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Inhibition effect of Tea *(Camellia Sinensis)* extract on the corrosion of mild steel in dilute sulphuric acid

C. A. Loto [1,2]

[1]*Department of Mechanical Engineering, Covenant University, Canaan Land, PMB 1023, Ota, Nigeria*

[2]*Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, Pretoria, South Africa*

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* Corresponding author. E-mail Address: *akinloto@gmail.com ; akinloto@yahoo.com*

Abstract

The effect of green tea extract as an organic 'green' inhibitor on the corrosion of mild steel in dilute sulphuric acid was studied at ambient temperature. Weight loss/corrosion rate and potential measurement techniques were used for the experimental work. The tea extract was obtained from the green tea leaves. The results obtained showed effective corrosion inhibition of the extract on the mild steel test specimens in the different concentrations of sulphuric acid used. There was no apparent significant difference in the corrosion inhibition performance of the selected extract's concentrations. The different acid strength used did not give any clear adverse corrosive effect on the performance of the inhibitor.

Key words: Inhibition, inhibitor, green tea, sulphuric acid, corrosion, tea, extract, mild steel, weight loss, corrosion rate, potential measurement.

Introduction

Investigative research work on the inhibitive properties of plants has of recent been receiving increasing attention [1-9]. 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 regarding 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 [10]. These compounds may account for up to 30% of dry weight. The other green tea polyphenols are flavonols, commonly known as catechins – the tea tannins. Green tea leaves contain six major catechins: (+)-catechin, (C), (-) – epicatechin (EC), (-)- gallocatechin (GC) , (-)- epicatechin gallate (ECG), (-)- epigallotechin (EGC), (-)- epigallocatechin gallate (EGCG) ( ). Catechins make approximately one- quarter of fresh dried green tea leaves of which EGCG comprises 60%. Green tea polyphenols include groups of compounds of different chemical structure and also possess variable biological properties. The green tea polyphenols' chemical structure is based on the conformation of the heterocyclic oxygen ring of the molecule.

Monomeric flavanols, the major components in green tea, are precursors of condensed tannin [10]. 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 [10]. 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 acid – 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 sulphuric acid with two different concentrations – 0.2M and 0.5M H_2SO_4 at ambient temperature..

The need for a possibility of using plant extracts as a natural source of inhibitor to mitigate against the corrosion of metals in corrosive environments necessitates this investigation. In addition, an effective inhibition of a plant extract such as this will be very environment friendly. 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.

Experimental procedure

Preparation of specimens

The mild steel specimen used as test specimens was obtained from a local rolling mill in Nigeria. It had a per cent nominal composition of 0.13C, 0.029Si, 0.018S, 0.0067P, 0.397Mn, 0.025Ni, 0.0076Cr, 0.0020Mo, 0.0010V, 0.036Cu, 0.0010Sn, 0.0057Co, 0.126Al, 0.023Zn, 0.0020Mg, 0.0046Nb, and 0.0025Bi, the rest Fe. The steel plate was cut into average dimension of 25 x 20 x 1mm. A wire brush was used to descale the test specimens. They were then ground with silicon carbide abrasive papers, polished, cleaned thoroughly, rinsed in ultrasonic cleaner, dried and kept in a desiccator for further weight- loss tests. Some of the specimens, after spot – welding to the connecting insulated flexible wire, were in turns, mounted in araldite resin. These specimens were prepared for potential measurements of the steel in the test environments.

Test media
The experiment was performed separately in 0.2M and 0.5M H_2SO_4 of AnalaR grade. The extracted solution of the green tea in different concentrations, was used as the corrosion inhibitor as explained below.

Green tea solution extract
The green tea extract was obtained directly from the tea bags of Lipton green tea. Some bags of the green tea were soaked in ethanol and left standing for 5 days. The solution was filtered and further distilled at 79^{o}C to remove the ethanol from the tea solution extracts and concentrate the inhibiting chemicals. The solution extract was further diluted and separately stored in a clean bottle and covered as 100% extract (as obtained), 50% green tea and 25% green tea extract concentrations.

Preparation of test media and the solution extract
350ml of 0.2M and 0.5M H_2SO_4 were separately measured into four different beakers each. The solution extract from the green tea in different concentrations of 100%, 50% and 25% was separately put in the first three beakers of each acid medium. No extract was added to the fourth beaker. These preparations were separately used for subsequent corrosion experiments.

Weight- loss experiment
Weighed test pieces were fully immersed, separately for 21 days in each of the beakers containing the 0.2M sulphuric acid and the solution extract for the three sets of the experiment described above, and the acid medium without the extract addition. The same process as above was done for the beakers containing 0.5M H_2SO_4 acid. Each of the test specimens was taken out every three days, washed with distilled water, rinsed with methanol, dried, and re-weighed. Plots of weight loss vs. exposure time and corrosion rate vs. exposure time were made (Figs. 1- 6).
The percentage inhibitor efficiency, P, for each of the corrosion rate results obtained for every experimental reading was calculated from the relationship:

$$P = 100[1 - W_2/W_1] \quad (1)$$

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). All the experiments were performed at the ambient temperature.

