



Inhibitive properties of *Carica papaya* leaf extract on Aluminium in 1.85M HCl

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ABSTRACT

The inhibition of aluminium metal corrosion in 1.85 M hydrochloric acid solution using extract of *Carica papaya* leaf was studied using gasometric technique. Aluminium coupons were immersed in test solutions of un-inhibited 1.85 M HCl and those containing extract concentrations of 10 %, 20 %, 30 %, 40 % and 50 % (v/v) at room temperature. The volume of hydrogen gas evolved as a result of the rate of reaction between aluminium coupons and the acid extracts was recorded. The inhibition efficiency of the extract was determined and the adsorption isotherm of the process was estimated using Temkin, Freundlich, Frumkin and Langmuir adsorption theories. The microstructure examination was also determined. The result of the investigation induced that the *Carica papaya* leaf extract retarded the acid induced corrosion of aluminium with a reduction in the volume of hydrogen gas evolved per increasing extract concentrations. The adsorption studies revealed Langmuir isotherm as the best model for the adsorption of *Carica papaya* extract ($R^2 = 1$) on aluminium surface. The adsorption result with the microstructure of the coupons implied an involvement of chemisorption process in the interaction of the extract with aluminium metal.

Indexing terms/Keywords

Corrosion inhibition; *Carica papaya*; Isotherms; Morphology; Aluminium.

Academic Discipline And Sub-Disciplines

Chemistry

SUBJECT CLASSIFICATION

Corrosion Study

TYPE (METHOD/APPROACH)

Adsorption and surface morphological study of ecofriendly corrosion inhibitors

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INTRODUCTION

The deterioration of materials due to their chemical or electrochemical interactions with the surrounding environment is generally understood as corrosion. This is as a result of the natural tendency for metals to revert to more stable mineral form in its natural state [1]. Typical instances are seen in aluminum and iron, when attacked by oxygen to form aluminum oxide and iron oxide. Virtually all metals, with the exception of gold and platinum, will corrode in an oxidizing environment forming compounds either in their oxides, hydroxides or sulphides state. Even though it is a natural process for metallic materials to corrode, the speed at which it occurs depends greatly on the type of environment to which the material is exposed [2], [3], [4].

Corrosion inhibitors are substances that are added in small concentrations to corrosive media to decrease or prevent the reaction of the metal in the media [5], [6]. Quite a number of ways have been deployed in controlling corrosion via material selection, coatings, designs, inhibitors and cathodic protection. The use of inhibitors has been one of the most practical methods for protection against corrosion in acidic environment [7]. Basically, there are various types of corrosion inhibitors such as anodic inhibitors, cathodic inhibitors, mixed inhibitors and volatile corrosion inhibitors [8]. There are also classification based on synthetic (organic), metallic (inorganic) and green inhibitors (natural product). However, research has confirmed that some of the synthetic and inorganic inhibitors are toxic thereby causing failure of kidney and liver as well as mutation of the enzymes to mention few [6].

In recent times, there has been an increasing awareness on the use of environment friendly substances as corrosion inhibitors in place of the harmful synthetic chemicals. This has orchestrated the drive on the development of green corrosion inhibitors from plant extracts. These inhibitors turns out to be inexpensive, rich in natural biodegradable chemicals which are environmentally friendly, nontoxic and available in large quantities with good efficiency [9], [10], [11], [12], [13], [14]. The availability of organic compounds, such as tannin, saponins, alkaloids, in the natural plants is what is majorly responsible for the inhibitive traits that is found in the green inhibitors [15], [16].

Several plants extracts, have been tested as corrosion inhibitors for metals. A few of them are karanj (*Pongamia pinnata*), Kalmegh (*Andrographis paniculata*) *Xylopi ferruginea*, *Occimum viridis*, *Hibiscus subdariffa*, henna, *Acalypha indica*, *Phyllanthus amarus* and ginkgo [17]. In addition, other researchers have confirmed the inhibiting effect of Al-Mg alloy in chloride solution using Rosemary leaves [18], aluminium alloy in 0.5M HCl solution using *Euphorbia hirta* and *Dialum guineense* leaf extracts [19], aluminium in 2 M HCl using *Chromolaena odorata* leaf extract [20], [21], aluminium in 1 M solution of HCl using extract of *Ipomoea involucreta* [20], aluminium in 0.5 M HCl using *Vernonia amygdalina* plant extract [12] and aluminium in 0.1 M solution of HCl using *Zenthoxylum alatum* extract [22]. The present study aims at investigating the inhibitive, adsorptive characteristics of *Carica papaya* leaf extract and the surface morphology of the extract inhibition on aluminium specimen in 1.85 M HCl solution using gasometric technique.

