THE INTERNATIONAL JOURNAL OF
SCIENCE & TECHNOLEDGE

Corrosion Inhibition Efficacy of *Cninodosculus chayamansa* Extracts on Aluminum Metal in Acidic and Alkaline Media

Okeke P. I.
Assistant Lecturer, Alvan Ikoku Federal College of Education, Owerri, Imo State, Nigeria
Maduka O. G.
Assistant Lecturer, Department of Basic Science,
Alvan Ikoku Federal College of Education, Owerri, Imo State, Nigeria
Emeronye R. U.
Assistant Lecturer, Department of Basic Science,
Alvan Ikoku Federal College of Education, Owerri, Imo State, Nigeria
Akalezie C. O.
Lecturer, Department of Chemistry, Federal University of Technology Owerri, Imo State, Nigeria
Mughele K.
Lecturer, Department of Chemistry, Federal University of Technology Owerri, Imo State, Nigeria
Achinihu I. O.
Assistant Lecturer, Department of Chemistry,
Alvan Ikoku Federal College of Education, Owerri, Imo State, Nigeria
Azubuike N. E.
Lecturer, Alvan Ikoku Federal College of Education, Owerri, Imo State, Nigeria

Abstract:
The corrosion behavior of extracts of Cninodosculus chayamansa(CC) on aluminum in 0.5 M NaOH and 1 M HCl was investigated using gravimetric technique. The effects of temperature, concentration and the addition of KI on the inhibition performance of the extracts were assessed. The experimental findings revealed that the extracts of CC inhibited corrosion reaction in both the acidic and alkaline environments with the effect becoming more vivid as the CC extract concentration increased, weight loss increased as temperature increased. The addition of KI to the extracts of CC significantly reduced the rate of corrosion in the alkaline environment and slightly in the acidic environment. Experimental data was seen to fit the Langmuir isotherm, this revealed that the organic constituents of the extracts chemically adsorbed on the metal/surface interface.

Keywords: *Acid and alkaline corrosion inhibition, gravimetric technique, aluminum, Cninidosculus chayamansa, adsorption*

1. Introduction

Aluminum and its alloys find widespread industrial, structural and scientific research applications. Unfortunately like many metals, aluminum and its alloys are susceptible to corrosion when they are put to use in acidic and alkaline environments, this is often associated with considerable safety hazards and economic losses since the massive breakdown of engineering structures resulting from the corrosion of metals have been reported [1-3]. A practical approach to reduce corrosion damage in hostile fluid environments involves the use of corrosion mitigating additives to lessen the corrosion rate. One of the methods commonly used is the addition of organic corrosion inhibitors to the corrosive media.

A number of heteroatom-containing organic compounds as well as compounds with extensive conjugation have been reported to effectively hinder the corrosion metals in acidic and alkaline environments [3-6]. The addition of such organic inhibitors consisted in the adsorption of the molecules into the metal/solution interface where the adsorbed file acts as a protective barrier between the metal surface and the corroding medium deactivating the active corrosion sites [7-9]. Attention has been shown in the use of these organics derived from the relative ease of synthesis and safer handling compared to the heavy metal-based inorganic inhibitors. However, the widespread use of these organic corrosion inhibitors is often limited because it is cost effective and quite toxic. As a result, great interest and focus is been directed towards organic corrosion inhibitors that are eco-friendly, inexpensive readily available, and renewable. In this regard, lots of research effort has been put into natural products of plant origin, such as extracts from roots, barks, leaves, and seeds for corrosion inhibition efficacy in the scientific community. It has been reported that these plant extracts are highly effective in the inhibition of corrosion of aluminum and its alloys. This has been linked with the organic constituents in these plant extracts therein, including alkaloids, tannins, fats and oils, proteins, pigments, resins, flavonoids, and carbohydrates with molecular structures bearing close similarities with those of conventional organic inhibitors [10-13]. Such plant extracts could thus serve as sources of non-toxic and inexpensive corrosion inhibiting additive in acidic and alkaline environments. The use of natural products of plant origin as corrosion inhibitors has been widely investigated by several authors [14-22].

