shell encloses one or two seeds embedded in a dry, brownish edible pulp asshown in fig. 1.

Figure 1: Velvet Tamarind Fruit

The fruits are also used in medicinal remedies, as source of vitamin C, as flavour in snacks and non-alcoholic beverages [9-11]. In our previous report, VT has been established to be a green inhibitor of low carbon steel corrosion in HCl and copper in sulphuric acid[12-13] using weight loss method. A thorough review of the literature revealed that VT has not yet been tested on low carbon steel corrosion in acetic or any organic acid.

The paper reports the inhibitory action of VT on low carbon steel corrosion in 0.5M acetic acid using gravimetric method.

2. Experimental

2.1. Preparation of Metal and Test Solutions

Themetal coupons used in this study was obtained from a 0.3cm thick flat sheets of low carbon steel which is chemically composed of carbon, manganese, sulphur, phosphorus, silicon and iron in the following percentages respectively, 0.12%, 0.90%, 0.066%, 0.050%, 0.10% and 98.764%.The coupons were cut into 4.0cm x 4.0cm dimension. They were prepared as reported earlier [12].

Acetic acid was of analytical grade and 0.5M solution of the acid was employed as the corrosive medium for this study. Different concentrations of VT (0.05 - 0.25g/500ml) were prepared with the 0.5M acetic acid as solutions for the tests.

2.2. Weight Loss Measurements

In our earlier report [12, 13], weight loss measurements details were given.

Previously weighed mild steel coupon were dropped into 250mlconical flasks which contained 100ml of 0.5M acetic acid (blank) and then the different concentrations of VT (0.05 - 0.25g/500ml) prepared with the 0.5M acetic acid solution. These text solutions were maintained at 30^{o}C, 40^{o}C and 50^{o}C in a water bath with thermometer to regulate the temperatures studied. The low carbon steel coupons were retrieved from the test solutions every24hours for 168hours. The coupons were washed inmild solution of sodium hydroxide, cleansed in distilled water, oven-dried and weighed. The difference between the initial and the final weight was calculated and recorded as the weight loss. The experiments were repeated and the average values of the weight loss were determined and used to evaluate the rate of corrosion (millimeter/year), inhibition efficiency (% E) and surface coverage (Ɵ) from the respective equations (1), (2) and (3) below:

Rate of corrosion (millimeter/year) = $\frac{87.6W_l}{\rho At}$ ………… (1)

$$\%\,E = \frac{\Delta Wlf - \Delta W_l I`}{\Delta Wlf} \quad x\ 100 \quad \text{……… (2)}$$

$\Theta = \frac{\%E}{100}$ …………….. (3)

The terms W_1 represents the weight loss of the low carbon steel coupon (mg);ρ, density of low carbon steel (gcm^{-3}); A, area of coupon (cm^2); t, the immersion time (hr.);while ΔWlf and $\Delta W_l I`$ stands for the weight loss of the coupons in the absence and presence of VT (the inhibitor) respectively.

3. Results and Discussion

3.1. The Influence of Time and VT Concentration on Low Carbon Steel Corrosion

The variation of weight loss with time for low carbon steel corrosion in acetic acid solution (0.5M) in different concentrations of VT at 30^{o}C is displayed in figure 2. Generally, the weight loss of the metal coupon increases with time. The figure also revealed a conspicuous decrease in the weight loss of the metal with the addition of VT (inhibitor). However, as the concentration of the additive

(VT) increases, the weight loss of the metal coupon continues to decrease. Hence 0.25g/500ml VT gave the least weight loss while 0.05g/500ml VT gave the highest. Similar plots were obtained at 40°C and 50°C.

