




## ORIGINAL RESEARCH PAPER



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# The inhibitive action of *Plukenetia conophora* plant extract on the corrosion of Al–Zn–Cu alloy in different acidic media

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## ABSTRACT

*Plukenetia conophora* (Nigerian Walnut) leaf extract was studied as a corrosion inhibitor on Al–Zn–Cu alloy in acidic (HCl and H<sub>2</sub>SO<sub>4</sub>) media using gravimetric, gasometric and electropotential techniques. The study showed that the inhibition efficiency (IE) increased as the concentration of the leaf extract increased and reached the peak (94.8%) at 0.8 g/L in 1 M HCl. In the two acidic media, *P. conophora* leaf extract exhibited good corrosion inhibition properties on the Al–Zn–Cu alloy samples due to adhesion of the extracts on the samples' surfaces. The adsorption process of the extract on the alloy sample surfaces was found to be spontaneous and perfectly obeyed the Langmuir isotherm model. Thus, *P. conophora* leaf extract is recommended for utilisation as a potential replacement for toxic inorganic inhibitors and for application in paint and coating industries.

## KEYWORDS

Al–Zn–Cu alloy, corrosion inhibitor, electropotential, gasometric, weight loss

## 1. INTRODUCTION

The study on aluminium and its alloy in line with its corrosion behaviour in various hostile environments have continuously generated extensive concern due to the innumerable utilisation of the alloy [1–4]. For aluminium to resist corrosion, a passive oxide adherent film is usually formed in various environments. The amphoteric nature of the oxide film causes it to dissolve significantly when the metal is placed in a high concentration of acidic or basic media [5]. After the oxide film breakdown, the surface sites of the bared metal become unprotected and exposed to the corrodent. This always causes an electrochemical reaction due to the metal leading to an electrochemical reaction as the metal dissolution. In strong acidic solutions, the evolution of hydrogen gas is principal due to numerous cathodic processes that are associated with corrosion [6–8]. These acid solutions have been used for aluminium pickling as well as for its chemical and electrochemical etching. These procedures generally bring about significant metal loss mainly because of corrosion when the quantities used were not properly regulated [8, 9].

One of the main strategies to mitigate corrosion of metals is to excellently perform metal segregation from corrosive elements [10–12]. This strategy of mitigation by metal segregation involves the usage of corrosion inhibitors. Phosphates, chromates, dichromate and arsenates, which are inorganic inhibiting substances of metal corrosion, however, they are very toxic. Therefore, their usage as metal corrosion inhibitors has raised severe criticisms [10]. As a result of these criticisms, some green inhibitors of plant origin (natural products) have been discovered as they exhibit good corrosion inhibiting properties in different corrosive environments [13–30].

The utilisation of these green inhibitors as corrosion inhibitors become vital as they have been known to be readily available, non-toxic, environmentally friendly, renewable material sources and ecologically acceptable. The organic nature of these plant products contains active constituents such as alkaloids, saponins, essential oils, flavonoids, organic and amino-acids; in which their presence have been established in literature to be advantageous in inhibiting corrosion [16, 17, 20–23].

Recent studies [21–23] have shown that *Jatropha curcas* and *Moringa oleifera* leaves extracts possessed good corrosion inhibiting properties on mild steel when immersed into acidic media. Odusote and Ajayi [21] stated that in a sulphuric acid solution, the increasing concentration of *J. curcas* extracts gave a high inhibitive efficiency. It was concluded that the inhibitive capacity was dependent on the concentration of the leaf extract in the corrosion environment, especially acidic solution. In another work by Ajayi et al. [23], where the inhibition of the degradation of mild steel in 4 M HCl and 4 M H<sub>2</sub>SO<sub>4</sub> aqueous solutions was studied, it was stated that the extract was a good and safe inhibitor in both solutions. Continuous effort is being drawn to the major constituent and reactivity of these green inhibitors that make them effective against corrosion. Matamala et al. [18] used the extracts from acacia and pin bark, and reported that the tannins in the extract of these green inhibitors play a major role in their effective usage as a corrosion inhibitor. However, as a developing nation with abundant sources of these green inhibitors, there are several of them that have not been at the limelight of observation scientifically. Thus, this study examined the corrosion inhibiting effect of *Plukenetia conophora* leaf extract on aluminium alloy in acidic media through gasometric, gravimetric and potentiodynamic polarisation techniques. This is aimed at furthering the development of environmentally friendly green corrosion inhibitors from plant leaves that contain similar active constituents such as alkaloids and saponins. These green inhibitors could successfully serve as replacement for synthetic inhibitors, which are toxic and obtained from non-renewable sources.

## 2. MATERIALS AND METHOD

### 2.1. Materials

The materials used in this study include Al, Zn and Cu scraps, which are melted to produce Al–Zn–Cu alloys samples (7,093 series). Other materials include *P. conophora* leaf, HCl and H<sub>2</sub>SO<sub>4</sub> acids. Ethanol, filter paper, air tight plastic containers were all used during the extraction of active ingredients from the *P. conophora* leaf to produce the inhibitor.

### 2.2. Experimental procedure

**2.2.1. Alloy preparation.** Al–Zn–Cu alloy test samples of dimensions 15 × 10 mm used in this study were produced using permanent mould. The casting was carried out

according to the procedure in a previous study [28]. Chemical composition analysis of the cast Al–Zn–Cu alloy was carried out at a private foundry in Lagos, Nigeria using optical light emission spectrometer (SPECTRO-06000939).

**2.2.2. Plant extract preparation.** Nigerian walnut (*P. conophora*) fresh green leaves were collected and thoroughly washed in distilled water. These washed leaves were air-dried for five days. Afterward, manual grinding machine was used to pulverise the dried leaves. Five hundred gram (500 g) of the pulverised *P. conophora* leaf sample was soaked in a flat bottom flask holding 1,000 ml of 99% ethanol. The flask was enclosed and allowed to remain in a cool desiccated cabinet for a duration of 48 h, as reported in previous studies [20]. This was then followed by filtration of the mixture via filter paper usage. To concentrate the filtrates, the ethanol content of the filtrate using a water bath was vapourised at 70°C. The obtained concentrates were then applied to formulate different inhibitor concentrations (0.2, 0.4, 0.6 and 0.8 g/L) with distilled water. Air-tight plastic containers were then used to keep the formulated inhibitors from contamination.

