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Technical Note

Adsorption and Inhibitive Properties of *Camellia Sinensis* for Aluminium Alloy in HCl

C.A. Loto[1,2,], O. O. Joseph[1], R.T. Loto[1,2]*

[1]Department of Mechanical Engineering, Covenant University, Ota, Nigeria
[2]Department of Chemical, Metallurgical & Materials Engineering, Tshwane University of Technology, Pretoria, South Africa
[*]E-mail: akinloto@gmail.com, cleophas.loto@covenantuniversity.edu.ng

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This study reports the effect of *Camellia Sinensis* (green tea) extract as a green inhibitor on the corrosion of aluminium alloy in 0.5M hydrochloric acid. Weight loss/corrosion rate and potential measurement techniques were used for the experimental work. The results were further analysed using the two-factor ANOVA test. Potential measurement was performed using a digital voltmeter and a saturated calomel reference electrode. The tea extract was obtained from the green tea leaves. The results obtained showed effective corrosion inhibition of the extract on the aluminium alloy test specimens in the different concentrations of hydrochloric acid used. The extracts gave appreciable corrosion inhibition performance of aluminium at 100 and 80% concentrations with the weight loss of 652mg (0.652g) and 674 mg (0.674g) respectively. ANOVA test confirmed the results at 95% confidence, and further showed that concentration of green tea extract had greater effect on potential measurements whereas test exposure time had greater influence on weight loss measurements. The value of Gibb's free energy of adsorption obtained signified that the mechanism of adsorption of plant extract molecules on the metal surface was by physiosorption. The adsorption of *Camellia Sinensis* extract on the surface of aluminium obeys the Freundlich isotherm model.

Keywords: Corrosion inhibition, *Camellia sinensis*, Aluminium, ANOVA, Adsorption, Gibb's free energy

1. INTRODUCTION

Metals have a natural tendency to become combined with other chemical elements and return to their lowest energy states. By so doing, the metals frequently combine with oxygen and water, of which both are abundant in most natural environments, to form hydrated iron oxides (rust) similar in chemical composition to their original ores [1]. Nevertheless, metallic materials such as bronze, brass, stainless steels, zinc, and pure aluminium play a great role in the construction of equipment used in agriculture, oil and gas, petrochemical, process and allied industries as well as in medical services. However, research into corrosion of these metals; its processes and its means of prevention, have been and is continually being undertaken by industry and academia [2]. The use of inhibitors is one of the best methods of preventing metals against corrosion. Inhibitors reduce corrosion rate by adsorption of ions/molecules onto the metal surface. Most of the corrosion inhibitors are synthetic chemicals, expensive and very hazardous to environments. Therefore, it is desirable to source for environmentally safe inhibitors which surpass the cost benefits, performance and versatility of conventional products [3].

Plants represent a class of interesting source of compounds currently being exported for use in metal corrosion protection in most systems. More so, investigations of corrosion inhibiting abilities of tannins, alkaloids, organic, amino acids and organic dyes of plant origin are of interest. In addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable sources of materi.als [4]. The use of phytochemicals as corrosion inhibitors can be traced back to 1960s when tannins and their derivatives were used to protect steel from corrosion [3]. Up till now, extracts of plant leaves also known as green inhibitors such as Pectin[5]; *Coriandum sativum L.* [6]; *Euphorbia hirta* [7]; Apricot juice[8]; *Spirulina platensis* [9]; *Tithonia diversifolia* [10]; *Laurus nobilis L.* ([11]; *Ocimum sanctum* [12]; Tryptamine [13]; *Cola Acuminata* and *Camellia Sinensis* [14]; *Neolamarckia cadamba* alkaloids [15]; *Vernonia Amygdalina* [16,17]; *Barbiturates* [18]; *Petersianthus macrocarpus* [19]; *Camellia Sinensis* [20]; henna extract [21], amongst others have been studied for corrosion inhibition of metals in various media. The present study aimed at investigating the inhibitive properties of *Camellia sinensis* (green tea) extract on the corrosion of aluminum alloy in 0.5M HCL solution. Tea from the leaves of *camellia sinensis*, a plant of the *Theaceae* family, is consumed by more than two thirds of the world's population and is the most popular beverage next only to water.

As previously reviewed [2], tea leaves contain many compounds, such as polysaccharides, volatile oils, vitamins, minerals, purines, alkaloids (e.g. caffeine) and polyphenols (catechins and flavonoids). Green tea contains polyphenols which are mainly flavonoids and are subdivided into flavones, flavonones, isoflavonones, flavanols – flavandiols, anthocyanins, and phenolic acids. The other green tea polyphenols are flavonols, commonly known as catechins – the tea tannins. Green tea polyphenols include groups of compounds of different chemical structure and also possess variable biological properties. Monomeric flavanols, the major components in green tea, are precursors of condensed tannin. Tea polyphenols also have high complexation affinity to metals, alkaloids, and biologic macromolecules such as lipids, carbohydrates, proteins, and nucleic acids. Green tea has very powerful antioxidant properties.

