INHIBITIVE ACTION OF ETHYL ACETATE EXTRACT OF *Corynocarpus laevigatus* ON THE CORROSION OF MILD STEEL IN 2 M HCl SOLUTION

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ABSTRACT

The inhibitive action of leaves extract of *Corynocarpus laevigatus* on mild steel in 2.0 M HCl solutions was investigated using Gravimetric (weight loss) technique. The results obtained indicate that the extract of *Corynocarpus laevigatus* functioned as a good inhibitor in Hydrochloric acid solutions. The inhibition efficiency is found to increase with increase in the extract concentration and decrease with increase in temperature with the highest inhibition efficiency being 89.96%. The kinetic considerations confirmed the reaction process to be a first order reaction. The finding from this study is an indication that ethyl acetate extract of CL (*Corynocarpus laevigatus*) is a good and suitable corrosion inhibitor.

1. INTRODUCTION

Corrosion processes are responsible for numerous losses mainly in the industrial and engineering scope. It is clear that the best way to combat it is prevention rather than cure, cause the cost of prevention is lesser than the cost of curing corrosion. Among the various methods to avoid or prevent destruction or deterioration of metal surface, the corrosion inhibitor is one of the best-known methods of corrosion protection and one of the most useful on the industry (Patni *et al.*, 2013). This method is following stand up due to low cost and practice method. Important researches have been conducted with government investment mainly in large areas such as development construction of new pipelines for shale gas and growth in construction (Al-Otaibi *et al*., 2012). The focus of these researches has been the inhibitors applications in water and concrete for the protection of metals in order to reduce material loss (Al-Otaibi *et al*., 2012).

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1.1 Corrosion

Corrosion is the deterioration or degradation of metals and alloys by chemical or electrochemical means in an environment. In simple terminology, corrosion processes involve reaction of metals with environmental species. “Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, and polymer) with its environment which results in the dissolution into the material into components (Ahmad, 1996).

Often, but not necessarily, corrosion results in effects which hampers the usage of the material considered. Exclusively physical or mechanical processes such as melting and evaporation, abrasion or mechanical fracture are not included in the term corrosion” With the knowledge of the role of various microorganisms present in soil and water bodies, the definition for corrosion need be further elaborated to include microbially induced factors (Daobing *et al.*, 2011).

Corrosion can be classified in different ways such as:

- Chemical and electrochemical
- High temperature and low temperature
- Wet corrosion and dry corrosion.

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Dry corrosion occurs in the absence of aqueous environment, that is to say that it doesn’t occur in wet environments, usually in the presence of gases and vapours, mainly at high temperatures, while wet corrosion occurs in the presence of aqueous environment (Balamurugan *et al.*, 2008).

1.2 Inhibitors

Inhibitors are substances or mixtures that when added in low concentration and in aggressive environment inhibit, prevent or combat the rate of corrosion (Obike *et al.*, 2012).

The corrosion inhibitors can be chemicals either synthetic or natural and could be classified by:

- The chemical nature as either organic or inorganic
- The mechanism of action as either anodic, cathodic or an anodic-cathodic mix and by adsorption phenomenon
- As oxidants or anti-oxidants.

The natural and synthetic inhibitors have been deployed severally in the fight against corrosion, but most scientist have adopted the natural inhibitor such as green inhibitors (plant extracts) rather than its synthetic counterpart, this is due to the fact that natural inhibitors poses little or no threat to the environment unlike the synthetic inhibitors which are toxic to man and the environment (Obike *et al.*, 2016).

Karaka or New Zealand laurel (*Corynocarpus laevigatus*) is an evergreen tree of the family *Corynocarpaceae endemic* to New Zealand. The species are scattered all over the world of which two are indigenous to Africa. This plant was used as an inhibitor in the present study.