**2.2.3. Leaf extract phytochemical screening.** The phytochemical screening to determine the constituents/active compounds in the *P. conophora* leaf extract was done using different reagents following the procedures described by Oloyede [24] and Mojab, Kamalinejad [25]. Distilled hydrochloric acid was used to dissolve the extract before being filtered. Afterwards, a potassium mercuric iodide solution was used in treating the filtered extract. A whitish-yellow precipitate was formed, which was an indication of alkaloids presence. Bluish black colouration formation showed phenol presence when four drops of ferric chloride-solution were applied on the extract. The presence of saponins was determined with the dilution of the extract in 20 ml distilled water and shaken for 15 min in a graduated test tube. The presence of saponins is known by the formation of foam layers. The presence of tannins was determined by the appearance of a brownish-green colour. This was obtained as a result of the addition of 0.1% ferric chloride in a few drops to the filtrate after boiling the leaf extract in a test tube that holds 20 mL of distilled water tube. The extract was treated with a ferric chloride solution in a few drops. Flavonoid presence was observed with the appearance of an intense green colouration. The appearance of a reddish-brown colouration at the layer interface was formed when the pulverised *P. conophora* leaf extract was added through the mixture of chloroform (2 mL) and sulphuric acid (3 mL). This indicated the presence of terpenoid.

**2.2.4. Gravimetric method.** The specimens were metallographically prepared to have a smooth and mirror-like surface before immersion. The initial weight of the specimens was determined through an electronic balance before immersing in 50 mL of 1 M HCl and H<sub>2</sub>SO<sub>4</sub>, respectively, with different leaf extract concentrations (ranging between 0.2 and 0.8 g/L). Samples were immersed in different solutions containing varying inhibitors concentration for 15 days duration. Each sample was being taken out of the solutions at 3 days interval, washed thoroughly with distilled water,



dried and weighed. The control experiment was void of inhibitor (leaf extract) usage. Eqs. (1)–(3) were utilised to determine the weight loss, the corrosion rate ( $CR$ ), surface coverage and inhibition efficiency ( $IE$ ) (%) of the plant extract in different media [21, 23].

$$\text{Corrosion rate (gcm}^{-2}\text{h}^{-1}) = \frac{\Delta W}{AT} \quad (1)$$

where  $\Delta W$  is weight loss (g),  $A$  is surface area of alloy sample ( $\text{cm}^2$ ) alloy sample and  $T$  is time of exposure (hour).

$$\text{Inhibition efficiency, } IE(\%) = \left( \frac{CR_B - CR_w}{CR_B} \right) \times 100. \quad (2)$$

$$\text{Surface coverage, } (\theta) = \left( \frac{CR_B - CR_w}{CR_B} \right), \quad (3)$$

where  $CR_B$  and  $CR_w$  are corrosion rates in the absence and presence of the inhibitor, respectively.

**2.2.5. Gasometric method.** The procedure set-up described by Odusote and Ajayi [21] was adopted for the measurement of hydrogen evolution. Using a delivery tube, a reaction vessel and burette were connected. The 3 M HCl and  $\text{H}_2\text{SO}_4$  solutions (higher concentration of the acids was used to increase the  $CR$ ) were passed into the mylius cell. The initial burette air volume was recorded. The prepared Al–Cu–Zn alloy was separately released into the HCl and  $\text{H}_2\text{SO}_4$  solutions. This was immediately followed by the quick closure of the mylius cell. The hydrogen gas volume evolving was observed based on the corrosion reaction via the volume change in water level in the burette. Recording of volume change was done every 10 min after 1 h absorption time for the alloy for up to 1 additional hour. For acid solutions with inhibitor presence, a similar approach was adopted. Eq. (4) was used to determine the  $IE$  while Eq. (5) was employed to estimate the surface coverage degree [21, 23]:

$$IE(\%) = \left( \frac{VH_0 - VH_1}{VH_0} \right) \times 100 \quad (4)$$

$$\text{Surface coverage, } (\theta) = \frac{VH_0 - VH_1}{VH_0}. \quad (5)$$

where  $VH_0$  is volume of hydrogen gas evolved in the absence of the inhibitors and  $VH_1$  is volume of hydrogen gas evolved in the presence of the inhibitors.

**2.2.6. Potentiodynamic polarization method.** The measurements of potentiodynamic polarisation and open circuit potential (OCP) were done using AUTOLAB PGSTAT 204N instrument, as shown in Fig. 1. The electrochemical studies were done at room temperature with the aid of a three-electrode cell assembly. Al–Cu–Zn alloy sample (with  $1 \text{ cm}^2$  area dimension) was the working electrode and was embedded in resin, as shown in Fig. 1a. A platinum electrode served as a counter electrode and the reference saturated utilised was silver/silver chloride. The electrolytes were 1 M HCl and  $\text{H}_2\text{SO}_4$  (See Fig. 1b). The working electrode was ground with 1,200 grit emery papers to have a smooth surface. Before the potentiodynamic polarisation measurement, the open-circuit corrosion potential (OCP) measurements were done for 30 min after it was established that the set up will be appropriate to achieve a steady value of  $E_{\text{corr}}$  by the appearance of –ve sign on the screen (Fig. 1c). The cathodic potential to anode potential range of  $-250 \text{ mV}$  to  $+250 \text{ mV}$  with  $1.0 \text{ mV s}^{-1}$  scan rate was used in the linear polarisation study. This was used to evaluate the current density,  $CR$  and  $IE$ . The results are presented in Table 5.