Furthermore, the complex nature of green tea's chemical composition and structure is expected to prove its effectiveness in corrosion inhibition of aluminium in HCL, a strong acid. This work therefore, reports the results obtained in the evaluation of the corrosion inhibitive effectiveness of the tea extract on the corrosion of aluminium specimens immersed in 0.5M dilute hydrochloric acid at ambient temperature. This study has also yielded some insight into the adsorption mechanisms responsible for the inhibitive property of *camellia sinensis* in the same corrosive environment. The equation for corrosion rate according to [21] is given by

$$C = {}^{k\Delta W}\!\big/_{\rho At} \quad \text{.. (1)}$$

Where K = Rate constant equal 534 mpy; mpy means mils per year

W= Weight loss in mg

ρ = Density of material in g/cm^3

T = Exposure time in hours

A = Exposed area of coupon in in^2 noting that 1 in^2 = 6.5416cm^2.

2. EXPERIMENTAL DETAILS

2.1 Specimen Preparation

Aluminium sheets of composition (wt %) Al (99), Si (0.157), Mn (0.024), Cr (0.023), Mg (0.51), Cu (0.0025), Ni (0.001), Co (0.001), Ti (0.0049), V (0.0035), Sn (0.001), Zn (0.001), Ca (0.0011), Zr (0.002) and Fe (0.282) were employed for this study. The aluminium sheets were cut into an average size of 2.5cm x 2.5cm coupons for weight loss measurements and 1cm x 1cm coupons for potential measurements. A total number of 12 samples used for the weight loss experiment were de-scaled with a wire brush, ground with various grades of emery paper and then polished. They were further rinsed in distilled water to remove any corrosion products and then cleaned with acetone to degrease. The samples were fully immersed thereafter preventing further exposure to moisture in the atmosphere. Another set of 12 samples for the corrosion potential experiment were cleaned in the same manner as those for the weight loss experiment except that they were mounted in resin to ensure that only the surface of the samples were exposed to the corrosive medium. Before mounting, copper wire was spot welded to each of the samples.

2.2 Preparation of plant extracts and test media

The experiment was performed in hydrochloric acid medium (0.5M HCL) of AnalaR grade. 0.5M HCL was prepared by diluting 41.39cm3 of concentrated HCL in 1 liter of distilled water.

Camellia sinensis (Green tea) was purchased at a local supermarket. The leaves were removed from the bags stored in a container for further use. The plant extract was obtained by the acid extraction method which involved boiling a weighted quantity of leaves in the concentration of sulphuric acid required for a period of two hours and then leaving the mixture to cool. After cooling, the tea leaves are filtered out leaving the solution which contains the leached out constituents of the green tea. The ratio of green tea to acid was 1:10; therefore, for every 40g of green tea leaves used, it was boiled in 400ml of 0.5M HCL solution. From the stock solution produced, inhibitor test solutions were prepared in the percentage concentrations of 20, 40, 60, 80 and 100 respectively. 100ml of the stock inhibitor solution was used as 100% inhibitor concentration. 80% concentration of inhibitor in acid was obtained by mixing 80ml of stock with 20ml of 0.5M HCL, 60% was also obtained by mixing

60ml of stock with 40ml of 0.5M HCL. The same procedure was followed to obtain 40% and 20% inhibitor concentrations.

2.3 Weight loss experiment

Weighed test specimens were totally immersed in each of the test media contained in a 250ml beaker for 24 days. Experiments were performed with 0.5M hydrochloric acid test medium in which some had the green tea extract added. Test specimens were taken out of the test media every 2 days, washed with distilled water, rinsed in methanol, air-dried, and re-weighed. Plots of weight loss and of calculated corrosion rate versus exposure time respectively (Figs. 1 and 2) were made. Corrosion rate was calculated from the formula in equation 1. The inhibitor efficiency (%) was also calculated for all the inhibitors for every 2 days of the experiment (Fig. 6).

2.4 Potential measurements

Potential measurements were performed on the mounted specimens in turns by immersing them in each of the acid test medium with and without inhibitor. The potential was recorded at 2 – day intervals using a digital voltmeter and saturated calomel reference electrode. Plots of variation of potential (vs. SCE) with the exposure time were made, and these are presented in Fig. 4.

3. RESULTS AND DISCUSSION

3.1 Weight loss method

The results obtained for the variation of weight loss and corrosion rate with exposure time respectively for the aluminium specimens immersed in 0.5M hydrochloric acid with varied concentrations of green tea extract are presented in Figs. 1 and 2.