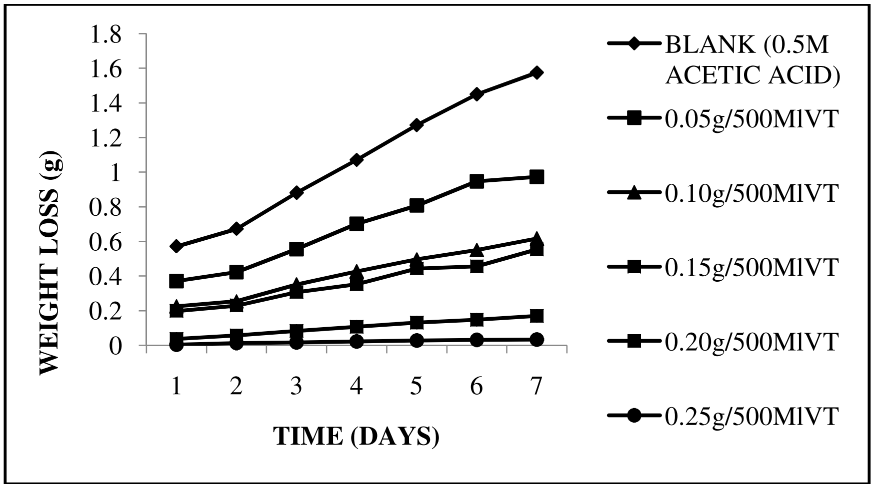

Figure 2: Weight loss of the low carbon steel coupons (g) versus time of immersion (days) at 30◦C.

3.2. Temperature Influence on the Efficiency of VT.

The effect of temperature increase on the corrosion of low carbon steel in 0.5M acetic acid was studied at 30- 50 °C with and without VT. The temperature influence on the efficiency of VT as inhibitor of the metal corrosion is shown in Fig. 3 below.

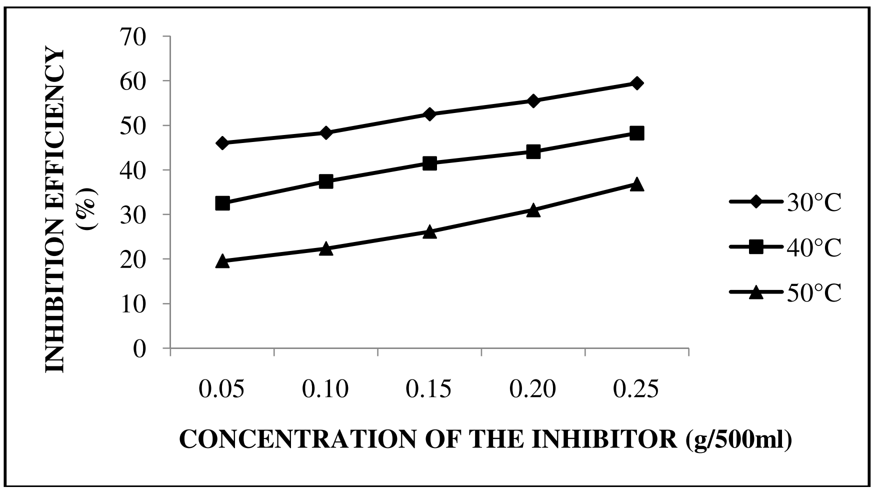

Figure 3: The inhibition efficiency of VT versus concentration of the inhibitor at30o - 50oC.

The efficiency of VT decreases as the temperature is raised from 30° - 50°C. It is therefore evident that a rise in temperature does not favour the efficiency of VT as corrosion inhibitor of low carbon steel in 0.5M acetic acid solution.

Furthermore, table 1 portrays a decrease in the corrosion rate of the metal which signified increased inhibition efficiencies and surface coverage of VT as its concentration increases in the acid solution. Thus, VT is an excellent corrosion inhibitor of low carbon steel in acetic acid with 99.46% inhibition at 0.25g/500ml inhibitor-acetic acid solution.

This outstanding inhibition property of VT might be as a result of its adsorption on the surface of the metal, thus blocking the active sites responsible for the metal corrosion.

