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Technical Report

Effect of *Cola Acuminata* and *Camellia Sinensis* Mixed Extracts on the Corrosion Inhibition of Mild Steel in 0.5M Sulphuric Acid

C.A. Loto[1, 2,] and A.P.I. Popoola[2]*

[1] Department of Mechanical Engineering, Covenant University, Ota, Nigeria
[2] Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, Private Bag X680, Pretoria, South Africa.
[*]E-mail: akinloto@gmail.com

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The corrosion inhibition effect of extracts of kola plant *(cola acuminata)* and green tea *(camellia sinensis)* in mixed form on the protection of mild steel specimens immersed in sulphuric acid solution was studied at ambient temperature by gravimetric and potential monitoring methods. The electrode potential monitoring was performed using a digital voltmeter and a saturated calomel electrode (SCE) as the reference electrode. Extracts of kola plant and green tea in different concentrations and combinations were used as 'green' inhibitors. There was significant reduction in the weight loss and in the corrosion rate of the test samples, particularly at the added extracts concentration of 100% and also at the concentrations of 50 and 25%. Some very good inhibitor efficiency values were obtained which suggested good corrosion inhibition performance of the added extracts at the concentrations used. Potential measurement values recorded showed a reduction in active corrosion reactions for all the combinations of the extracts. This behavior was attributed to the protective film provided on the steel's surface by the complex chemical constituents of the plants extracts. The best corrosion inhibition performance for mild steel was obtained using the combined extracts of kola leaf and green tea at100% concentration. The combination of kola leaf, kola nut and green tea at the same concentration was also effective in corrosion inhibition performance.

Keywords: Inhibition, corrosion, mild steel, kola tree, green tea, sulphuric acid, protection

1. INTRODUCTION

In a previous study [1, 2], the extracts of kola tree and green tea were separately investigated in acid chloride, sulphuric and hydrochloric acids. The results obtained were very encouraging and this necessitated the interest in undertaking the present study to look into the possible reactions synergism of these extracts when used in different combinations at about the same previous per cent concentrations.

The use of plant extracts as inhibitors for the corrosion of metals/alloys, has gained very wide interest among researchers in recent time [1-7]. In very many cases, the corrosion inhibitive effect of some plants' extracts has been attributed to the presence of tannin in their chemical constituents [7-9]. Also associated with the presence of tannin in the extracts is the bitter taste in the bark and /or leaves of the plants.

As previously reviewed [2], 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.

Also, kola nut tree's chemical composition consists of caffeine (2.0 - 3.5%), theobromine (1.0 – 2.5%), theophylline, phenolics – such as phobaphens, epicachins, D- catechin, tannic acid (tannin), sugar – cellulose, and water [11]. As reported in some previous studies and also mentioned above [2-7], tannin is known to possess corrosion inhibitive properties on metals – particularly, mild steel.

With the very complex structural chemical compounds of the extracts of the two plants, a reasonable amount of corrosion inhibition of the mild steel in the very corrosive acid environment used in this work is expected. Such a positive result will be economically and technologically beneficial.

2. EXPERIMENTAL PROCEDURE

The experimental procedure here follows that of other previous investigations [7]. The mild steel specimens used has the nominal composition of: 0.08 C, 0.34 Mn, 0.012 P, 0.008 S, 0.023 Si, 0.053 Al, 0.03 Cu, 0.002 Sn, 0.0024 N, 0.02 Cr and 0.01 Ni, the rest being iron. The mild steel samples were cut into dimension of 20 x 40 x 1.5 mm. A 1.5 mm diameter hole was drilled about 5 mm from the top of the 20 mm edge. The clean test specimens were ground with silicon carbide abrasive paper of 240, 320, 400 and 600 grits; polished to 1 micron, thoroughly cleaned and rinsed in ultrasonic cleaner, dried and kept in a desiccator for further tests. Selected specimens were, in turn spot welded to a connecting insulated flexible wires and mounted in araldite resin. They were subsequently used for potential measurement.

2.1. Preparation of test media and the plants extracts

The experiment was performed in sulphuric acid medium (0.5M H_2SO_4) of AnalaR grade. The separately extracted juices from the nuts and leaves of the kola tree and from green tea were used as the corrosion inhibitor, in different concentrations: 100% (as extracted), 50% and 25% respectively. .

The nuts and leaves of the kola tree (Cola acuminata) each weighing 1Kg, were collected. The nuts were pounded and ground to a coarse powder. The leaves were cut, oven dried at 72^{o}C and blended to fine powders using a blending machine. 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.

2.2. The test media

150 ml of sulphuric acid (0.5 M) was put into different 250ml beakers. The first beaker contained only the acid test medium. Extracts of kola nuts and kola leaves, each with the addition of green tea extract; in three different concentrations as mentioned above, were put in the other beakers separately. Further, extracts of kola nuts, kola leaves and green tea (*c. sinensis*) were added together in three different combinations/concentrations for another set of tests for synergism effect.

