Inhibition Effect of Extracts of *Carica Papaya* and *Camellia Sinensis* Leaves on the Corrosion of Duplex (α β) Brass in 1M Nitric acid

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The effect of *C. Papaya* (pawpaw) leaves and *C. Sinensis* (tea) extracts as an organic 'green' inhibitor on the corrosion of α β (duplex) brass (65-35% Cu-Zn alloy) in $1MHNO_3$ (nitric 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 extracts on the brass test specimens in the 1M nitric acid used. The different combined extracts concentrations also gave good corrosion inhibition performance. They also exhibited effective corrosion reactions synergism. The test specimen (duplex brass) gave some appreciable corrosion resistance in the test environment.

1. INTRODUCTION

The interest in research work on the corrosion inhibition properties of plants has increased tremendously in recent time [1-12]. Extracts from kola nut, leaves and bark; mango, tobacco, cashew, and neem plants, among others, have been studied and are further receiving more investigation [1, 2; 6-8]. The presence of tannin, polyphenols and flavonols in the solution extracts of some various plants, have been associated with the effective corrosion inhibition performance of the different plants extracts investigated [6-8]. In this work, *C. Papaya* (pawpaw) of the *Caricaceae* family and *C. Sinensis* (tea) – family of *Theaceae,* extracts were used as inhibitors.

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. Papaya (pawpaw) contains numerous chemical constituents which include the fermenting agent myrosin, alkaloids, rutin, resin, tannins, carpaine, dehydrocarpaines, pseudocarpaine, flavonols, benzylglucosinolate, linalool, malic acid, methyl salicylate, chymopapain, papain, calcium, iron, magnesium, manganese, phosphorus, potassium, zinc, beta-carotene, B-vitamins and vitamins A, C, and E, anthraquinones (bound and free), philobatinins, and saponins [13].

As previously reviewed [14], 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]. The other green tea polyphenols are flavonols, commonly known as catechins – the tea tannins. Green tea leaves contain six major catechins: catechin, epicatechin, gallocatechin, epicatechin gallate, epigallotechin, and epigallocatechin gallate. 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]. 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 chemical compositions and structures of pawpaw and tea is expected to exhibit electrochemical reactive property and prove effective in corrosion inhibition of 65-35% Cu-Zn duplex brass alloy in the strong nitric acid. The need for possibility of using plant extracts as a natural source of inhibitor to reduce/stop the corrosion of metals in corrosive environments necessitates this investigation. An effective corrosion inhibition performance of extracts of plants 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; and with economic and technological benefit.

2. EXPERIMENTAL PROCEDURE

2. 1. Preparation of specimens

The 65 – 35% Cu-Zn alloy (α β brass) sample used as test specimens was obtained from a supplier in Lagos, Nigeria. Further analysis confirmed the chemical composition to be:
0.020% C,0.0025% Si, 0.0046% S, 0.0014% P, <0.0005% Mn, 0.0043% Ni, 0.0006% Cr, 0.0018% Mg, <0.0010% Ag, 0.015% Sb, 0.0035% Bi, 0.0043% As, <0.0005% Sn, 0.020% Co,

0.027% Al, 0.0006% Cd, 35.31% Zn, 0.0041% Pb, 0.0050% Fe, <0.0001% Be, <0.0000% Zr, 0.0060% Au, <0.0005% B, 0.0013% Ti and 64.6% Cu

The brass plate was cut into average dimension of 25 x 20 x 1mm. 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 were connected to the connecting insulated flexible wire, and were in turns, mounted in araldite resin. The specimens were similarly ground with silicon carbide papers, polished, cleaned and rinsed in ultrasonic cleaners. These specimens were prepared for potential measurements of the brass in the test environments.

2.2. Test media

The experiment was performed separately in 0.1M nitric acid of AnalaR grade. The extracted solutions of the pawpaw and green tea in different concentrations and combination of concentrations, were used as the corrosion inhibitor as explained below.

2.3. Green tea and pawpaw solution extracts

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°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. The leaves of the pawpaw *(carica papaya)* were cut, oven dried at 72°C and blended to fine powders using a blending machine. The powdered sample (100g) was then soaked in a 400 ml container containing ethanol. This was filtered and the solution was left to evaporate at room temperature for three days to concentrate the juice extract. The plant extract was stored in clean airtight bottle and refrigerated. The solution extract was further diluted and separately stored in a clean bottle and covered as 100% extract (as obtained), 50% and 25% pawpaw extracts concentrations.

2.4. Preparation of test media and the solution extract

200ml of 0.1M HNO$_3$ were separately measured into eight 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.

The same process was done separately for the pawpaw leaves extract. No extract was added to the fourth beaker for each of the extracts. In addition, a combination of each of the two extracts concentrations were similarly prepared as mentioned above for each of the extracts concentrations. They were prepared to test for synergistic corrosion inhibition performance. These prepared specimens were separately used for subsequent corrosion experiments.

2.5. Weight- loss experiment

Weighed test pieces were fully immersed, separately for 23 days in each of the beakers which contained the 1M nitric acid and the solution extracts for the different sets of the experiments described above, and the acid medium without the extract addition. Each of the test specimens was taken out every 3 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:

$$P = 100[1 - W_2/W_1], \text{ where}$$

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.

2.6. 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 pawpaw (*C. Papaya*) green tea (*C. Sinensis*) inhibitors and also of the combined concentrations of the extracts. The same tests were also performed in the acid 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.

