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Electrode Potential Evaluation of Effect of Inhibitors on the Electrochemical Corrosion Behaviour of Mild Steel Reinforcement in Concrete in H_2SO_4

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Abstract
The electrochemical corrosion behaviour of mild steel embedded in concrete, and partially immersed in 0.2M H_2SO_4, was studied in this investigation at ambient temperature by potential monitoring technique. The experimental work was performed with a digital multimeter and a *Cu/CuSO4* electrode (CSE) as the reference electrode. Extracts of *carica papaya* leaves and sodium nitrite ($NaNO_2$) in different concentrations were separately and in combination, used as inhibitors. This paper reports the observed electrochemical response from the electrode potential monitoring of the embedded steel rebar during the experiments. The results obtained, showed a reduction in the active corrosion reactions behaviour of the embedded mild steel in concrete with added different concentrations of sodium nitrite and the pawpaw leaves extracts in the acidic test environment. This reduced active corrosion reaction was an indication of corrosion inhibition / protection characteristic. The observed inhibition was associated with the protective film provided on the embedded steel's surface in the concrete by the complex chemical compounds of the plant leaves' extracts and of the sodium nitrite with the alkaline composition/environment of the concrete constituents. The protective film prevented and/or reduced the chloride ions penetration to the steel surface. The combination of *c. papaya* extracts and the $NaNO_2$ solution also provided effective corrosion inhibition of the embedded steel by synergism. The 100% concentration of each of the inhibitors and when in combinations, exhibited the most effective corrosion inhibition performance in the sulphuric acid test environment.

Key words: Inhibitors, corrosion, mild steel, *carica papaya,* concrete, sulphuric acid, sodium nitrite.

Introduction
Many research studies on corrosion and protection of steel rebar concrete reinforcement had been undertaken by researchers that have also generated a lot of literatures worldwide [1-10]. The scientific research interest is due in part to the importance of steel reinforced concrete as one of the most widely used materials of construction everywhere. The 0.2M sulphuric acid used for this investigation simulates the municipal concrete structures such as in sewage; and also in sulphur/sulphur dioxide polluted industrial and agricultural

environments where corrosion of reinforced concrete structures remains prominent. The present study is a contribution to the already existing knowledge in this research field.

This investigation makes use of extract of pawpaw leaves as an environment friendly 'green' inhibitor from a natural source and also sodium nitrite– a chemical compound that had already been tested in some other works for corrosion inhibition of embedded steel in concrete. It is anticipated that the extracts of *c. papaya* leaves will possess chemical properties through their various chemical constituents/composition that could provide inhibitive film on the embedded rebar just as the sodium nitrite also in anticipation. The film will then serve as a barrier for the steel – concrete environment interfacial reaction(s) and hence mitigate the corrosion reactions on the steel surface.

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 [11]. These combined constituents may exhibit electrochemical activity such as corrosion inhibition performance [12].

Sodium nitrite is expected to form complex chemical compound(s) with the concrete environment constituents that could confer passive corrosion reactions at the steel/ concrete environment interface through the formation of strong adherent film on the steel surface.

It is expected that a reasonable amount of corrosion inhibition of the embedded metal in the concrete will be obtained separately from the sodium nitrite chemical compound and *c. papaya* extracts; and even more when these inhibitors are used in combination. The very complex structural chemical compounds of the extracts of *carica papaya* could exhibit effective corrosion inhibition performance.

Experimental Procedure

Preparation of pawpaw leaves extract(s) and the sodium nitrite concentrations

Fresh leaves of pawpaw *(c. papaya)* were obtained and oven dried at 110^{o}C for two hours. The dried leaves weighing 0.5kg were ground into powder and put in a container. Ethanol was added to the container. The resulting solution was boiled for two hours and then left overnight to settle while it cooled down. It was filtered with filter papers after about a day and a half. The filtered substance was put into 100ml beaker to make different solutions. From these, three different concentrations of 40, 70 and 100% respectively were made for further use as inhibitors –mixed with concrete.

100g of $NaNO_2$ was obtained. From this, three different per cent concentrations of 40, 70 and 100 (as received) were made using distilled water.

Preparation of concrete block samples

Preparation of concrete block samples follows the same process as previously reported [3, 4, 6, 8]. Concrete blocks made of Portland cement, Sand, Gravel and Water, each with a reinforcing steel rebar embedded in it were used for the experiment. Each concrete block was 160 mm long, 100 mm wide and 100 mm thick. All the blocks were prepared with 1:2:4 (C: S: G) – cement, sand, gravel ratio. The formulation for the reinforced concrete specimens used, in kg/m^3, was: Cement 320; Water 140; Sand 700 and Gravel 110. The water cement (W/C) ratio was 0.44.

Two sets of reinforced concrete were cast without inhibitors (the control test samples) and 9 sets of steel reinforced concrete were cast with different inhibitor concentrations admixed The sets were prepared with different percent concentrations of inhibitors as presented Table 1.

The steel rebar used for the reinforcement was DIN-ST 60mm. It has the chemical composition of: 0.3%C, 0.25%Si, 1.5%Mn, 0.04%P, 0.04%S, 0.25%Cu, 0.1Cr, 0.11%Ni, and the rest Fe. The sodium chloride and sodium nitrite used were of AnalaR grade.

The steel samples were cut into several pieces each with a length of 160mm and 16mm diameter. An abrasive grinder was used to remove any mill scale and the rust stains on the steel specimens before embedded in the concrete. Each steel rebar was symmetrically placed across the length of the block in which it was embedded and had a concrete cover of 42 mm. Only about 140 mm was embedded in each concrete block. The remaining 20mm protruded at one end of the concrete block, and was painted to prevent atmospheric corrosion, Fig.1. This part was also used for electrical connection. The test medium used for the investigation was 0.2M H_2SO_4.