EXPERIMENTAL

Aluminium Plate Sample

Aluminium specimen of chemical composition 0.57% Silicon, 1.18% Iron, 0.01% Magnesium, 0.11% Titanium, 0.31% Strontium, 0.01% Copper, 0.012% Lead and the remaining 93.10% being aluminium were used for the corrosion studies. The aluminium plate were mechanically pressed cut into coupons of dimension 24 mm x 14 mm with a thickness of 1 mm. The coupons were examined carefully to check for rough edges, which could influence the monitoring process. Each coupon was degreased by washing with ethanol, dried with acetone and preserved in desiccator to avoid moisture. All reagents used for the study were analar grade and distilled water was used for their preparation.

Acid Extraction and Preparation of Inhibitor Solutions

Leave of *Carica papaya* were air dried and pulverized into powder form. 10 g of the powder was refluxed with 200 cm³ of 1.85 M HCl solution for two hours and left overnight before it was filtered with filter paper. Extract concentration of 10 %, 20 %, 30 %, 40 %, 50 % volume/volume (v/v) were prepared through serial dilution using 1.85% HCl filtrate for further use to study the inhibition abilities of the extract. The experimental set up (Figure 1) is similar in literature with that elsewhere [11].

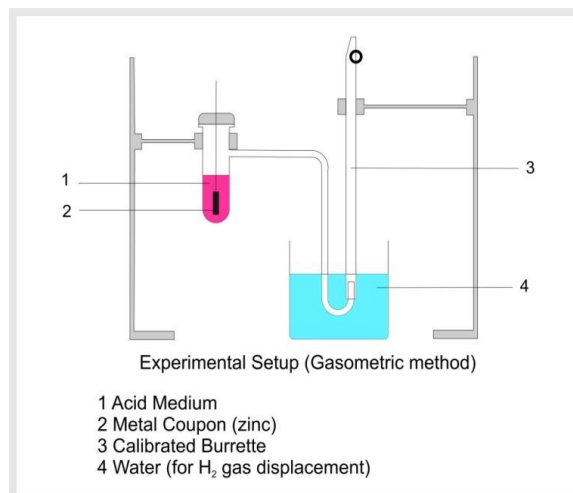


Figure 1: Experimental set up for gasometric method

Gasometric Measurement

The gasometric (gas-volumetric) technique provides a rapid and reliable means of ascertaining any perturbation by the inhibition with regard to gas evolution at the corrodent interphase. Each weighed specimen was dropped into the mylius cell containing 50 cm³ of the blank solution, 1.85 M HCl, as the control and also in the presence of the various extract concentrations (10% - 50%) for *Carica papaya* extract at room temperature, the principle of which hydrogen gas is given off as a result of aluminium reacting with HCl. The volume of hydrogen gas evolved per minute interval was recorded in each volume/volume dilutions. At the end of each experiment of hydrogen gas evolution, each aluminium specimen was withdrawn from the mylius cell and weighed. The process is in resemblance with method used somewhere else [21] which connote that rate of reaction corresponds to rate of corrosion damage of the aluminium in uninhibited and inhibited solutions. However based on the assumption made in the literature[21], the following relationships were also obtained. The basis for this is represented in Equation 1.

$$\Delta V \propto \Delta W \quad (1)$$

$$\frac{d\Delta V}{dt} \propto \frac{d\Delta W}{dt}$$

but

$$\frac{R \propto dW_m}{dt} \propto \frac{d \Delta V_{H_2}}{dt} \quad (2)$$

Where

α = proportionality sign

ΔV = Volume of hydrogen gas evolved

ΔW = Metal weight loss due to corrosion

R = Corrosion rate

t = Time (sec)

Thus to determine Equation 2, it is important to develop a relationship between volume evolved and time of evolution. This was attained by a polynomial regression analysis of the volume of hydrogen gas against time leading to Equation 3 [23].