Potential measurements
The mounted and polished specimens were tested for potential measurements. They were immersed in turns in each of the different test media containing different concentrations of the extracted green tea inhibitor. The same tests were also performed in the acid (with two different concentrations) without the extract addition. The potential was recorded at 3 – day intervals using a digital multimeter and saturated calomel electrode (S.C.E.) as the reference electrode. Curves of variation of potential (mV) vs. S.C.E with exposure time obtained are presented in Figs.5 and 6.

Results and discussion

Weight-loss method
The results obtained for the variation of weight loss with exposure time for the steel specimens immersed in 0.2M H_2SO_4 with and without the addition, separately, of varied concentrations of green tea extract are presented in Fig.1. The first curve with the highest magnitude of weight loss (mg) throughout the days of the experiment contained no juice extract addition: it served as the control experiment. Apparently, there was no corrosion inhibition of the test specimens for the 21 days duration of the experiment. The green tea extracts addition to the test medium reduced corrosion significantly throughout the experimental period. The results showed no weight loss at all in the first 3 days of the experiment; but rising just a little to 0.50×10^2 mg on the 21st day. The results obtained for the 100%, 50% and 25% green tea extract concentrations addition to the test medium were all very similar and bear very close relationship in corrosion inhibition behavior; thus indicating little extract concentration effect. However, the results confirmed the very good effect of the green tea solution extract on the corrosion inhibition of mild steel in sulphuric acid at its concentration of use.

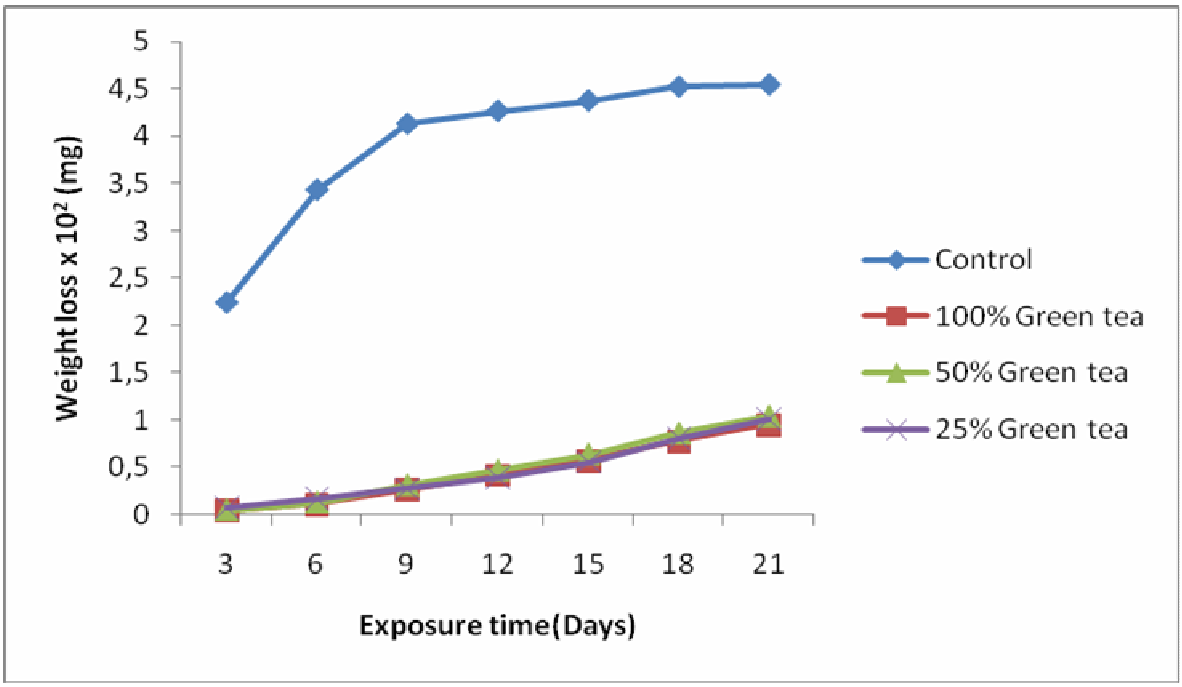

Figure 1: Variation of weight loss with exposure time for the mild steel specimen immersed in 0.2M H_2SO_4 and addition of different concentrations of green tea extract.