The evaluation of inhibitor efficiency was done using Eq. (6) [16]:

$$IE(\%) = \left( \frac{I_{\text{corr}} - I_{\text{corr}}^*}{I_{\text{corr}}} \right) \times 100 \quad (6)$$

where  $I_{\text{corr}}$  and  $I_{\text{corr}}^*$  are corrosion current in the absence and presence of inhibitors, respectively.

## 2.3. Adsorption isotherm

Adsorption is a surface-based process where adsorbate film is created on the adsorbent surface. The metal corrosion reaction inhibition mechanism can be determined through adsorption isotherms, which include Langmuir, Frumkin, Temkin, Freundlich, Flory Huggins isotherm, and so on. The value and the sign of the standard Gibbs free energy obtained from any of the isotherm models can be used to evaluate the spontaneity of the corrosion reaction and nature of the bonding as either physisorption or chemisorption.

**2.3.1. Langmuir adsorption isotherm.** The determination of the Langmuir adsorption isotherm was done using Eq. (7) [26]. More so, the term that reveals the interaction type occurring between the surface of the metal/alloy and the molecules of the inhibitor was evaluated using Eq. (8) [27].



Fig. 1. Electropotential method experimental set up: (A) Embedded sample in resin. (B) Electrodes set up. (C) Monitor showing OCP measurements

This term is known as the standard Gibbs free energy value,  $\Delta G_{ads}$ .

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C. \quad (7)$$

where  $C$  is aqueous extract concentration;  $\theta$  is surface coverage and  $K_{ads}$  is the adsorption process equilibrium constant.

$$\Delta G_{ads} = -RT \ln 55.5K_{ads} \quad (8)$$

where  $R$  is universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is thermodynamic temperature in K. however, 55.5 is a constant which represents the molar concentration of water in the solution.

A linearly fit curve of  $C/\theta$  against  $C$  when plotted expresses the Langmuir isotherm model is obeyed with the adsorption of the extracts onto the metal surface.

### 3. RESULTS AND DISCUSSION

#### 3.1. Chemical composition of the alloy sample

The chemical composition analysis of the cast Al–Zn–Cu alloy done is presented in Table 1.

#### 3.2. Leaf extract phytochemical screening

Table 2 shows the obtained results for the *P. conophora* leaf extract when the phytochemical analysis was done. The results revealed that there are active constituents of alkaloids, phenol and saponins in higher amount in comparison to the other constituents present in the extract. Saponins, tannins and alkaloids have been reported to be active constituents of most green inhibitors [18, 21, 23, 28, 29].

#### 3.3. Gravimetric method

**3.3.1. Weight loss measurement.** Figs. 2 and 3 show the weight loss variation with exposure time for the Al–Zn–Cu alloy specimens inserted in the acidic solutions when the

Table 1. Al–Cu–Zn alloy chemical composition (wt.%)

Elements	Weight (%)	Elements	Weight (%)
Al	86.200	Mn	0.010
Cu	1.860	Cr	0.002
Zn	8.930	Ni	0.001
Fe	1.780	Pb	0.041
Si	0.880	Mg	0.089
Sn	0.001	V	0.206

Table 2. Leaf extract of *Plukenetia Conophora* phytochemical screening

Constituents	Bioassays	Constituents	Bioassays
Alkaloids	+++	Terpenoids	+
Cardiac glycosides	+	Anthraquinone	+
Saponins	++	Phenols	++
Tannins	+	–	–
Flavonoids	+		

concentrations of the extracts were varied. From the figures, the loss in weight of aluminium alloy increased as the exposure period increases but reduced as the inhibition concentration increases. The rate of weight loss is faster in inhibitor-free media (HCl and  $\text{H}_2\text{SO}_4$  solutions) compared with those with inhibitors. However, more weight is lost especially at lower inhibitor concentrations up to 0.4 g/L in HCl solution compared with  $\text{H}_2\text{SO}_4$  solution indicating higher corrosive nature of the HCl medium. The weight loss results (Figs. 2 and 3) indicate that the *P. conophora* leaves extract inhibited the aluminium alloy corrosion and thus reduced the rate of corrosion of the specimens as the inhibitor concentration increases. The original weight reduction of the alloy coupons placed in the aggressive media (HCl and  $\text{H}_2\text{SO}_4$ ) also indicated that the constituents of the alloy, aluminium, zinc, and copper are being dissolved and corroded.

Based on the results, the  $\text{H}_2\text{SO}_4$  medium was observed to be less corrosive than the HCl medium. Hence, the rate of corrosion of any metal in acidic media is largely dependent on the type of radicals present in the acids. In the current study, during initial exposure time up to 9 days, the samples in sulphuric acid began to react vigorously leading to a fast rate of weight loss as compared to the hydrochloric acid solution. The colour of the acid solution changes based on the constituent metals in the alloy at different concentrations of each inhibitor; the zinc and copper constituents of the coupons gave blue-black colouration, which turned black as the immersion time increases. This may be due to the formation of zinc and cupric chloride ( $\text{ZnCl}_2$  and  $\text{CuCl}_2$ ) resulting from the reaction of zinc and copper with chloride ions of HCl media [18]. The result here followed the same pattern as observed for zinc as well as for other metals including aluminium in acidic solutions as reported in previous studies [9, 17]. The inhibitive action can be attributed to the adhesion of the active constituents in the leaf extract on the cathodic sites on the metal surface. Thus, the corrosion inhibitive action rises with increasing concentration of the inhibitor in the electrolyte. Plant extracts active constituents such as alkaloids, tannin, phenol and saponins have been described to display changeable inhibition mechanisms and efficiency [5, 20]. A function of these extracts' inhibition tendency is their molecular constituents, which in turn affect the molecular reactivity and its absorbability. This may be responsible for the inhibition efficiencies differences and mechanisms reported for different inhibiting agents.