2.3. Weight loss experiment

Weighed test specimens were totally immersed in each of the test media contained in a 250ml beaker for 21 days. Experiments were performed with 0.5M sulphuric acid test medium in which some had the mixed solution extracts added. Test specimens were taken out of the test media every 3 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 to 6) were made. The corrosion rate calculation is from this formula:

$$mm/yr = 87.6W/DAT \text{……….} \ (1)$$

where W is the weight loss in milligrams, D is the density in g/cm^2, A is the area in cm^2, and T is the time of exposure in hours. All the experiments were performed at ambient temperature(s). The percentage inhibitor efficiency, P, was calculated from relationship: P = 100 (1-W_2)/ (W_1)………. (2): where;

W_1 and W_2 are the corrosion rates in the absence and presence, respectively, of a predetermined concentration of inhibitor. The inhibitor efficiency (%) was calculated for all the inhibitors for every 3 days of the experiment, (Figs. 10-12).

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 mixed plant extracts. The potential was recorded at 3 – 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 Figs. 7 to 9.

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 mild steel specimens immersed in 0.5M sulphuric acid with varied concentrations of kola leaf, kola nut and green tea in combinations are presented in Figs. 1 to 6.

3.2. Kola nut and green tea mixed extracts

The results obtained for the variation of weight loss with exposure time for the mild steel test - specimens immersed in 0.5M sulphuric acid with addition of varied concentrations of kola nut and green tea extracts in different combinations are presented in Fig. 1. The corresponding corrosion rate vs. the exposure time curves are presented in Fig. 2. The acid test medium with 25% concentration extract addition had the least corrosion inhibition effect of the immersed specimens by the end of the 21st day achieving a weight loss value of 397mg. At this value it could be considered to be fairly protective; even when compared with the specimen without added mixed extracts. The control experiment (without added extracts) recorded a weight loss value of 542mg at the 21st day of the experiment. The test medium with added 50% concentration of mixed extracts performed better than that of the 25%'s. It recorded a weight loss value of 244mg on the 21st day of the experiment.

The acid test medium with 100% concentration of extract addition recorded the lowest weight loss with a value of 191mg. These weight loss values showed that the mixed extracts exhibited very good corrosion inhibition at the end of the experiment on the 21st day.

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.

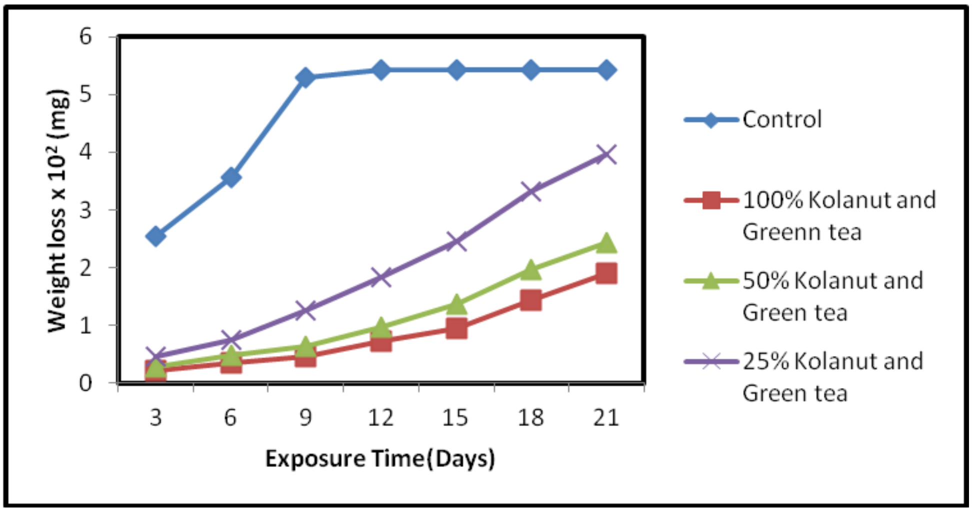

Figure 1. Variation of weight loss with exposure time for the mild steel specimen immersed in 0.5M H_2SO_4, with added varied percent concentrations of mixed kola nut and green tea extracts.

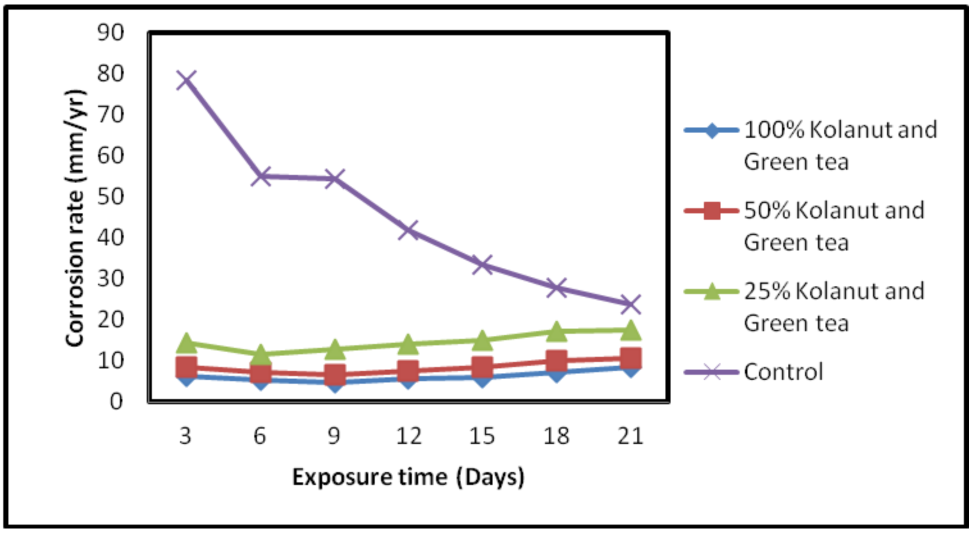

Figure 2. Variation of corrosion rate with exposure time for the mild steel specimen immersed in sulphuric acid with varied percent concentrations of mixed kola nut and green tea extracts addition.