Cninodosculus chayamansa(CC) is nicknamed tree spinach but it contains more than twice as much proteins, calcium, vitamin C, iron, fiber, caronteniods as spinach. It is very easy to grow and readily available, like many tropical plants, it contains hydrocyanic glucosides in its leaves. It is used in traditional remedy for the treatment of diabetes, rheumatism, gastrointestinal disorders and inflammation-related diseases [23]. Ihebrodike *et al*,[24] reported experimental and theoretical assessment of the inhibiting action of *aspilia africana* extract on corrosion of aluminum alloy AA3003 in 0.4 and 0.5 M HCl, the result showed that the plant extract effectively inhibited the corrosion of aluminum in acidic environments, with inhibition efficiency increasing with extract concentration and temperature rise. To the best of our knowledge, *CC* has not been studied for corrosion inhibition abilities on aluminum. The present study investigates the inhibitive efficacy of *CC* leaves on aluminum in acidic and alkaline environments and the effect of addition of KI to the solutions using the gravimetric technique.

2. Materials and Methods

2.1. Materials Preparation

2.2.1. Metal Specimen

The aluminum metal was obtained from First Aluminum Company Ltd, Port Harcourt, Rivers State, Nigeria. The weight percentage composition is given in table 1

Element	Si	Fe	Cu	Mn	Mg	Zn	Ti	Cr	Ni	Va	Pb	Al
Weight %	0.247	0.658	0.03	0.079	0.01	0.037	0.016	0.004	0.003	0.007	0.014	98.894

Table 1: Weight percentage composition of aluminum metal

The aluminum metal sheets of thickness 1mm were cut into coupons of dimension 3cm x 3cm with a hole drilled on its side for easy suspension into the corroding solution. They were degreased in absolute ethanol, rinsed with water, dipped into acetone, air dried, labeled properly and stored in moisture free desiccators prior to use. The chemicals and reagents used for the study were of analytical grade.

2.1.2. Preparation of Plant Extracts

Leaves of *C. chayamansa* were collected, washed, air dried to a constant weight, ground to a fine powder, and then stored in labeled glass jars before use. The stock solutions of the leaves were prepared by dissolving 50g in 1500cm^3 of 0.5 M NaOH and 1 M HCl solution. The resultant solutions were boiled under reflux for 3 hours, allowed to cool to room temperature, then filtered and stored in air tight containers and kept away from sunlight, from the stock solution concentrations of 50mg/L, 100mg/L, 200mg/L, 300mg/L, 400mg/L and 500mg/L were prepared for gravimetric analysis.

2.2. Gravimetric Experiments

Aluminum coupon sheets of 3cm x 3cm x 1cm were used for the weight loss measurements. The total geometric surface area of the coupons exposed was 0.1911dm^2 and the weight loss of the aluminum coupons was calculated as 3.31675g.

2.2.1. Blank Experiment

For the weight loss measurements, two beakers labeled A and B containing 300mL of 0.5 M NaOH solution served as the blank corrodent for the alkaline medium while same containing 1 M HCl served as blank for the acidic medium. The aluminum coupons were carefully weighed, tagged, and suspended in the reaction beakers containing the respective test solutions via the 3mm diameter hole on the coupon with the aid of twine rope and glass rod. They were retrieved at 6 hour interval, chemically cleansed immediately using HNO_3, washed with bristle brush in water, dipped in ethanol and then acetone for drying. They were then air dried and reweighed. The weight loss in W was calculated in grams as the difference between the initial weight prior to immersion and the final weight after retrieval of the coupons. The weight loss in g/dm^2 was then obtained by dividing the weight loss W in gram by the total surface area (A) of the coupons.

2.2.2. Inhibitor Experiment

A second experiment set-up tagged inhibitor experiment was conducted with the same procedure as with the blank experiment but with the introduction of various amounts of plant extracts as the inhibitor, concentrations ranging from 50mg/L to 500mg/L were used. We had six beakers containing 300mg/L each of 0.5 M NaOH + inhibitor and 1 M HCL + inhibitor. These served as the corrosion inhibition experiment for the alkaline and acidic media. Coupons were retrieved after 6 hours cleansed chemically and the weight loss calculated as in the blank experiment.

2.2.3. KI Experiment

A third experimental set up tagged the KI experiment was carried out, here, one beaker containing 0.000001 M KI + 0.5 M NaOH served as the blank for KI in alkaline medium and another containing 0.000001 M KI + 1 M HCl served as the blank for KI in the acidic medium. The same set up was done but with the introduction of 200mg/L and 400mg/L of the inhibitor, coupons were retrieved after 6 hours of immersion and reweighed, then weight loss calculated.