2. METHODS

2.1 Materials and Equipments

The materials for this study were: Ethyl acetate, H_2O (water), Methanol/ethanol, Hydrochloric acid, Acetone, Mild steel coupons, Ice block, Handkerchief, Foil, Thread, Emery sand paper (320 and 800 grit size), *Corynocarpus laevigatus*, Beakers (100, 150, 250 ml), Separation funnel, Retort stand, Soxhlet extractor, Measuring cylinder (100 ml, 1000 ml), pH meter, Water bath, Digital scale, Reagent bottle (1000 ml), Masking tape, Volumetric flask (1000 ml), Bristle brush

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2.2 Preparation of mild steel coupons

The mild steel coupons used in this work were obtained from Urata market, Aba in Abia State, Nigeria. They were mechanically cut into 5.0 x 1.5 x 0.07 cm^2. The surfaces of the mild steel coupons were polished with fine grade emery paper (Grit size 320 and 800). The polished coupons were then washed thoroughly with distilled water, degreased with methanol, dried with acetone. The dried coupons were weighed using a digital Atom 2.0 weighing balance. The weights were recorded as the initial weights. The weighed coupons were used for the gravimetric (Weight loss) analysis.

2.3 Sample Collection, Identification and Preparation

The leaves of *Corynocarpus laevigatus* were collected within the environment of Abia State University, Uturu. Nigeria. The leaves were identified by Dr. Paschal Etusim of the department of Plant Science and Biotechnology of Abia State University Uturu. The leaves of *Corynocarpus laevigatus* were air dried in the laboratory under room temperature away from direct sunlight. The leaves were pulverized using a mechanical grinder to fine powder, the pulverized leaves material was stored in an air tight container. Stock acid solution of 2.0 M of HCl was prepared using 35% Conc. HCl (analytical grade). The stock acid solution was used to prepare the corrosive media. The distilled ethyl acetate plant extract (1.0 g) was dissolved in 1000 mL of 2.0 M HCl and left to stand for 24 hours. The resultant solutions were filtered and stored in a 1.0 L volumetric flask each. Similarly, 2.0 g, 3.0 g, 4.0 g and 5.0 g of the leaf extracts were dissolved in 1000 mL of the 2.0 M HCl. These solutions were then used for the corrosion inhibition test.

2.4 Experimental

The weighed mild steel coupons were suspended in beakers containing 100 ml of the test solution at room temperature. The mild steel coupons were completely immersed in the test solutions and retrieved every 24 hours for 24-120 hours. The retrieved coupons were washed, scrubbed with bristle brush under fast flowing water, degreased in methanol, dried using acetone, re-weighed and re-immersed in the corrodent. The weight loss of the mild steel was evaluated in grams as the difference in the initial and final weight of the coupons and also the average of the weight loss was taken due to the triplicate immersion. The experiment was carried out for the *corynocarpus laevigatus* leaves extract using concentrations of 1.0 g/L, 2.0 g/L, 3.0 g/L, 4.0 g/L, and 5.0 g/L at ambient temperature. As the coupons corrode, there is a reduction in the weight of the coupon and this reduction is directly related to the corrosion rate.

From the weight loss data, the corrosion rates (CR) were calculated using equation 1 (Okafor *et al.*, 2007).

$$CR = \frac{Wl}{At} \qquad 1$$

Where Wl is weight loss in mg, A is the metal surface area and t, the time of immersion in hours. From corrosion rate, the surface coverage (ϴ) as a result of adsorption of inhibitor molecules and inhibition efficiencies of the plant extracts (I%) were determined using equation 2 and 3 (Obike *et al*., 2016).

$$\theta = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \qquad 2$$

$$I\% = \left[\frac{CR_{blank} - CR_{inh}}{CR_{blank}}\right] \times 100 \qquad 3$$

Where CR_{blank} and CR_{inh} are the corrosion rates in the absence and presence of the plant extracts respectively.

In the present study of mild steel in HCl solution, a plot of the logarithm of the initial weight of the mild steel coupon divided by the weight after post treatment against immersion time was used to know the order of reaction (Obike *et al*., 2016).

$$Log\left(\frac{wo}{wf}\right) = \text{kt} \qquad 4$$

Where W_o and W_f are weight in grams before and after post treatment of the mild steel coupons respectively, k is the rate constant obtained from the slope of the graph and t is the time in hours. From the rate constant values, the half-life values $t_{1/2}$ of the metal in the test solutions were calculated using the equation: (Obike *et al*., 2016).