3. RESULTS AND DISCUSSION

3.1. Weight-loss method

3.1.1. Carica Papaya (Pawpaw) extracts

The results obtained for the variation of weight loss and corrosion rate with exposure time respectively for the duplex brass test specimens immersed in 1M nitric acid with varied concentrations of added pawpaw extracts are presented in Figs. 1 and 2. The acid test medium with 25% concentration of pawpaw extracts addition showed the best corrosion inhibition effect of the immersed specimens, and together with the 100% extracts concentration addition, achieved weight loss values of 0.800g at the 23rd day (end) of the experiment. For most days of the experimental period, the extract's 50%
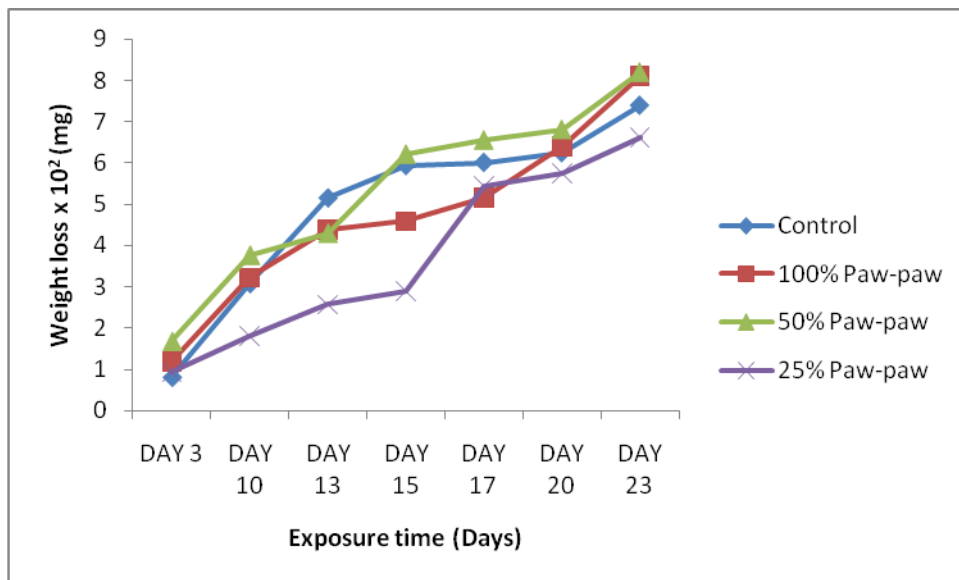
Figure 1. Variation of weight loss with exposure time for the brass specimen immersed in 1M HNO_3 and addition of different concentrations of paw-paw extracts
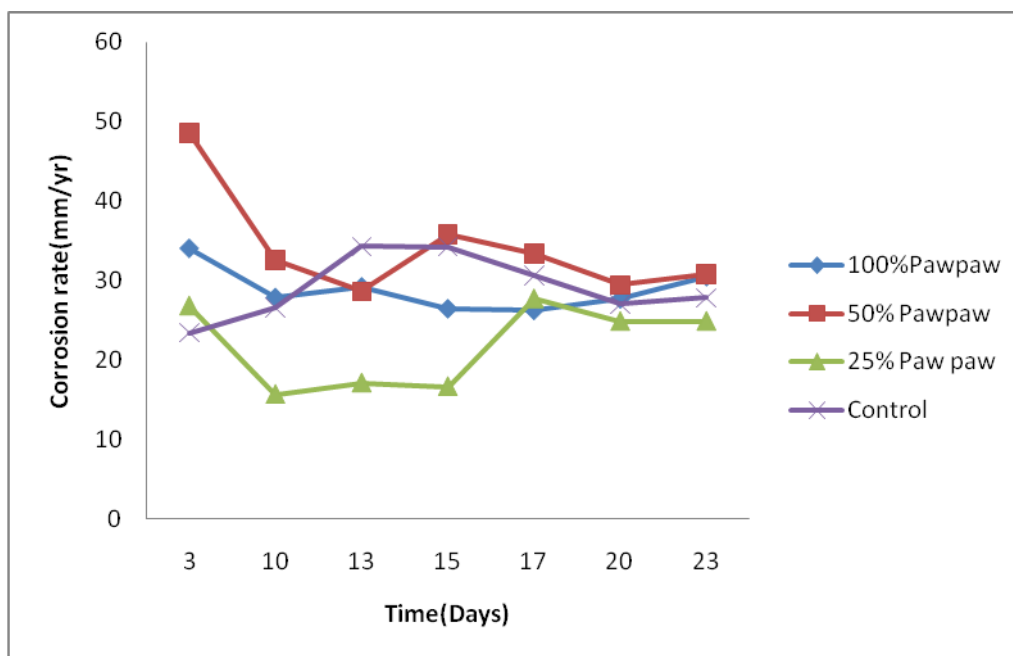

Figure 2. Variation of corrosion rate with exposure time for the brass specimen immersed in 1M HNO_3 and addition of different concentrations of paw-paw extracts

concentration addition to the test medium performed better than the extract's 100% concentration addition, though it achieved a comparative lower weight loss value of 0.75g on the 23rd day of the experiment. However, this extract's concentration was lower in inhibition performance than the 25% concentration addition. The nitrate ions ($NO_3^=$) caused the corrosion of the brass test specimens in the environment. It is difficult to explain why the lowest concentration of 25% extracts concentration

addition had the best corrosion inhibition effect. In general, an apparent corrosion inhibition of the test specimen was achieved when the results of the tests with the different extracts concentration addition were compared with the results of the tests performed without extracts addition.