The test medium with added 100% concentration of solution extract gave the least corrosion rate, which ranged between 8.59 mm/yr at the beginning to 10.77 mm/yr on the 21st day. The test medium with 25% concentration of extract addition gave the highest corrosion rate of 17.53mm/yr at the last day of the experiment.

3.3. Kola leaf and green tea mixed extracts

The results obtained for the variation of weight loss with exposure time for the mild steel test specimen immersed in 0.5M sulphuric acid with addition of varied concentration of kola leaf and green tea extracts combined (25%, 50%, 100% concentrations) are presented in Fig. 3. The corresponding corrosion rate vs. the exposure time curves are presented in Fig. 4.

While the test with 25% concentration mixed extracts addition had a weight loss value of 241.58mg on the 21st day of the experiment that with added 50% concentration of solution extract recorded a weight loss value of 209.83mg. The acid test medium with 100% concentration of solution extract addition recorded the lowest weight loss with a value of 157.1mg. Apparently, this can be described as very protective, especially when compared with the test without extracts addition in which a weight loss value of 541.83mg was obtained on the 21st day of the experiment.

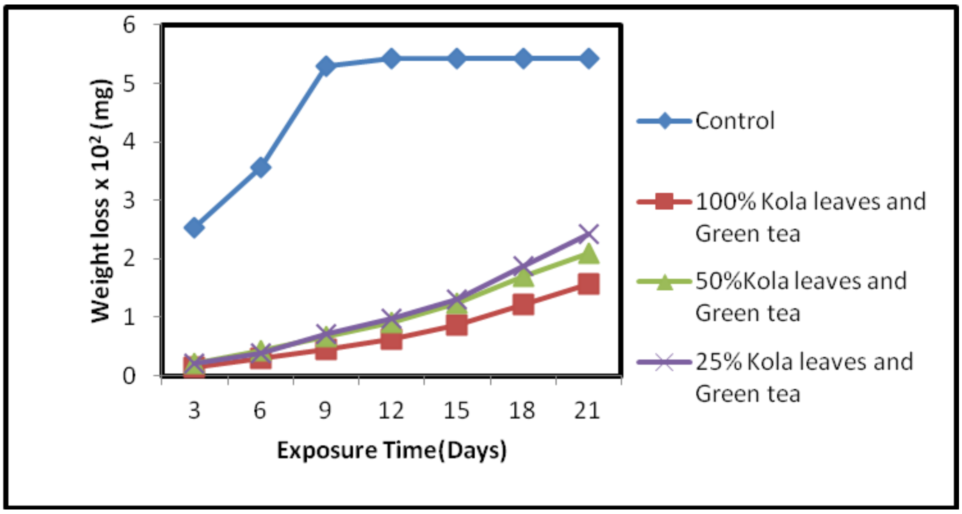

Figure 3. Variation of weight loss with exposure time for the steel specimen immersed in $0.5H_2SO_4$ and addition of different concentrations of mixed kola leaves and green tea extracts.

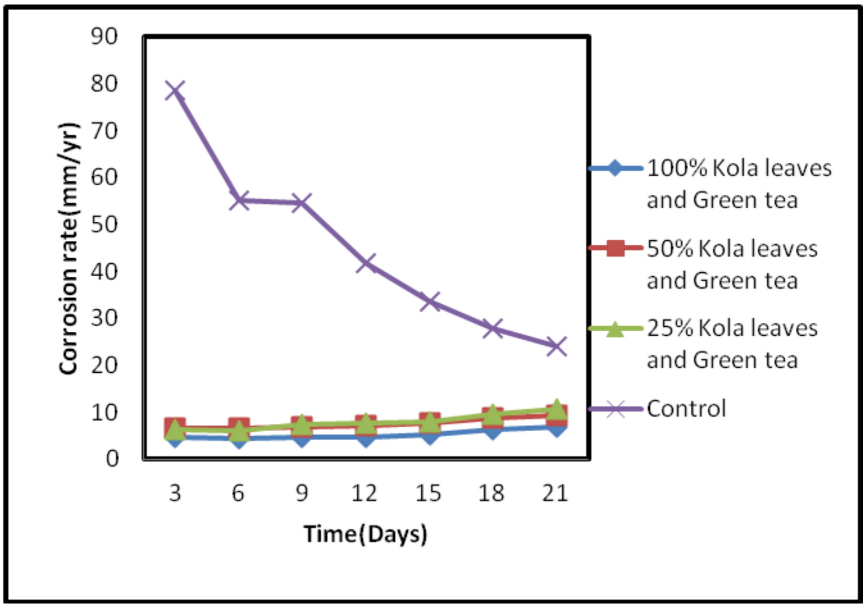

Figure 4. Variation of Corrosion rate with exposure time for the steel specimen immersed in 0.5M $H_2SO_4$and addition of different concentrations of Kola leaves and Green tea extracts