$$V = c + bt + at^2 \quad (3)$$

Thus

$$R = \frac{dv}{dt} = b + 2at \quad (4)$$



Adapting Equations 3 and 4 to the volume-time measurement for individual concentration and using the example for measurement relating to 50 cm³ concentration of *Carica papaya* extract in 1.85 M HCl, the corrosion rate model can be shown as:

$$V = 0.325t^2 - 2.725t + 1.375 \quad (5)$$

$$\frac{dv}{dt} = 0.650t - 2.725 \quad (6)$$

The corrosion rate R, is derived from the second differential of V_{in} as in $d^2V_{in}/dt^2 = \pm C$. The rate of evolution of the gas was determined from the slope of the graph of volume of gas evolved against time. The inhibition efficiency (IE) and inhibitor surface coverage (θ) was then determined using equations 7 and 8 respectively [24].

$$I.E(\%) = \frac{V_H - V_{HI}}{V_H} \times 100 \quad (7)$$

V_H = Volume of hydrogen evolved without inhibitor

V_{HI} = Volume of hydrogen gas with inhibitor

$$\theta = \frac{IE}{100} \quad (8)$$

RESULTS AND DISCUSSION

Gasometric Data

The free corrosion of the aluminium metal in 1.85 M HCl was characterized by rapid effervescence resulting from hydrogen evolution in the presence of the blank solution (0% extract) and the various extract concentrations (10% - 50%) for the *Carica papaya* leaf extract. Figure 2 shows the volume of hydrogen evolved during the corrosion reaction of aluminium in 1.85 M HCl containing different concentration of *Carica papaya* leaf extract into the corrodent indicating that the extract actually inhibits corrosion of aluminium in the acidic environment when compared to the blank. Further reduction in the volume of hydrogen gas was observed as the extract concentration increased 10% - 50%, v/v; suggesting the inhibitive action was concentration dependent. The plot revealed slow rate of hydrogen evolution at the commencement of the reaction and after an incubation period, which correspond to the time interval needed by the corrodent to break down the pre immersion oxide film on the aluminium surface. It was observed that the volume of the hydrogen gas varies directly with reaction time, which as well, is in line with observations made elsewhere in literature [25], [26], using *Ananas sativum* as an inhibitor for aluminium metal in HCl media.

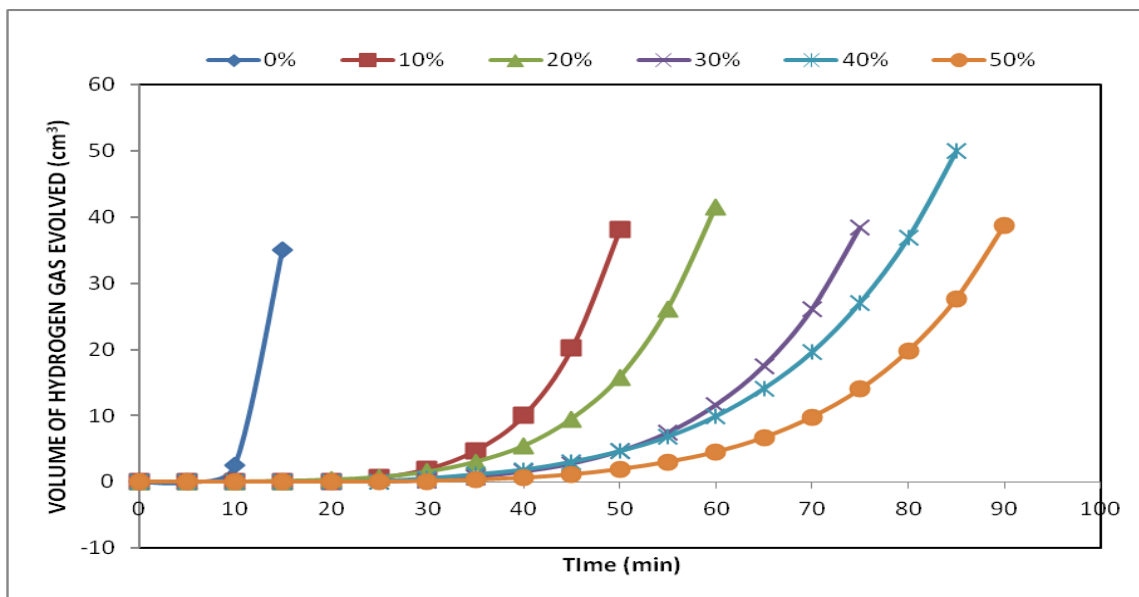


Figure 2: Variation of volume of evolved hydrogen gas (cm³) with time (min) for aluminium coupon of different concentration of *Carica papaya* leaf extract in 1.85 M HCl solution at room temperature.