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 tended to decrease with time, though with fluctuations. The test with 25% extract concentration addition had the lowest corrosion rate achieving corrosion rate value of 33.50mm/yr on the 23rd day of the experiment. The test performed with 100% concentration addition had the same corrosion rate value with the former at the end of the experiment though the overall performance was lower. Nitric acid is a very strong acid and the duplex brass is a very strong corrosion resisting alloy, these characteristics could account for the haphazard corrosion rate and hence corrosion reactions behaviour observed.

3.1.2 Camellia Sinensis (Green Tea) extracts

The results obtained for the variation of weight loss with exposure time for the brass specimens immersed in 1M HNO_3 with and without the addition, separately, of varied concentrations of green tea extracts are presented in Fig.3. 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 23 days duration of the experiment.
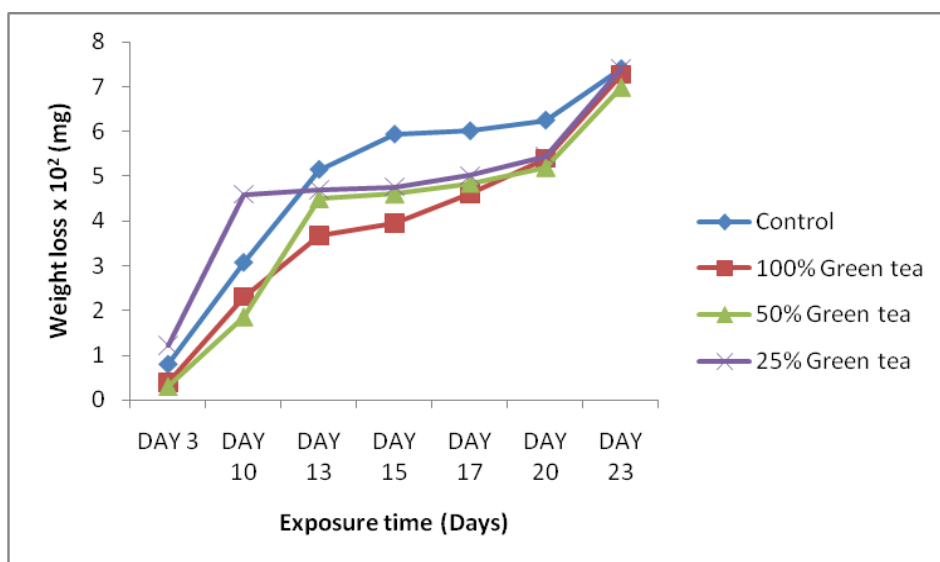

Figure 3. Variation of weight loss with exposure time for the brass specimen immersed in 1M HNO_3 and addition of different concentrations of green tea extracts

The green tea extracts addition to the test medium reduced corrosion significantly up to the 20th day out of the 23 days of the experimental period. The results obtained for the 100%, 50% and 25% green tea extract concentrations addition to the test medium seemed very close in weight loss values at

the 20th and 23rd days of the experiment achieving values of 0.55, 0.53 and 0.55g respectively. However, the results confirmed the effectiveness of the green tea solution extract on the corrosion inhibition of duplex brass in nitric acid at its concentrations of use. The extract concentration of 50% addition appeared to perform best on the 20th and 23rd days of the experiment, albeit, marginally achieving a weight loss value of 0.70g and others, 0.76g on the 23rd day of the experiment.
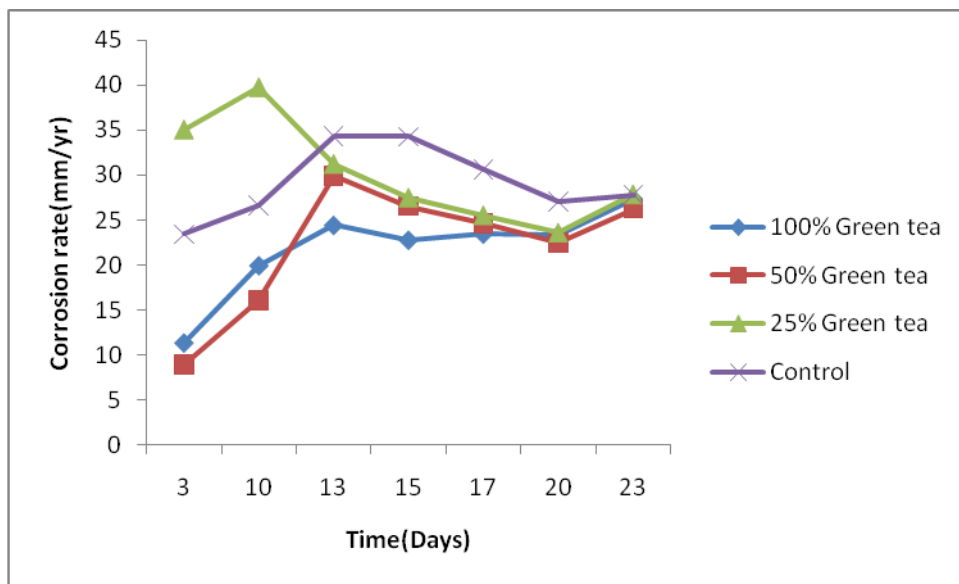