2.2.4. Temperature Experiment

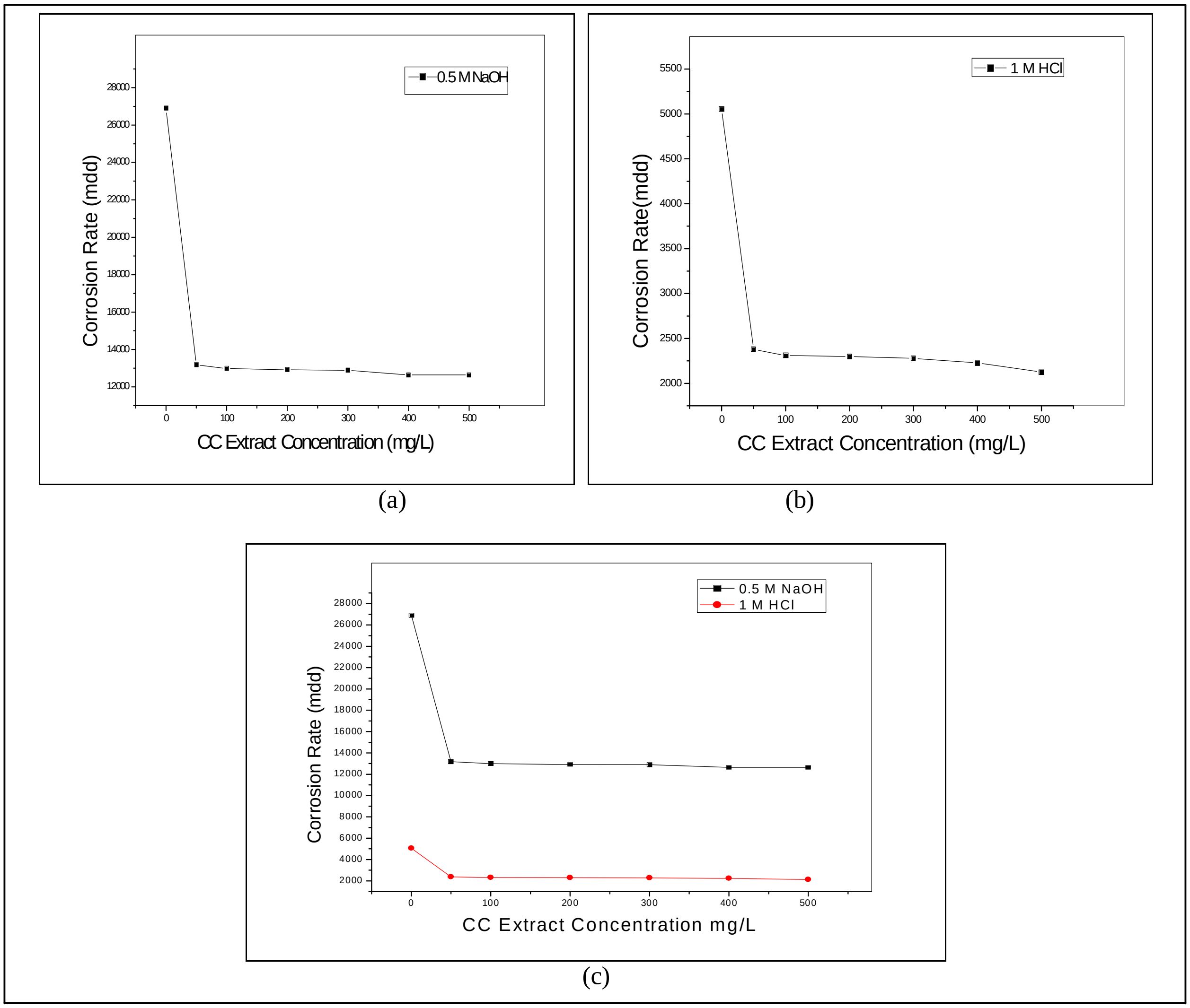
The fourth experimental set up was carried out using the highest concentration of 500mg/L. two beakers each of 300mg/L of 500mg/L inhibitor + 0.5 M NaOH were set up at temperatures of 30^0 and 60^0 using a hot water bath for the alkaline medium and another beaker was set up as above but with 1 M HCl for the acidic medium. Also, coupons were retrieved after 6 hours of immersion and reweighed, and then weight loss calculated.