The corresponding corrosion rate vs. the exposure time curves obtained by calculation from the weight-loss data are presented in Fig. 2. The corrosion rate curve for the test medium without the green tea addition showed high corrosion rate in the first 3 days of the experiment, achieving a magnitude of 70mm/yr. This phenomenon was found, however, to decrease significantly with time till the end of the experiment. As expected, sulphuric acid is a very strong acid and it has very drastic corrosion effect on unprotected mild steel. The corrosive action produced a lot of dissolution of the steel into the solution and thus weakening the test medium. In consequence, the corrosion reactions became shifted with the increasing days of the experiments. With the addition of the varied concentrations of the green tea extracts, the corrosion rate became significantly reduced and achieving a magnitude of about 2 mm/yr in the first 3 days and increasing to 5 mm/yr in the 21st day of the experiment.

Very similar results as above were obtained for the weight loss and corrosion rate vs. exposure time experiments when the H_2SO_4 concentration was increased from 0.2M to 0.5M, Figs.3 and 4. At this acid concentration and for all per cent of green tea extract concentrations, green tea extract in 0.5M H_2SO_4 showed excellent inhibiting behavior. The weight- loss readings recorded were minimal due to the addition of the different inhibitor concentrations.

The curve of the test medium without green tea extract addition showed great increase in weight loss with increase in exposure time. The corrosion rate also behaved similarly. Addition of green tea extract as inhibitor showed very much reduced weight loss and corrosion rate. The effect of varied acid concentration on the corrosion of mild steel when this green inhibitor was used was very minimal. That is, the use of 0.2M or 0.5M H_2SO_4 did not affect the weight loss or the corrosion rate of mild steel in any significant way when the green tea extract in different concentrations were used, Figs.3 and 4.

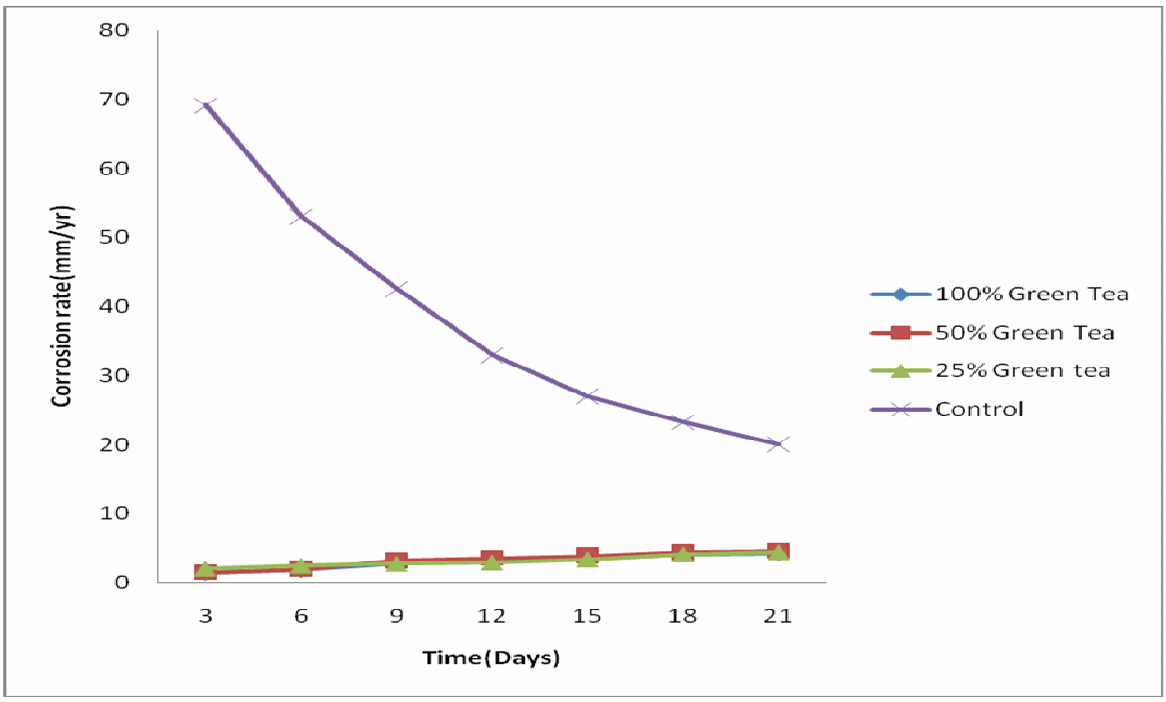

Figure 2: Variation of corrosion rate with exposure time for the mild steel specimen immersed in 0.2M H_2SO_4 and addition of different concentrations of green tea extract

