Chrysophyllum albidium extracts as corrosion inhibition for aluminium in 0.5 M H2SO4 solution

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ABSTRACT

The inhibition performance of Chrysophyllum albidium (CA) extracts on aluminium in sulphuric acid solution was evaluated by gravimetric and polarisation techniques. Extracts from the barks and leaves were employed in this study. The results obtained showed that the bark extracts are a better corrosion inhibitor for aluminium in sulphuric acid than the leaf extracts. The polarisation studies revealed that both the CA bark and leaf extracts act as a mixed-type inhibitor. The inhibitors on an aluminium surface obeyed the Temkin adsorption isotherm with respect to weight loss data and were best fitted by Langmuir for the polarisation experiment. The microstructural investigation results showed that CA extracts confer considerable protection on the aluminium samples in a sulphuric acid environment.

Introduction

The serious consequences of corrosion have become a problem of worldwide significance. Corrosion prevention and control have become a perpetual struggle between man and nature, particularly in view of the modern age, technological development and the increasing need for, and use of, metallic materials in all facets of technology. This has necessitated increasing interest in research into the metal-environment interface reaction and ways of mitigating the damaging effects of corrosion on metals and alloys (Loto and Mohammed, 2000). The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media (Trabanelli, 1991). The present study focuses on acidic media owing to the increasing demand for acids in process industries, such as mineral processing, fertiliser manufacture, oil refining, wastewater processing and chemical synthesis, among others. Most of the corrosion inhibitors are synthetic chemicals, which are expensive and highly hazardous to the environment, hence the need for research into non-toxic organic corrosion inhibitors (Broussard et al., 1997).

A comprehensive review of the application of natural products as corrosion inhibitors for numerous metals in different aggressive media was conducted by Raja and Sethuraman (2008). It was stated that, owing to their environmental acceptability, availability and possibility of being naturally renewable, there is an increase in research into plant extracts to replace toxic chemical packages. Gece (2011) X-rayed the potentials of drugs from phytochemicals as corrosion inhibitors and it was noted that substructures of drugs and corrosion inhibitors share so many similarities. This accounts for the recent momentum in elucidating information about the application and mechanism of plant extracts as corrosion inhibitors. Several researchers have also employed natural products as corrosion inhibitors for aluminium in acidic media (Li et al., 2012; Satapathy et al., 2009; Loto et al., and Ramirez-Arteaga et al., 2013).

The present paper describes a study of the corrosion inhibition of Chrysophyllum albidum (African Star Apple) bark and leaf extracts on aluminium in 0.5M H2SO4 using the gravimetry (weight loss) and potentiostatic polarisation techniques. A literature search revealed that Chrysophyllum albidum fruit has been employed in mitigating acidic corrosion of aluminium substrate at different concentrations (Madufor et al., 2012; 2013) and it was reported that the fruit can be an effective corrosion inhibitor. However, the fruit is (not?) perennial and is affected by climatic changes. This paper considers the use of Chrysophyllum albidium leaves and barks as corrosion inhibitors.

Experimental procedures

The purpose of this experiment was twofold: to evaluate the corrosion inhibition of Chrysophyllum albidium extracts in 0.5 M H2SO4 solution for aluminium and to establish the data obtained from a locally designed potentiostat.

Materials

The aluminum 6063 used for this study was obtained from Nigerian Aluminum Extrusion Limited, in Lagos, and the chemical composition is as presented in Table 1. The coupons were mechanically prepared into 1.8 x 1.5 x 0.7 coupons and ground with silicon-carbide abrasive paper, with the surface further prepared using emery cloth. The samples were degreased using ethanol and water. Each coupon was subsequently weighed. The 0.5 M H2SO4 solution was prepared by diluting analytical-grade (98%) sulphuric acid with distilled water.

