Adsorption and Inhibitive Properties of Camellia Sinensis for Mild Steel in 0.5M HCl and 0.8M H2SO4

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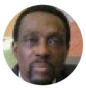

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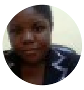

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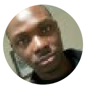

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Adsorption and Inhibitive Properties of *Camellia Sinensis* for Mild Steel in 0.5M HCl and 0.8M H_2SO_4

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ABSTRACT

The effect of *Camellia Sinensis* (green tea) extract as a 'green' inhibitor on mild steel corrosion in 0.5M HCl and 0.8M H_2SO_4 was studied at ambient temperature. Weight loss/corrosion rate and potential measurement techniques were used for the experimental work. The results were further analyzed using the two-factor ANOVA. Potential measurement was performed using a digital voltmeter and a saturated calomel reference electrode. Results obtained showed effective corrosion-inhibition of the extract on the mild steel test-specimens in the different concentrations of HCl and H_2SO_4 used. There was increasing inhibition performance with increasing concentration of inhibitor. In 0.5M HCl, 100% green tea gave the optimal performance with weight loss and corrosion rate of 246mg and 0.63 mm/yr respectively. A similar result was observed in 0.8M H_2SO_4 where 100% green tea gave the best results of 1226 mg weight loss and 3 mm/yr corrosion rate. ANOVA test confirmed the results at 95% confidence, and further showed that concentration of green tea extract had greater effect on potential and weight loss measurements. The Gibb's free adsorption energy signified physisorption in HCl and chemisorption in H_2SO_4 as the adsorption mechanism of plant extract molecules on the metal surface.

Key words: Corrosion inhibition, *Camellia sinensis*, Mild steel, ANOVA, Adsorption, Gibb's free energy

INTRODUCTION

Investigative research work on the inhibitive properties of plants has of recent been receiving increasing attention.[1-19] Extracts from mango, cashew, pawpaw and neem plants, among others, have been studied and are further receiving more investigation.[1,2,6-8] In most cases, the results obtained have been satisfactory. The presence of tannin in the solution extracts has been associated with the corrosion inhibitive effect of the different plants extracts investigated.[6-8]

In this work, green tea extract was used as inhibitor. 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. The plant is cultivated in more than 30 countries. Teas differ based on how they are produced. Green tea production involves steaming fresh leaves at elevated temperatures, followed by a series of drying and rolling, so that the chemical composition essentially remains as that of fresh leaves. This process makes commercial green tea. 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.[20] Monomeric flavanols, the major components in green tea, are precursors of condensed tannin.[20] The flavanols are easily oxidized to the corresponding O – quinones. These flavanols and quinones can function as either hydrogen acceptors or hydrogen donors. In addition, tea polyphenols effectively interact with reactive oxygen species. In flavanol structure, the 5- and 7- dihydroxy groups and 1- oxygen make the carbons at positions six and eight strongly nucleophilic. 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.[20] In green tea, caffeine, theobromine, and theophylline, the principal alkaloids, account for about 4% of the dry weight. In addition, there are phenolic acids such as gallic acids and characteristic amino acids such as theanine.

The complex nature of the tea's chemical composition and structure is expected to prove effective in corrosion inhibition of mild steel in the strong acids: HCl and H_2SO_4. This work, therefore, reports the results obtained in the evaluation of the corrosion inhibitive effectiveness of the tea extract on the corrosion of mild steel test specimens immersed in dilute 0.5M hydrochloric acid and dilute 0.8M H_2SO_4 at ambient temperature. The need for a possibility of using plant extracts as a natural source of inhibitor to militate against the corrosion of metals in corrosive environments necessitates this investigation. It is anticipated that the study will make a contribution to the present research interest in this area of studies. Economic and technological benefit is envisaged from a positive result in this work.

Table 1
Summary of per cent nominal composition of mild steel

C	Si	S	P	Mn	Ni	Cr	Mo	V	Cu	Sn	Al
0.171	0.209	0.04	0.025	0.55	0.141	0.067	0.011	0.002	0.252	0.01	0.003
Zn	**Nb**	**Ti**	**W**	**Pb**	**B**	**Ca**	**Ce**	**Zr**	**Bi**	**Co**	**Fe**
0.003	0.012	0.0004	0.004	0.0004	0.001	0.0007	0.008	0.002	0.001	0.009	98.48

EXPERIMENTAL PROCEDURE

Preparation of Specimens

The mild steel specimen used as test specimens was obtained from a local rolling mill in Nigeria. It has a per cent nominal composition as shown in Table 1.

The steel plate was cut into 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 24 samples used for the weight loss experiment were de-scaled with a wire brush, ground with various grades of emery paper and then polished to 6 μm,. 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 24 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.

Preparation of Plant Extracts and Test Media

The experiment was performed in (i) hydrochloric acid medium (0.5M HCl) and (ii) sulphuric acid medium (0.8M H_2SO_4) both of AnalaR grade. 0.5M HCl was prepared by diluting 41.39 cm^3 of concentrated HCl in 1 liter of distilled water while 0.8M H_2SO_4 was prepared by diluting 44.44cm^3 of concentrated H_2SO_4 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 40ml of green tea leaves extract used, it was boiled in 400ml of 0.5M HCl solution and 400ml of 0.8MH_2SO_4 solution respectively.