3. Results and Discussion

All tests were conducted under total immersion conditions in 300mg/L of aerated and unstirred test solutions. Each test was run in triplicate to ascertain the reproducibility of the data with standard deviation ranging from 0 to 00031.

3.1. Corrosion Rates and CC Extract Concentrations

The corrosion rates of aluminum coupons in the various test solutions were evaluated from the gravimetric results.



(a)

(b)

(c)

Figure 1: Corrosion rate of aluminum in (a) 0.5 M NaOH (b)1 M HCl (c)Relationship between the corrosion rate of aluminum in 1 M HCl and 0.5 M NaOH as a function of CC extract concentration

Fig. 1(a) illustrates the corrosion rate of aluminum in 0.5 M NaOH as a function of *CC* extract concentration, the plot shows Al coupons corroding in 0.5 M NaOH without and with 50, 100, 200, 300, 400, and 500mg/L of *CC*. the result indicates that *CC* extracts clearly retarded the corrosion rate of Al in this alkaline medium at all concentrations with corrosion rate decreasing with increase in concentration. *CC* extract reduced the corrosion rate of Al sharply from 26894.9mdd to 13173.6mdd for addition of 50mg/L of the extract, increasing the concentration continued to reduce the corrosion rate as can be seen above. Fig. 1(b) shows the corrosion rate of Al in 1 M HCl as a function of *CC* extract concentration, the result showed that *CC* extract reduced the corrosion rate from 5054.9mdd to 2376.6mdd for addition of 50mg/L and down to 2125.5mdd for 500mg/L. Fig. 1 (c) depicts the relationship between the corrosion rates of Al in the alkaline and acidic environments. The result indicates that the corrosion rate in the acidic medium was steadily decreasing with increasing concentration up to 300mg/L concentration and then went up to an optimum at 500mg/L whereas in the alkaline medium, the corrosion rate decreased steadily in 50mg/L and up to 500mg/L.