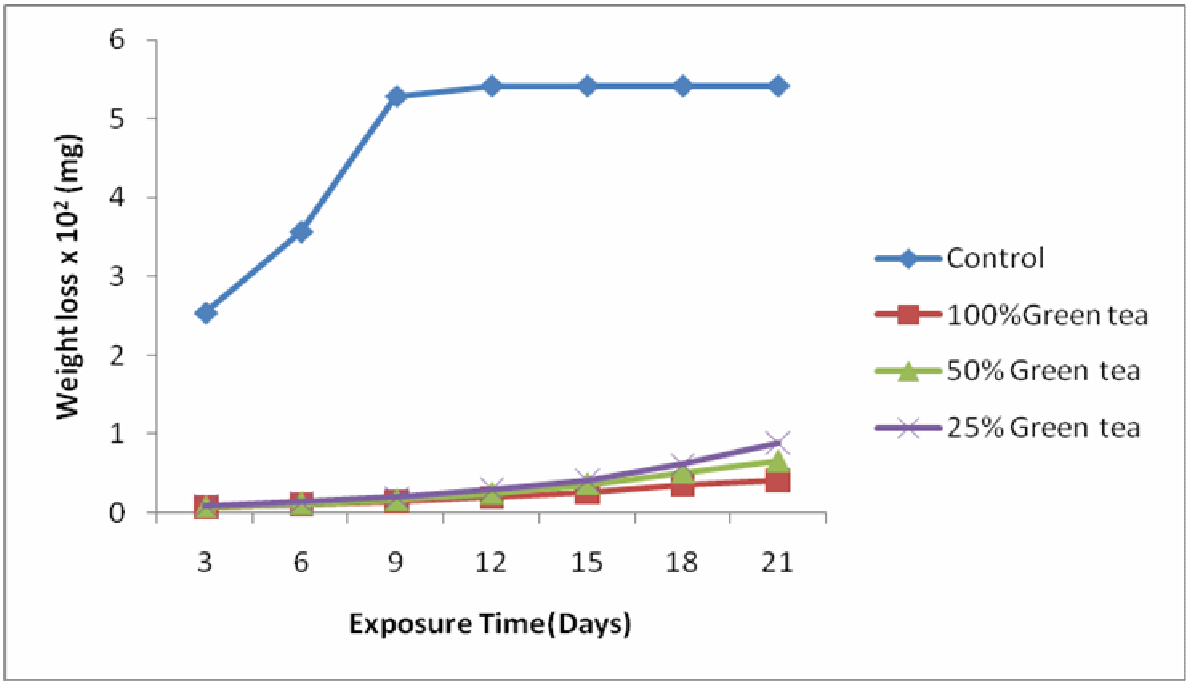

Figure 3: Variation of weight loss with exposure time for the mild steel specimen immersed in 0.5M H_2SO_4 and addition of different concentrations of green tea extract

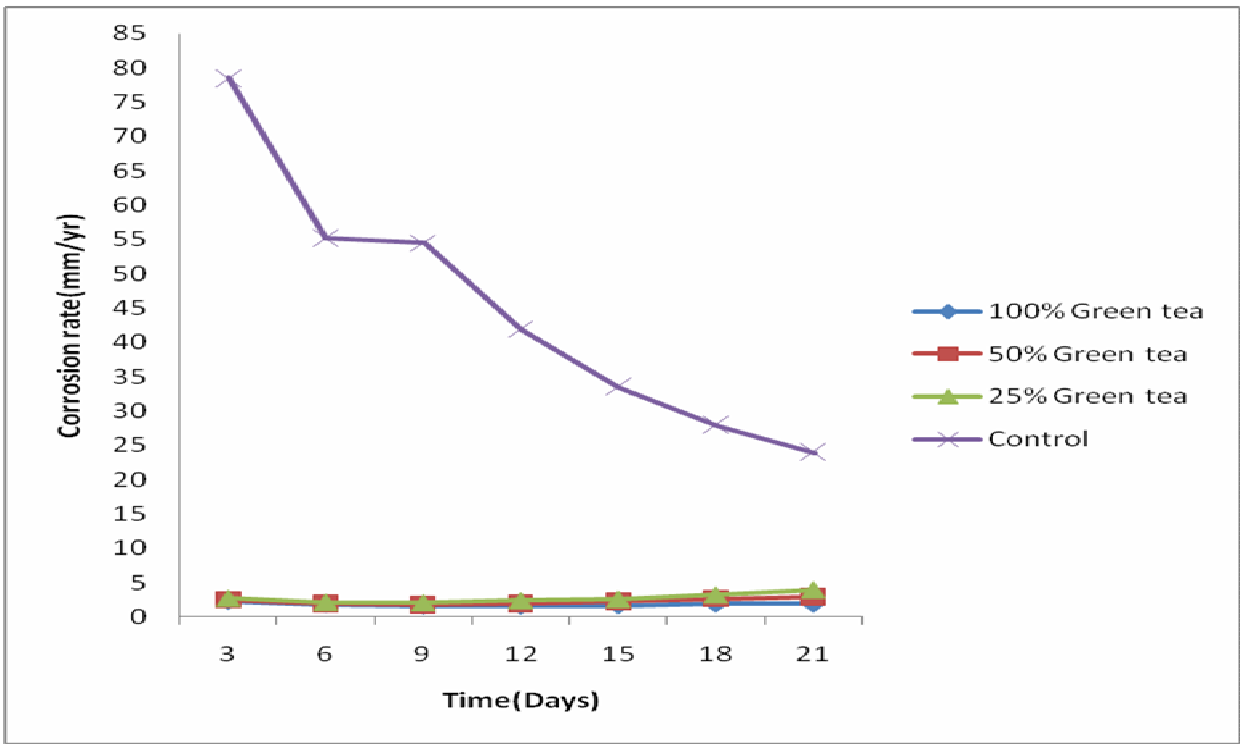

Figure 4: Variation of corrosion rate with exposure time for the mild steel specimen immersed in 0.5M H_2SO_4 and addition of different concentrations of green tea extract