Corrosion Rate

The corrosion rate value of *Carica papaya* extract on Aluminium was calculated (Equation 4) for the blank and also for the extract concentrations. Figure 3 shows a plot of corrosion rate of *Carica papaya* extract with respect to time. From the results obtained, it was observed that the corrosion rates drastically decreased with increase in concentration of the extracts in comparison to the blank. The 50% v/v extract have the lowest corrosion rate, which depict that the inhibitive action of the extract is concentration dependent.

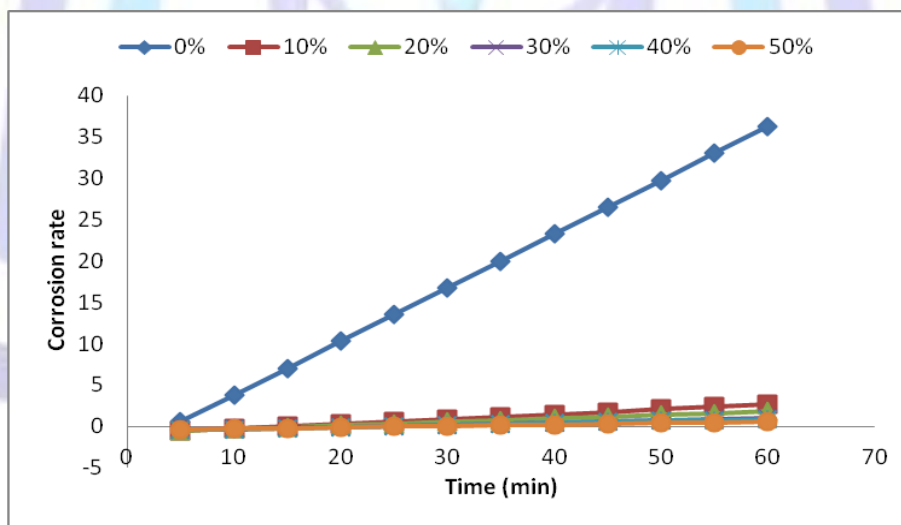


Figure 3: Corrosion rate of varying concentrations of *Carica papaya* leaf extract with time (min) on aluminium coupon in 1.85M HCl solution at room temperature.

Effect of Extracts Concentration on Inhibition Efficiency

The inhibition efficiency was determined from rate of hydrogen evolution result using equation 7. Figure 4 shows the plot of the inhibition efficiency against time of *Carica papaya* extract in 1.85 M HCl. It was observed that the inhibition efficiency values increased with increasing extract concentration. All extract concentrations had maximum I.E (%) values between 10 - 16 min thus indicating the period for highest optimization/exposure time range. This obtained result follows the same pattern reported [9] in the study of the inhibitive effect of plant extracts on the corrosion of aluminium in acidic media.

Carica papaya leave was reported to contain alkaloids, cyanogenics glycosides, flavanoids (aurone, chalcone, flavones and flavanol), phytates saponins and tannins while phytic acid and tannins are seen as non-toxic inhibitors for metal in aggressive media [27]. Hence anti-corrosion activity of *Carica papaya* extract in this study can be ascribed to phytic acid binding unto the cathodic sites on the metal surface. Tannin containing extracts are reported to contain varying inhibition efficiency and inhibition mechanism [28]; however tannins had demonstrated that inhibitive tendency is a function of molecular properties (absolute electronegativity, absolute hardness and the electron donating ability) of its constituent molecules. This accounts for the inhibition efficiency observed for *Carica papaya* extract in the work which agrees with literature [29], that observed natural tannins extract as better corrosion inhibition by virtue of better adherence to metallic substrates.