The corresponding corrosion rate vs. the exposure time results in Fig.4 gave a good correlation with the results in Fig. 3. The corrosion rate decreased with time. That the corrosion rate decreased with time is an indication of the progressive weakness of the corroding medium due to the stifling action of the corrosion deposits. It could also be explained to be due to the adhesion of the extracts inhibiting surface film on metal's test specimens that acted as barrier for the penetration of the reacting Cl^- and $SO4^=$ species. The test medium with added 100% concentration of mixed solution extracts gave the least corrosion rate of 6.94 mm/yr.

3.4. Kola nut, Kola leaf and Green tea mixed extracts

The results obtained for the variation of weight loss with exposure time for the mild steel test specimen immersed in 0.5M sulphuric acid with addition of varied concentrations of combined kola nut, kola leaf and green tea extracts (25%, 50%, 100% concentrations) are presented in Figure 5. The corresponding corrosion rate vs. the exposure time curves are presented in Fig. 6. The acid test medium with 25% concentration extracts addition provided the least corrosion inhibition of the immersed specimen.

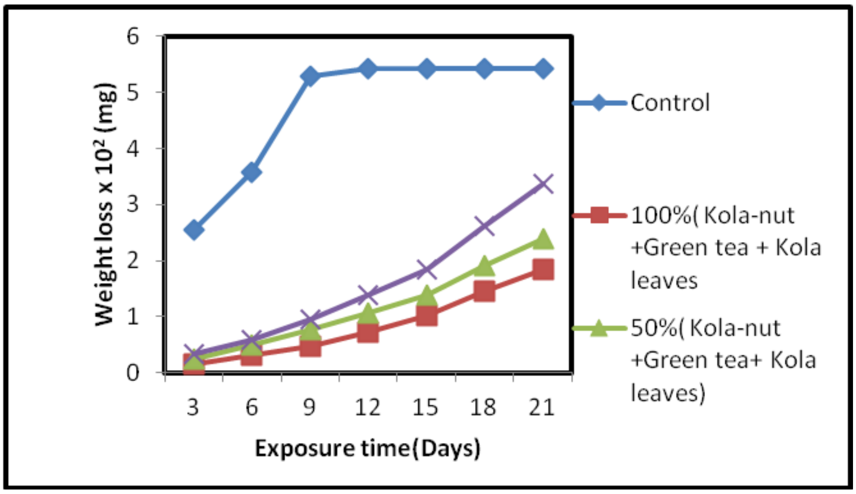

Figure 5. Variation of weight loss with exposure time for the steel specimen immersed in 0.5M H_2SO_4 and addition of different concentrations of mixed kola-nut, kola leaves and green tea extracts.

By the end of the 21st day, the test sample achieved a weight loss value of 338mg. However, it could still be considered as very fairly protective when compared with the control experiment (without extracts addition) in which a weight loss of 541.83mg was recorded during the same duration of the experimental period.

The test with added 50% concentration of mixed extracts recorded a value of 238.77mg by the 21st day; and the test medium with 100% concentration of extracts addition recorded the lowest weight loss with a value of 184.01mg at the same test period. These extract combinations, apparently showed significant effect of corrosion inhibition particularly at the concentration of 100% mixed extracts.

The corresponding corrosion rate vs. the exposure time results in Fig. 6 correlated with the results in Fig. 5. The corrosion rate increased with time. The test medium with added 100% concentration of solution extract gave the least corrosion rate, which ranged between 8.17mm/yr on the 21st day. The test medium with 50% concentration of solution extract addition recorded a corrosion rate value of 10.55mm/yr; while with the 25% extracts concentration the highest corrosion rate of 14.93mm/yr was achieved on the last day (21st day) of the experiment. The control experiment recorded very high corrosion rate (78.52mm/yr) at the beginning and ended with a value of 23.93mm/yr.