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 each acid, 60% was also obtained by mixing 60ml of stock with 40ml of each acid. The same procedure was followed to obtain 40% and 20% inhibitor concentrations.

Weight loss experiment

Weighed test specimens were totally immersed in each of the test media contained in a 250ml beaker for 24 days. Two test coupons were used for each test and the average weights used. Experiments were performed with 0.5M hydrochloric acid and 0.8M sulphuric acid test media 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 and then re-immersed in the test solution for continued tests during the whole experimental period. The plots of accumulated weight loss and of correspondingly calculated corrosion rate versus exposure time are respectively presented in Figure 1 and Figure 2. Corrosion rate was calculated from the formula in equation 1.[21]

$$C.R.\ (mm/y) = 87.6 \times (W / DAT) \quad \text{............................(1)}$$

where:

W = weight loss in milligrams

D = metal density in g /cm^3

A = exposed area of sample in cm^2

T = time of exposure of the in hours metal sample

The percentage inhibitor efficiency, P, for each of the corrosion rate results obtained for every experimental reading was calculated from the relationship:

$$P = 100[1 - W_2/W_1] \quad \text{.. (2);}$$

Where:
W_1 and W_2 are, respectively the corrosion rates in the absence and presence of the predetermined concentration of the inhibitor. The results obtained are used to plot the curve(s) of % inhibition efficiency vs. exposure time (days).

Potential Measurements

Potential measurements were performed on the mounted specimens in turns by immersing them in each of the acid test media 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 Figure 4.

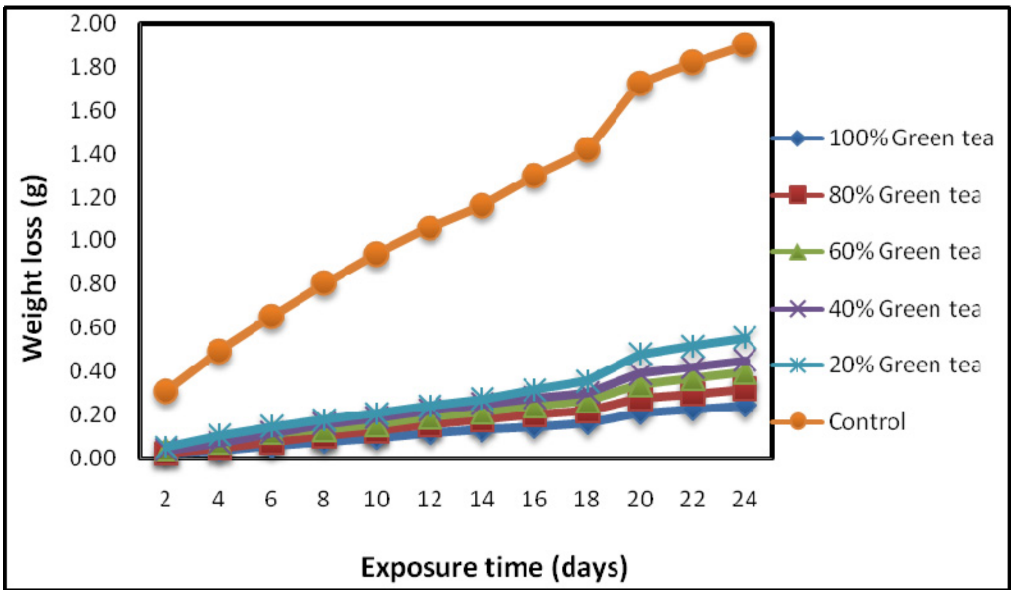

Figure 1: Variation of weight loss with exposure time for mild steel immersed in 0.5M HCl solution with varying concentrations of inhibitor

RESULTS

Weight Loss Method

<u>*Camellia Sinensis* with mild steel in HCl.</u>

The results obtained for the variation of weight loss with exposure time for the mild steel specimens immersed in 0.5M hydrochloric acid with varied concentrations of green tea extract are presented in Figure 1.

From Figure 1, it is clear that the mild steel sample immersed in the solution without any inhibitor lost the most weight within the 24 day duration of the experiment with a total weight loss of 1.89 g. The weight loss increased in the order of the concentration of the inhibitor in each of the solutions. This could have been due to a larger concentration of the inhibiting species contained in the solution with 100% having the greatest inhibiting effect with a total weight loss of 246 mg.