The control experiment (without added extracts) recorded a weight loss value of 853mg at the 24^{th} day of the experiment. The acid test medium with 20 and 40% concentration of extract addition had the least corrosion inhibition effect of the immersed specimens by the end of the 24^{th} day achieving a weight loss value of 734mg and 729mg respectively. At this value it could be considered to be averagely protective. The test medium with added 60% concentration of green tea performed better than that of the 40%'s, recording a weight loss value of 680mg on the 24^{th} day of the experiment.

The acid test medium with 100% concentration of extract addition recorded the lowest weight loss with a value of 652mg. These weight loss values showed that the green tea extract exhibited very good corrosion inhibition at the end of the experiment on the 24^{th} day. Furthermore, it was noted that the effectiveness of the inhibitor increased with increased inhibitor concentration.

The corresponding corrosion rate vs. the exposure time results in Fig. 2 gave a good correlation with the results in Fig. 1. The corrosion rate decreased with time.

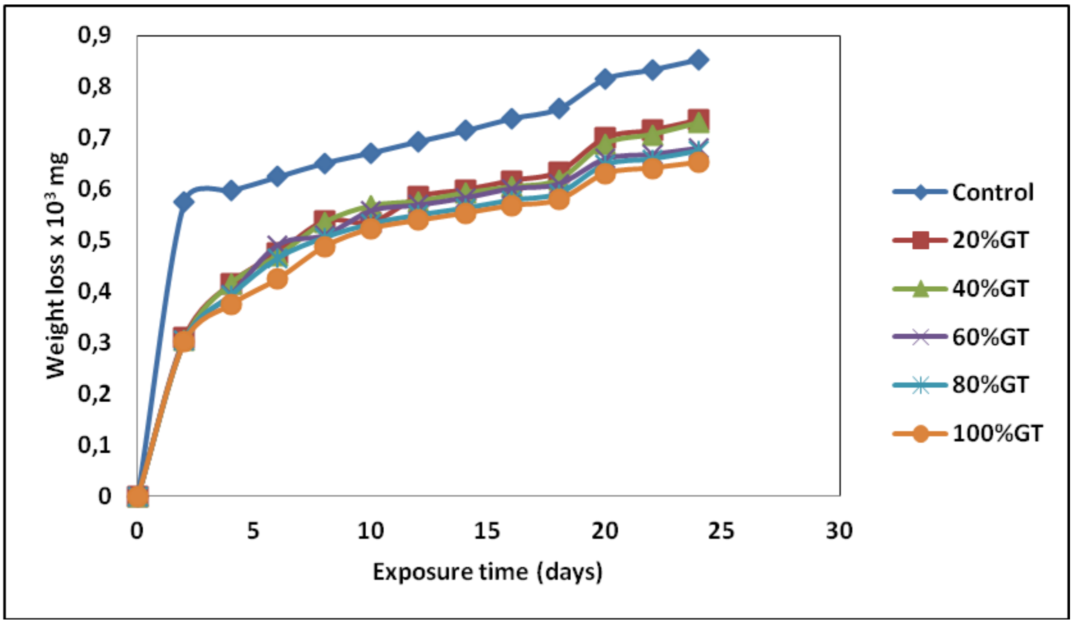


Figure 1. Variation of weight loss with exposure time in days for aluminium immersed in 0.5M HCL in addition of different concentrations of green tea.