Element	Al	Si	Fe	Cu	Mn	Mg	Zn	Cr	Ti	V
Wt %	93.95	0.3613	0.1353	0.002	0.004	0.0051	0.0002	0.0006	0.0118	0.008

Table 1: Chemical Composition of Al 6063

Inhibitor extraction

The barks and leaves of Chrysophllum albidium were obtained from the experimental farm of Obafemi Awolowo University, in Ile-Ife, Nigeria. The barks and leaves were dried, ground and blended into powder, before being weighed separately. The molecular structure of the inhibitor is as presented in Figure 1 and it was identified as myricetin 3- rhamnoside (Adebayo et al., 2011). The dried powders were soaked in separate conical flasks; 250 ml of ethanol was poured in the conical flasks and covered for four days. Thereafter, the samples were cooled and filtered using cotton wool and filter paper.
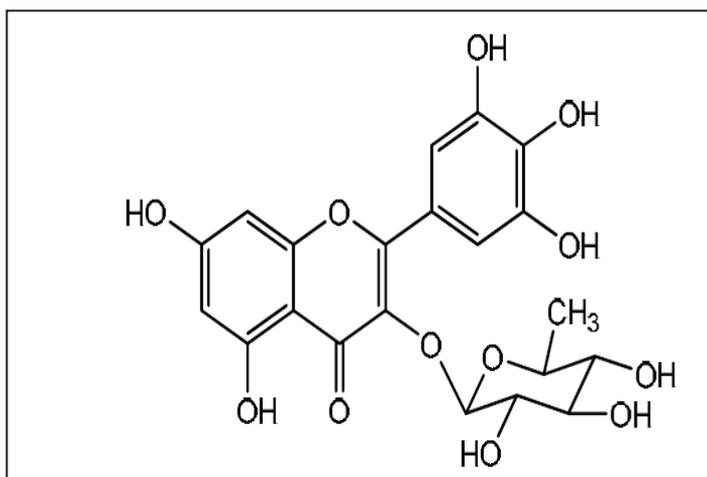
myricetin 3 - rhamnoside
Figure 1: The molecular structure of the inhibitor use in this study (Adebayo et al., 2011)

The filtrates were then subjected to fractional distillation at temperatures of about 55 0C in rotary distillation equipment to ensure the samples were free of the ethanol (Loto et al., 2011). The inhibitor concentrations were varied between 0.1 g/l and 0.5 g/l for the gravimetric technique and the preliminary results showed that a higher concentration above 0.3 may not be required. The inhibition concentrations for potentiostatic measurements were, however, varied between 0.05 g/l and 0.3 g/l, with the former aimed at evaluating the corrosion resistance of the extracts at lower concentrations.

Weight loss measurements

Each of the cleaned and weighed aluminium 6063 alloy coupons was immersed in the acidic solution (0.5 M H2SO4) and CA inhibited solutions with varied concentrations (0.1 – 0.5 g/l). The setup was carried out at room temperature. Each sample was removed at 48-hour intervals (NACE 1984) and the total exposure duration was 504 hours. The coupons were retrieved and scrubbed with a bristle brush under running water in order to remove corrosion products. They were then dried with acetone and reweighed. The differences in weight were noted in accordance with the ASTM method (Deng, 2012). The inhibition efficiency percentages (IE%) were evaluated from the corrosion rate data. The average corrosion rates of the coupons in various environments were determined using the established relation (Ovri and Ofeke 1998; Osarolube, et al., 2004):

$$CR \ (mm/yr) = \frac{87.6 \ W}{\rho AT} \qquad [1]$$

where W is the weight loss in mg, p is the metal density in mg/m^3, A is the exposed area of the test coupon in m^2, T is the exposure time in hours.

The inhibition efficiency of the inhibitor was calculated using the following expression:

$$IE\% = \frac{CR_i}{CR_0} \ X \ 100\% \qquad [2]$$

where, CRo and CRi are the corrosion rates of the aluminium coupons in the absence and presence of an inhibitor respectively in H_2SO_4 at the same temperature.