$$T_{1/2} = \frac{0.693}{K} \qquad 5$$

3. RESULTS AND DISCUSSION

The result of gravimetric analysis (weight loss) is presented in table 1. The inhibition efficiency and weight loss of the study is presented in Table 1. The results from the weight loss shows that the there was a decrease in the dissolution of the coupon as there was an increase in the concentration of the inhibitor in the acid media and an increase in the dissolution of the metal as the immersion time increased. The inhibition efficiency followed the same trend as the weight loss, where the efficiency of the inhibitor was seen to increase with an increase in the ethyl acetate concentration of the plant extract in the corrosive media and decreased with increase in time of the immersion in the acid media. The results show that the extract of Cl was able to effectively restrict the acid from degrading the mild steel coupons in the corrosive media. This is an implication that there is an increasing surface coverage of the inhibitor molecules on the metal surface which may have occurred with an increasing inhibitor concentration. The observation made from this research was similarly observed by (Obike *et al.*, 2012; Samuel *et al.*, 2015) in an investigation as such. They observed that the corrosion inhibition efficiency was observed to increase with increase in the concentration of the extracts of the leaf and decreased with the increase in time

Table 1: Weight loss results and Percentage Inhibition efficiency for ethyl acetate of *Corynocarpus laevigatus*

	Weight loss (g)					Inhibition efficiency (%)				
	1hr	**2hrs**	**3hrs**	**4hrs**	**5hrs**	**1hr**	**2hrs**	**3hrs**	**4hrs**	**5hrs**
Blank	0.29	0.68	1.19	1.33	1.45					
1.0g/L	0.09	0.29	0.56	0.76	0.83	68.97	57.35	52.94	42.86	42.76
2.0g/L	0.05	0.21	0.43	0.54	0.7	82.76	69.12	63.87	59.4	51.72
3.0g/L	0.04	0.14	0.27	0.41	0.53	86.21	79.41	77.31	69.17	63.45
4.0g/L	0.04	0.1	0.21	0.37	0.45	86.21	85.29	82.35	72.18	68.97
5.0g/L	0.03	0.08	0.19	0.27	0.32	89.66	88.24	84.03	79.7	77.93

The plot of weight loss against concentration is shown in figure 1 and 2 respectively. From the plots, it was observed that the weight loss increased with increase in time of immersion and decreased concentration of the extract. The decrease in weight loss with increase in the extract concentration showed that the extract was able to restrain the corrosion of mild steel in the 2.0 M HCl acid solution.

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3.1 Mechanism of Reaction

The increase in weight loss with temperature and time is an indication that inhibition efficiency decreased with increasing temperature, it can be inferred from the trend that the mechanism is physical adsorption. This trend may be due to the fact that most effects at elevated temperatures are adverse to corrosion inhibition by increasing the corrosion rate (Ejikeme *et al.*, 2014; Nnanna *et al.*, 2010).

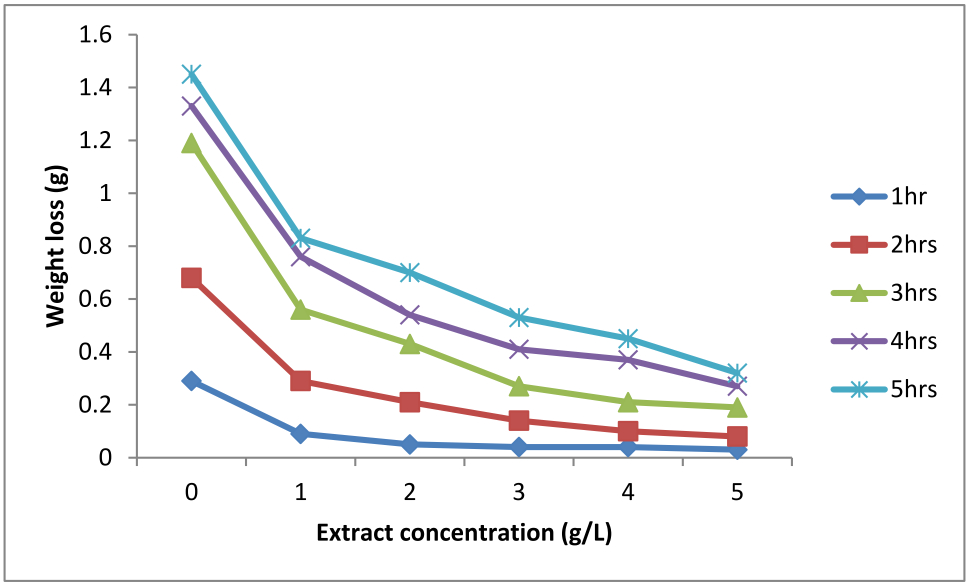

Figure 1. Plot of weight loss against extract concentration of Ethyl Acetate extract of CL in 2.0 M HCl.

