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Kinetics and Equilibrium Assessment of Anticorrosion Efficiency of Palm Kernel Oil as Green inhibitor on Aluminium Sheet in Acidic Medium

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ABSTRACT: Chemical industries are currently looking for environmentally friendly, reliable inhibitors to stop different metals or alloys from corroding in both acidic and basic media. Therefore, the aim of this paper was to assess the kinetic and equilibrium models of anticorrosion efficiency of palm kernel oil as green inhibitor on aluminium sheet in acidic medium using weight loss method at various concentrations of the oil (2-10 ml) and different time interval of 24 – 120 h. The oil was extracted using Soxhlet extraction method and characterized using Fourier Transform Infrared Spectrophotometer (FTIR). The result revealed maximum inhibition efficiency of approximately 96% at 6 ml concentration of the oil and at the time interval of 24 h. The FTIR analysis showed the presence of C=C-H, Ar-H bending out of plane, C-H bending in plane, C-O, N-O asymmetric stretch, C=C stretch, C=N stretch, and O-H functional groups at various peaks (wave numbers). The adsorption of the oil extract on the surface of the test coupon obeyed Langmuir adsorption isotherm and the kinetic study of the anticorrosion process obeyed pseudo first order kinetic model. However, based on the outcome of this study, palm kernel oil is considered as an excellent corrosion inhibitor and can be used as an alternative inhibitor to replace the non-biodegradable ones.

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Many researchers around the globe have noted with great care that metallic materials like steel, iron, aluminum, and copper are rapidly disappearing from use in a variety of chemical industries as a result of corrosion (Garai *et al.*, 2012; Ali *et al.*, 2016; Obi *et al.*, 2016). Eventually, there will undoubtedly be a metal crisis in the long run. Nevertheless, researches indicate that nearly every metal used in industry, with the exception of noble metals, is unstable to variable degrees in the natural environment due to corrosion (Al-Otaibi *et al.*, 2012; Patel *et al.*, 2013; Sluger *et al.*, 2014). Furthermore, a lot of aspects of our lives are impacted by corrosion and the damage it causes is enormous and detrimental to our lives and properties. It is evident that corrosion has significant financial effects our economy. Thus, according to the World Corrosion Organization (WCO) reported by Rajendran *et al.* (2009), approximately $ 2.2 trillion is lost to corrosion worldwide each year, and 25% of these losses might be avoided by using straightforward, well-understood preventative measures. However, corrosion prevention should also be viewed as a matter of health and safety rather than just a costly one since according to Patel and Šnita (2014), corroded buildings, ships, bridges, and other metal constructions can result in harm or even death.

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Aluminium is a white silvery metallic element of boron family. It has a good thermal and electrical properties. As a result, aluminium was reported to be the most widely used non-ferrous metal in various industries such as Nigerian Bottling Company, beverages among others (Safak *et al.*, 2012). However, frequent exposure of this metal to some of the raw materials, finished product or environmental conditions can to lead corrosion (Mohammed *et al*., 2022).

Corrosion inhibitor, according to Garai *et al*. (2012), is a chemical or mixture of chemicals that, when introduced in extremely low concentrations to a corrosive environment, successfully prevents or lowers corrosion without significantly reacting with the surrounding materials. However, synthetic inhibitors have been used successfully for many years to shield metals from the destructive effects of corrosion, but their usage was long discouraged due to their negative effects on the environment and human health (Adejo *et al*., 2013). Consequently, researchers are now focusing more on green inhibitors as better alternative which proved to be economical and environmental friendly. Therefore, this research work is aimed at assessing the kinetic and equilibrium models of anticorrosion efficiency of palm kernel oil as green inhibitor on aluminium sheet in acidic medium.

MATERIALS AND METHODS

Sample Collection and Preparation: The Palm kernel sample was purchased in keffi market, Keffi LGA, Nasarawa State. It was broken down with mortar and pestle to remove the nuts from the kernel. The nuts were rinsed with water and was further grinded into fine particles for extraction.

Metal Preparation: The Al metal was cut into coupons of 3.0 × 2.0 × 1.0 cm. The coupons were cleaned followed by polishing with sand paper to expose shining polished surface. The specimen were washed with distilled water and air drilled. The weight of each coupon was taken using electronic weighing balance and the initial weight was recorded (Safak *et al*., 2011).

Extraction of the Palm Kernel Oil: The extraction was carried out according to the method adopted by Mohammed *et al*. (2022) using soxhlet extractor, 30 g of the sample was loaded into the soxhlet extractor containing 250 ml of n-hexane and the mixture was heated at reflux for 3 h. The oil extract obtained was poured in a beaker and transferred to a hot plate for heating, to get the desired oil. The obtained oil from the kernel nut was pale yellowish in colour.