**3.3.2. Corrosion rate.** The variations of CR with immersion time for varying concentrations of the *P. conophora* leaves extract in 1 M HCl and  $\text{H}_2\text{SO}_4$  solutions are shown in Figs. 4 and 5. The figures revealed that the CR of the aluminium alloy decreases with increasing concentration of the extracts. It was observed, as shown in Fig. 4, that after day 3, the CR was very fast compared to the other days. This may be due to the very aggressive direct reaction between the metal surface and the acid. The CR in the HCl environment declined with rising inhibitor concentration and was higher in the blank



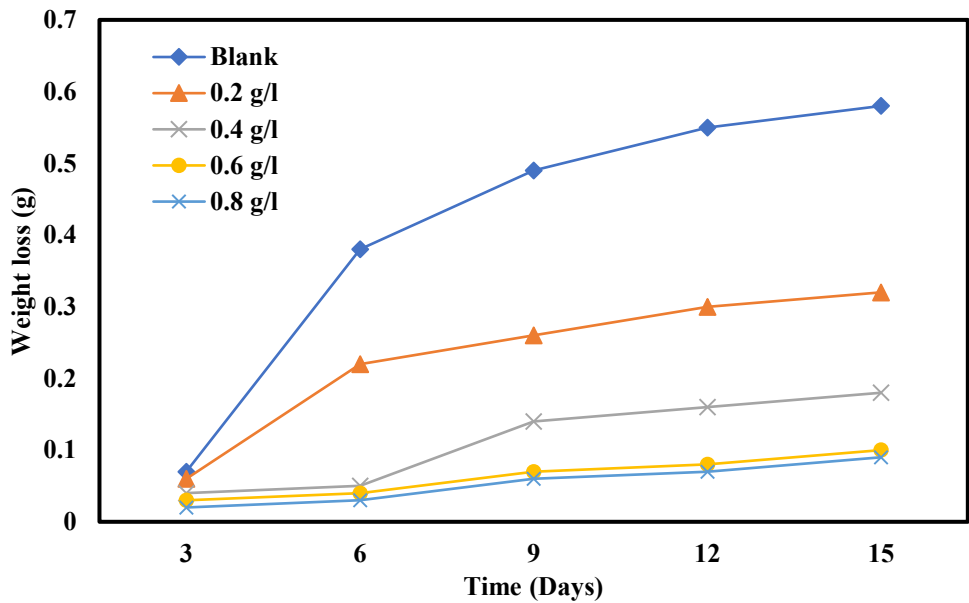


Fig. 2. Effect of inhibitor concentrations in 1 M HCl on weight loss of the Al-Zn-Cu alloy at different exposure time

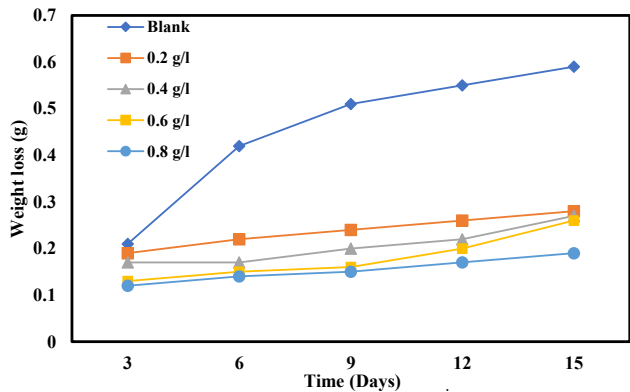


Fig. 3. Effect of inhibitor concentrations in 1 M H<sub>2</sub>SO<sub>4</sub> on weight loss of the Al-Zn-Cu alloy at different exposure time

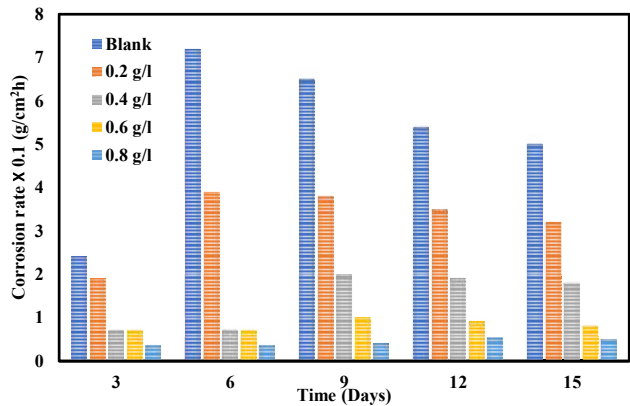


Fig. 4. Corrosion rate vs. exposure time of Al-Zn-Cu alloy in 1 M HCl using *Plukenetia conophora* leaves extracts





solution at all exposure time. However, the CR after 3 days of exposure was slower compared to longer days of exposure. This observation may be due to the delay in penetration of the acid into the alloy surface resulting from the presence of passive oxide films on the sample surface. Above this exposure period (6 days), the CR was very fast possibly because of the breaking of the initial passive film on the surface, which allows for a direct reaction between the alloy sample surface and the penetrated  $\text{Cl}^-$  [30]. This observation shows that the initial passive oxide film on Al alloy will be broken after a maximum of 3 days exposure to an aggressive environment such as  $\text{Cl}^-$ , justifying that 15 days exposure is enough to determine the preliminary behaviour of Al alloy in an acid environment. At longer exposure time (Fig. 4), the CR became reduced because of the formation of a protective passive film on the alloy surface since aluminium is a passive metal. However, after the protective film formation owing to the action of the inhibitors, the CR continuously reduces with increasing exposure time (9–15 days). Also, the increment in the concentration of the inhibitors results in a gradual decline of the CR. This is an indication of the effectiveness of the inhibitors. Furthermore, it can also be inferred that the CR of the samples in *P. conophora* leaves extracts is far lesser as there was an increment in concentration of the leaves extract probably because of the active agents present in *P. conophora* such as alkaloids and phenol that are present in large quantities.