Figure 4. Variation of corrosion rate with exposure time for the brass specimen immersed in 1M HNO$_3$and addition of different concentrations of green tea extracts

The corresponding corrosion rate vs. the exposure time curves obtained by calculation from the weight-loss data are presented in Fig. 4. The corrosion rate curve for the test medium without the green tea addition showed high corrosion rate throughout the days of the experiment except the first 10 days achieving a magnitude of 34mm/yr on the 15th day. Though, nitric acid is a very strong acid, the excellent corrosion resistance of duplex brass in the acid, did not allow severe magnitude of corrosion of the test specimens. In general, the corrosion rate results showed good correlation with the weight loss data. All the corrosion rate values after the 10th day of the experiment, for the inhibited tests were lower than the values obtained for the uninhibited specimens in the experiments. There was a convergence of corrosion rate values on the 20th day and also on the 23rd day. While the corrosion rate value for the uninhibited specimens was 28mm/yr on the 20th day, others were 24mm/yr.

3.1.3 The combined pawpaw and green tea extracts

The results obtained for the variation of weight loss with exposure time for the brass specimens immersed in 1M HNO$_3$ with and without the addition, separately, of varied concentrations of combined pawpaw and green tea extracts are presented in Fig.5. The corresponding corrosion rate vs. the exposure time curves obtained by calculation from the weight-loss data are presented in Fig. 6. The

test specimen without extracts addition recorded the highest weight loss values throughout the experimental period, with values ranging between 0.0718 at the beginning to 0.739g at the end of the experiment on the 23rd day.
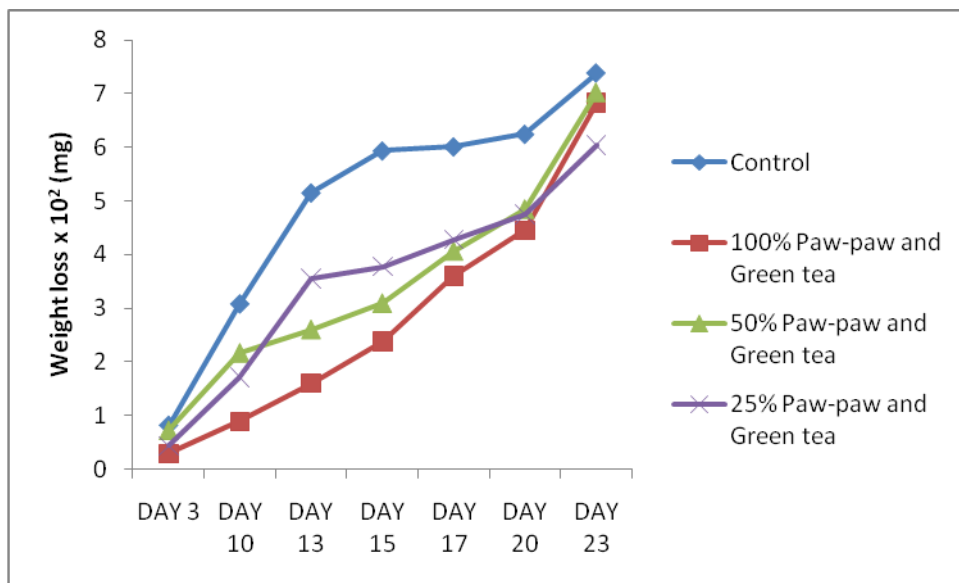

Figure 5. Variation weight loss with exposure time for the brass specimen immersed in 1M HNO_3 and addition of different concentrations of paw-paw and green tea extracts
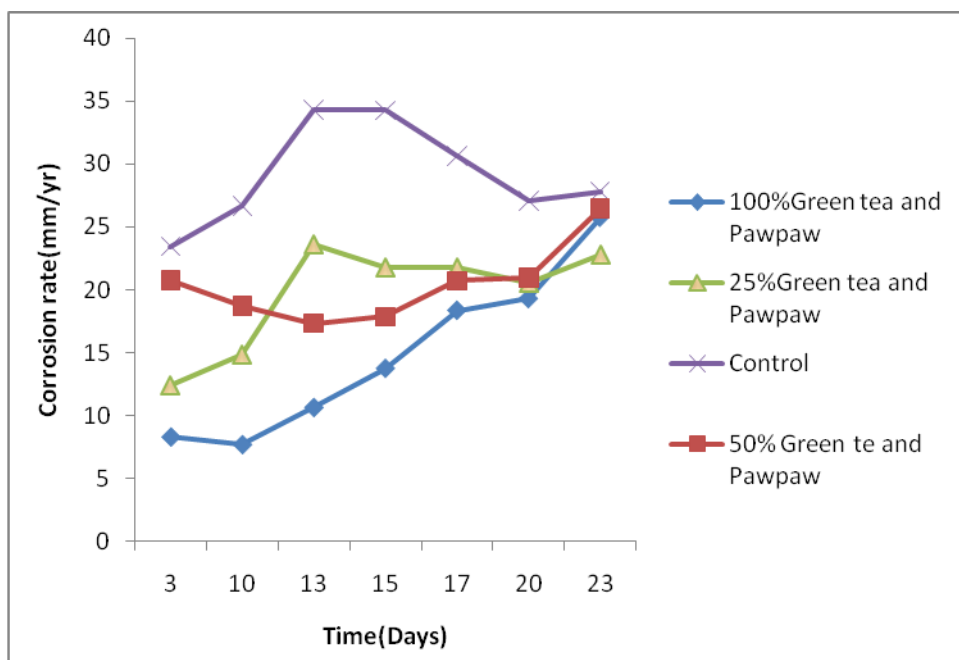