Potentiostatic polarisation measurements

The potentiostatic polarisation experiment was carried out using a three-compartment electrode cell. An Ag/AgCl electrode was used as the reference electrode and the aluminium was the working electrode, while the counter electrode was carbon (graphite). The steady-state potentiostatic polarisation experiments were done through a locally designed and constructed potentiostat (Aremo, 2012) by applying potentials of 10 mV increments after every minute, with the corresponding current values being recorded one minute after the potential was applied. The specimens were first immersed in the test solution for 35 minutes to attain a stable state (Awizar et al., 2013). The inhibitor concentrations were varied for potentiostatic polarisation readings and the setup was repeated twice for each set and data recordings. The inhibitor efficiency was computed according to the work of Fouda et al. (2012):

$$\% \ IE = 100\theta = \frac{i_{corr(free)} - i_{corr(inh)}}{i_{corr(free)}} \ x \ 100 \qquad [3]$$

where, $i_{corr(free)}$ and $i_{corr(inh)}$ are the corrosion current densities in the absence and presence of an inhibitor respectively.

Results and discussion

Weight loss measurements

The effects of inhibition on the metal samples are as shown in Figure 2. The corrosion rates for the uninhibited solution were in the range of 10-2 mm/
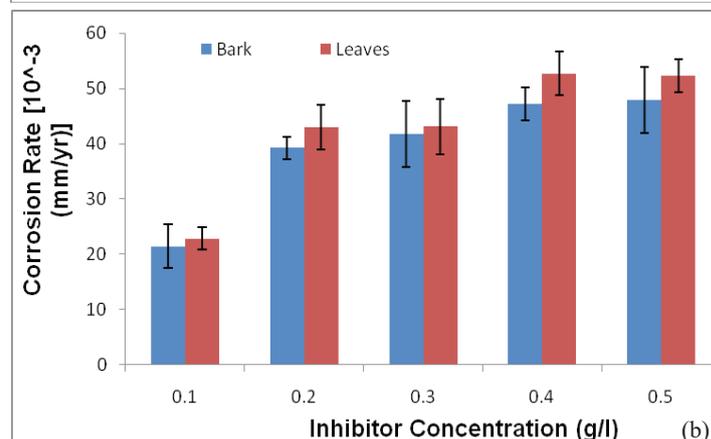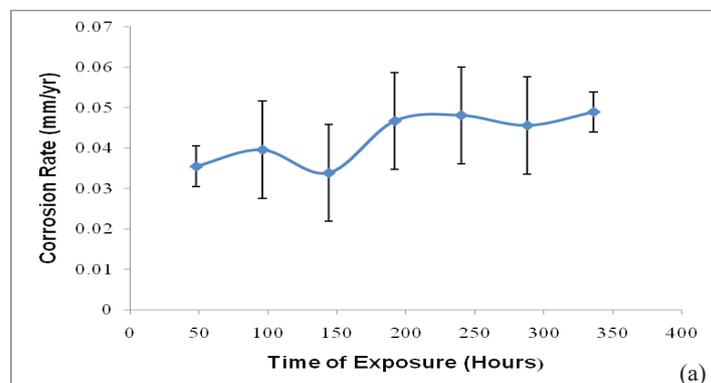

Figure 2: The corrosion rates as a function of time from gravimetric technique for the (a) Uninhibited and (b) Inhibited solutions

yr, while those for the bark-extract and leaf-extract-inhibited solutions were in the range of 10-4 mm/yr. This implies that the CA barks and leaves significantly reduced the corrosion rates in the studied environment. It was also noticed that, with an increase in the inhibition concentration, the corrosion rates also increased in the case of both barks and leaves.

The optimal inhibitor concentration for both barks and leaves was observed at 0.1 g/l. Preliminary investigations showed that the corrosion rates decreased as the inhibitor concentrations increased up to 0 - 0.1 g/l. Interestingly, it was only at this concentration that the leaves outperformed the barks, unlike at other concentrations, where the converse was noticed. It was also observed from the preliminary investigations that the corrosion rates were seemingly on the high side for inhibitor concentrations less than 0.1 g/l.

Potentiostatic measurements
Tafel plots (Figure 3) were extrapolated from the linear portion of the cathodic curve up to the horizontal line drawn from the Eoc. Actually, the region of activation control did not display the required linearity over one order of magnitude of current; consequently, a modified approach of extrapolation from the activation-controlled region was adopted.