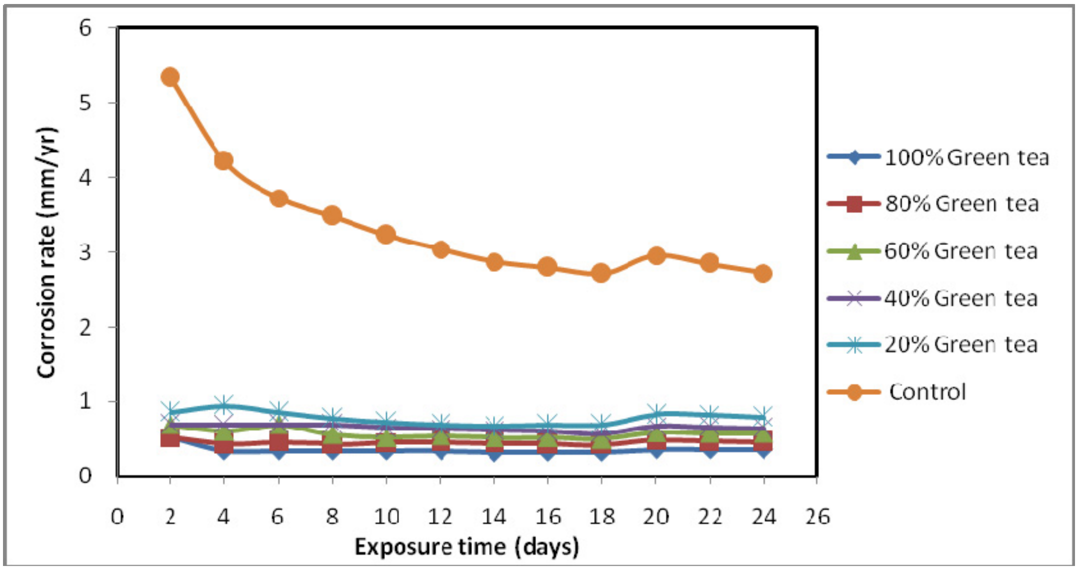

Figure 2: Variation of corrosion rate with exposure time for mild steel immersed in 0.5M HCl solution with varying concentrations of inhibitor

The specimen with no inhibitor had the highest corrosion rate throughout the experiment and the samples with inhibitor all had low corrosion rates with the specimen in 100% inhibitor having the least corrosion rate throughout the experiment with a corrosion rate of approximately 0.36 mm/yr on the 24th day.

Camellia Sinensis with mild steel in H_2SO_4

Results obtained for the variation of weight loss with exposure time for the mild steel specimens immersed in 0.8M sulphuric acid with varied concentrations of green tea extract are presented in Figure 3. From the graph, it is clear that the mild steel sample immersed in the solution without any inhibitor lost the most weight within the 24 day duration of the experiment as was the case in Figure 1, with a total weight loss of 6.43g. The weight loss also increased in the order of the concentration (100, 80, 60, 40 and 20%) of the inhibitor in each of the solutions. This could have been due to a larger concentration of the inhibiting species contained in the solution with 100% having the greatest inhibiting effect with a total weight loss of 1226 mg. It was noted however, that there was a decrease in weight loss with 40% inhibitor concentration which was not quite significant since it was only less than the preceding value.

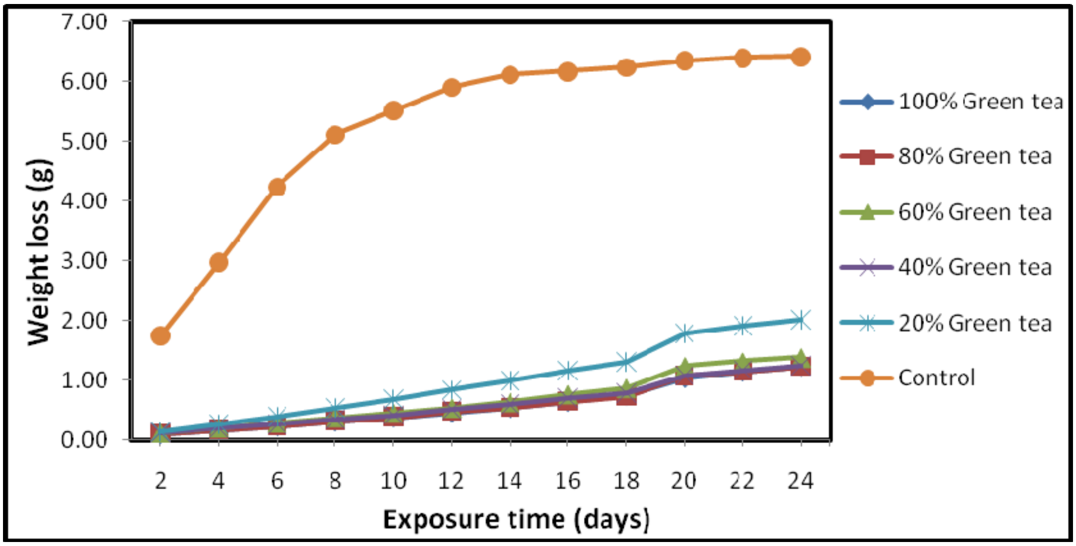

Figure 3: Variation of weight loss with exposure time for mild steel immersed in 0.8M H_2SO_4 solution with varying concentrations of inhibitor