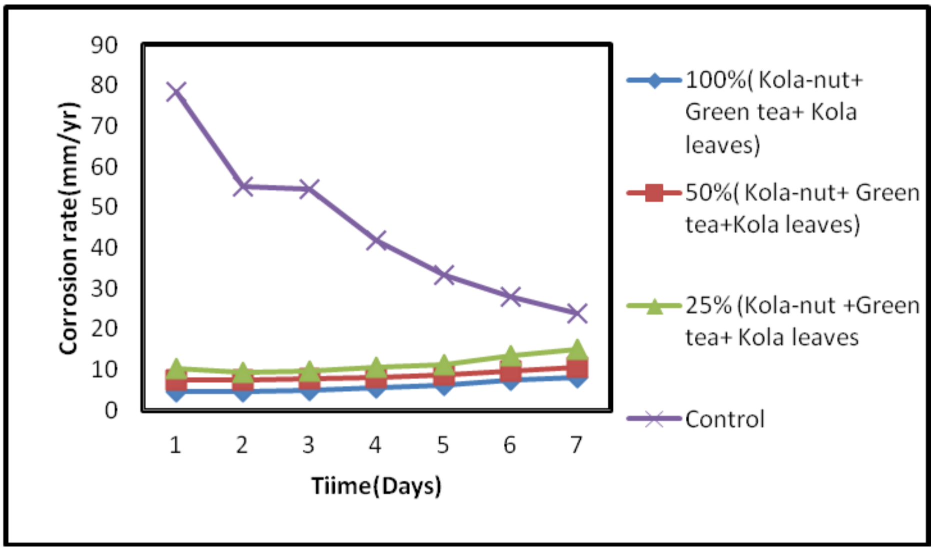

Figure 6. Variation of Corrosion rate with exposure time for the steel specimen immersed in 0.5M H_2SO_4 and addition of different concentrations of mixed extracts of kola nut, kola leaves and green tea.

3.5. Potential measurement

Potential readings for the mild steel specimens were taken over a period of 18 days at an interval of 3 days. The curves obtained for the variation of potential (mV) vs. saturated calomel electrode (SCE) with the exposure time are presented in Figs 7 to 9. The specimens were immersed separately, in 0.5M H_2SO_4 with different mixed extracts concentrations (25, 50, and 100%) of kola nut and green tea; kola leaf and green tea; and kola nut, kola leaf and green tea respectively.

In Fig. 7, the test medium without the mixed extracts addition recorded the most negative potential in the first 12 days of the experiment with a potential value of – 500mV on the 12th day. 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 50% concentrations showed effective corrosion protection throughout the experimental period. The extracts with the 100% concentration showed the best corrosion inhibition performance with potential values of -474mV on third day of the experiment and -465mV on the 15th day and on the 18th day, the potential value was -480mV. All these values fell within the passive corrosion reactions range with respect to SCE. The potential values for the 50% concentration extracts were slightly more negative than the former and showed more active corrosion reactions – with a potential value of -484mVon the 3rd day and -494mV on the 18th day of the experiment.

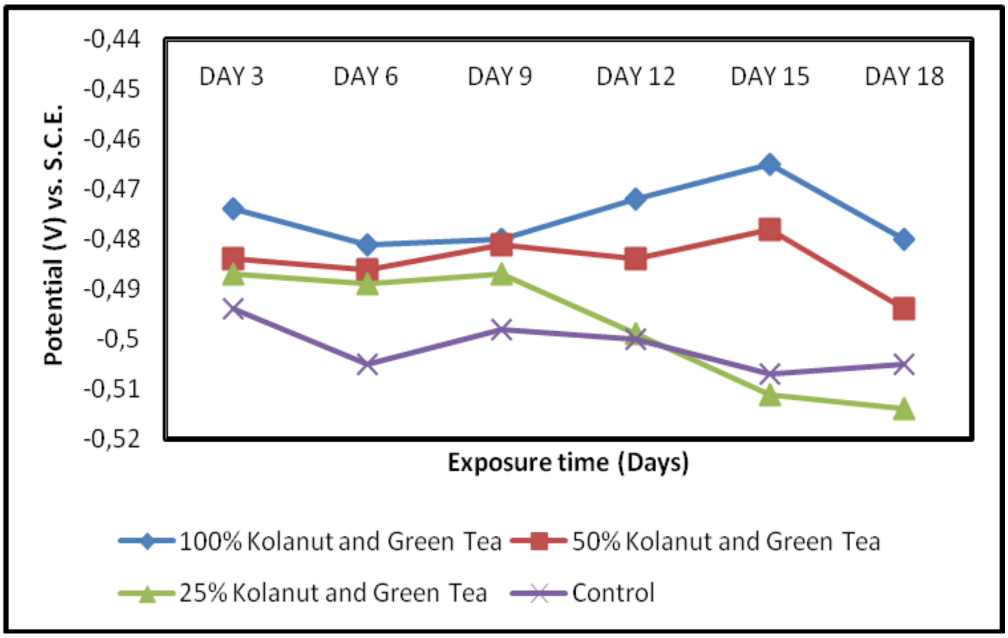

Figure 7. Variation of potential with exposure time for the mild steel specimen immersed in 0.5M H_2SO_4 with varied percent concentrations of added kola nut and green extracts.