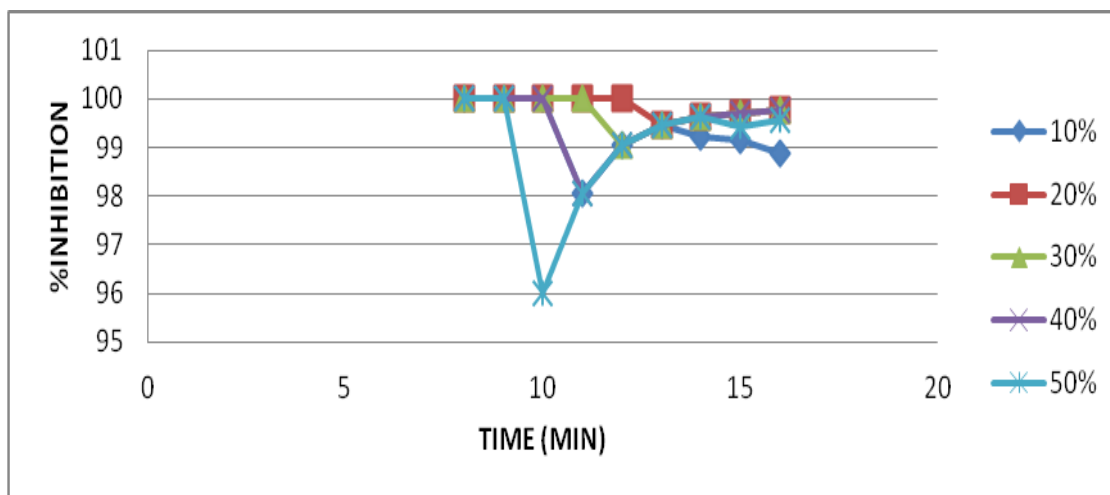


Figure 4: Percentage inhibition efficiency of varying concentration of *Carica papaya* leaf extract with time on aluminium coupons in 1.85 M HCl solution at room temperature.

Adsorption Isotherm

One possible mechanism for corrosion inhibition using organic compounds is the adsorption of the inhibitor on the metal surface which blocks the active sites and thus prevents further corrosion of the metal from taking place. The principle of which provides information about interaction among the adsorbed molecules themselves as well as with their metal surface [30]. Two main types of interaction can describe the adsorption of organic compounds namely; physical adsorption and chemical adsorption.

The degree of surface coverage value for *Carica papaya* was obtained from the hydrogen evolution measurement (Equation 8). The assumption of direct relationship between surface coverage and inhibition efficiency fitted into adsorption isotherms of Temkin, Freundlich, Frumkin and Langmuir and the correlation coefficients obtained (R^2) were used to conclude and validate the best fitted isotherm. The unity value of correlation coefficient obtained in the Langmuir isotherm is an indication that the adsorption of *Carica papaya* extract onto aluminium surface best fits into the Langmuir adsorption isotherm. The Langmuir isotherm has been observed to characterize chemisorptions of the adsorbed species and is expected to have a correlation coefficient of unity [25]. The R^2 value (Figure 5) indicated that the monolayer of the *Carica papaya* extract must have been attached to aluminium surface without lateral interaction between the adsorbed species.

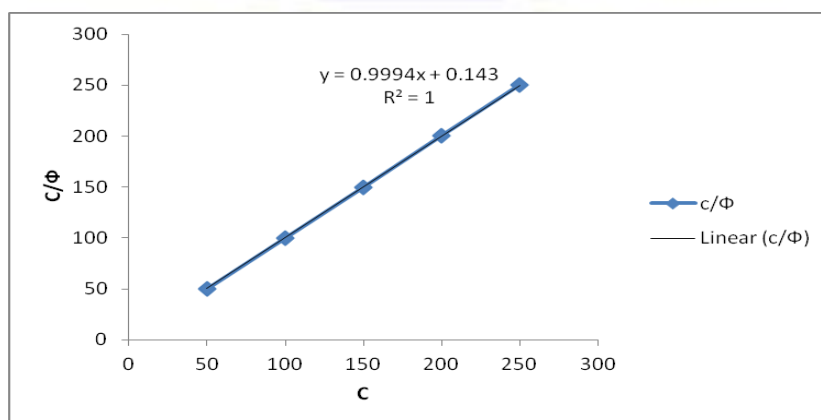


Figure 5: Langmuir adsorption plot for aluminium corrosion in *Carica papaya* leaf extract in 1.85 M at 15 min.

Result of the study shows that *Carica papaya* leaf extract inhibited the acid induced corrosion of aluminium by virtue of adsorption on its component onto the metal surface. This inhibition process is a function of the aluminium metal as well as the *Carica papaya* extract concentrations which is so much dependent on the number of adsorption sites observed. This could be attributed to the fact that *Carica papaya* leaf extract contains different chemical compounds.