3.2. Effect of Addition of KI

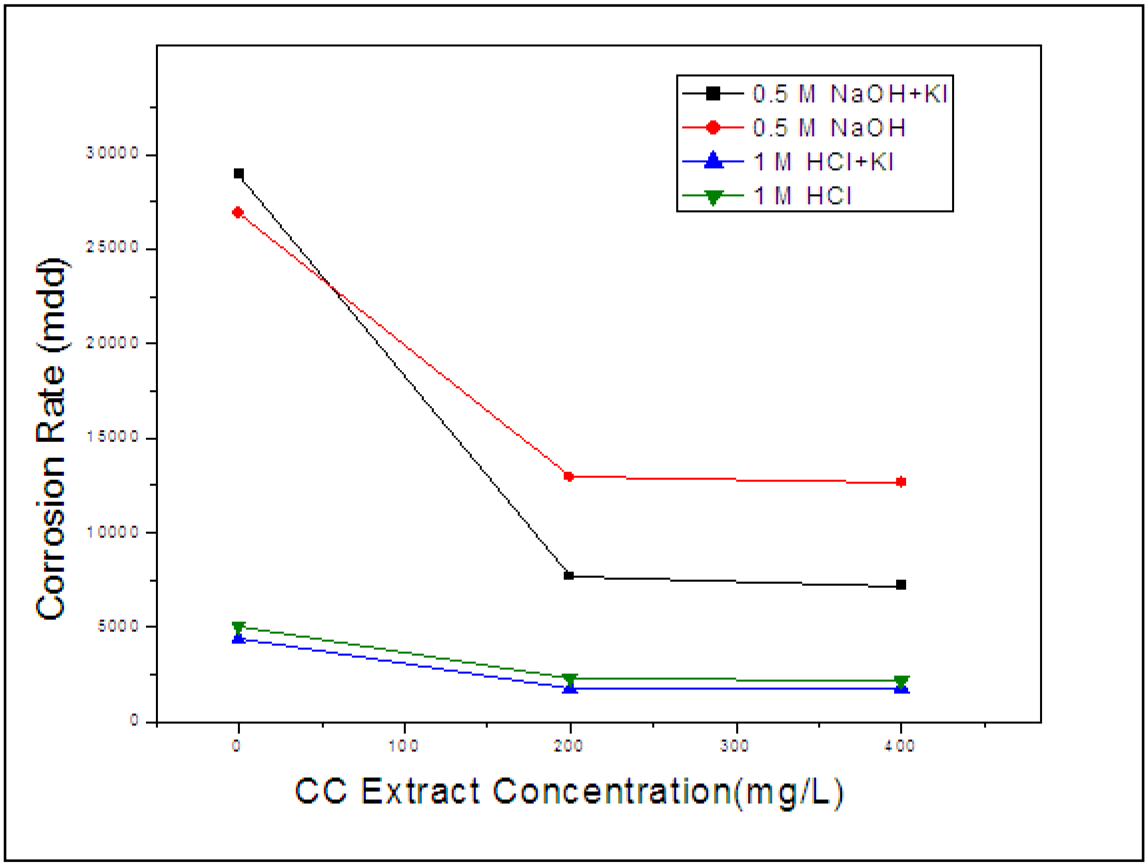
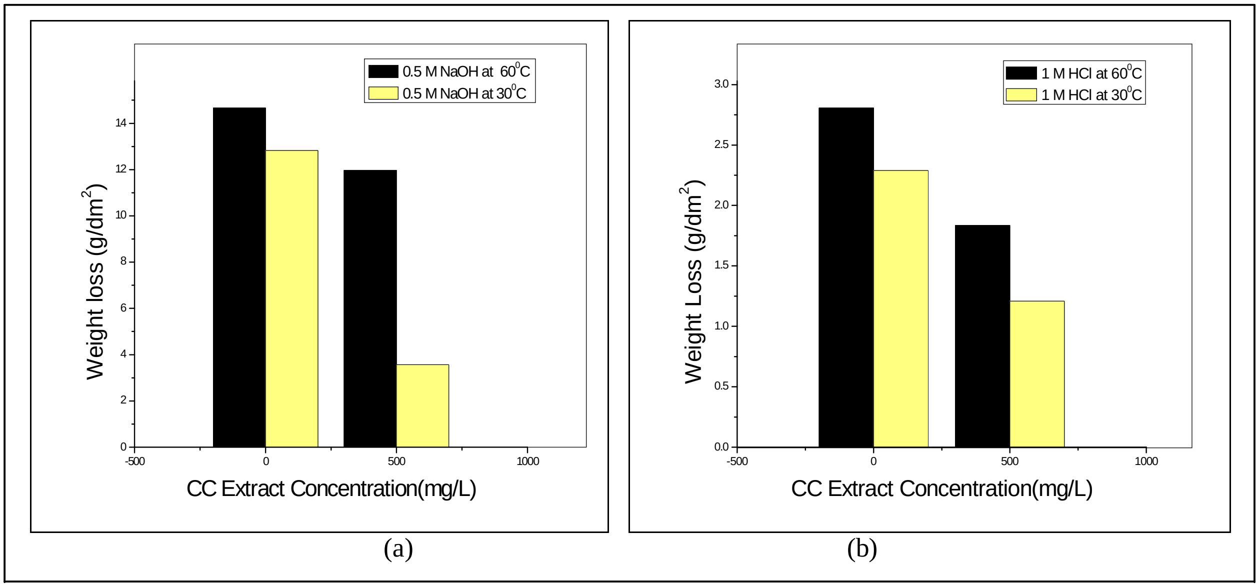


Figure 2: Corrosion rate of aluminum in 1 M HCl and 0.5 M NaOH with and without KI as a function of CC extract concentration

Fig. 2 illustrates Corrosion rate of aluminum in 1 M HCl and 0.5 M NaOH with and without KI as a function of CC extract concentration. This was done to assess the influence of halide additives on corrosion rate. It has been proven that addition of halide ions facilitates adsorption of organic-cation-type inhibitors during metal corrosion in acidic and alkaline solutions, the quality increases in the order $Cl^- < Br^- < I^-$ and it is also initiated by the specific adsorption of the anion onto the metal surface [25-26]. Consequently, if the protonated species contribute optimally to the reduction of the corrosion rate of the metal and the effectiveness of the extract, a synergistic decrease in the corrosion rate should be observed in the presence of the halide additives. On the other hand, if the molecular species in the extracts are more active, the halide additive will have a negligible effect [27]. Fig. 2 vividly describes how those iodide ions remarkably reduced the corrosion rate of aluminum. It showed that the effect is more in the alkaline medium with corrosion rate reducing with the addition of KI in 0.5 M NaOH in concentrations of 200mg/L and 400mg/L of *CC* extract. Where as, in the 1 M HCl medium the effect is less compared to the 0.5 M NaOH medium. However, the result depicts that corrosion rates reduced with increase in the concentration of the extracts for both the alkaline and the acidic medium as can be seen in Fig. 2. This can be due to the presence of more molecular species in the acidic medium. This phenomenon is referred to as synergistic effect as was described above.