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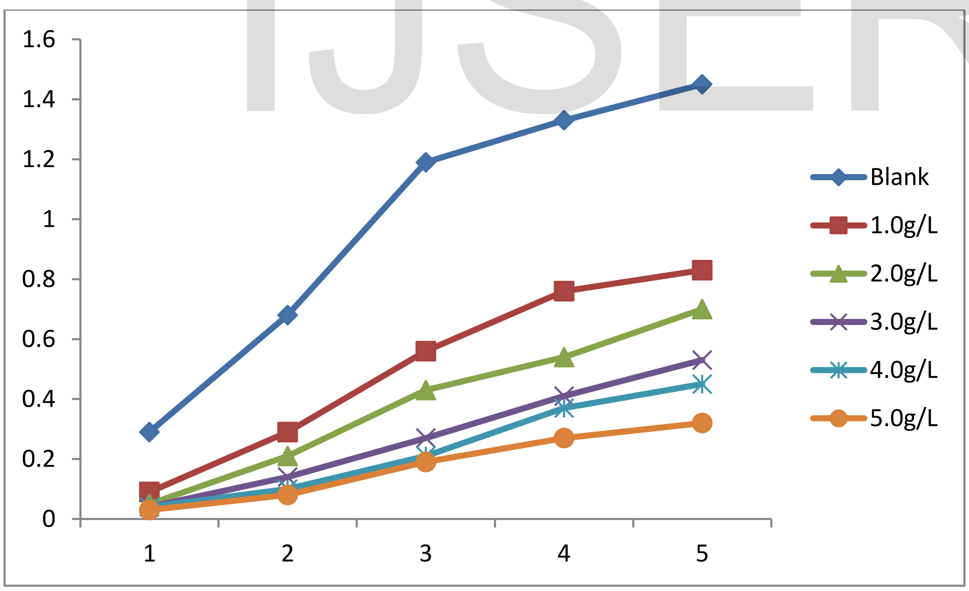

Fig. 2. plot of weight loss against time for Ethyl Acetate extract of CL in 2.0 M HCl

The results from table 1 aided to obtain information about the rate of corrosion of the coupons in the acid media. The values of the rate of corrosion was plotted against the concentration of the extract and time of immersion as represented in figure 3 and 4. From the plots the rate of corrosion was seen to increase with an increase in time of immersion and decreased with increase in the concentration of the ethyl acetate extract of Cl in the corrosive media as seen in figures 4 and 3 respectively. This collaborates with the result displayed in Table 1.