In the sulphuric acid environment, the CR of the sample reduced with exposure time increment and concentration of the inhibitor (Fig. 5). Since  $\text{SO}_4^{2-}$  is not as aggressive as  $\text{Cl}^-$ , the passive film on the Al alloy sample surface serves as a barrier and prevents the acid solution ( $\text{SO}_4^{2-}$ ) from reaching the sample surface, resulting in a decrease in CR [1]. Formation of protective film on sample surfaces during corrosion usually slows down the corrosion reaction as the exposure time increases provided the passive film is continuously acting as a barrier between the metal alloy surface and the environments [10]. The more time the inhibitors spend in the environment the less active they become due to a reduction in the phytochemical constituents of the inhibitor. Finally, it can be deduced from the figures that, for 0.8 g/L inhibitor concentration, the rate at

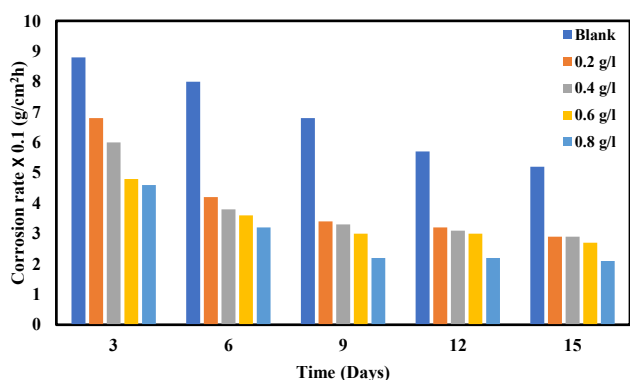


Fig. 5. Corrosion rate vs. exposure time of Al-Zn-Cu alloy in 1 M  $\text{H}_2\text{SO}_4$  using *Plukenetia conophora* leaves extracts

which the CR keeps reducing is more significant compared to the other concentrations. This suggested that the aluminium alloy surface has formed a strong barrier which has disallowed, through inhibition ability of the extract, the active agents present to penetrate. This can be ascribed to the fact that there is a proportional rise between chemical reaction rate and acid concentration [31].

**3.3.3. Inhibition efficiency.** Tables 3 and 4 show the results of inhibition efficiencies of *P. conophora* leaves extracts on aluminium alloy corrosion alloy in the acidic solutions of 1 M HCl and  $\text{H}_2\text{SO}_4$  solutions at different immersion times. It is observed that there was a rise in IE as the concentration of the extracts increases at all the exposure times. The inhibition efficiencies were constant at some points, which may be due to little or no effect of higher concentration of the leaves extract at those exposure times. In the HCl solution, the IE after 3 days of exposure was very low at different concentrations of the extract, because the acid is very aggressive. Thus, it reacted very fast with the Al alloy sample surfaces to remove the initial passive film and increased the CR. However, after the reaction of the acid with the Al alloy sample surfaces, there was protective film formation owing to the inhibitive actions of the *P. conophora* leaves extract. The presence of protective films lowered the CR leading to increased inhibition efficiencies as shown in Tables 3 and 4. The IE at 0.2 g/L inhibitor concentration was very low compared to other concentrations agreeing with weight loss results (Figs. 2 and 3). This is referred to as the latency period. This may be due to the presence of passive oxide film on the aluminium alloy sample surfaces. The period it took to remove this initial film may be referred to as the latency period, which lasted for about 3 days.

For instance, Tables 3 and 4 show some drop of efficiencies as exposure time increases in both HCl and  $\text{H}_2\text{SO}_4$

Table 3. Inhibition efficiency of Al-Zn-Cu alloy at different extract concentration in 1 M HCl

Time (Day)	Inhibition efficiency in HCl solution (%)			
	0.2 g/L	0.4 g/L	0.6 g/L	0.8 g/L
3rd	17	66.5	66.5	83.5
6th	44.7	89.4	89.4	94.8
9th	45.1	68.6	86.3	92.2
12th	43.1	65.8	84.5	89.7
15th	41.7	63.5	83.4	88.5

Table 4. Inhibition efficiency of Al-Zn-Cu alloy at different extract concentration in 1 M  $\text{H}_2\text{SO}_4$

Time (Day)	Inhibition efficiency in $\text{H}_2\text{SO}_4$ solution (%)			
	0.2 g/L	0.4 g/L	0.6 g/L	0.8 g/L
3rd	21.7	30.5	43.4	47.7
6th	45.3	52.4	57.2	64.3
9th	50.0	51.9	59.6	67.4
12th	43.9	47.3	49.2	59.6
15th	44.3	44.3	47.5	54.1

probably because of the rate at which the environment attacks the samples as well as the reaction of the alloy constituents with the active agents,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , present in the environment. However, the effects of the  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  on the alloy sample surfaces varied as indicated by higher *IE* for HCl at the same concentration of inhibitor and exposure time (Table 4). This may be due to the presence of different radicals in the acid solutions used, which determine their rate of reactions in the same media [13].

The higher *IE* of HCl compared with that of  $\text{H}_2\text{SO}_4$  may be due to the slow rate of reaction of  $\text{H}_2\text{SO}_4$  on the sample surfaces leading to reduction of the effects of the inhibitors in forming passive film to protect the sample surfaces. Furthermore, the leaf extract of *P. conophora* gave the highest value of *IE* of 94.8% in 0.8 g/L concentration in hydrochloric acid compared to sulphuric acid with the highest efficiencies of 67.4%. This is probably due to the faster rate of formation of the passive layer on the surface of the metal substrate, which serves as a barrier between the Al–Zn–Cu alloy sample surface and the environment resulting in lower *CR* and higher *IE* compared to sulphuric acid [19]. The *IE* of the leaf extract could be associated with the presence of complex chemical compounds of the active constituents, which include tannins, alkaloids and saponins [15, 20]. Finally, it can be deduced from the tables that the highest value of inhibition efficiencies was achieved at the inhibitor concentration of 0.8 g/L. This suggests that an indestructible obstruction has been established on the aluminium alloy surface restricting the active agents' penetration present in the environments. This can be attributed to the fact that the *IE* of inhibitor is directly proportional to the concentration, that is, an increase in inhibitor concentration will lead to a rise in *IE*. Therefore, *P. conophora* can be said to be an adsorption corrosion inhibitor for aluminium in aggressive media. Hence, the physical adsorption mechanism was favoured due to the adhesion of the inhibitor on the aluminium surface [32–34].