Concentration of VT (g/500ml)	**Rate of corrosion (millimeter/year)**	**Percentage VT efficiency (E %)**	**Surface coverage of VT (θ)**
0.0	97.76	-	-
0.05	61.00	38.27	0.38
0.10	39.22	62.00	0.62
0.15	35.51	72.00	0.72
0.20	11.08	93.56	0.94
0.25	2.15	99.46	0.99

Table 1: The rate of corrosion, percentage VT efficiency and surface coverage of VT on low carbon steel in acetic acid solution at 30°C for 168 hours' immersion period.

3.3. The Chemical Constituents in VT as active Ingredients for Its Corrosion Inhibitory Property

The inhibitory effect of the VT is due to the electron rich active components (Fig. 4) present in it as its chemical constituents. The VT actually contains several heavy organic molecules with electronegative atoms enriched with electrons embedded in their structures which can serve as adsorption sites to the metal surface.

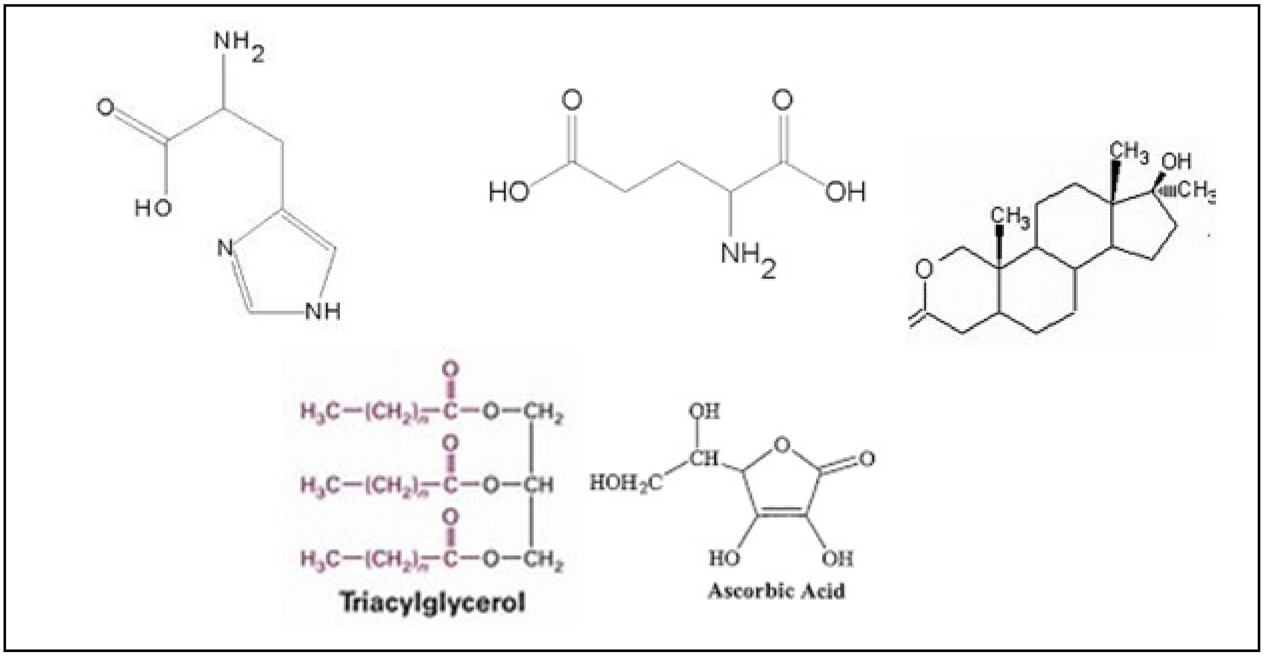

Figure 4: Chemical structures of the compounds in African black velvet tamarind.

These include glutamic acid (amino acid), histidine (crude protein), triacylglycerol, a high content of vitamin C (ascorbic acid), sterols among others [14-15]. However, the inhibition efficiency of VT may have been enhanced by the synergistic effects of the several compounds it contains. These chemical constituents in VT can further be characterized with some analytical methods (SEM, EDX and XRD) to determine the active sites responsible for the inhibition.