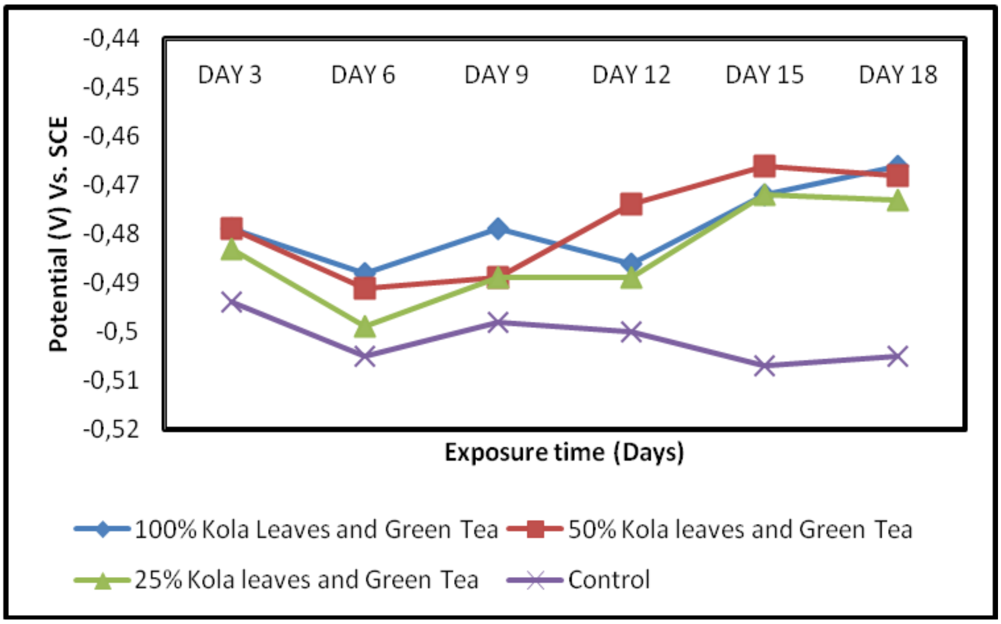

Figure 8. Variation of potential with exposure time for the steel specimen immersed in 0.5M H_2SO_4 and addition of different concentrations of kola leaves and green tea mixed extracts

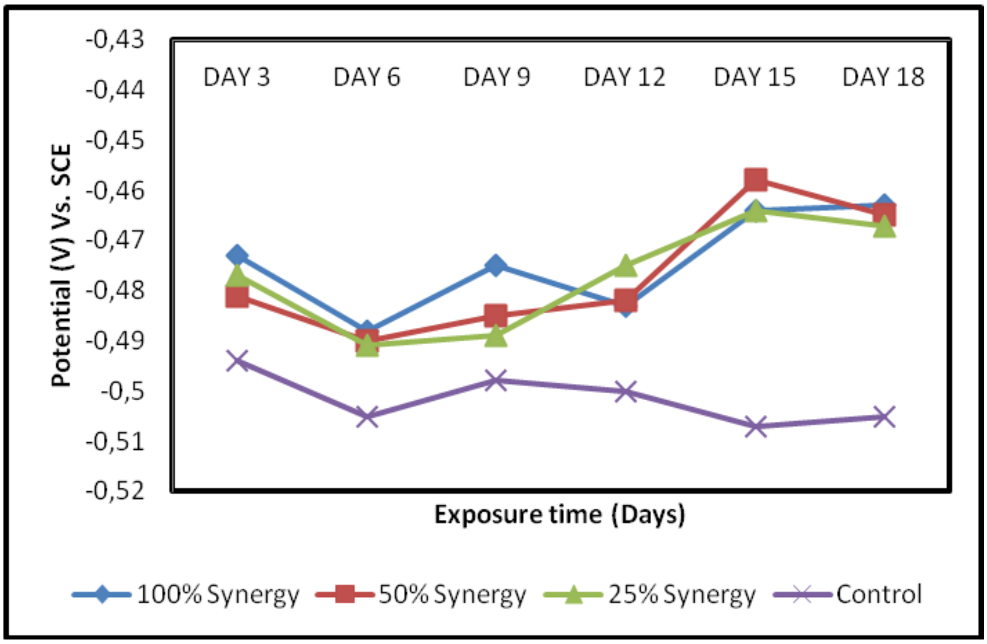

Figure 9. Variation of potential with exposure time for the mild steel specimen immersed in H_2SO_4 with varied percent concentrations of added kola nut, kola leaf and green tea mixed extracts.

Fig.8 shows the variation of potential with exposure time for the steel specimen immersed in 0.5M H_2SO_4 and addition of different concentrations of kola leaves and green tea mixed extracts. The control experiment, that is, the one without extracts addition, remained in active corrosion reactions throughout the duration of the experiment. Though with fluctuations, it recorded the potential values that ranged between -494mV on the 3rd day to -505mv on the 18th day (which was the last day) of the experiment. This confirmed the increasing corrosion of the tested electrode in the acid without any inhibition.

The tests with 100 and 50% concentrations of added mixed extracts gave very close corrosion inhibition performance as indicated by the obtained potential values. Both had the same potential values (-479mV) on the 3rd day of the experiment and also almost the same value at the end of the experiment on the 18th day, achieving potential values of -468 and -466mV for the 50 and 100% extract concentrations respectively. These results showed increasing passive corrosion reactions and thus exhibition of effective corrosion inhibition performance that was far better than the one recorded for the control experiment. The test with the 25% extract concentration addition also showed close corrosion inhibition performance to the 50 and 100% concentrations with potential values that ranged between -483mV at the 3rd day to -472mV on the 18th day. The mixed extracts at this concentration could be considered as very fairly inhibitive.