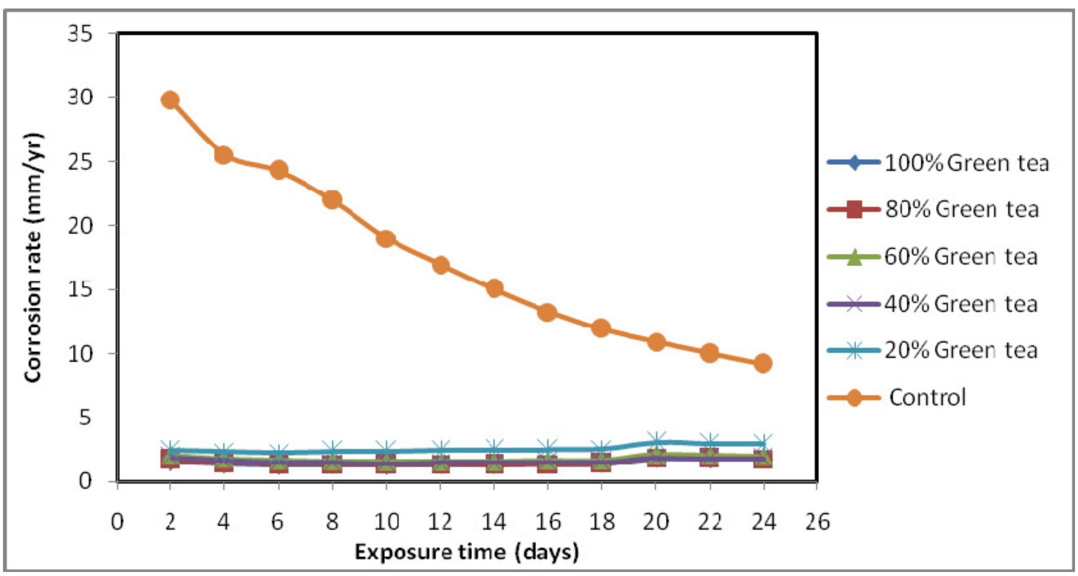

Figure 4: Variation of corrosion rate with exposure time for mild steel immersed in 0.8M H_2SO_4 solution with varying concentrations of inhibitor

The specimen with no inhibitor had the highest corrosion rate throughout the experiment and the samples with inhibitor all had low corrosion rates with the specimen in 100% inhibitor having the least corrosion rate throughout the experiment with a corrosion rate of approximately 3 mm/py on the 24th day.

Statistical Analysis

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 mild steel in 0.5M HCl and 0.8M H_2SO_4 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 study[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):

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

Total Sum of Squares:

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

The calculation using the ANOVA test is tabulated (Table 2 and 3) as shown.

Table 2
Summary of ANOVA analysis for weight loss measurements in 0.5M HCl

Source of Variation	SS	Df	MS	F	Significance F
Exposure Time	2.23	11	0.20	7.15	1.97
Concentration of *Camellia Sinensis*	8.74	5	1.75	61.63	2.38
Residual	1.56	55	0.03		
Total	12.53	71			

Table 3
Summary of ANOVA analysis for weight loss measurements in 0.8M H_2SO_4

Source of Variation	SS	Df	MS	F	Significance F
Exposure Time	23.31	11	2.12	8.38	1.97
Concentration of *Camellia Sinensis*	210.64	5	42.13	166.69	2.38
Residual	13.9	55	0.25		
Total	247.86	71			

On the basis of the results in Table 2 and 3, it can be concluded with 95% confidence that the exposure time and concentration of *Camellia Sinensis* partially affects the corrosion rate of mild steel in 0.5M HCl and 0.8M H_2SO_4 environments. This gave good correlation with the scatter plots obtained in Figure 1, Figure 2, Figure 3 and Figure 4. It was further observed that the concentration of *Camellia sinensis* extract had greater significant effect on the corrosion rate (Figure 5 and Figure 6).

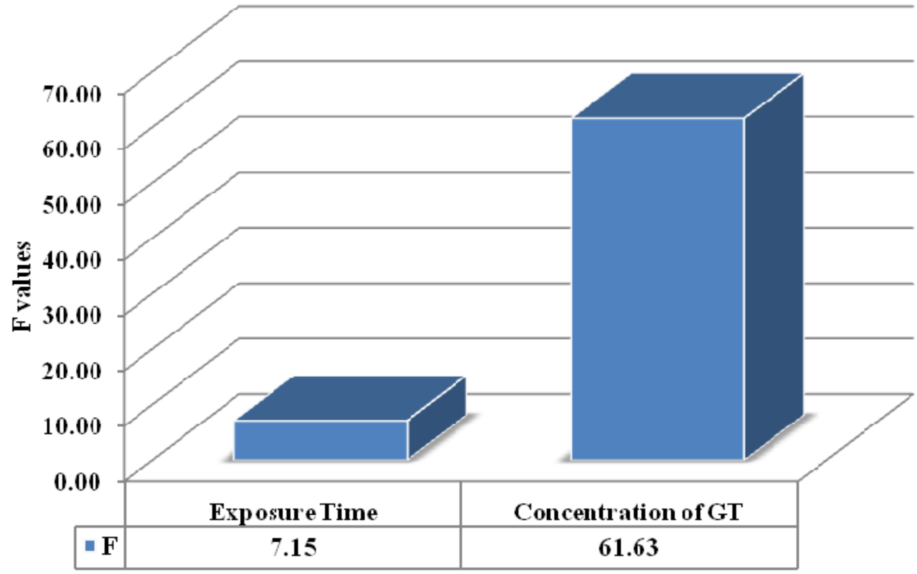

Figure 5: F values showing the influence of exposure time and GT concentration on Weight Loss measurements in HCl