Potential measurement

Curves of the variation of potential (mV) vs. saturated calomel electrode (SCE) with the exposure time for the mild steel specimen immersed in 0.2M H_2SO_4 with different per cent concentrations of green tea extract, are presented in Fig.5.

The curve obtained without the extract addition is also shown in the same figure. The test medium without the addition of tea extract showed active corrosion reactions behavior for the most part of the experimental period. The weakening of the acid corrosive medium by the corrosion products in solution and the deposits on the test specimens' surface slowed down the rate of the metallic test specimens' anodic dissolution. The addition of the tea extract to the test medium shifted the potentials more positively into almost passive state of corrosion reactions. This observed behavior was an indication of the effective corrosion inhibition performance of the green tea extract. In general, the results obtained bear a close relationship with those obtained with the weight loss method, Figs 1 and 2.

The curves of the variation of potential (mV) versus saturated calomel electrode (SCE) with exposure time for mild steel specimens immersed in 0.5M H_2SO_4 with different concentrations of added green tea extract are presented in Figure 6. In this figure, all the curves bear a very close relationship to the weight loss and corrosion rate, (Figs. 3 and 4).

In Fig. 5, all the green tea extract concentrations used, showed very good corrosion inhibition effect as all the potentials range from -490mV to -460mV vs. SCE. All the potential values, throughout the experiment were less negative than in the specimen immersed in the acid without added green tea extract. The curve without added green tea extract showed negative potentials that ranged between -495 to -505mV vs. SCE.

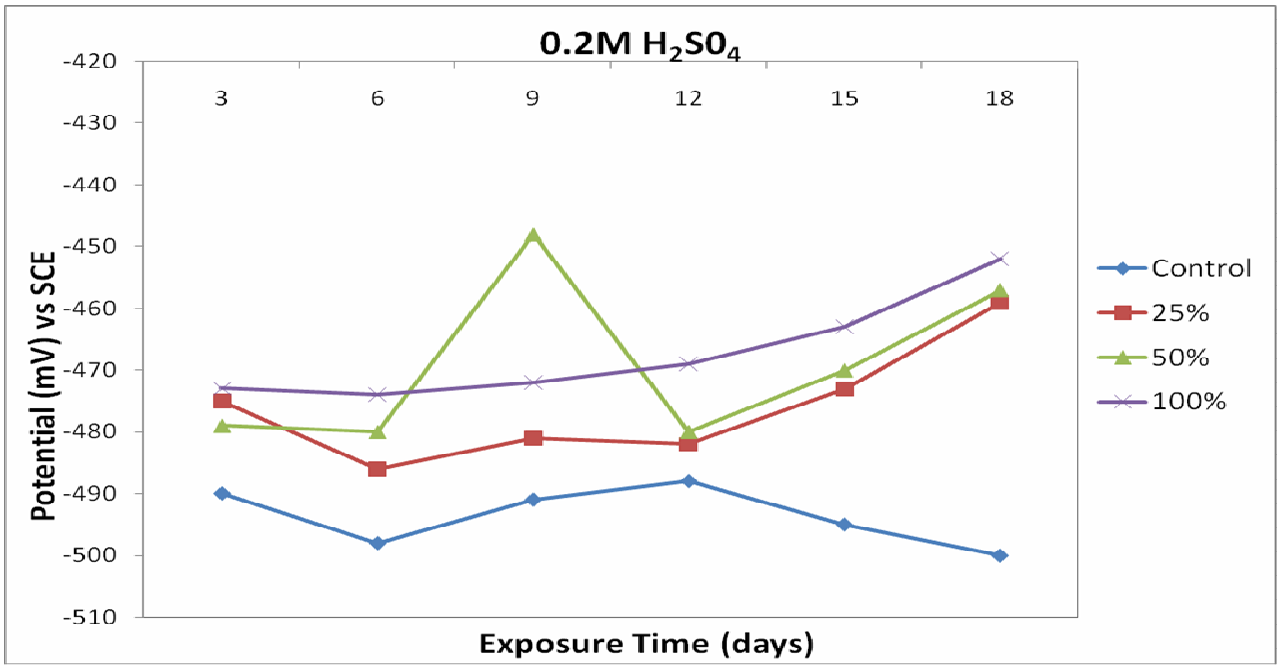

Figure 5: Variation of potential with exposure time for mild steel in 0.2M H_2SO_4 and tea extract