The variation of potential with exposure time for the mild steel specimen immersed in H_2SO_4 with varied percent concentrations of added kola nut, kola leaf and green tea combined extracts is presented in Fig. 9. The 100% concentration of the three combined extracts showed good corrosion inhibition performance that ranged from -473mV on the 3rd day to -463mV on the 18th day of the experiment. Similarly, the 50% concentration addition of the combined extracts gave very close and effective inhibition like the former with the potential values ranging between -481mV and -465mV on the 3rd and 18th day of the experiment respectively. The tests in 25% concentration of the combined extracts addition also gave very close results as in in the 50 and 100% concentrations addition. The achieved potential values ranged between -477 and -467mV from the beginning and end of the experiment. All the results obtained here remained in the passive corrosion reactions, thus indicating effective corrosion inhibition with reference to the saturated calomel electrode used. A clear case of synergism was exhibited here as the combined extracts in different concentrations gave improved potential values and better corrosion inhibition.

3.6. Inhibitor Efficiency

The results of the inhibitor efficiency obtained by calculations are presented in Figs. 10 to 12.

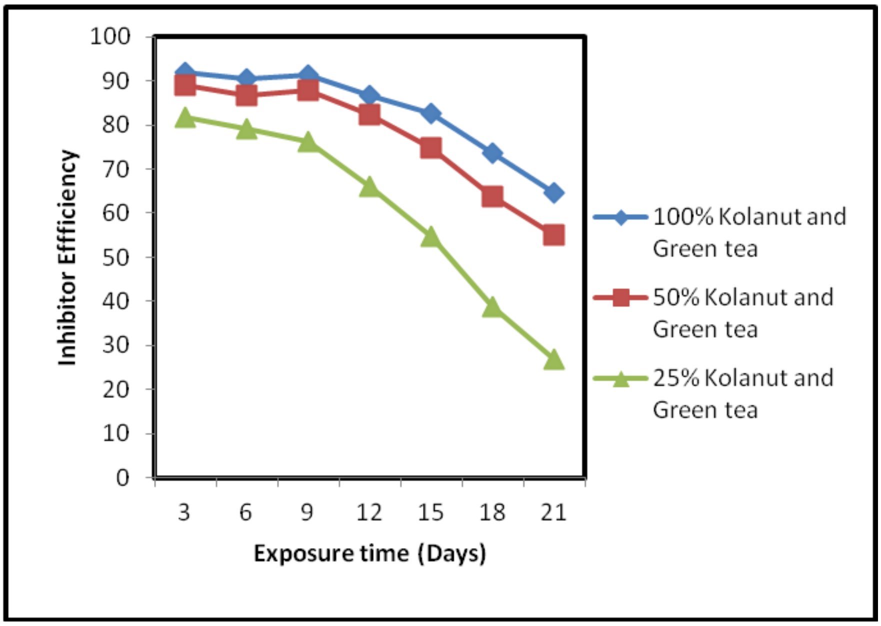

Figure 10. Variation of inhibitor efficiency with exposure time for the steel specimen immersed in 0.5M H_2SO_4 and addition of different concentrations of kola-nut and green tea mixed extracts.

All the inhibitor efficiency values at all the per cent concentrations and at all the combinations used decreased with the exposure time throughout the whole experimental period. This could be due to the progressive weakness of the plants extracts by the contamination caused by the corrosion reactions causing some metal dissolution in the test medium. These reactions phenomena would tend to stifle not only the corrosion reactions but the formation and stability of the protective inhibition films from the extracts' chemical constituents.

In spite of the above observation, very good result was, however, obtained for the mild steel specimen by each of the respective mixed extracts concentrations, and particularly very high in the first 12 days of the experiment. In Fig. 10, the mixed extracts of kola nut and green tea addition to the test medium, gave the inhibitor efficiency of 86.72% for 100% concentration on the 12th day of the experiment and 64.76% on the 21st day. At the same periods as above, the 50% concentration gave the inhibitor efficiency of 82.21% on the 12th day and 54.99% on the 21st day; while 25% concentration addition gave the results of 66.00 and 26.75% respectively. In Fig. 11 the combination of green tea and kola leaf extracts at all the concentrations used presented the same trend of decreasing inhibition efficiency with exposure time as in Fig. 10.

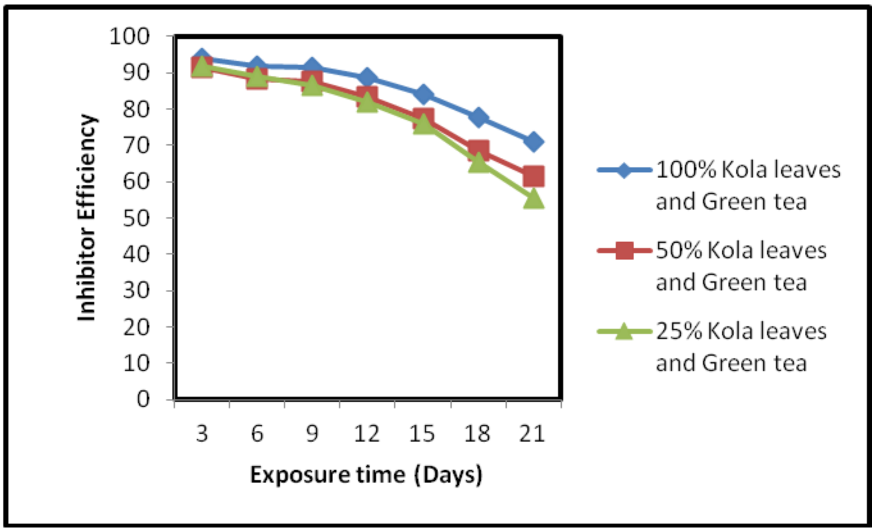

Figure 11. Variation of inhibitor efficiency with exposure time for the steel specimen immersed in 0.5M H_2SO_4 and addition of different concentrations of kola leaves and green tea mixed extracts