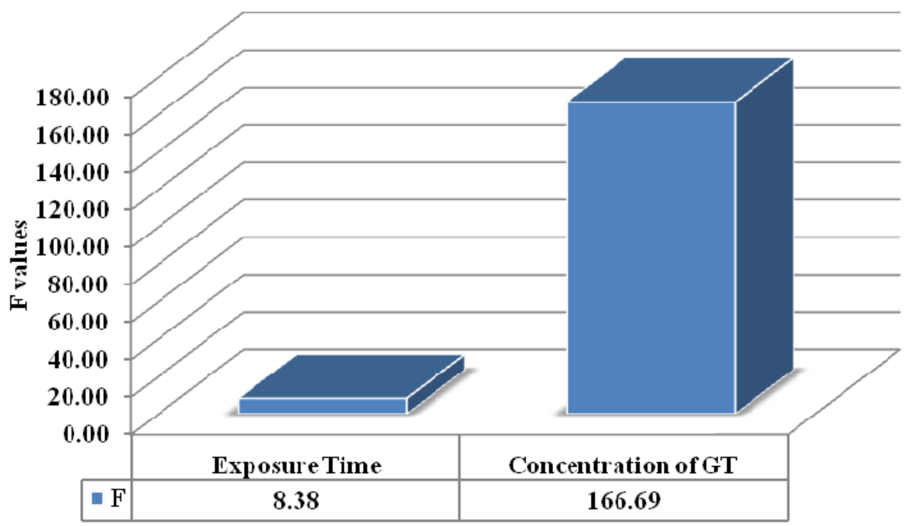

Figure 6: F values showing the influence of exposure time and GT concentration on Weight Loss measurements in H_2SO_4

Potential Measurement

Camellia Sinensis with mild steel in HCl

Potential readings for the mild steel 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 Figure 7. 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 throughout the experiment with a range of potential value from –466 to –602mV.

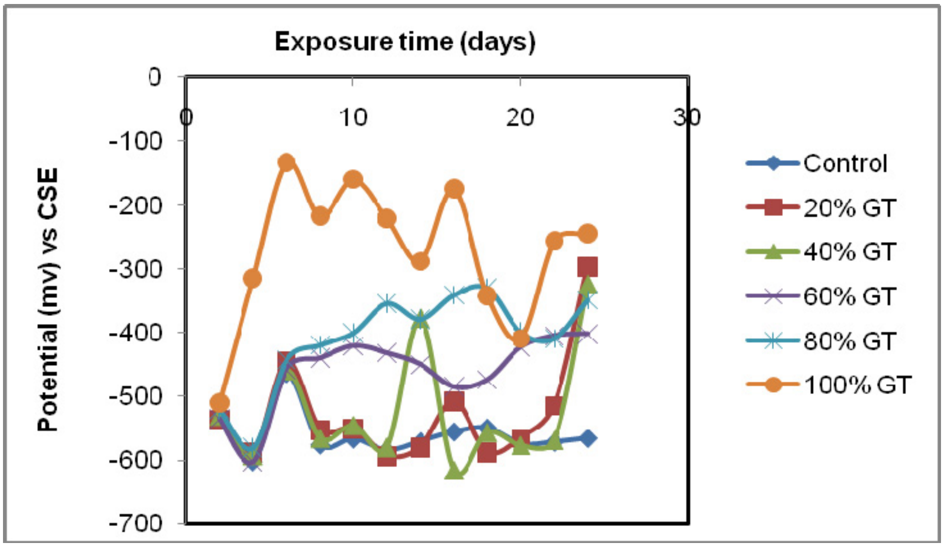

Figure 7: Variation of potential with exposure time for mild steel immersed in 0.5M HCl in addition of different concentrations of green tea

There was increasing positivity and decrease in corrosion reactions with increasing concentrations of green tea. The optimal performance was obtained with 100% concentration. This has potential values of –133mV on 6th day of the experiment, –342mV on the 18th day and –245mV on the 24th day. These values, in spite of the fluctuations, indicated passive range of corrosion reactions.

Camellia Sinensis with mild steel in H_2SO_4

Results obtained for the variation of potential with exposure time for the mild steel specimens immersed in 0.8M sulphuric acid with varied concentrations of green tea extract are presented in Figure 8.