Preparation of 1M HCl: The preparation of 1 M HCl was carried by dissolving 83 ml of concentrated hydrochloric acid in 1 dm^3 volumetric flask containing distilled water and made up to mark.

FTIR Analysis of the Oil Extracts: After extraction of the oil from the palm kernel nut, the oil extract was subjected to Fourier Transform Infrared Spectrophotometer (FTIR) for the identification of the functional groups present in the oil extract.

Experimental Procedure: Gravimetric method was adopted to examine the inhibitive efficiency of the oil extract at various concentrations. In this method, the pretreated coupons of size 3.0×2.0×1.0 cm were separately immersed into 100 ml beaker containing 30 ml of the test solution of 1M HCl in the presence and absence of the inhibitor. The coupons were withdrawn from the test solution, washed thoroughly with distilled water and completely dried. The final weight of the coupons was taken at the difference in weight of the coupons before and after the immersion at the time intervals of 24, 48, 72, 96 and 120 h respectively. The weight loss by the coupons were calculated as the difference between the initial weight before immersion and the final weight after the removal of the coupons from the solution. From the weight loss measurement, the corrosion rate, inhibition efficiency (IE)% and surface coverage (Θ) of the extract were calculated using equations 1, 2 and 3 respectively (Solmaz *et al*., 2009; E-Haddad, 2013).

$$CR\ \left(gcm^2h^1\right) = \frac{W - W_1}{AT} \qquad (1)$$

Where CR is the corrosion rate, W and W_1 are the initial and final weight, A is the surface area of the coupon (cm^2) and T is the time of exposure or immersion.

$$IE(\%) = \frac{CR_B - CR_W}{CR_B}\ x\ 100 \qquad (2)$$

$$\text{Surface coverage } (\Theta) = \frac{CR_B - CR_W}{CR_B} \qquad (3)$$

Where IE = inhibition Efficiency, CR_B and CR_W = Corrosion rates in the absence and presence of the inhibitor respectively.

Adsorption Study: Langmuir adsorption isotherm was adopted to evaluate the mechanism of the adsorption process of the inhibitor onto the aluminum surface in

1 M HCl. The Langmuir isotherm equation is given in equation 4 (Hakeem *et al*., 2016).

$$LogC_{inh} = \frac{\log C_{inh}}{\theta} - \log K \quad (4)$$

Kinetic Study: Pseudo first order kinetic model was applied to evaluate the kinetics of the corrosion inhibition process of the study using equation 5 (Muthukrishnan *et al.,* 2013).

$$lin\Delta w = - k_1 T \quad (5)$$

Where, ΔW is the weight loss (g), K_1 is the rate constant (h^{-1}) for first order reaction and T is the exposure time (h).

RESULTS AND DISCUSSION

Corrosion Inhibition Analysis: The results of the experiment are shown in Tables 1 – 3. However, Table 1 shows the variation of corrosion rate with time of immersion in 1 M HCl, Table 2 shows variation of corrosion rate with immersion time at different concentrations of the oil extract and Table 3 shows the effect immersion time of the coupons on corrosion rate in acidic medium containing 6 ml of the inhibitor (oil extract). Perceptible inspection of the experiment's coupons reveals color changes, surface deterioration, microcracks, and pits that signify corrosion attack by the acidic medium. Even with the color shifts, the coupons submerged in the blank solution had more noticeable pits and fissures. However, similar observations were also reported in the literature (Martinez and Štern, 2001; Loto, 2005).

Table 1: Variation of Corrosion Rate with Time of Immersion in 1 M HCl

Coupon	Immersion Time (h)	Weight loss (g)	CR (g/cm^3h^{-1})
C1	24	0.40	0.0047
C2	48	0.50	0.0019
C3	72	0.60	0.0011
C4	96	0.50	0.0009
C5	120	0.70	0.0006

Table 1 shows the variation of corrosion rate with time of immersion of the coupons in 1 M HCl acid solution. It was observed that the coupons immersed in the acidic medium without inhibitor shows the highest corrosion rates compared to those immersed in the acidic medium containing various concentrations of the inhibitor. It was obvious that there was increase in the corrosion rate as the time of immersion increased from 24 h to 72 h and a pronounced decrease in the corrosion rate as the immersion time was increased from 96 h, a slight increase was observed at 120 h. This result was in agreement with those by Olusegun *et al*. (2013) and Mohammed *et al*. (2022) respectively.