Fig 3: Plot of voltage versus log of current for (a) uninhibited sample (b) inhibited with 0.1g/l CA leaves (c) inhibited with 0.1g/l CA barks

It must also be noted that the cathodic polarisation data are preferred in the Tafel analysis since these are easier to measure experimentally (Ningshen and Mudali, 2002; Sequeira, 2010). The summarised electrochemical corrosion kinetic data, which include corrosion current density (i_{corr}) and corrosion potential (E_{corr}), are presented in Table 2. It is evident that the anodic metal dissolution reactions were inhibited with the addition of CA bark and leaf extracts.

	Concentrations	Corrosion Potential (-E_{corr}) mV	Corrosion current i_{corr} (mAcm^{-2})
Control Experiment	-	560	1252
Leaves	0.05	500	540.08
	0.1	511.6	428.67
	0.2	552	773.4
	0.3	540	619.86
Barks	0.05	540.12	363.5
	0.1	569	328.99
	0.2	589.64	394.1
	0.3	630	511

Table 2: Potentiostatic polarization data from corrosion of aluminum in H_2SO_4 with different concentrations of CA bark and leaves

The results indicated that, upon the addition of the extracts, the corrosion current density decreases, and it can be inferred that the corrosion rates decreases. A compound can be classified as an anodic or a cathodic type inhibitor when the change in the E_{corr} value is greater than 85 mV (Li et al., 2008). Since the largest shift in E_{corr} caused by the addition of the inhibitors was less than this value (Table 2), it may be concluded that the two inhibitors should be considered as a mixed-type inhibitor.

Cathodic and anodic reactions of the aluminium electrodes were inhibited inconsistently with an increase in Chrysophyllum albidum bark and leaf extract concentration. This may be due to the adsorption and formation of a good protective film by the inhibitors on the aluminium surface, thus blocking both anodic and cathodic sites indirectly.

In the second part of this study, electrochemical impedance spectroscopy (EIS) data that can provide more information on inhibition mechanism and the corrosion behaviour of the metal with time will be presented.

Inhibition efficiency
It is observed from Figure 3a that the order of inhibition efficiency of CA bark concentrations is 0.1 > 0.05 > 0.15 > 0.2 > 0.3 > 0.4 > 0.5 (g/l), while that of CA leaves on aluminium in the acidic medium is 0.1 > 0.05 > 0.15 > 0.2 > 0.3 > 0.5 > 0.4 (g/l). The IE% using the gravimetric technique follows the same pattern as the corrosion rates data (Figure 1) such that the optimal efficiency was observed at 0.1 g/l for both bark- and leaf-inhibited samples (42% and 55% respectively).