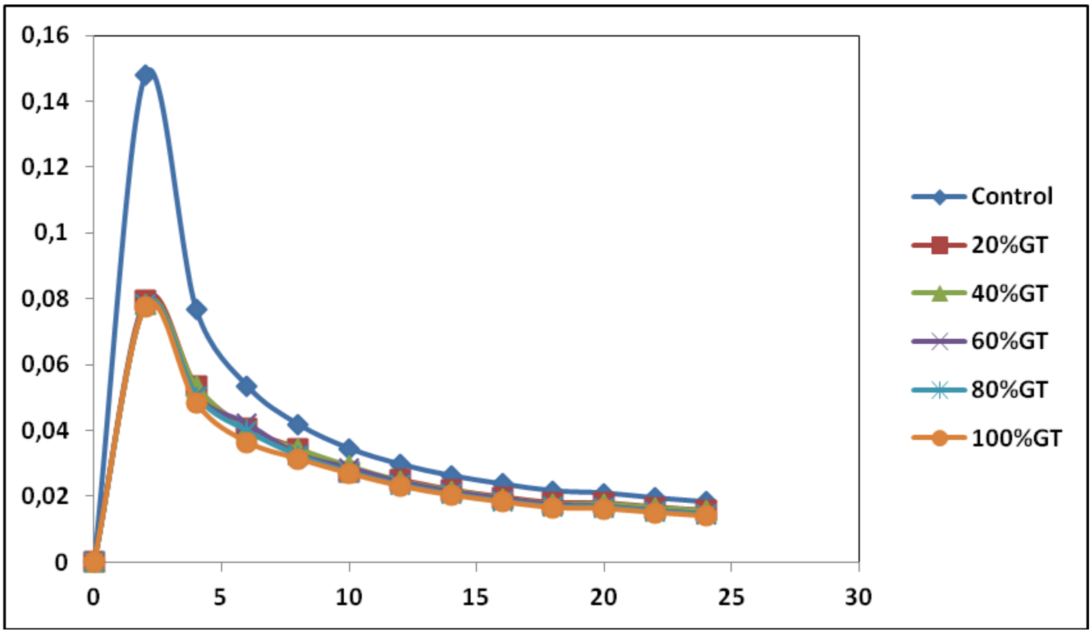


Figure 2. Variation of corrosion rate with exposure time in days for aluminium immersed in 0.5M HCL in addition of different concentrations of green tea.

The corrosion rate bears the same relationship as the weight loss with the specimen immersed in the 100% inhibitor having the least corrosion rate throughout the duration of the experiment. Among all the specimens immersed in solutions containing inhibitor, the sample with 20% inhibitor had the highest corrosion rate from the beginning up until the end of the experiment. The poor effect in low concentration of inhibitor signifies that inhibiting effect of green tea on aluminium in 0.5M HCL increases with increasing amount of the inhibitor.

3.1.1. Statistical Analysis

Table 1. Summary of ANOVA analysis for weight loss measurements

Source of Variation	SS	Df	MS	F	Significance F
Exposure Time	0.82	11	0.07455	205	1.97
Concentration of GT	0.27	5	0.05400	148.5	2.38
Residual	0.02	55	0.00036		
Total	1.11	71			

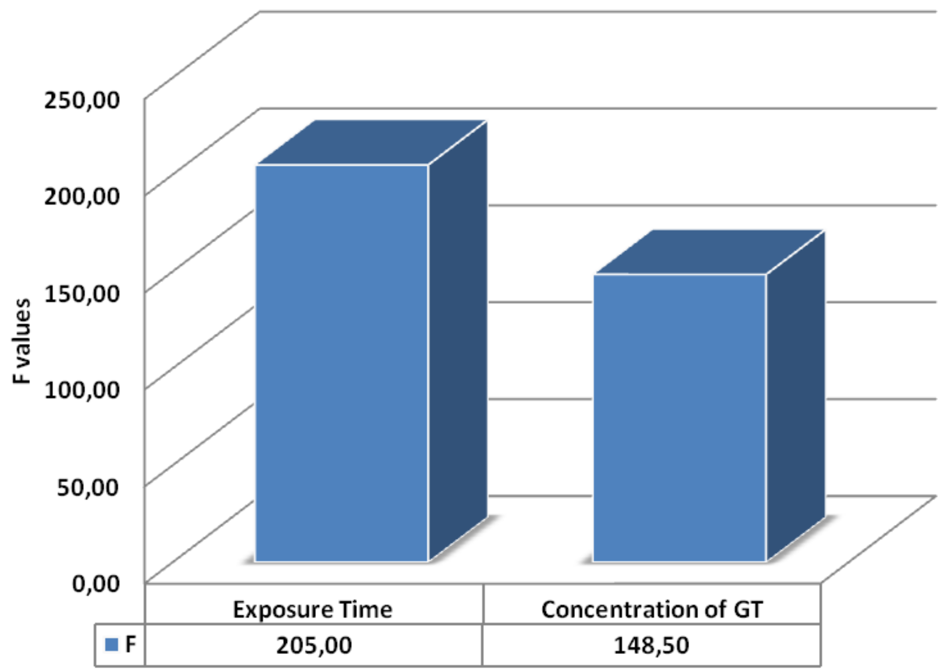


Figure 3. F values showing the influence of exposure time and GT concentration on Weight Loss measurements

Two-factor single level experiment ANOVA test (F-test) was used to evaluate the separate and combined effects of concentration of green tea (GT) extracts and exposure time on the weight loss of the aluminium in 0.5M HCL solution. The F-test was used to examine the amount of variation within each of the samples relative to the amount of variation between the samples. As previously used by [22], the Sum of Squares among columns (exposure time) was obtained with the equation:

$$SS_c = \frac{\sum T_c^2}{nr} - \frac{T^2}{N} \quad \text{.. (2)}$$

Sum of Squares among rows (concentration of GT):

$$SS_r = \frac{\sum T_r^2}{nc} - \frac{T^2}{N} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

Total Sum of Squares:

$$SS_{Total} = \sum x^2 - \frac{T^2}{N} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4)}$$

The calculation using the ANOVA test is tabulated (Table 1) as shown.