Table 2: Variation of Corrosion Rate with Immersion Time at Different Concentrations of Oil Extract

Conc. (ml)	CR (g/cm^2h^{-1})	I.E (%)
2.0	0.0018	62.10
4.0	0.0004	76.99
6.0	0.0001	86.99
8.0	0.0001	85.95
10.0	0.00005	90.99

Table 2 shows the variation rate with immersion time at different concentrations of oil extract. It was observed that the efficiencies of the oil extract ranges approximately from 62-91% respectively. Thus, it was observed that an increase in concentration of the oil extract decreases the corrosion rate except for the concentrations between 6- 8 ml which indicates a slight decrease in inhibitive efficiency as the concentration increased. This could be due to experimental errors. However, the variation in the corrosion rate with time of immersion of the test coupons in the acidic medium containing various concentration of the extracts (oil) could be attributed to the presence of functional groups presence in the oil extract as shown in figure 4, chemical species in the extract which may have worked to inhibit both the cathodic and anodic reaction. The lower the corrosion rate exhibited by the coupons at higher concentration of the extract and time of immersion, the higher the inhibitor efficiency. Maximum protection was achieved by the inhibition efficiency at a certain concentration and immersion time.The maximum efficiencies of 87 and 96% were obtained at 96 and 120 h of immersion time in 1 M HCl solution containing 2 ml-10 ml of the extract respectively. The effect in the inhibition efficiency could be attributed to the functional groups present in both samples which may be affected by the concentration of the corrosion inhibitor, thereby making it unstable (Umoren *et al.*, 2008; Otaibi *et al.*, 2012).

Table 3: Effect of Immersion Time using 6 ml of the Oil Extract in 1 M HCl

Time (h)	CR (g/cm^2h^{-1})	I.E (%)
24	0.0001	95.61
48	0.0005	82.45
72	0.0009	74.09
96	0.0017	64.10
120	0.0049	54.07

Although, the results revealed that the inhibition efficiencies of the oil extract from the palm kernel nut ranged approximately from 54-96%. Thus, it was observed that increase in time of immersion of the coupons in the acidic medium at fixed concentration of the extract (6 ml) increased the corrosion rate while the inhibitive efficiency decreased. However, similar observations were reported by many researchers on corrosion studies (Salasi *et al.*, 2007; Olusegun *et al.*, 2013; Sylvester *et al.*, 2013).

Adsorption Isotherm Analysis: Adsorption isotherm analysis provides vital information used to identify and also describe the mechanism of the anticorrosion process. Figure1 shows the Langmuir adsorption isotherm for the palm kernel oil (PKO) as corrosion inhibitor against aluminium sheet in 1M HCl. The plot revealed a strong negative Pearson's correlation coefficient (R^2) = -0.9971.This implies that the corrosion inhibition study obeyed Langmuir adsorption isotherm model which suggests monolayer adsorption of the oil on the aluminium surface.

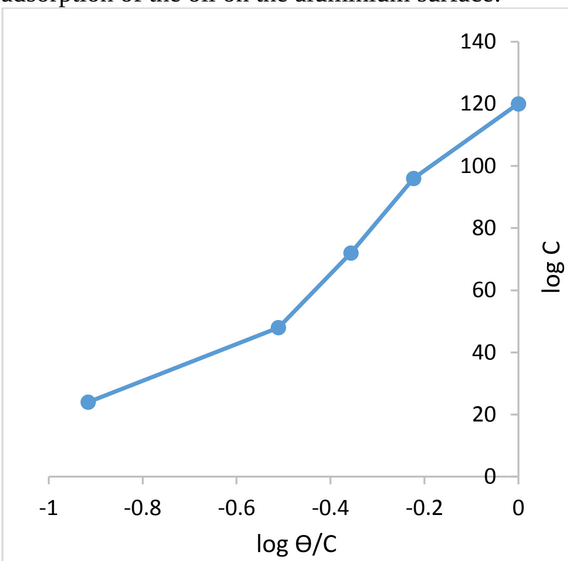

Fig 1: Langmuir adsorption isotherm for the anticorrosion process

Kinetic Analysis: Kinetic analysis provides valuable information on the kinetics of corrosion inhibition process. Figure 3.2 shows the kinetics plot of corrosion inhibition study. The plot revealed strong positive Pearson's correlation coefficient (R^2) = -0.9971.This also implies that the corrosion inhibition study obeyed pseudo first kinetic model as shown in figure 3.2. However similar result was reported by Okewale and Adesina (2020) on Kinetics and thermodynamic study of corrosion inhibition of mild steel in 1.5M HCl Medium using Cocoa leaf extract as inhibitor.