Figure 6. Variation of corrosion rate with exposure time for the brass specimen immersed in 1M HNO_3 and addition of different concentrations of paw-paw and green tea extracts

The lowest recorded weight loss was achieved with the 100% combined concentrations of the pawpaw and green tea extracts with values ranging between 0.043 at the beginning and 0.475g at the 20th day of the experiment before a sudden jump to 0.727g on the 23rd day of the experiment. All the other recorded values for the 25 and 50% extracts concentration addition performed better throughout the experimental period than the test in which there was no extracts addition. These results confirmed that the combined extracts exhibited corrosion inhibition synergism and also proved effective in corrosion inhibition performance.

The corrosion rate curve for the test medium without the combined pawpaw and green tea extracts' addition showed high corrosion rate throughout the days of the experiment. Corrosion rate value of 23.44 mm/yr was recorded on the 3rd day of the experiment which rose to 34.30mm/yr on the 13th and 14th day and ending with a value of 27.83mm/yr on the 23rd day of the experiment. The lowest recorded corrosion rate was achieved with the 100% combined concentrations of the pawpaw and green tea extracts with values ranging between 8.305mm/yr at the 3rd day of the experiment and 19.284 / 25.726 mm/yr on the 20th and 23rd day of the experiment respectively. The other extract concentrations of 25 and 50% also had lower corrosion rates (Fig. 6) than the test performed without the combined extract addition.

3.2 Potential measurement

3.2.1 Carica papaya (pawpaw) solution extract

Potential readings for the duplex brass specimens were taken over a period of 15 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.
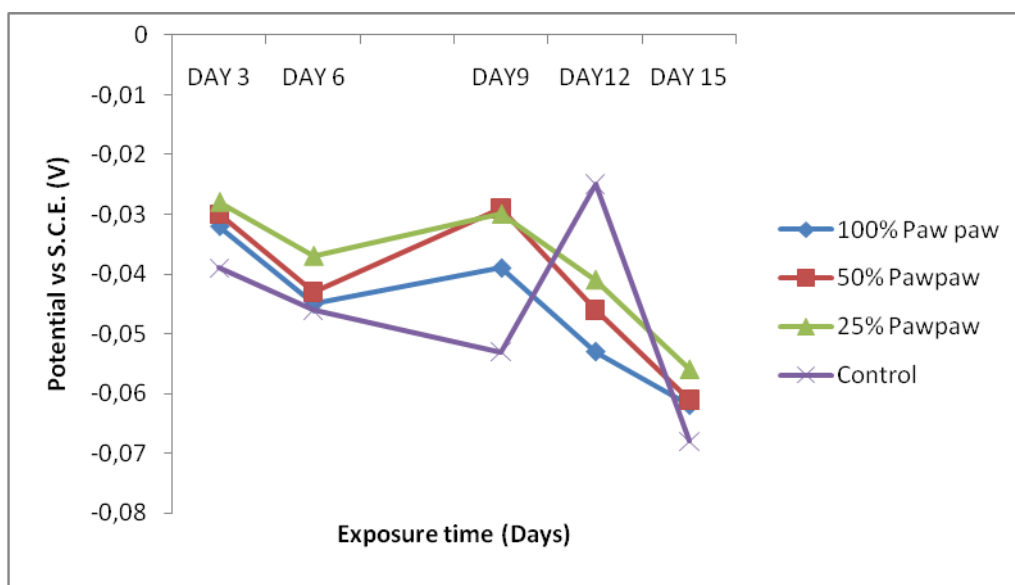

Figure 7. Variation of potential with exposure time for the brass specimen immersed in 1M HNO_3 and addition of different concentrations of paw-paw extracts

In Fig. 7, the specimens were immersed separately, in nitric acid (1M HNO$_3$) with different extract concentrations of pawpaw. The test medium without the solution extract addition increased negatively in potential from -39mV (0.039V) and attained a value of -68mV at the end of the 15 days of the experiment. The observed spike (the sudden positive jump) on the 12th day was completely out of the corrosion reactions' trend. The 'abnormality' could be due to instrumentation or human error. The results obtained for the solution extract of pawpaw at 100% concentration gave a very reasonable corrosion inhibition performance with the potential values   of -31mV at the beginning; -39mV on the 9th day and attaining the values of -53 and -68mV on the 12th and 15th day respectively.

The addition of 50% concentration extract of pawpaw also gave a fairly good indication of effective corrosion inhibition performance. Potential values ranging from -30mV at the beginning to -61mV at the end of the experiment on the 15th day showed it to have a better performance than that of 100% extract of pawpaw addition to the test medium. The addition of 25% extract concentration gave the best inhibition performance in this test with values ranging at the beginning from -28 to -56mV at the end of the experiment. These results were in close correlation with the results of the weight loss method where the order of corrosion inhibition performance was similar.