On the basis of the results in Table 1, it can be concluded with 95% confidence that the exposure time and concentration of GT significantly affects the corrosion rate of aluminium in 0.5M HCL environment. This gave good correlation with the scatter plots obtained in Figs. 1 and 2. It was further observed that the test exposure time had a greater significant effect on the corrosion rate (Fig.3).

3.2 Potential measurement

Potential readings for the aluminium specimens were taken over a period of 24 days at an interval of 2 days. The curves obtained for the variation of potential (mV) vs. saturated calomel electrode (SCE) with the exposure time are presented in Fig. 4. The specimens were immersed separately, in 0.5M HCL with different concentrations (20, 40, 60, 80 and 100%) of green tea.

The test medium without the inhibitor addition recorded the most negative potential on the first day of the experiment with a potential value of – 743mV. Afterwards, there was a gradual decrease in negativity up till the 6^{th} day. Thereafter, a sudden increase in negativity was observed. A similar trend was observed for the test media with 20% and 40% inhibitor concentrations.

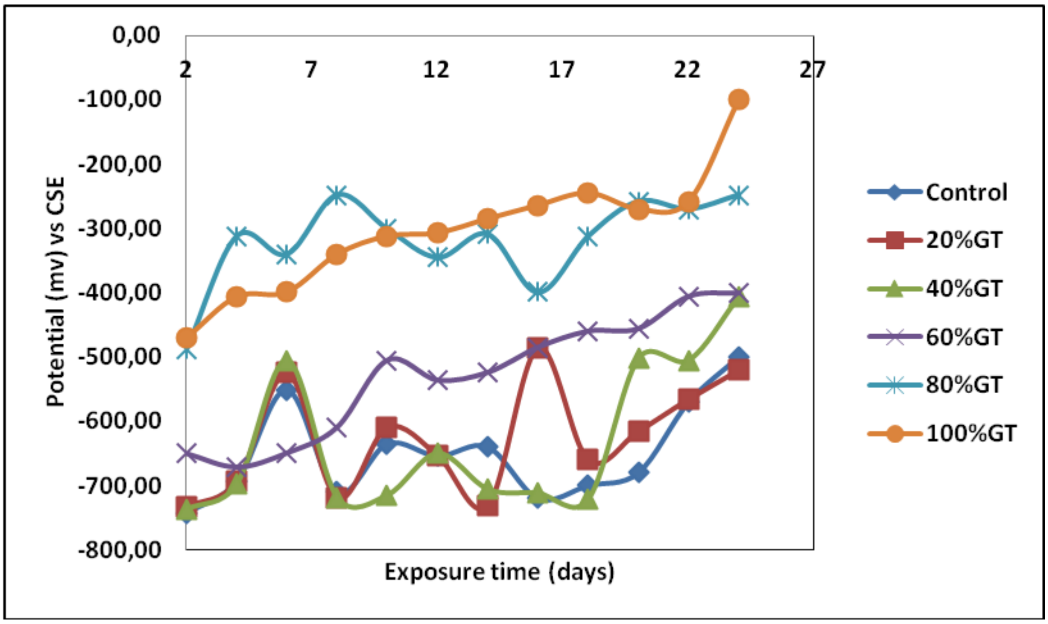


Figure 4. Variation of potential with exposure time for aluminium immersed in 0.5M HCL in addition of different concentrations of green tea.

This was a clear indication of active corrosion reactions and can thus be correlated with the results obtained in the weight loss experiments. The curves for variation of potential with exposure time in the test media for the extracts of 100 and 80% concentrations showed effective corrosion protection throughout the experimental period. The extracts with 100% concentration showed the best corrosion inhibition performance with potential values of -399mV on 6th day of the experiment and -245mV on the 18th day and on the 24th day, the potential value was -100mV. All these values fell within the passive corrosion reactions range with respect to SCE. The potential values for the 80% concentration extracts showed more passive corrosion reactions than for 100% concentration during the first 10 days. Afterwards, it exhibited less passive reactions in comparison to 100% inhibitor concentration for the next 8 days and until the end of the experiment where a potential value of -248mv was attained.

The effect of these variables on the corrosion potential of the aluminium alloy was further confirmed with the ANOVA test using equations (2) – (4) as stated earlier. The results are displayed in Table 2.