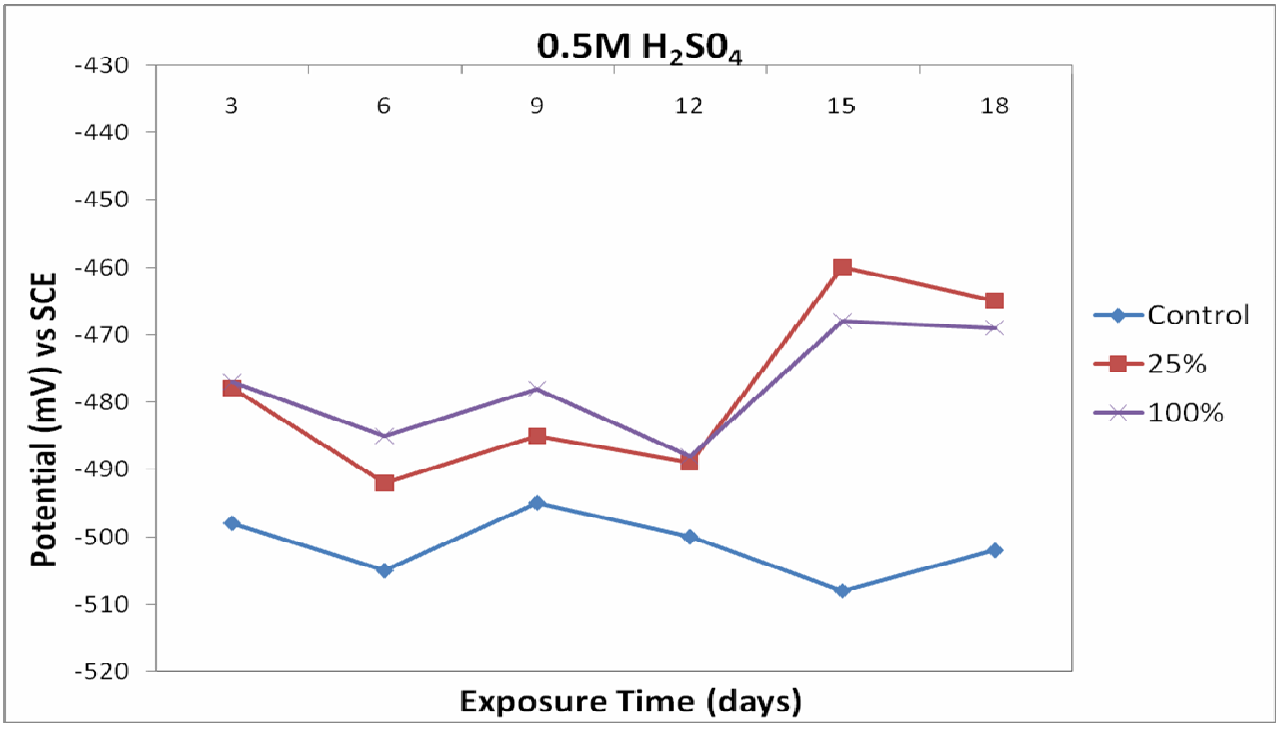

Figure 6: Variation of potential with exposure time for mild steel specimen in 0.5M H2SO4 and addition of different concentrations of green tea extract.

Inhibitor efficiency

The per cent inhibitor efficiency data obtained by calculation are presented in Figs. 7 and 8 for the experiment in 0.2M H_2SO_4 and in 0.5M H_2SO_4 respectively. In Fig.7, at the end of the experiment (21 days), inhibitor efficiency in order of 79%, 71% and 78% were obtained at 100%, 50% and 25% green tea extract concentrations respectively. This shows the green tea possesses a very good corrosion inhibition characteristic in the 0.2M H_2SO_4 medium for mild steel at ambient temperature.

In 0.5M H_2SO_4 experiment, the inhibitor efficiency at the 21st day of the experiment, for all the green tea extract concentrations, achieved values of 94%, 87% and 83% at 100%, 50% and 25% extract concentrations respectively, (Fig. 8).

All the results obtained for the inhibitor efficiency follow the same trend as the results obtained with the weight-loss and potential measurements.

The tea composition effect

Tea consists of many compounds with different complex chemical composition. A plausible explanation, therefore, for the effective corrosion inhibition performance of green tea extract for the mild steel specimen in sulphuric acid concentrations used can be associated with these complex compounds and diverse chemical composition [10]. Tea contains tannin which had been known [1, 2; 6, 7] to be an effective corrosion inhibitor. Tannins are a group of chemicals usually with large molecular weights and diverse structures. Monomeric flavanols, the major components in green tea, are precursors of condensed tannins [10]. In the flavanol structure, the 5- and 7- dihydroxy groups and 1 –oxygen make the carbons at positions 6 and 8 strongly nucleophilic. During enzyme oxidation or non enzyme oxidation, including autoxidation or coupled oxidation, tea flavanols may undergo oxidative condensation via C-O or C-C bond formation in oxidative polymerization reactions and thus producing the condensed tannin.