Surface Morphological Studies

The surface morphology of the aluminium metal was studied using scanning electron microscope (SEM). The SEM pictures are useful for examining the fine structure of cells and can show the depth of rear surface aluminium alloyed layer with an advantage of provision for practical range of magnifications that is suitable for investigation. The images at 10 μ m of the aluminium surfaces at uninhibited (0%) and inhibited (10%; 30% and 50% v/v) are shown in Figure 6. The structural distinctive of the aluminium metal increases with the *Carica papaya* extract concentrations. The surface of the metal is rapidly oxidized in the control (A) and the glint effect of the aluminium metal is appreciated in the 50% (D) and partially superficial in the 30% (C). This spine-like array observed in D and C was totally battered in B and A, with insinuation that 10% is not enough concentration to effect inhibition. Possible consequence of this may result in fracture surfaces and intergranular fracture which may result in precipitation of a second phase particles along the weakened grain boundaries if the aluminium metal is used in the studied acidic environment without inhibition.

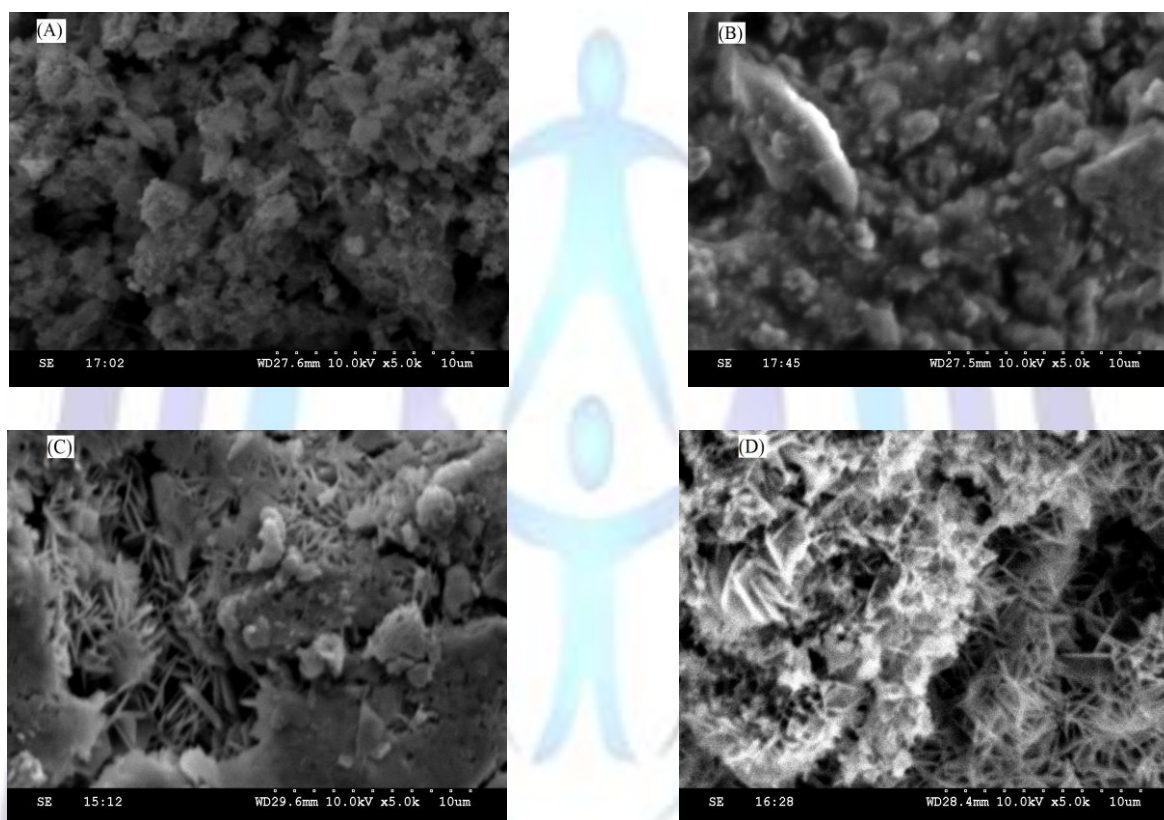


Figure 6: SEM images of aluminium coupons in 0% (A); 10% (B); 30% (C) and 50% (D) *Carica papaya* leaf extract in 1.85 M HCl solution

Conclusion

The crude leave extract of *Carica papaya* as inhibitor for aluminium corrosion in 1.85M HCl has been studied in this work. Inhibition efficiency of the extract increases with increase concentration of the extract with 50% v/v observed as the optimum inhibition concentration. The corrosion inhibition was due to the photochemical constituents of the extract on the metal surface which blocks its active sites by phenomenon of chemical adsorption. The extract obeyed Langmuir adsorption isotherm in all concentrations studied and the morphological images inferred chemisorption as the surface adsorption route in the inhibition process.

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