Chemical compounds having –OR, -COOH and NR2 have inhibited metal corrosion in acid solutions in the past [16-17] by getting adsorbed on to the metal surface, preventing the metal ions from ionizing and thus retarding its corrosion in the acid solutions. The reduction in the weight loss of the low carbon steel shown in fig.2 as the VT concentration increases and the decrease in corrosion rate coupled with an increase in surface coverage (Table1) is a proof of the adsorption of VT on the metal to effect inhibition. The literature reports similar observation [18].

3.4. Adsorption Consideration

The adsorption mechanism was considered by plotting the different equations of adsorption isotherms graphs using the surface coverage values. Plotting C/θ versus C (as shown in Fig.7) gave a straight line, signifying a linear correlation whose coefficient is greater than 0.9625.

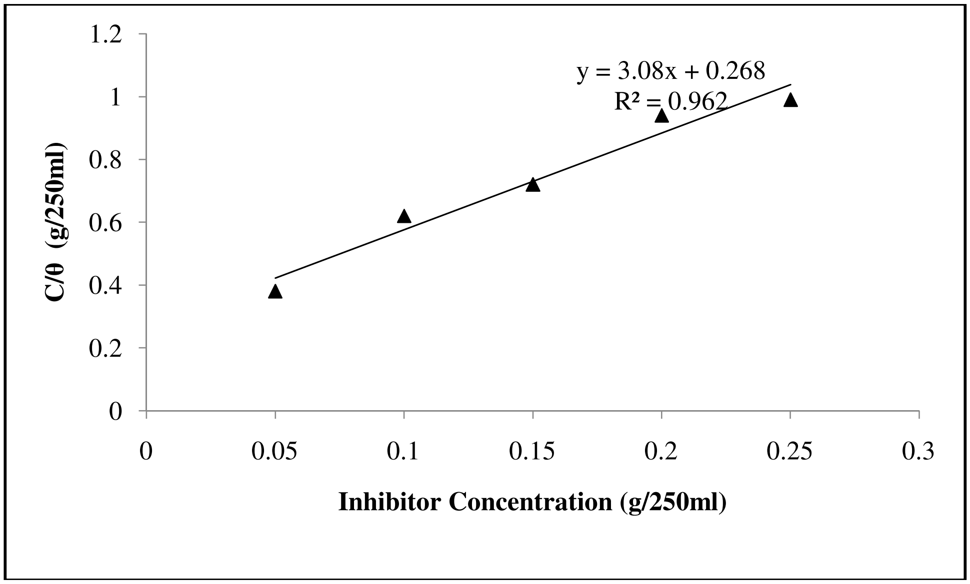

Figure 5: Langmuir adsorption model of VT on the surface of low carbon steel in 0.5M acetic acid solution at 30^{o}C for 168 hours' immersion period.

This is a good data that confirms that VT inhibited the corrosion of the metal by being adsorbed onto the surface of the metal. The linear relationship of the parameters plotted also showed that the adsorption can be fitted into the Langmuir isotherm whose equation is given as (4):

$\frac{C}{\theta} = C + \frac{1}{K}$ ………….. (4)

C=VT concentration and K, the equilibrium constant of the corrosion inhibition process.

The Gibb's free energy of adsorption (ΔG_{ads}), calculated from equation (5) [19]:

$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G^0_{ads}}{RT}\right)$ …………………. (5)

was found to be -10.43 kJ / mol. The negative value of ΔG_{ads} *proves the spontaneity of the inhibition reaction and the stability of VTmolecules on the surface of the low carbon steel. This calculated* ΔG_{ads} *value also shows that VT inhibited the corrosion of the metal* in 0.5M acetic acid *solution through the mechanism of physical adsorption.*

4. Conclusion

The African Black velvet tamarind is an excellent eco-friendly inhibitor of low carbon steel corrosion in 0.5M acetic acid solution. It gave an inhibition efficiency as high as 99% at 0.25g/250ml concentration. The inhibition is as a result of the adsorption of VT on the metal surface which obeyed the adsorption isotherm of Langmuir. A negative ΔG_{ads} *value was obtained indicating that adsorption process was spontaneous and feasible.*

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