3.3. Effect of Temperature



(a) (b)

Figure 3: Effect of temperature on the weight loss of aluminum in (a) 0.5 M NaOH and (b) 1 M HCl at 60^0C and 30^0C with and without CC extract

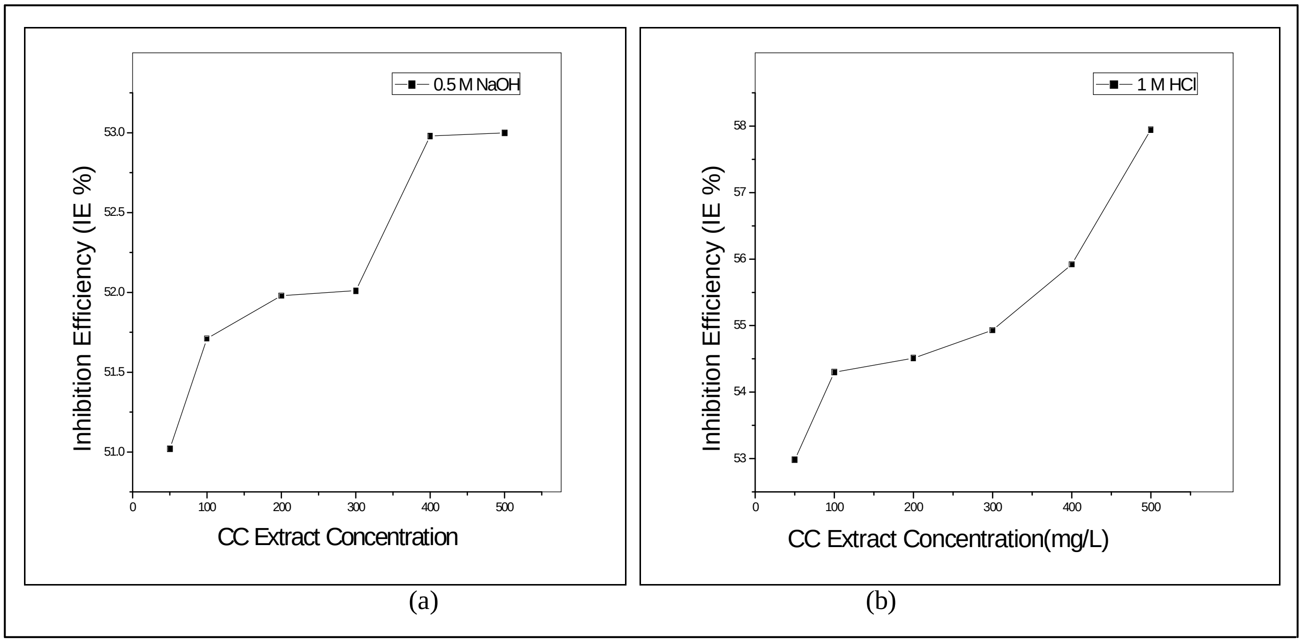
This was conducted to assess the effect of temperature on the corrosion processes of aluminum in the alkaline and acidic media. Experiments were carried out in both the inhibited and uninhibited systems. Fig. 3(a) showed the effect of temperature on the weight loss of Al in 0.5 M NaOH at 60^0C and 30^0C while Fig. 3(b) showed that for 1 M HCl, the results showed that weight loss increased with rise in temperature for both systems however, the effect is more in the alkaline medium with weight loss increasing from 3.56g/dm^2 to 14.66g/dm^2 from 30^0C to 60^0C but it went from 1.20g/dm^2 to 1.83g/dm^2 in the acidic medium. Nevertheless *CC* extracts were observed to retain their inhibitory ability at both temperatures as can be seen above that weight loss reduced with increase in concentration. This kind of phenomenon has been reported by Oguzie E. E. *et al* [28].