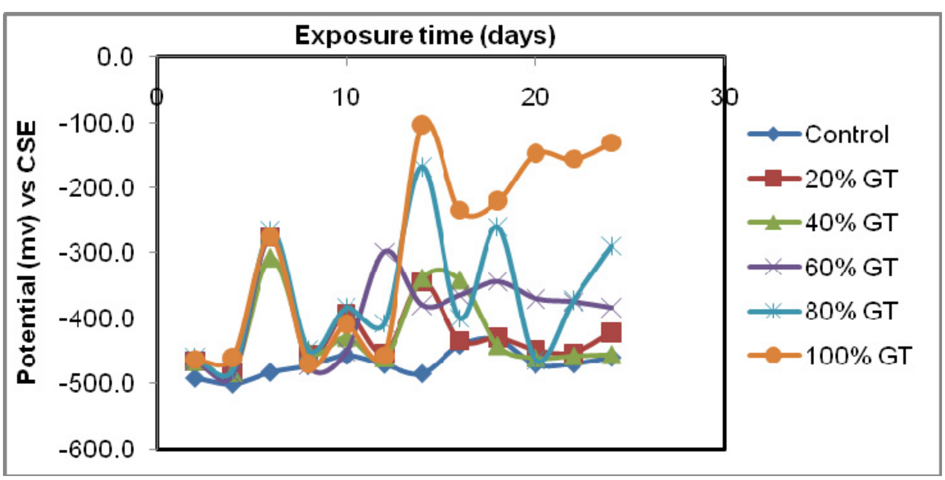

Figure 8: Variation of potential with exposure time for mild steel immersed in 0.8M H_2SO_4 in addition of different concentrations of green tea

At the start of the experiment, there were active corrosion reactions for all test situations. Subsequently, however, corrosion reaction in the presence of the different Green tea concentrations exhibited fluctuations into the passive potential ranges. The control experiment exhibited active corrosion reactions throughout the duration of the experiment within a potential range of –433mV and –501mV. From the 12th day of the experiment, an increasing inhibitor performance was observed with increasing concentration of camellia sinensis, resulting into a similar trend with the case of mild steel in 0.5M HCl. The 100% GT concentration gave the best performance with more passive reactions, followed by 80% GT, though highly fluctuating.

The effect of these variables on the corrosion potential of mild steel was further confirmed with the ANOVA test using equations (2) – (4) as stated earlier. The results are displayed in Table 4 and 5.

Table 4
Summary of ANOVA analysis for potential measurements in 0.5M HCl

Source of Variation	SS	Df	MS	F	Significance F
Exposure Time	163506.94	11	14864.27	6.89	1.97
Concentration of GT	671431.78	5	134286.36	62.21	2.38
Residual	118717.22	55	2158.49		
Total	953655.94	71			

Table 5
Summary of ANOVA analysis for potential measurements in 0.8M H_2SO_4

Source of Variation	SS	Df	MS	F	Significance F
Exposure Time	23.31	11	2.12	8.38	1.97
Concentration of GT	210.64	5	42.13	166.69	2.38
Residual	13.9	55	0.25		
Total	247.86	71			

On the basis of the results in Table 4 and 5, it can be concluded with 95% confidence that the exposure time and concentration of *Camellia Sinensis* significantly affects the corrosion potential of mild steel in 0.5M HCl and 0.8M H_2SO_4 environments. This gave good correlation with the scatter plots obtained in Figure 7 and Figure 8. It was further observed that the concentration of *camellia sinensis* extract had greater significant effect on the corrosion potential (Figure 9 and Figure 10).

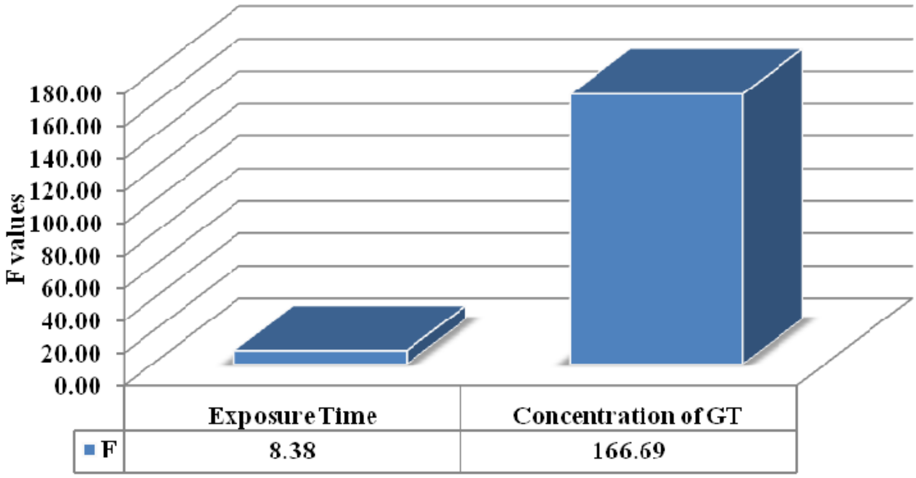

Figure 9: F values showing the influence of exposure time and GT concentration on Potential measurements in HCl