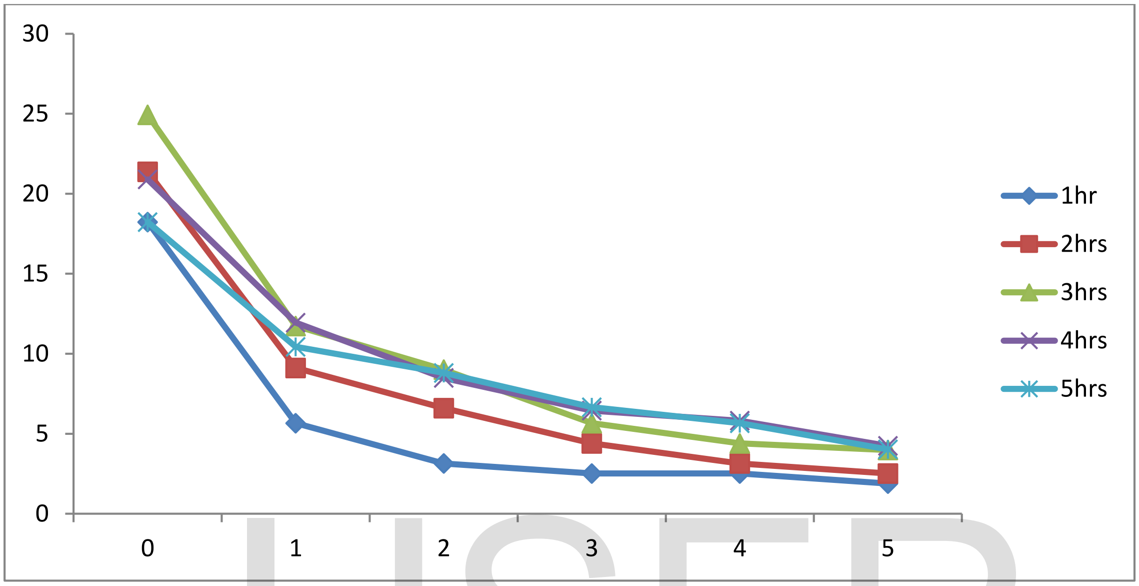

Fig 3. Plot of corrosion rate against Ethyl Acetate extract of CL in 2.0M HCl.

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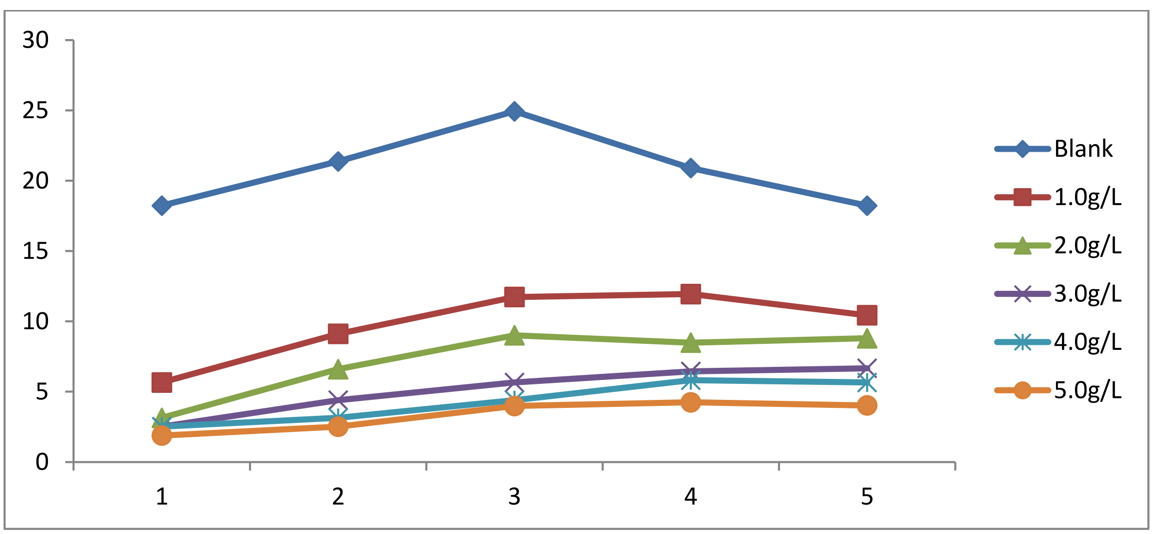

Fig 4. Plot of Corrosion rate against Time for Ethyl Acetate extract of CL in 2.0M HCl