3.4. Inhibition Efficiency (IE %) and CC Extract Concentration.

The inhibiting effect of *CC* on aluminum corrosion was quantified and assessed by evaluating the inhibition efficiency IE (%) as given:

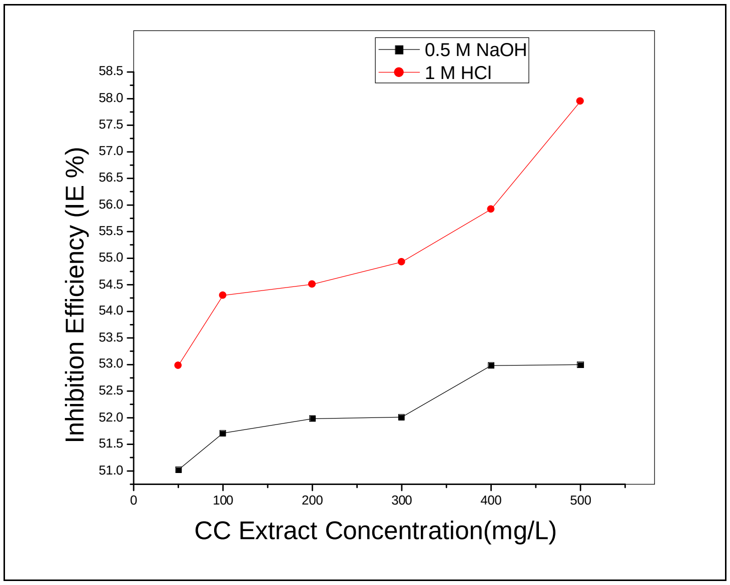
$$IE(\%) = \left(1 - \frac{W_1}{W_2}\right) x\, 100 \qquad (3.1)$$

Where W_1 and W_2 are the weight losses in inhibited and uninhibited corrodent, respectively



(a) (b)

Figure 4: Inhibition efficiency of CC extract for aluminum corrosion in (a) 0.5 M NaOH (b) 1 M HCl as a function of extract concentration



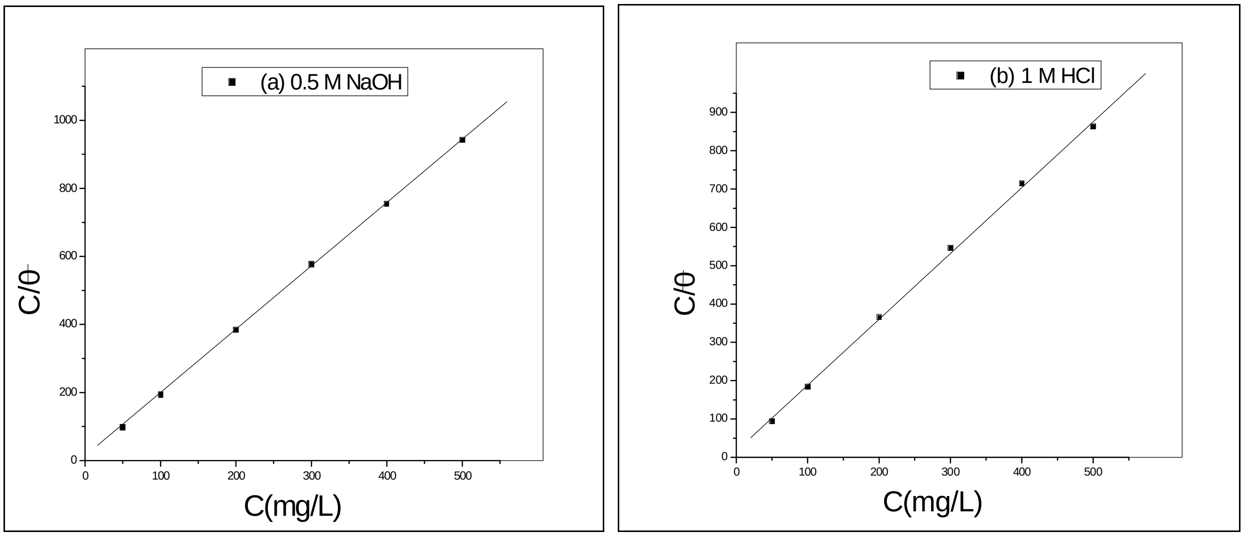
(c)