Table 2. Summary of ANOVA analysis for potential measurements

Source of Variation	SS	Df	MS	F	Significance F
Exposure Time	451294.38	11	41026.76	5.83	1.97
Concentration of GT	1749467.13	5	349893.43	49.75	2.38
Residual	386826.38	55	7033.21		
Total	2587587.88	71			

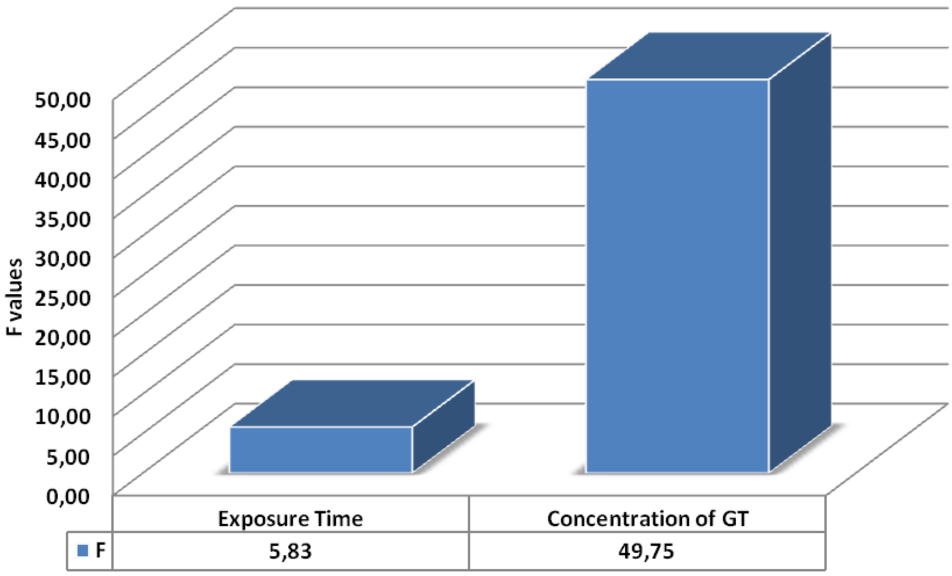


Figure 5. F values showing the influence of exposure time and GT concentration on potential measurements.

On the basis of the results in Table 2, it can be concluded with 95% confidence that varied concentration of GT significantly affects the corrosion potential of aluminium in 0.5M HCL, the effect of GT concentration being exceedingly significant (Fig. 5).

3.3 Inhibitor Efficiency

The results of the inhibitor efficiency obtained by calculations are presented in Fig. 6. There was increased inhibitor efficiency with increased per cent concentration of inhibitor and increased exposure time throughout the whole experimental period. The extracts with 100% concentration addition gave the optimal inhibition efficiency of 90.57% on the 24th day of the experiment. Similarly, the 80% concentration addition gave inhibition efficiency of 90.25% on the 24th day of the experiment. Also, the 60% concentration addition gave a high inhibition efficiency of 90.16% on the 24th day of the experiment. It was observed that the inhibition efficiencies increased with increasing exposure time and inhibitor concentration respectively.