3.2.2. Green Tea solution extract

Curves of the variation of potential (mV) vs. saturated calomel electrode (SCE) with the exposure time for the duplex brass specimen immersed in 1M nitric acid with different per cent concentrations of green tea extract are presented in Fig.8.
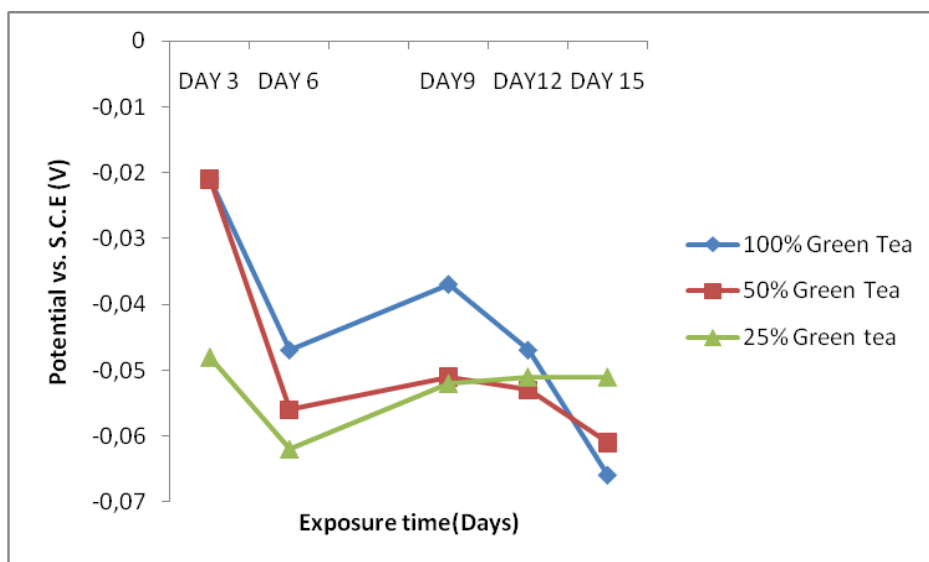

Figure 8. Variation of potential with exposure time for the brass specimen immersed in 1M HNO$_3$ and addition of different concentrations of green tea extracts

The results of the test medium without the addition of tea extract were of the same values (ranging from -39 and -68mV) as in Fig. 7 and hence not reported here. Up to the 12th day of the

experiment, the solution extract of 100% had the best corrosion inhibition performance in terms of potential values achieved (-21 to -47mV) and followed very closely by the 50% concentration of extract addition (-21 to -53mV); while the 25% concentration extract addition had the least performance (-48, -62 and -51mV). However, on the 15th day, the recorded potential values changed with the 25% concentration extract now having the best corrosion inhibition performance (-51mV) and followed by the 50% concentration extract (-61mV) and 100% concentration extract the lowest value of -68mV. The reason for this change in performance is difficult to explain. In all, the green tea solution extract gave some measure of effective corrosion inhibition of duplex brass in 1M nitric acid. In general, the results obtained bear a close relationship with those obtained for the weight loss method, Figs. 3 and 4.

3.2.3 The combined pawpaw and green tea solution extracts

The curves obtained for the variation of potential (mV) vs. saturated calomel electrode (SCE) with the exposure time for the combined different percent concentrations of the extracts of *C. Papaya and C. Sinensis* are presented in Fig. 9. With the exception of the 'spike' on the 12th day of the experiment for the test without any extract addition, a clear case of synergism is exhibited with the results obtained here not only with the values of potentials recorded but with clear orderliness of corrosion inhibition performance of each of the combined extracts concentrations.
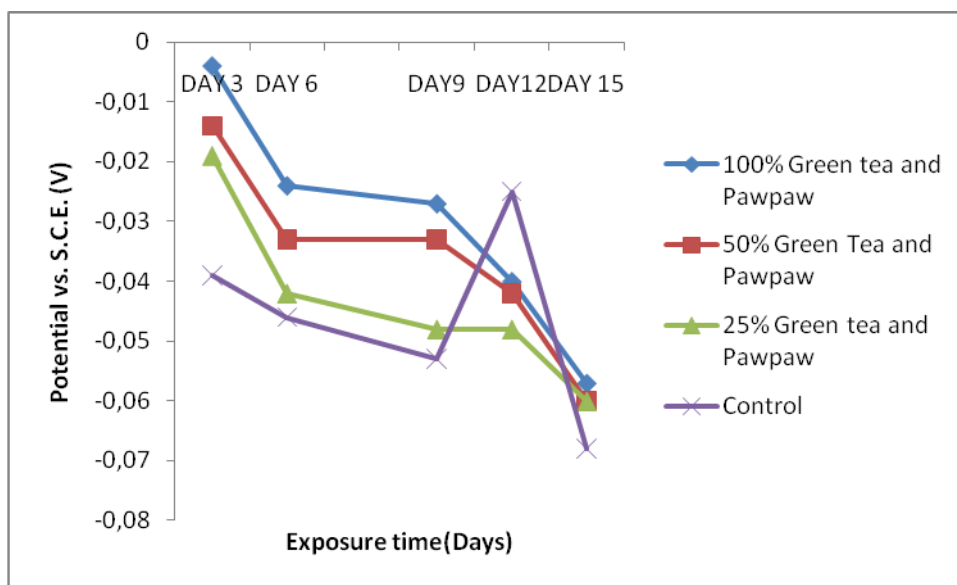

Figure 9. Variation of potential with exposure time for the brass specimen immersed in 1M HNO$_3$ and addition of different concentrations of paw-paw and green tea extracts

The test performed with the combined 100% concentration extracts gave the best corrosion inhibition performance. The obtained values recorded ranged from -3mV at the beginning to -24mV on the 6th day, -27 and -40mV on the 9th and 12th day respectively and achieving a value of -57mV on

the 15th day – the last day of the experiment. The test performed with 50% concentration of extracts followed the former in corrosions reaction performance with values ranging from -3mV (initial) to -60mV at the last day of the experiment. The 25% concentration of extracts, though still maintained effective inhibition, had the most negative values and hence more tendency towards active corrosion reactions.