### 3.4. Gasometric method

**3.4.1. Hydrogen gas evolution.** Figs. 6 and 7 illustrate the volume variation of hydrogen gas evolved with increment in time when the Al–Zn–Cu alloy was immersed in 3 M HCl and  $\text{H}_2\text{SO}_4$ . The results show that the *CR* of the blank Al–Zn–Cu alloy gave the maximum value when compared to the other environments with the presence of inhibiting agents. The gasometric measurements revealed that the amount of hydrogen gas evolved reduced as the quantity of the extract increased. This can be due to inhibiting effects of the *P. conophora* leaf extract, which depends on its concentrations as it ranges between 0.2 and 0.8 g/L in the three media. This suggests that the extract in the solution slowed down the *CR* of aluminium alloy in these aggressive environments. Therefore, the dissolution of copper in aluminium alloy is low in HCl as well as in  $\text{H}_3\text{PO}_4$  acidic medium compared to other pure aluminium. Nevertheless, the comparison in different acidic strengths makes Cu more reactive in HCl acid than in  $\text{H}_3\text{PO}_4$  acid or in any other

media [19, 35]. From this, it can be construed that the adherent passive oxide film on aluminium alloy will be reduced to some extent, which will give rise to a high *CR* compared to the pure aluminium sample. After the absorption time, a high volume of hydrogen gas started evolving both in HCl and sulphuric acid, after 120 min. It was observed that in HCl 19.1  $\text{cm}^3$  of hydrogen gas evolved in the control sample while 7.8  $\text{cm}^3$  evolved in 8 g/L *P. conophora* inhibitor. In sulphuric acid, 22.1  $\text{cm}^3$  of hydrogen gas was evolved in the control sample while 16.5  $\text{cm}^3$  evolved in *P. conophora* leaf extracts. Therefore, the hydrogen gas evolution rate was found more reduceable at the 8 g/L concentration of the inhibitor as a result of more adsorption layer formation on the alloy surface. This agrees with a previous study that reported that as the volume of hydrogen gas evolved decreased, the concentrations of *J. curcas* increased [36].

**3.4.2. Inhibition efficiency.** Figs. 8 and 9 show the *IE* variation with immersion time. It was observed that as there was a rise in the extract concentration, there was a proportionate increment in *IE*. As shown in the figures, the optimum *IE* was reached after 60 min of exposure of the samples after the latency period, which is a period of initiation of reaction between the acids and the sample surfaces,

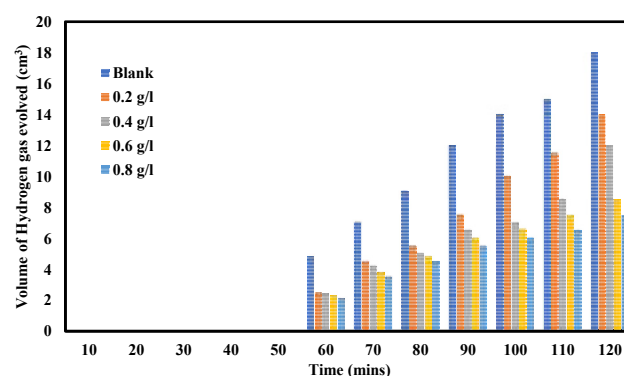


Fig. 6. Evolution of  $\text{H}_2$  volume with time for Al–Zn–Cu alloy in 3M HCl using *Plukenetia conophora* leaf extract as inhibitor

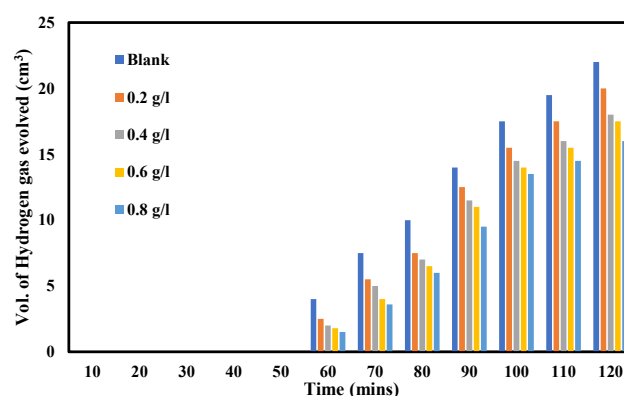


Fig. 7. Evolution of  $\text{H}_2$  volume with time for Al–Zn–Cu alloy in 3M  $\text{H}_2\text{SO}_4$  using *Plukenetia conophora* leaf extract as inhibitor



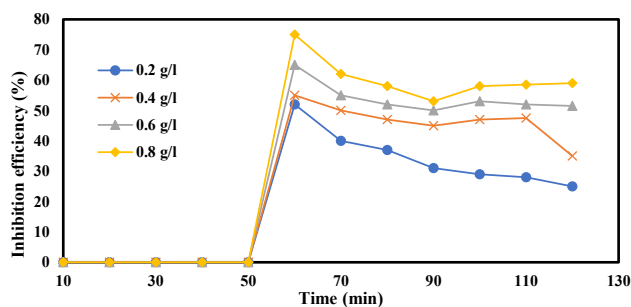


Fig. 8. Inhibition efficiency vs. immersion time of Al-Zn-Cu alloy in 3 M HCl via *Plukenetia conophora* leaf extract