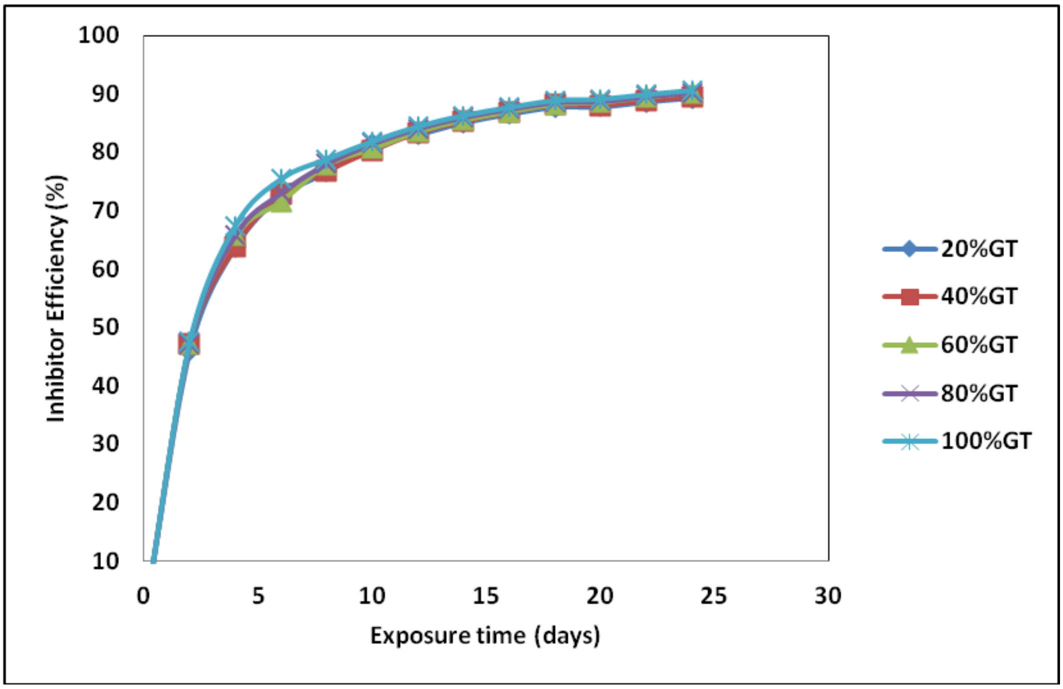
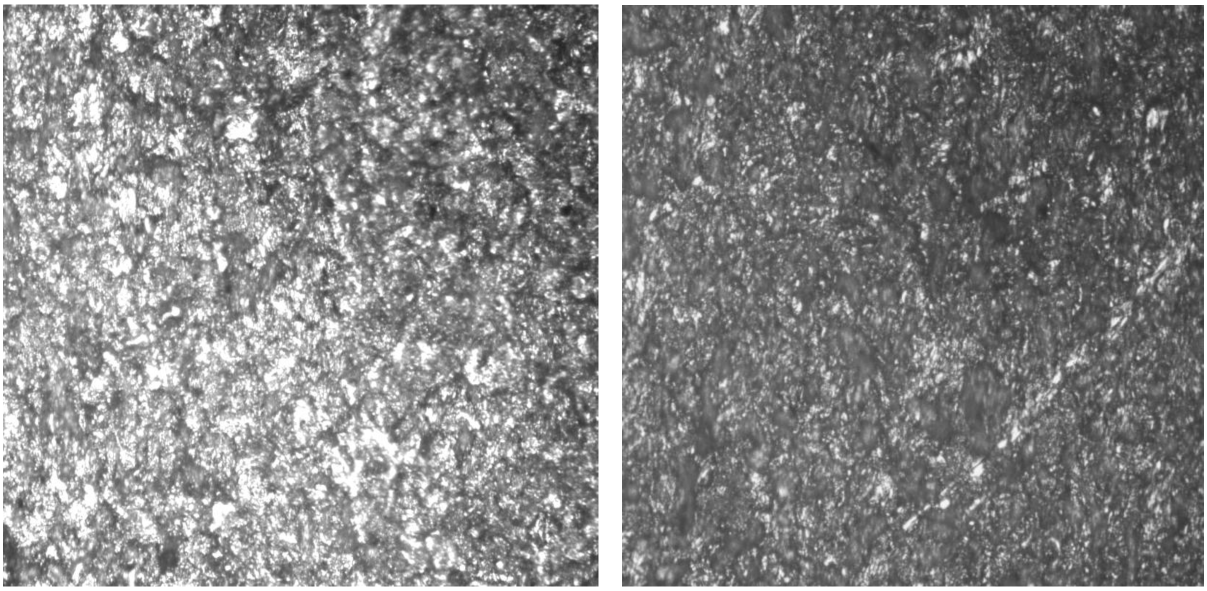


Figure 6. Variation of inhibitor efficiency with exposure time in days for aluminium immersed in $0.8MH_2SO_4$ in addition of different concentrations of green tea.

After removing the samples from solution at the end of the experiment, severe corrosion

was observed (Fig. 7a) by inspecting the surface of the sample without inhibitor under the microscope. This suggests that hydrochloric acid can be aggressive for the aluminium alloy to induce corrosion.



(a) (b)

Figure 7. Micrograph of aluminium immersed in 0.5M HCL a) without inhibitor, b) with 100% Green tea inhibitor.

A positive change was observed by using the green tea inhibitor (Fig. 7b), indicating suppressed corrosion.

3.3.1. Thermodynamics and Adsorption Studies

Corrosion inhibition of aluminium alloy in 0.5M HCL by green tea can be further explained based on molecular adsorption. The adsorption process is influenced by the chemical structures of organic compounds, the distribution of charge in molecule, the nature and surface charge of metal and the type of aggressive media [23]. It was therefore, necessary to investigate the likely mode of adsorption by putting to test the experimental data obtained with several adsorption isotherms. The value of k which is the adsorption equilibrium constant and the standard free energy of adsorption ΔG^o_{ads} were evaluated based on the relation given by [21]:

$$k = \frac{1}{55.5}\exp\left(-\frac{\Delta G^o_{ads}}{RT}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where ΔG^o_{ads} is the standard free energy of adsorption

R is the molar gas constant and

T is the absolute temperature

The negative values of ΔG^o_{ads} obtained implies that the adsorption process was spontaneous and there was stability of the absorbed inhibitor layer on the metal surface. The values of the standard free energy of adsorption for 20% to 100% plant extracts is within the range of -14 to -17kJ/mol, characterizing the physiosorption mode of adsorption. Studies have shown that ΔG^o_{ads} values that are -20kJ/mol and above, i.e. less negative are consistent with physical adsorption (physiosorption) which involves electrostatic interaction between charged atoms and the charged metal, while those around -40kJ/mol and more negative are generally associated with chemical adsorption[21,10].