Also at this concentration, the leaves have better efficiency than the barks as a corrosion inhibitor in the acidic medium. This is contrary to what was noticed at other concentration levels, where the barks produced a higher efficiency than the leaves.
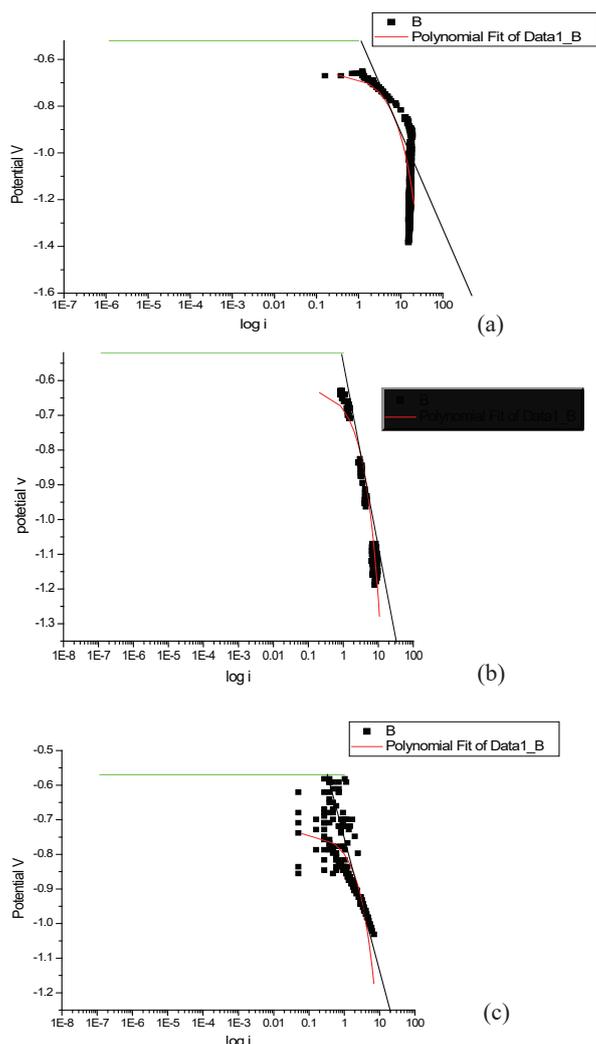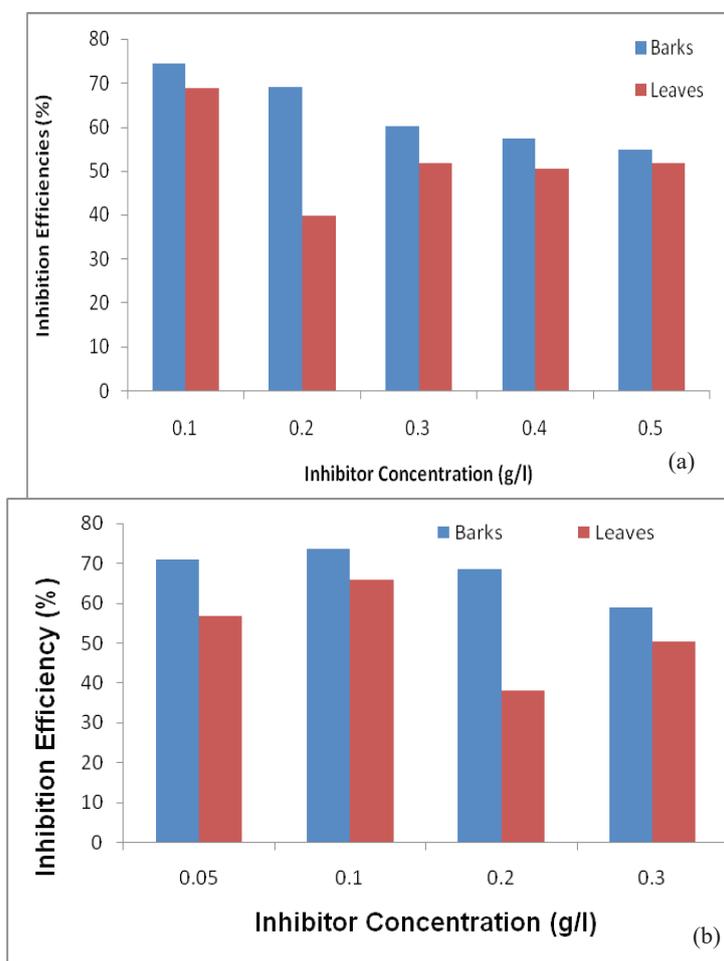
Figure 4: The inhibition efficiencies at various inhibition concentrations for (a)Gravimetric technique (b) Potentiostatic technique

The controlling step in anodic electrochemical reactions for aluminium in an acidic solution is the complexation reactions between the hydrated cation and the anion present. According to Figure 1, the molecular structure of the plant extracts has functional hydroxyl groups that enhance film formation between the metal-inhibitor surfaces. The presence of lone-pair electrons on the oxygen atoms of the functional group possibly boosts the interaction between the aluminium substrates and the plants extracts. This is in line with earlier reports that organic inhibitors have rich O, N, P and/or S atoms as an active centre (Bahrami et al., 2010 and Fouda et al. 1986).