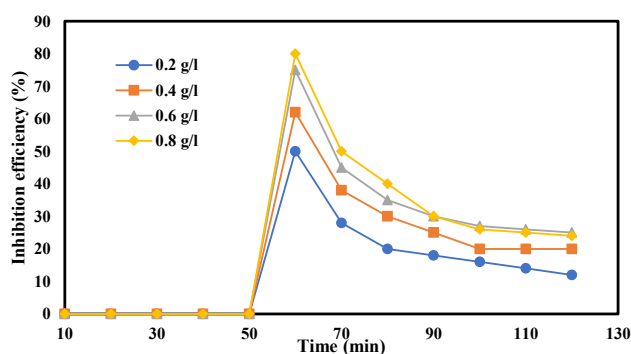


Fig. 9. Inhibition efficiency vs. immersion time of Al-Zn-Cu alloy in 3 M H<sub>2</sub>SO<sub>4</sub> using *Plukenetia conophora* leaf extract

absorption time of the acid into the alloy. At the latency period, below 60 min of exposure time, there was a slow reaction between the acid and the oxide film on the aluminium surface [37]. The passive oxide film serves as a barrier between the Al alloy surfaces and prevents the acid solution from reaching the sample surface, bringing about a decrease in CR and higher IE, as shown in Figs. 8 and 9. However, after the penetration of the acid into the surface, the CR increases while the IE was gradually decreasing. Similar trends were observed at all different inhibitor concentrations (0.2–0.8 g/L), which show that the CR reduces while there was a rise in IE owing to increment in the inhibitor concentration. Above 60 min of exposure, the inhibition efficiencies were gradually decreasing due to the reduction in the rate of corrosion. This can be due to the formation of a passive layer acting between the metal substrate and the environment [22].

The initial CR of HCl is faster leading to a faster rate of passive film formation on the Al alloy surface due to the presence of inhibitor. The passive film prevents a further reaction between the sample surface and the environment. This will lead to reduced CR at longer exposure times and thus higher IE. However, in the H<sub>2</sub>SO<sub>4</sub> environment, the initial CR is very slow because sulphuric acid is less aggressive and takes a longer time to remove the thin passive film on the Al alloy sample surface. At longer exposure time, the CR increased due to the direct reaction between the sample surface and the acid after removal of the initial passive film leading to lower IE. The inhibition action of the deposited plant extract on the surface

of aluminium alloy can be due to the presence of phytochemical constituents in the leaf extract, as shown in Table 2. From Figs. 8 and 9, it was observed that the inhibition efficiencies at different concentrations began to reduce and after some point became stable probably due to protective film formation on the Al alloy surface resulting from the interaction between the constituents of the extract and the Al alloy. Also, comparing the effectiveness of the inhibitors, it can be deduced that the inhibition efficiencies are highest at the 0.8 g/L inhibitor concentration (optimum value).

### 3.5. Electro-potential method

Potentiodynamic polarisation curves for aluminium alloy in 1 M HCl solution in the presence and absence of *P. conophora* leaves extract at room temperature are displayed in Fig. 10. The presence and increased amount of the inhibitors affect the corrosion potential, as shown in the figure. However, the higher the concentration of the extracts the more the curve shifts to the positive potential direction, thus indicating a corrosion inhibiting effect. The nature of the inhibitors, mode of action and mechanism of the reaction was determined through electrochemical measurements (Fig. 10). The effects of the extract in the absence and presence of inhibitors on the electrochemical behaviour of the Al-Zn-Cu alloy in 1 M HCl solution were studied. Parameters including corrosion potential ( $E_{corr}$ ), corrosion current density ( $I_{corr}$ ), anodic and cathodic Tafel slopes ( $b_a$  and  $b_c$ ), CR and percentage of the IE were determined, as shown in Table 5. It was observed that the extract addition into 1 M HCl solution revealed limited significant change in  $E_{corr}$ . This implies that both the anodic and cathodic reactions of the corrosion are being controlled by the plant extracts. This means that the corrosion inhibition of the aluminium alloy in 1 M HCl based on the extract used is under mixed-type inhibitor [15]. With an increase in the concentration of the inhibitor, the  $E_{corr}$  values shifted to the negative side the more. It was also observed that the  $I_{corr}$  values of the inhibited acids are seen to be lower compared to uninhibited acid. This suggests that the corrosion inhibition property increment can be attributed to the increment in the blocked fraction by inhibitor molecules adsorption on the surface of the electrode [38]. Thus, a regular reduction in  $I_{corr}$  is observed as there is an increment in the

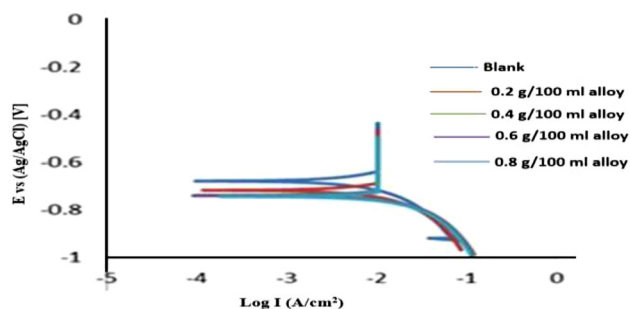


Fig. 10. Al-Zn-Cu alloy polarisation curves in different concentrations of inhibitor in 1 M HCl



Table 5. Potentiodynamic polarisation parameters for Al–Zn–Cu alloy in different concentrations of inhibitor in 1 M HCl

Inhibitor concentration (g/L)	$E_{corr}$ (mV versus SCE)	$I_{corr}$ ( $\mu\text{Acm}^{-2}$ )	$b_a$ (mV/dec)	$b_c$ (mV/dec)	$C_R$ (mm/y)	IE (%)
0	−741.70	16.67	148.74	174.49	170.49	–
0.2	−737.81	12.47	131.41	145.39	156.57	25.18
0.4	−738.65	11.61	126.64	107.05	151.87	30.39
0.6	−716.87	9.92	107.75	103.19	138.56	40.48
0.8	−741.95	6.22	99.72	132.80	83.86	62.71

concentration. This shows that *P. conophora* leaves extract in 1 M HCl can be considered as a very good inhibitor for aluminium alloy. However, based on the  $E_{corr}$  values, the inhibitor can be categorised to be a mixed type inhibitor [13]. This observation is in agreement with the study of Adeyeye [15], which suggested that the various organic compounds like phenols, flavonoids, alkaloids, tannins, phenols, trypsin, oxalate, terpenoids, anthraquinones and anthraquinone are present in the plant extract. The IE values were realised to increase as the concentration of the extracts increases. Hence, a maximum rise in the linear IE at a concentration value of 0.8 g/L of *P. conophora* leaves extract in 1 M HCl was found to be 62.71%.