Table 3. Thermodynamic parameters for aluminium in 0.5M HCL with green tea extracts

Inhibitor concentration	ϴ	K	log K	1-ϴ	ϴ/1-ϴ	ΔG (kJ/mol-1)
Control	0.00	0.00	0.00	1.00	0.00	0.00
20% GT	0.14	810.58	2.91	0.86	0.16	-16.60
40% GT	0.15	423.98	2.63	0.86	0.17	-14.99
60% GT	0.20	424.51	2.63	0.80	0.25	-14.99
80% GT	0.21	331.88	2.52	0.79	0.27	-14.38
100% GT	0.24	308.22	2.49	0.76	0.31	-14.20

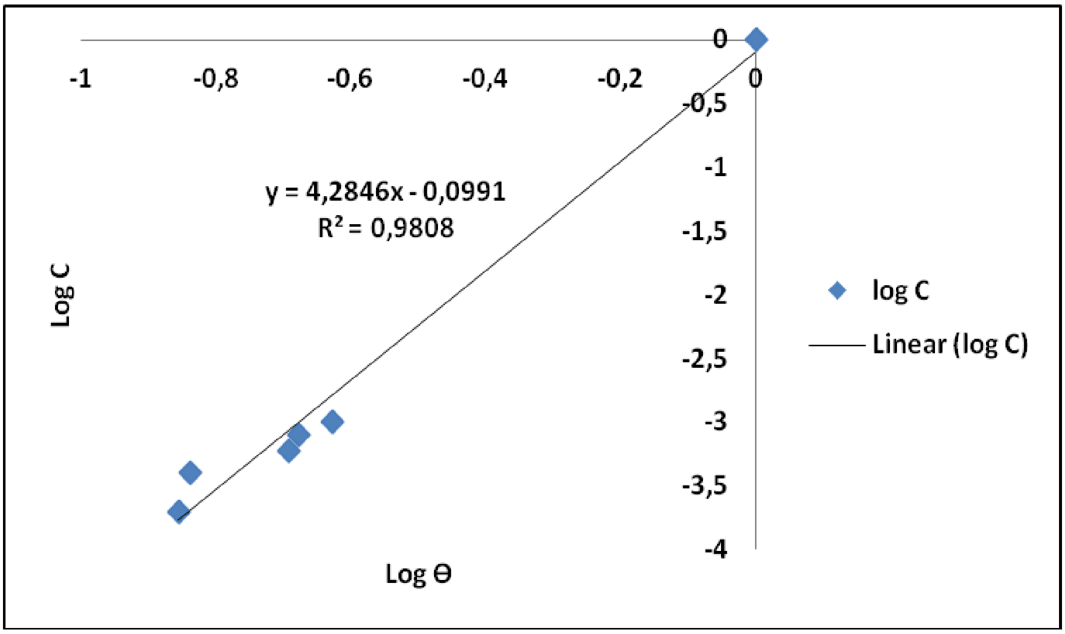


Figure 8. Freundlich adsorption isotherm for inhibition of aluminium in 0.5M HCL using green tea extracts

Langmuir, Temkin and Freundlich isotherms were used to test the experimental data. The best fit was obtained with Freundlich adsorption isotherm which is given by the relations [24]:

$$\theta = KC^n \qquad (6)$$

$$Log\ \theta = n\ Log\ C + \ln\ K \qquad (7)$$

Where θ is the degree of surface coverage, K and n are coefficients and C is the inhibitor concentration. The linear regression obtained by plotting the graph of $Log\ C$ against $Log\ \theta$ is 0.980.

3.4 Summary

The overall corrosion and inhibition profile showed that good corrosion inhibition was achieved with the use of green tea extracts. The potential values obtained as presented in the curves bear correlation with the results obtained gravimetrically. The potential values obtained for the green tea extracts of different concentrations fell within the accepted range for fairly good protection for aluminium with reference to saturated calomel electrode.

In general, the effective corrosion inhibition performance of green tea extract could be associated with their complex chemical compounds which include tannin and polyphenols. The action/reaction of this compound on the surface of the aluminium could hinder the sulphate ion species, promote more stable passive film formation and hence inhibit and stifle corrosion reactions at the aluminium /environment interface.

4. CONCLUSION

Green tea was found to be an effective natural corrosion inhibitor for aluminium in 0.5M HCL by using potential and weight loss methods. The results obtained from both methods were in good agreement. ANOVA test confirmed at 95% confidence that the exposure time and concentration of Green Tea significantly affects the corrosion rate and corrosion potential of aluminium in 0.5M HCL environment. Furthermore, the inhibition efficiency of the plant extract was found to increase with increasing inhibitor concentration. In addition, the value of Gibb's free energy of adsorption obtained signified that the mechanism of adsorption of plant extract molecules on the metal surface was by physiosorption and the adsorption of green tea on the alloy surface obeys the Freundlich isotherm model.

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