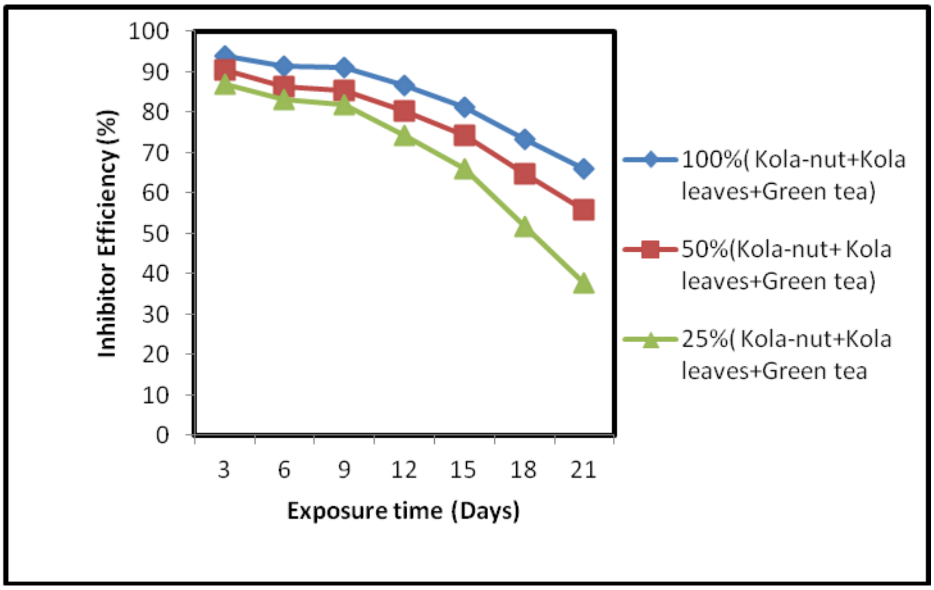

Figure 12. Variation of inhibitor efficiency with exposure time for the steel specimen immersed in 0.5M H_2SO_4 and addition of different concentrations of kola- nut, kola leaves and green tea mixed extracts

The extracts with 100% concentration addition gave an inhibition efficiency of 88.51% on 12th day and 71% on the 21st day of the experiment. Similarly, the 50% concentration addition gave inhibition efficiency of 83.28 and 61.27% on the 12th and 21st day of the experiment respectively. The 25% concentration addition gave the inhibition efficiency of 81.87 and 55.41% on the 12th and 21st day respectively. The combination of the extracts of the kola nut, kola leaf, and green tea, Fig. 12, gave good inhibition also at a concentration of 100% addition, with a percent inhibition efficiency of 86.63 and 66.03% respectively on the 12th and 21st day (the last day of the experiment). At the 12th day of the experiment, the addition of 50 and 25% separately also give good corrosion inhibition with the inhibition efficiency values of 80.39 and 74.32% respectively. The inhibition values at the 21st day of the experiment are comparatively much lower. There was synergism effect in the results of Fig. 12: the combined solution extracts of kola nut, kola leaf and green tea.

3.7. Summary

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

In general, the effective corrosion inhibition performance of kola tree and green tea extracts could be associated with their complex chemical compounds which include tannin and polyphenols. Also for kola leaf and nut extracts, constituents such as epicatechin, D-catechins, theophylline and theobromine contained in their constituents could be, or act as inhibiting passive film formers on the steel substrate surface. The synergistic action/reaction of these compounds on the surface of the steel could hinder the sulphate ion species, promote more stable passive film formation on the surface of the steel and hence inhibit and stifle corrosion reactions at the steel / environment interface.

4. CONCLUSION

The results obtained from the gravimetric and potential methods and by the calculation of the inhibition efficiency bore very close relationships. The different combinations of the extracts gave good corrosion inhibition of the test electrode in sulphuric acid at a concentration of 0.5M. At the ambient working temperature, the best corrosion inhibition performance for mild steel was obtained using the combined extracts of kola leaf and green tea at 100% concentration with an inhibition efficiency of 88.5 and 71% respectively on the 12th and 21st day of the experiment. The combination of kola leaf, nut and green tea at 100% concentration was also effective at an inhibition efficiency of 86.63 and 66.00% respectively on the 12th and 21st day. Similar corrosion inhibition performance was exhibited by the combined extracts of kola nut and green tea with inhibition efficiencies of 86.72 and 64.77% on the 12th and 21st day of the experiment respectively at the extracts addition concentration of

100%. In spite of the very strong sulphuric acid medium, the mixed extracts at 100% concentration, gave results that showed synergism in their corrosion inhibition reactions and protective performance of the tested mild steel.

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