### 3.6. Adsorption isotherm

*Plukenetia conophora* extract contains organic compounds with polar atoms or groups that adsorb themselves to metallic surface. The electron density of the functional group donor and polarisability of the organic compound such as tannins, saponins, alkaloids and lignin in the extracts affects the strength or weakness of the adsorption bond. The improved corrosion inhibition is caused by the replacement of H atom attached to the C in the ring by a substituent group such as COOH, CHO, NH<sub>2</sub>, OH, NH or NO<sub>2</sub> [13–15]. The Langmuir isotherm plots of *P. conophora* leaf extracts in both aqueous solutions of HCl and H<sub>2</sub>SO<sub>4</sub> displaying the variation of  $C/\theta$  against C after 12 days exposure were shown in Figs. 11 and 12, respectively. The plots showed that the adsorption mechanism of the leaf extract of *P. conophora* in both acidic media perfectly obeys the Langmuir adsorption

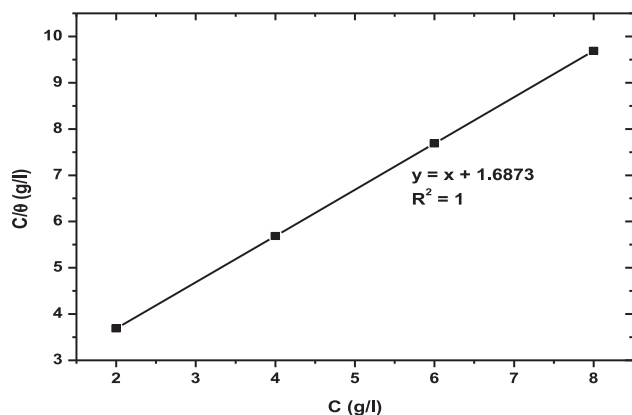
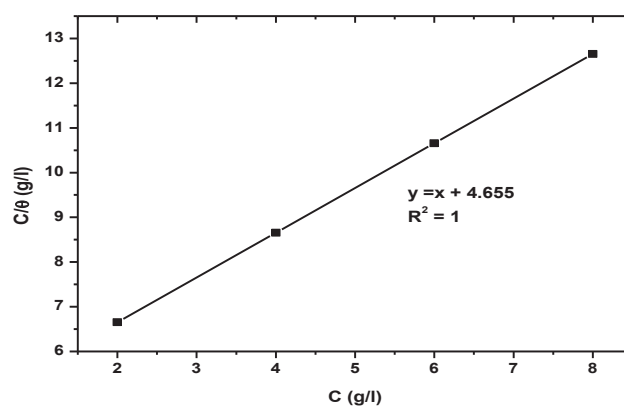


Fig. 11. Langmuir isotherm adsorption of the inhibitor on Al–Zn–Cu alloy surface in 1 M HCl after 12 days exposure

Fig. 12. Langmuir isotherm adsorption of the inhibitor on Al–Zn–Cu alloy surface in 1 M H<sub>2</sub>SO<sub>4</sub> after 12 days exposure

isotherm model. The experimental data were well fitted with a regression coefficient,  $R^2$  of 1 at a fixed slope of 1 in agreement with the model equation (Eq. 7). These results indicated that Langmuir adsorption isotherm is very suitable for the evaluation of the extract's adsorption mechanism of *P. conophora* leaf in the media. From the intercept, the adsorption isotherm equilibrium constant,  $K_{ads}$ , of the *P. conophora* leaf extract for both media were evaluated as shown in Table 6.

The standard Gibbs free energy values of the adsorption isotherm,  $\Delta G_{ads}$  were determined to be  $-81.54 \text{ kJ mol}^{-1}$  in HCl environment and  $-35.11 \text{ kJ mol}^{-1}$  in H<sub>2</sub>SO<sub>4</sub> solution, as shown in Table 6. These negative values indicated that the corrosion reaction is spontaneous in both media. The higher negative value of the  $\Delta G_{ads}$  in HCl environment agrees with the previous observation that the reaction is more aggressive and spontaneous in HCl medium than in H<sub>2</sub>SO<sub>4</sub> medium. In addition, since the slope of the isotherm did not deviate from unity in both media, this may indicate that there is little or no interaction among the adsorbed species on the metal surface [39]. This agrees with the Langmuir isotherm model assumption.

Table 6. Parameters of Langmuir adsorption isotherm for *Plukenetia conophora* (PC) extract in 1 M HCl and H<sub>2</sub>SO<sub>4</sub> aqueous solution at after 12 days exposure

Plant extract	Slope	$K_{ads}$ (g/L)	$R^2$	$\Delta G_{ads}$ (kJ mol <sup>−1</sup> )
PC in 1 M HCl	1.000	0.593	1.000	−81.54
PC in 1 M H <sub>2</sub> SO <sub>4</sub>	1.000	0.215	1.000	−35.11

## 4. CONCLUSION

The inhibitive property of the extract of *P. conophora* on the corrosion of Al–Zn–Cu alloy in acidic media has been investigated. The leaf extract of *P. conophora* acted to be a suitable and efficient corrosion inhibitor of aluminium alloy in acidic media. The *IE* was higher in the hydrochloric acid environment because the acid ionised more readily, and thus made the inhibitor more easily absorbed and formed a protective film on the Al alloy sample surfaces than in sulphuric acid. The inhibition of the corrosion of aluminium alloy by ethanol extract of *P. conophora* leaf was due to the phytochemical constituents in the plant extract. The negative standard Gibbs free energy values of the adsorption isotherm specified that the adsorption of leaf extract of *P. conophora* on the Al alloy sample surface was spontaneous. The adsorption mechanism of the inhibitor (*P. conophora*) in both acidic media perfectly obeys the Langmuir adsorption isotherm model.

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