The data obtained showed that there is a peak-value phenomenon of inhibitor concentration, which accounted for the negative efficiency noticed at inhibitor concentration levels above 0.4 g/l. This is associated with the adsorption mode of the inhibitor (Jiang et al, 2005; Durnie et al., 1999; Singh, 1993). There is realignment of the metal surface-inhibitor molecules interaction from parallel alignment to perpendicular as the inhibitor concentration increases. This resulted in a smaller surface area coverage for the inhibitor, and the material loss increased.

It is evident from polarisation measurements (Figure 3b) that the Chrysophyllum albidum bark extract has higher inhibition efficiencies than the leaf extract. The order of inhibition efficiency obtained from polarisation measurements for CA leaf extract is as follows: 0.1 > 0.05 > 0.2 > 0.3 (g/l). For CA bark extract, the order of inhibition efficiency is 0.1 > 0.05 > 0.3 > 0.2

(g/l). The optimal IE% was also obtained at 0.1 g/l for both barks and leaves (73.7 and 65.75%). Noticeably, the bark-inhibited samples performed better than leaves at all concentration levels. Also, the IE% decreased as the inhibitor concentration levels increased, which is in consonance with the weight loss data but the efficiencies for polarisation measurements are on the high side, when compared with those for the gravimetric technique at all inhibitor concentrations. This is in agreement with earlier reported works (Ige, et al., 2012; 2013; Wang and Neville, 2004).

In order to evaluate the inhibition mechanism, several adsorption isotherms were correlated with both the gravimetric and polarisation data. The results (Figure 5) for samples inhibited with leaf extract indicate that the Temkin isotherm is obeyed, which is in agreement with the work of Madufor et al., (2012 and 2013).
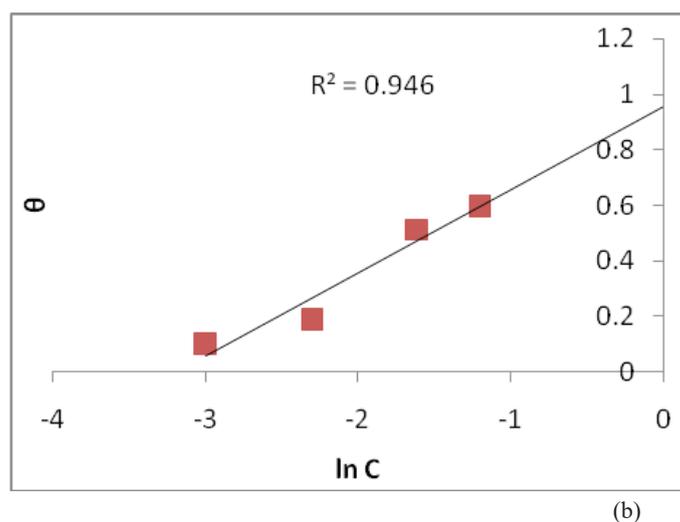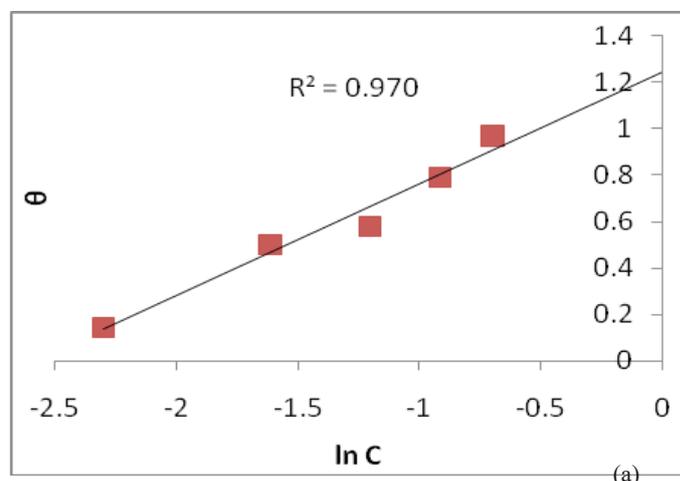
The Temkin isotherm is predicated on excellent prediction of the substrate-inhibitor interaction in a tightly packed structure where identical orientation is not necessary, that is, there is no lateral interaction between them. The adsorption process constants (Kads) for both techniques were positive (0.946 and 1.247 respectively), indicating that there is attraction between the inhibitors and the aluminium substrate. Specifically, the addition of the leaf extract increases the Kads, which implies that the chemical interaction