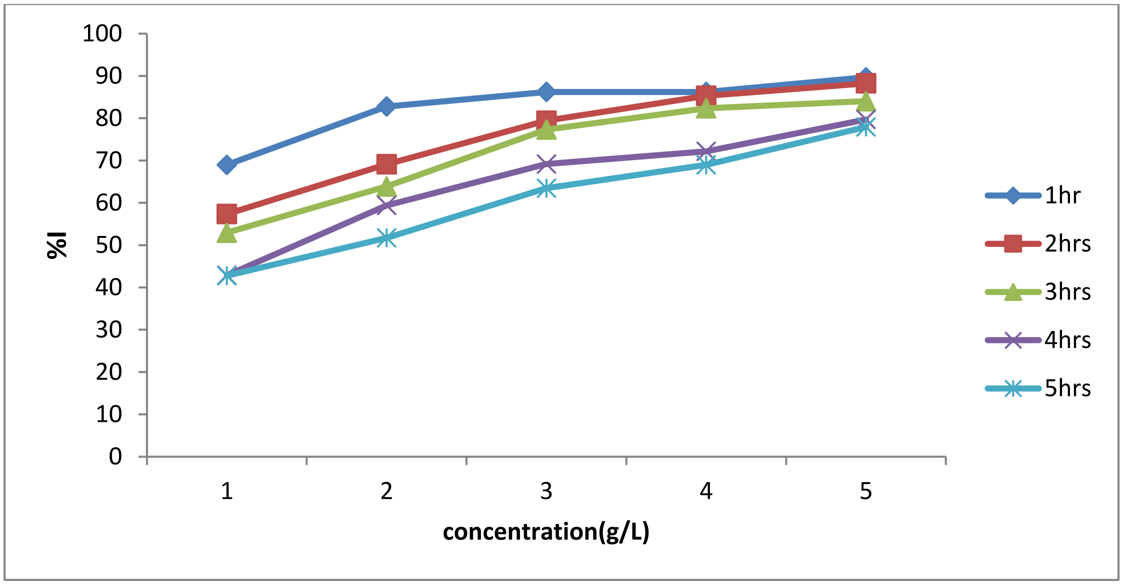

Fig 5. Plot of I% against Ethyl Acetate extract of CL in 2.0M HCl

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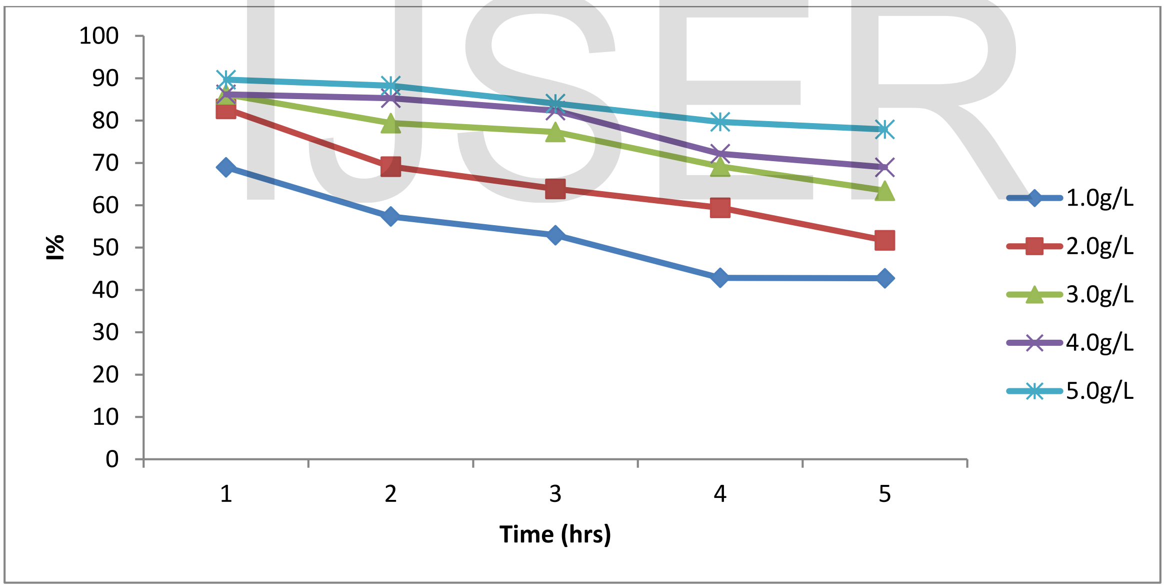

Fig 6. Plot of I% against time for Ethyl Acetate extract of CL in 2.0M HCl

Figures 5 and 6 is a representative data of the plots of the inhibition efficiency against concentration of extract and time respectively. The inhibition efficiency was seen to decrease with as the time intervals increased from 1 to 5 hours and increased uniformly as the concentration of the extract increased. This is still in line with the observation quoted earlier in the chapter by (Obike *et al.*, 2012; Ofoma *et al.*, 2018; Obike *et al.*, 2017; Nya *et al.*, 2018).