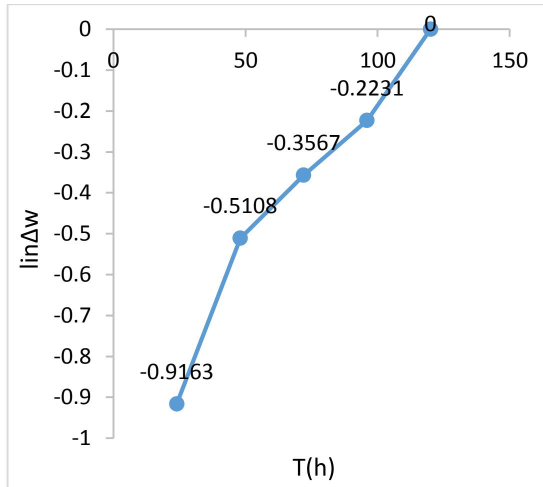

Fig 2: Kinetic plot of the corrosion inhibition study of PKO

The FTIR Spectra of the Oil Extract: Figure 3 shows the result of FTIR analysis of the palm kernel oil extract**.**

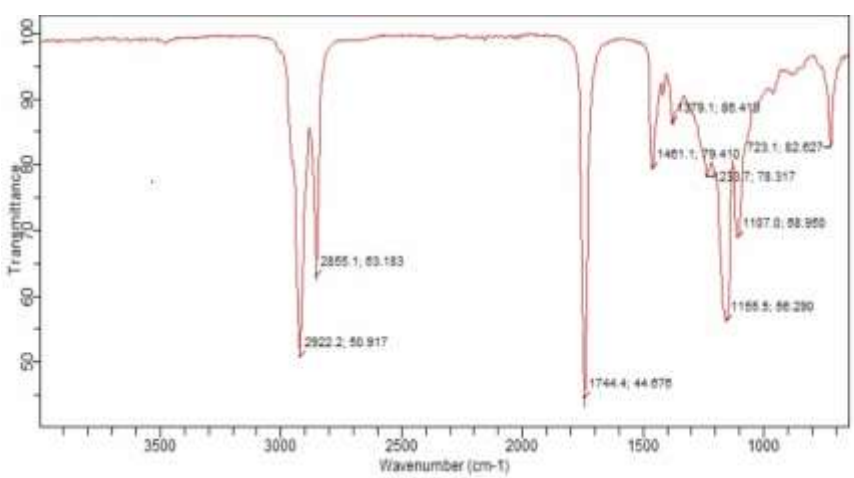

Fig 3: FTIR spectra of the oil extract

Figure 3 and Table 3 present the spectra, peak values, intensity and assigned functional groups corresponding to the peak values respectively**.** The peaks indicated the presence of C = C – H, C – O stretch, C = O, S = O stretch, N – O stretch, N = O, C = C, C = N stretch and O – H stretch functional groups in the oil extracts as clearly indicated in Table 3.4. However, according to literature heteroatoms (N–O), polar functional groups (-OH) electron donating (-CH_3) group, π electrons and aromatic rings are good adsorption centre (Nadia *et al*., 2019). However, the presence of these functional groups in the oil extract are however responsible for the corrosion inhibition since most of the adsorption centre mentioned above are identified in palm kernel oil.

Table 4: Peak, Intensity and Assignment Functional Group

Peak (cm^{-1})	Intensity	Assigned Functional Groups
723.1	82.63	C =C-H, C = O Stretch
1107.0	68.95	C - O Stretch
1155.5	56.29	C – O, CH_2 Stretch
1233.7	78.32	C – O, CH_2, C = O Stretch
1379.1	86.42	C – O, S = O, N = O Stretch
1461.1	79.41	C – O, N = O Stretch
1744.4	44.67	C = O, C =C, C = N Stretch
2855.1	63.18	C – H, O – H, N – H Stretch
2922.2	50.92	C – H, O – H, N – H Stretch

Conclusion: The study evaluated the anticorrosion efficiency of palm kernel oil on aluminium sheet in 1 M HCl and also assessed the kinetic and adsorption mechanism of the anticorrosion process using first order kinetics and Langmuir adsorption isotherm models respectively. From the result obtained, it was observed that the inhibition efficiency increased with increase in the concentrations of the oil extract until a maximum inhibition efficiency of approximately 96% was recorded. The kinetics and adsorption mechanism of the oil extract on the surface of the test coupon obeyed both models respectively. However, based on the outcome of this study, palm kernel oil is considered as an excellent corrosion inhibitor and can be used as an alternative inhibitor to replace the non-biodegradable ones.

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