enhances film formation and reduces the degradation rates. However, the data for bark-inhibited samples were best fitted with the Langmuir isotherm (Figure 6) and it is generally known that the Langmuir isotherm assumes that there is mono-layer adsorption.
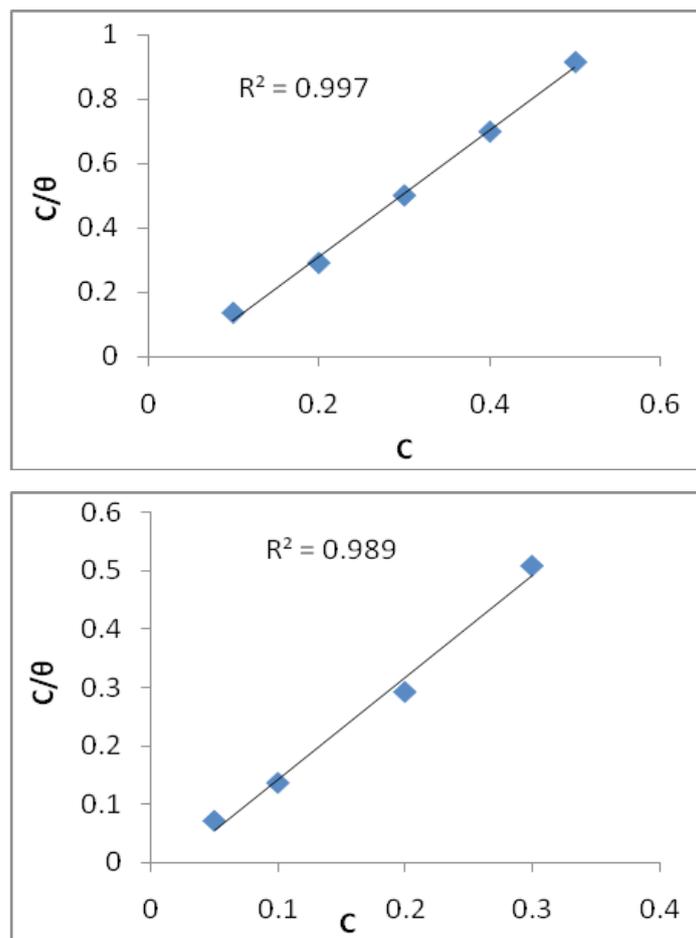

Figure 6: The experimental data was best correlated with Langmuir adsorption for barks inhibited samples (a) gravimetric and (b) polarization techniques

It is noticed that the molecular interaction, which is the inverse of the intercept for the Langmuir model, has negative values (–31 and –12) for the polarisation and gravimetric techniques respectively. The negativity indicated that there is virtually no interaction between the bark extract and the aluminium substrates.

Conclusion
A locally designed and constructed potentiostat was used to characterise Chrysophyllum albidium extracts as corrosion inhibitors for aluminium in 0.5 M H2SO4 solution. The following conclusions can be summarised from this research:
The results displayed by both the gravimetric and polarisation techniques revealed that the optimal inhibitor concentration is recorded at 0.1g/l for both CA bark and leaf extract in the studied environment.
•The samples inhibited with CA leaves offer more corrosion protection than those inhibited with CA barks at the optimal inhibitor concentration. However, at other concentration levels, the barks were more effective.

•CA bark and leaf extracts act as mixed-type inhibitors, with bark-inhibited samples being cathodic in nature, while the leaves are anodically inhibited.
•The experimental data for the leaf-inhibited samples are best fitted with the Temkin isotherm for both techniques, and the Langmuir isotherm correlated well with both gravimetric and polarisation data for samples with bark.

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