Figure 4(c): Relationship between the inhibition efficiency of CC extract for aluminum corrosion in 0.5 M NaOH and 1 M HCl as a function of extract concentration

Fig. 4 (a) demonstrates the inhibition efficiency of *CC* extract for aluminum corrosion in 0.5 M NaOH as a function of concentration, while Fig. 4 (b) demonstrates that for 1 M HCl. In Fig. 4 (a), inhibition efficiency increased steadily up to 300mg/L concentration and went sharply to 400mg/L and stabilized at 500mg/L this indicates that inhibition efficiency of *CC* extracts on aluminum is better at higher concentrations in this system. In Fig. 4 (b), inhibition efficiency increased steadily at all concentrations, showing that *CC* extract is effectively active at all concentrations in this system as has been studied by several authors on natural products for corrosion inhibition efficiency. Fig. 4 (c) illustrates Relationship between the inhibition efficiency of CC extract for aluminum corrosion in 0.5 M NaOH and 1 M HCl as a function of extract concentration. The result shows that inhibition efficiency is higher in the acidic medium compared to the alkaline medium, this indicates that *CC* extract is more effective in the acidic medium. However, inhibition efficiency increased with increase in concentration of the extracts for both

3.5 Adsorption Considerations

Surface coverage data are very useful in determining inhibitor adsorption characteristics, such data are applied in construction of adsorption isotherm. Which give detailed information on adsorption mechanism.



(a) (b)

Figure 5: Langmuir adsorption isotherms for CC extract on aluminum in (a) 0.5 M NaOH (b) 1 M HCl

The data obtained from gravimetric measurements can be used to determine the adsorption characteristic of *CC* on aluminum in the alkaline and acidic environments according to the Langmuir equation:

$$C/\Theta = 1/b + C$$

Where 1/b is the intercept, C is the inhibitor concentration and Θ is the surface coverage.

The plots of C/Θ against C are shown in Fig. 5(a) and 5(b) which illustrates Langmuir adsorption isotherms for CC extracts on aluminum in 0.5 M NaOH and 1 M HCl. A linear plot was obtained with a slope of 1.8721 for 0.5 M NaOH and 1.7705 for 1 M HCl suggesting the adsorption of extract organic matter follows the Langmuir adsorption isotherm, deviation of the slope from unity suggest interaction between adsorbed species on the metal surface and changes in the heat of adsorption with increasing surface coverage.

In the acidic and alkaline extracts used in this study, the majority of the organic constituents should exist as protonated species and others in the molecular form. The protonated species could be adsorbed onto cathodic sites on the corroding metal surface and reduce H_2 evolution, while the molecular species can be chemisorbed at active anodic sites and hinder the anodic dissolution reaction. It is possible that at low concentrations of 50mg/L the amount of the surface active organic matter of the extracts was insufficient, as the concentration increases, more of the organic matter becomes available for complex formation which subsequently diminishes the solubility of the surface layer leading to improved corrosion inhibition[36-41]. A comparism of the inhibition efficiency values for *CC* extract in 0.5 M NaOH and 1 M HCl reveals the principal mode of adsorption of the extract species.

The chemical interaction of some of the extract constituents with the aluminum surface at high *CC* concentrations is attributed to chemisorptions of inhibitor species at anodic and cathodic sites on the corroding metal surface.

4. Conclusion

The objective of this research was to ascertain the efficacy of exploiting *Cninodosculus chayamansa (CC)* for aluminum corrosion control. The results showed that *CC* extracts effectively mitigated the corrosion rates of aluminum in 0.5 M NaOH and 1 M HCl solutions, better results were obtained at higher concentrations of *CC* extract and at low temperature. The addition of KI was seen to enhance to effectiveness of the extracts by reducing further the corrosion rates of aluminum. *CC* extracts presented higher inhibition efficiencies in the acidic medium compared to the alkaline medium, however, inhibition efficiency increased as extract concentration increased in both media. Extract adsorption was further corroborated by the experimental data to fit the Langmuir isotherm. The result obtain from this research suggests that *CC* extract could find practical applications as an inexpensive and benign corrosion inhibitor for aluminum in aggressive acid and alkaline environments.

5. Acknowledgement

The authors are grateful to Dr. E. E. Oguzie for providing facilities for the measurements.

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