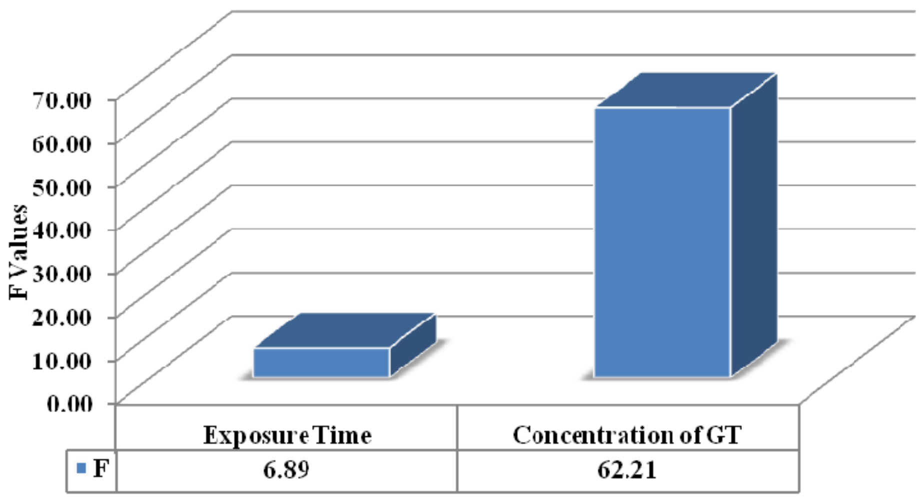

Figure 10: F values showing the influence of exposure time and GT concentration on Potential measurements in H_2SO_4

Inhibitor Efficiency

The results of the inhibitor efficiency obtained by calculations are presented in Figure 11 and Figure 12. Using both HCl and H_2SO_4, there was increased inhibitor efficiency with increased per cent concentration of inhibitor and increased exposure time throughout the whole experimental period. For mild steel in 0.5M HCl, the extracts with 100% concentration addition gave the optimal inhibition efficiency of 87% on the 24th day of the experiment. Similarly, the 80% concentration addition gave inhibition efficiency of 83.2% on the 24th day of the experiment. Also, the 60% concentration addition gave a high inhibition efficiency of 79.2% on the 24th day of the experiment. It was observed that the inhibition efficiencies increased with increasing exposure time and inhibitor concentration respectively. A similar trend was also observed for mild steel in 0.8M H_2SO_4. At the end of the 24^{th} day, all the specimens had the following inhibitor efficiencies, 80.9%, 80.9%, 78.5%, 80.7%, and 68.6% in order of the inhibitor concentrations starting with the 100% inhibitor specimen.

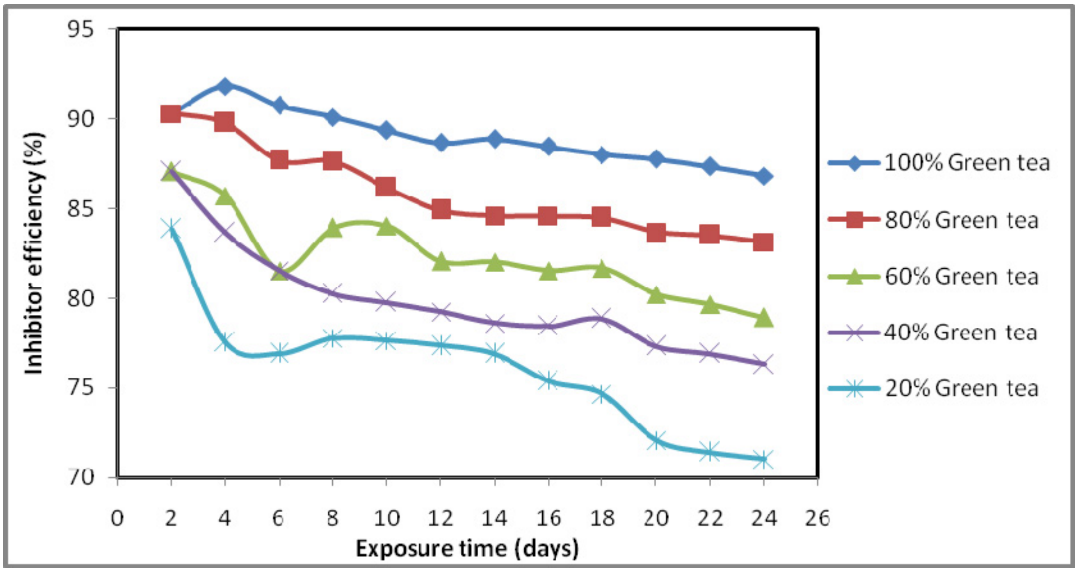

Figure 11: Variation of inhibitor efficiency with exposure time in days for mild steel immersed in 0.5M HCl in addition of different concentrations of green tea