As mentioned in the introduction section of this paper, tea polyphenols also have high complexation affinity to metals, alkaloids, and biologic macromolecules such as lipids, carbohydrates, proteins, and nucleic acids [10]. The high complexation affinity to metals in particular could be responsible for the effective metallic corrosion inhibition performance. The very likely strong adsorption of the tea compounds' film to the metal surface that was enhanced by the high complexation affinity of polyphenols to metals could be responsible for the effective corrosion inhibition performance.

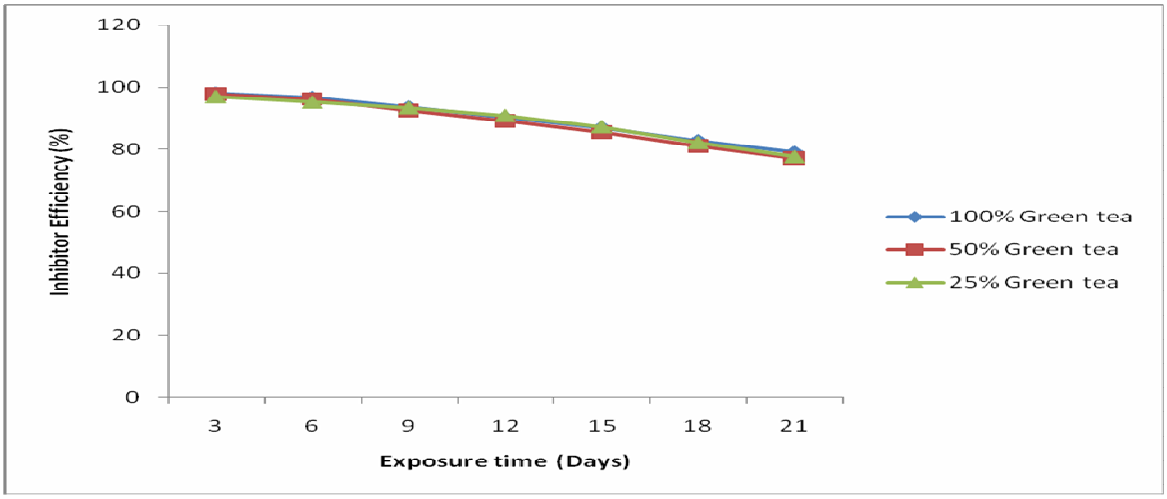

Figure 7: Variation of inhibitor efficiency with exposure time for the mild steel specimen immersed in 0.2M H_2SO_4 and addition of different concentrations of green tea extract