3.2 Kinetic Consideration

Table 2: Values of rate constant, half-life and the coefficient of correlation

	K	$t^1/_2$	R^2
Blank	0.04	17.325	0.9
1.0g/L	0.023	30.13043	0.994
2.0g/L	0.019	36.47368	0.952
3.0g/L	0.014	49.5	0.966
4.0g/L	0.012	57.75	0.976
5.0g/L	0.009	77	0.976

The values of the k and $t_{1/2}$ and R^2 are presented in Table 2. The $t_{1/2}$ values obtained from figure 7 and displayed in Table 2 is observed to increase with increase in the concentration of the extract. Also, the plot of Log (Wo/W_f) against time is shown in figure 7 below. This linear plot represents the first order kinetics. The rate constants (k) were gotten from the slope of the plots and they were used to calculate the half-life ($t_{1/2}$). The R^2 values obtained from the plots were very close to unity and this shows that the data is first order kinetics (Okafor *et al.,* 2007; Obike *et al*., 2012). The trend of increase in the half-life as the concentration increased is justification that the ethyl acetate extract of the plant *Corynocarpus laevigatus* is a good inhibitor.

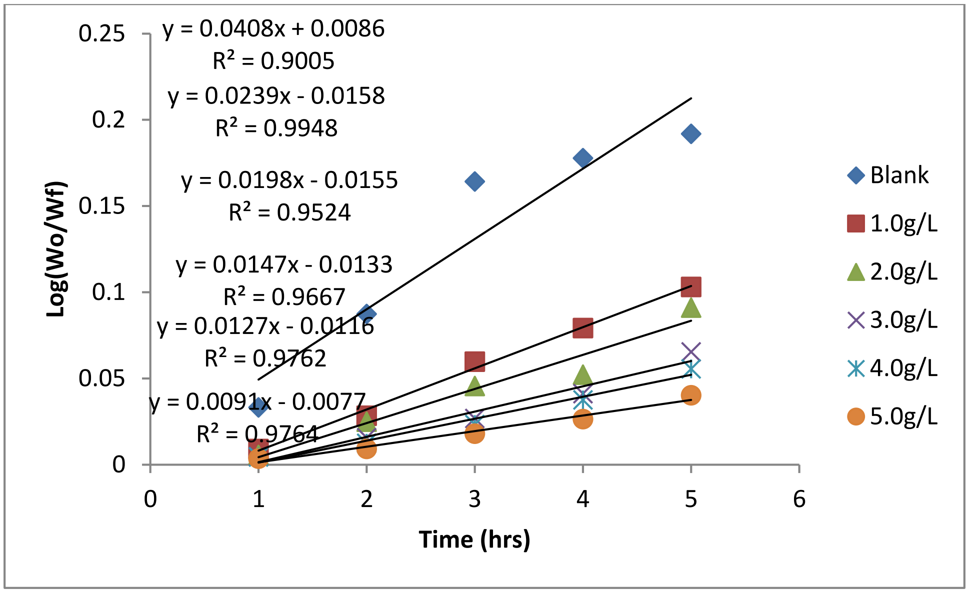

Fig 7. First order kinetics plot for Ethyl Acetate extract of CL in 2.0 M HCl

4. CONCLUSION

This study revealed that ethyl acetate extract of CL (*Corynocarpus laevigatus*) was able to inhibit corrosion of mild steel in the corrosive media of 2 M HCl. This research was strictly investigated using weight loss method, from which it was possible to determine the inhibition efficiencies, rate of corrosion and the order of reaction. The corrosion inhibition and weight loss of the coupons was seen to increase as the concentration of the plant extract increased and they also decreased as the time of immersion increased all at ambient temperature. Where *Corynocarpus laevigatus* had a maximum inhibition efficiency of 88.24%. While the rate of corrosion decreased with increase in the concentration of the plant extract. The plot of the log (W_o/W_f) against time confirmed the kinetics to be first order. The finding from this study is an indication that ethyl acetate extract of CL (*Corynocarpus laevigatus*) is a good and suitable corrosion inhibitor.

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