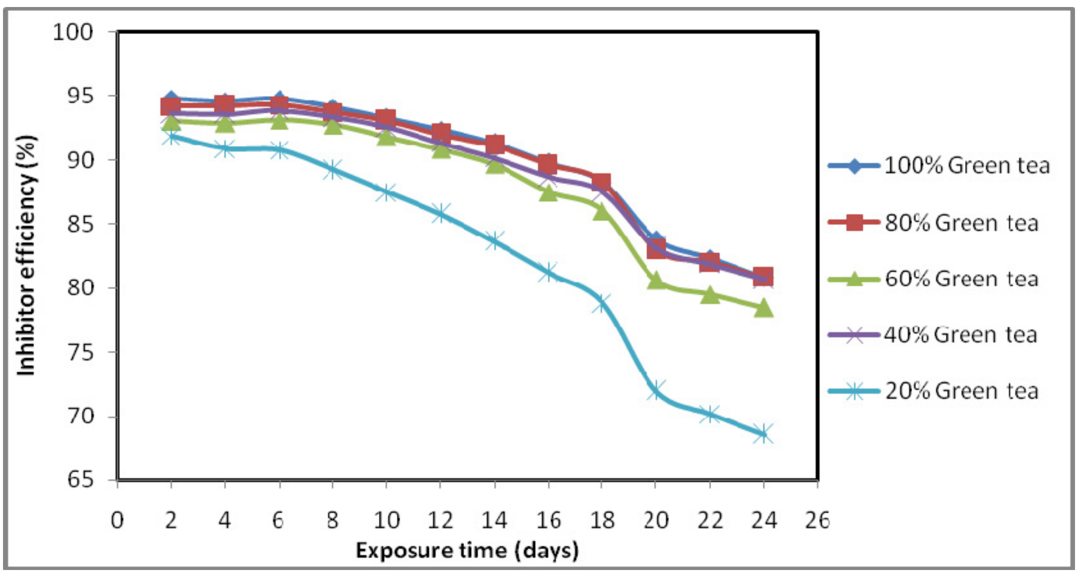

Figure 12: Variation of inhibitor efficiency with exposure time in days for mild steel immersed in 0.8MH_2SO_4 in addition of different concentrations of green tea

After removing the samples from solution at the end of the experiment, severe corrosion was observed by inspecting the surface of the samples without inhibitor under the microscope. A positive change was observed by using the green tea inhibitor indicating suppressed corrosion.

Thermodynamics and Adsorption Studies

Corrosion inhibition of mild steel in 0.5M HCl and 0.8M H_2SO_4 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, using the surface coverage parameter ϴ defined as:

$$\theta = IE\% \times 100 \qquad \text{……………………………………. (5)}$$

Where *IE%* is the inhibition efficiency. This was fitted to the Langmuir adsorption isotherm model given by:[24]

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad \text{……………………………………. (6)}$$

Where *C is Camelia Sinensis* concentration and K_{ads} is the adsorption equilibrium constant from which the standard free energy of adsorption $\Delta G^o{}_{ads}$ were evaluated based on the relationship:[21,24-25]

$$K_{ads} = \frac{1}{55.5}\exp\left(-\frac{\Delta G^o{}_{ads}}{RT}\right) \qquad \text{……………………………………. (6)}$$

Where R is the molar gas constant = 8.314 kJ/mol·K, and
T is the absolute ambient temperature ≡ 300K

The results of the fittings to the isotherm model for the mild steel in 0.5M HCl are presented in Table 6 while the results of the fittings for mild steel in 0.8M H_2SO_4 are presented in Table 7, through the 24-day experimental period.

Table 6
Thermodynamic parameters for mild steel in 0.5M HCl with green tea extracts

Immersion Time (days)	2	4	6	8	10	12	14	16	18	20	22	24
K_{ads}	0.27	0.17	0.15	0.16	0.17	0.16	0.16	0.15	0.15	0.13	0.12	0.12
$-\Delta G^o{}_{ads}$	15.62	12.91	12.15	12.51	12.78	12.53	12.43	12.21	12.11	11.23	11.04	10.89
r^2	99.85	99.78	99.58	99.76	99.78	99.71	99.70	99.71	99.74	99.73	99.72	99.71

Table 7
Thermodynamic parameters for mild steel in 0.8M H_2SO_4 with green tea extracts

Immersion Time (days)	2	4	6	8	10	12	14	16	18	20	22	24
K_{ads}	102.80	90.73	86.53	76.53	64.98	58.13	47.14	39.93	36.78	26.47	25.14	24.63
$-\Delta G^o{}_{ads}$	49.68	48.96	48.69	47.99	47.05	46.41	45.20	44.25	43.78	41.89	41.59	41.47
r^2	99.99	99.99	99.99	99.99	99.99	99.99	99.98	99.97	99.95	99.88	99.88	99.87

Both tables showed that, for the fittings, coefficient of determination r^2 > 99% in the HCl and in the H_2SO_4 media. This suggest excellent model fitting of the experimental results by the Langmuir adsorption isotherm assumption. Also, the negative values of $\Delta G^o{}_{ads}$ obtained from both media imply that the adsorption process was spontaneous in both media and there was stability of the absorbed inhibitor layer on the metal surface. However, the values of the standard free energy of adsorption obtained for the 0.5M HCl medium are less negative than –20 kJ/mol indicating physical adsorption or physisorption mechanism prevails in the HCl medium. In contrast, the standard free energy of adsorption obtained for the 0.8M H_2SO_4 medium are more negative than –40 kJ/mol thus indicating chemical adsorption or chemisorption mechanism prevails in the sulphuric acid medium.[21,24-25]

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 of mild steel 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 mild steel could hinder the sulphate and chloride ion species, promote more stable passive film formation and hence inhibit and stifle corrosion reactions at the steel /environment interface.

CONCLUSIONS

Green tea was found to be an effective natural corrosion inhibitor for mild steel in 0.5M HCl and 0.8M H_2SO_4 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 mild steel in 0.5M HCl and 0.8M H_2SO_4 environments respectively. 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 in the HCl medium and by chemisorption in the H_2SO_4 medium.

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