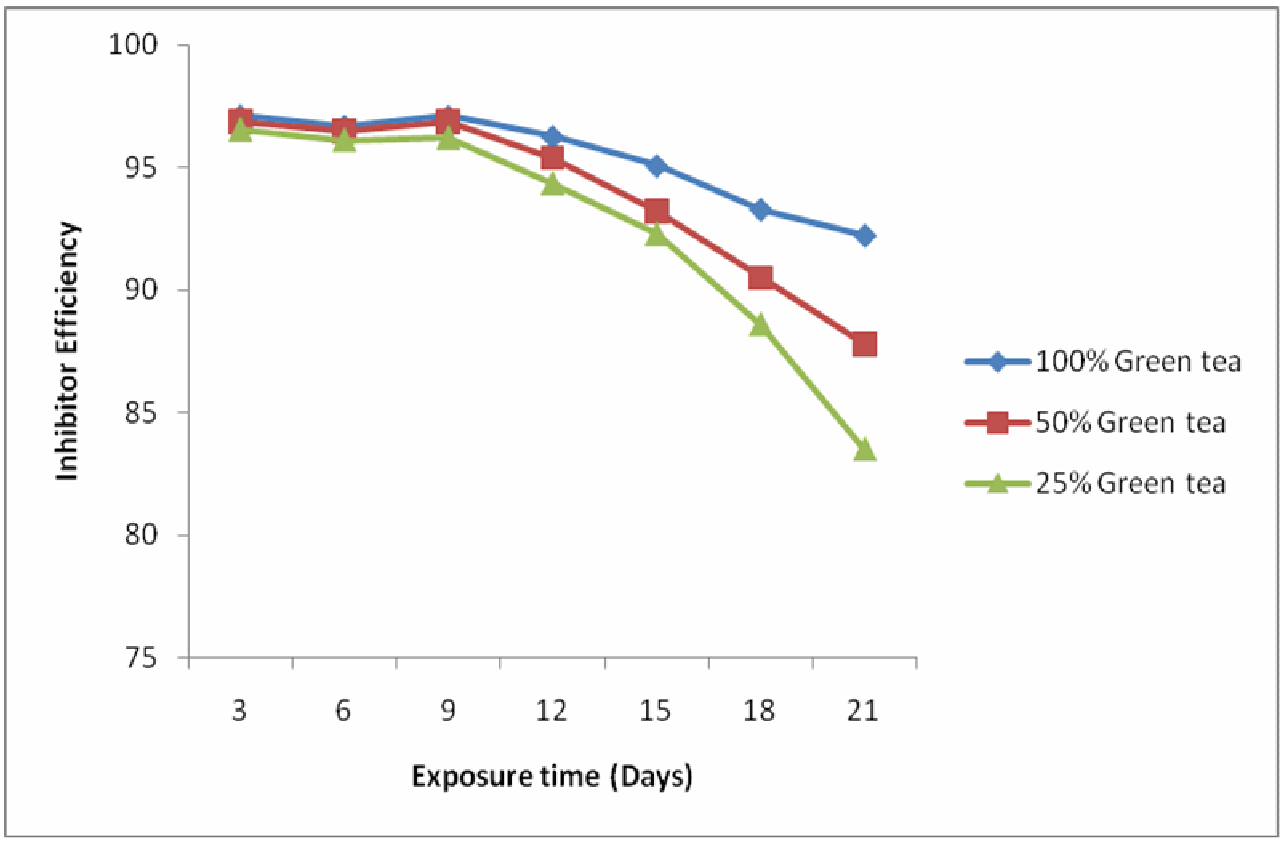

Figure 8: Variation of inhibitor efficiency with exposure time for the mild steel specimen immersed in 0.5M H_2SO_4 and addition of different concentrations of green tea extract

Conclusion

Working at the ambient temperature, the green tea extract gave an effective corrosion inhibition performance in both the 0.2M and 0.5M H_2SO_4 environments. The various per cent tea extract concentrations used, gave good results, though the best results were obtained with the 100% extract concentration in the two different sulphuric acid concentrations. The lower concentration of 0.2M H_2SO_4 did not give any clear advantage in the inhibition performance of the tea extract. Values of up to 94% inhibitor efficiency for 100% tea extract concentration in 0.5M sulphuric acid and 79% inhibitor efficiency for the same extract concentration in 0.2M H_2SO_4 were achieved.

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References

1. Loto, C.A., Mohammed, A.I. The effect of *Anacardium Occidentale* (cashew) juice extract on the corrosion of mild steel in hydrochloric acid. *Corrosion Prevention & Control J.* 47 (2000) 50-56.
2. Loto, C.A. The effect of mango bark and leaf extract solution additives on the corrosion

inhibition of mild steel in dilute sulphuric acid. *Corrosion Prevention & Control J. Part I.* 48 (2001) 38-40; Part II- 48 (2001) 59-64.
3. Davis, G.D. 'The use of extracts of tobacco plants as corrosion inhibitors', (2000) *DACCO SCI, INC*., Columbia, USA.
4. Abiola, O.K., Oforka, N.C., Ebenso, E.E. 'The Inhibition of Mild Steel Corrosion in an Acidic Medium by Fruit Juice of Citrus Paradisi', *Journal of Corrosion Science and Engineering*, 5 (2006) 1-7, University of Manchester, Manchester, England.
5. James, A.O., Ekpe, E.O. 'Inhibition of corrosion of mild steel in 2M hydrochloric acid by Aloe Vera', *International Journal of Pure and Applied Chemistry (IJPAC)*, 35 (2002) No 10, Oxbridge.
6. Loto, C.A. The effect of *Vernonia Amygdalina* (Bitter leaf) solution extract on the corrosion inhibition of mild steel in 0.5M hydrochloric and tetraoxosulphate (VI) acids. *Corrosion Prevention & Control J.* 50 (2003) 43-49.
7. Loto, C.A., Mohammed, A.I. and Loto, R O. Inhibition evaluation of *Mangifera Indica* (mango) juice extract on the corrosion of mild steel in hydrochloric acid. *Corrosion Prevention & Control J.* 50 (2003) 107-115.
8. Loto, C.A. Inhibition of cashew juice on the corrosion of mild steel in sulphuric acid. *Corrosion Prevention & Control J.* 52 (2005) 13-22.
9. Okafor, P.C et al. 'Eco-friendly corrosion inhibitors: inhibitive action of ethanol extracts of Garcinia kola for the corrosion of mild steel in H_2SO_4 solutions', *Pigment and Resin Technology*, 36 (2007) 5.
10. Chung, S. Yang, Zhi- Yuan Wang. The Chemistry of Tea, "The Tea Man", (1996). *www. Teatalk.com/science/chemistry.htm*