3.3 Inhibitor efficiency

The per cent inhibitor efficiency data obtained by calculation for the experiments performed with pawpaw and green tea extracts alone and for their combined percent concentrations are respectively presented graphically in Figs. 10 to 12. All the combined concentrations of extracts had initial negative values indicating their non effectiveness but rather, a tendency towards active corrosion reactions acceleration.

In Fig. 10, the 25% concentration of pawpaw extracts had the highest inhibitor efficiency at the 15th day of the experiment achieving a value of 51.32%. This, however, decreased to 10.57% from the 17th day to the 23rd day – the last day of the experiment. The 50% concentration of the extract showed negative values throughout the experimental period; except on the 13th day when an inhibitor efficiency value of 16.47% was obtained. This result was an indication of more inhibitor negative corrosion inhibition performance at that concentration for the test under the particular testing conditions.
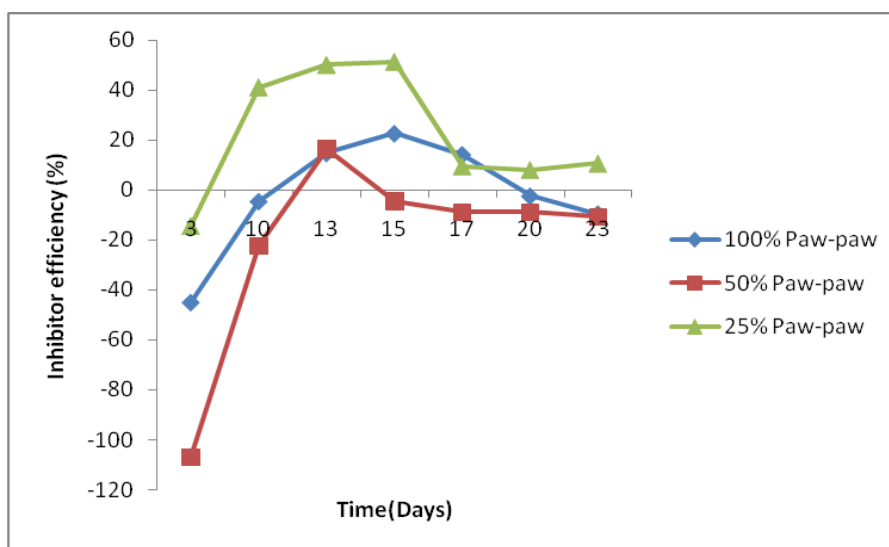

Figure 10. Variation of inhibitor efficiency with exposure time for the brass specimen immersed in 1M HNO$_3$ and addition of different concentrations of paw-paw extracts

A better result than that of 50% concentration of the extracts was obtained for the extract's100% concentration. It recorded its highest inhibitor of 23.73% on the 125th day of the experiment. From the 20th to the 23rd day, the recorded inhibitor efficiency values were negative.
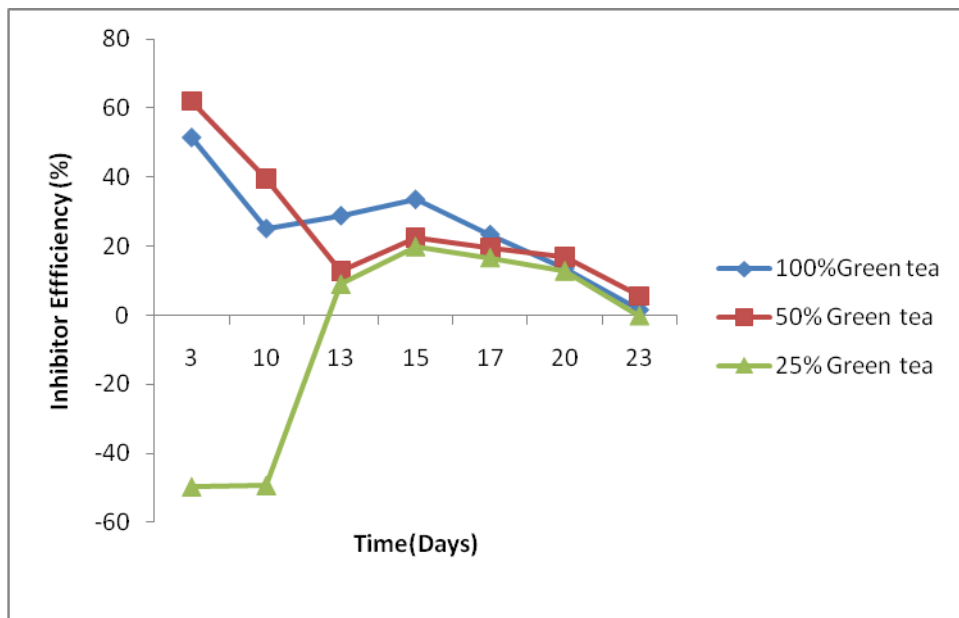
Figure 11. Variation of inhibitor efficiency with exposure time for the brass specimen immersed in 1M HNO$_3$ and addition of different concentrations of green tea extracts

Fig. 11 shows graphically, the results obtained for the calculated inhibitor efficiency data for the test performed with the extract concentrations of green tea.
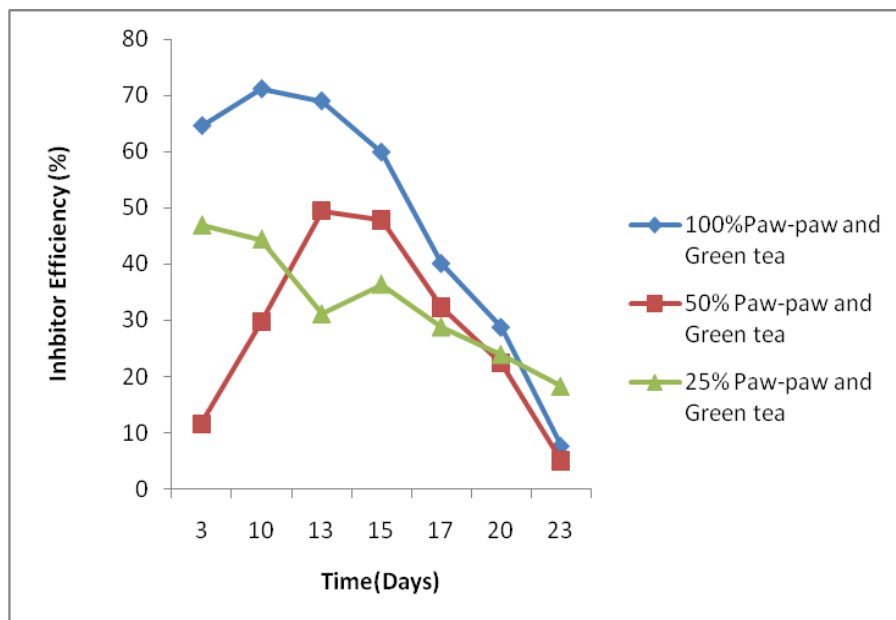

Figure 12. Variation of inhibitor efficiency with exposure time for the brass specimen immersed in 1M HNO$_3$ and addition of different concentrations of paw-paw and green tea extracts

The best results were obtained with the extract concentrations of 50 and 100% with the initial values of 61.99% and 51.35%; 19.77 and 33.50% on the 15th day; and 5.7 and 5.2% on the 23rd

respectively. The 25% concentration of green tea extract had initial negative value on the 3rd and 6th day. However, it recorded some magnitude of appreciable inhibitor efficiency values on the 15th day (19.77%) and 12.75% on the 20th day. However, its inhibitor efficiency on the 23rd day was 0%.

In Fig. 12, the highest inhibitor efficiency of 68.97% for the combined concentration of extracts was obtained with the 100% concentration of pawpaw on the 10th day of the experiment but this came down to just 7.56% on the 23rd day of the experiment. Just like with other results here, this very low inhibitor efficiency at the last day of the experiment could be associated with the weak test medium at that period due to its weakening by the corrosion deposit which stifled the corrosion reactions. The 50% concentration of the combined extracts had the inhibitor efficiency values of 49.46 and 47.88% on the 15th and 17th day respectively. On the last day of the experiment the value came down to 4.93%. The combined extract concentration of 25% had the initial inhibitor efficiency of 46.89%, 36.38% on the 17th day and 18.72% on the last day which was the highest at that particular period. The implication of this result was that with 25% concentration of combined extracts, inhibition of the test specimens could be obtained for a longer period of time under the experimental testing conditions.

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

In general, all the results obtained in this investigation showed that duplex brass is very corrosion resistant in 1M nitric acid at ambient temperature. All the weight loss values were minimal and hence the very low corrosion rates. The potential values from potential measurements showed that most of the obtained values were in the passive state of corrosion reactions but with continuous tendency towards active corrosion reactions behaviour. Apparently, in this work, the amount of corrosion of the test specimens in the acid was not very significant. A longer period of time of experimental work would be needed in subsequent investigation.

Pawpaw and tea (green) consist of many compounds with different complex chemical compositions. It could, plausibly, be explained, that the effective corrosion inhibition performance of pawpaw and green tea extracts for the duplex brass specimen in 1M nitric acid used can be associated with these complex compounds and diverse chemical compositions [10]. The extracts from both the pawpaw and green tea contain 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].

As mentioned in the introduction, (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.

4. CONCLUSION

At the ambient temperature, extracts pawpaw *(C. Papaya)* and green tea *(C. Sinensis)* gave effective corrosion inhibition performance in the 1M nitric acid environment. The various per cent

extracts concentrations used, gave good results, but not with a particular pattern as fluctuations were obtained in the various values obtained. With pawpaw extracts the best performance was more of 25% concentration addition to the test environment. With the extracts of green tea the best result for corrosion inhibition was obtained with the 100% concentration. The combined extract concentrations followed the same trend as the latter and with apparent exhibition of synergism. The duplex brass itself showed very good corrosion resistance in 1M nitric acid environment.

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