Table 1: Preparation of concrete sets

Test medium 0.2M H_2SO_4 / Control	Pawpaw leaves extracts concentrations (%)	Sodium nitrite concentrations (%)	Pawpaw extract + $NaNO_2$ (%)
No inhibitor (Control)	40	40	40
	70	70	70
	100	100	100

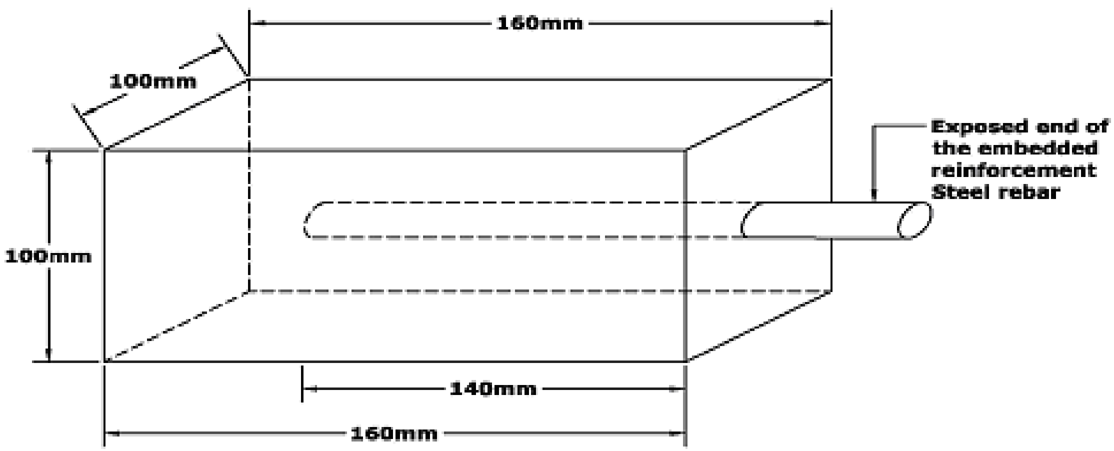

Fig. 1: A sample block (not to scale).

Potential measurement

Each concrete block was partially immersed in 0.2M sulphuric acid such that the medium level was just below the exposed reinforcing steel but not did not make contact with it. The potential readings were obtained by placing a copper sulphate electrode firmly on the concrete block, Fig.2. One of the two terminals of a digital voltmeter was connected to the copper sulphate electrode and the other to the exposed part of the embedded steel rebar to make a complete electrical circuit. The readings were taken at different points on each concrete block directly over the embedded steel rebar. The average of the three readings was computed as the potential reading for the embedded rebar in 3 –day intervals. All the experiments were performed under free corrosion potential and at ambient temperature.

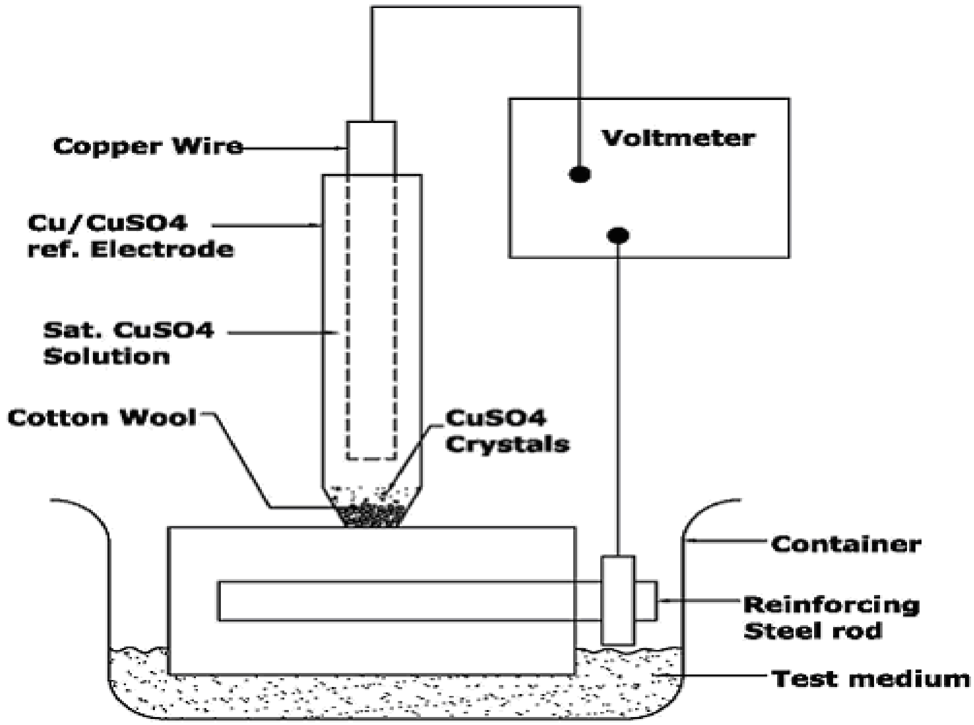

Fig. 2: Schematic representation of experimental set up.

Results and Discussion

Varied Percent Concentrations of $NaNO_2$ addition

The results obtained for the varied per cent concentrations of sodium nitrite addition – 40, 70 and 100%, mixed with the concrete test samples are presented in Fig.3 All the curves show the variation of potentials (mV) with exposure time (days) for the steel reinforced concrete samples partially immersed in 0.2M H_2SO_4. The curve for the 100% concentration addition showed a tendency towards active corrosion reactions from the 3^{rd} day to the 9^{th} day of the experiment. It however, moved into the passive state of corrosion reactions throughout the experimental period, achieving potential values of -227 and -153 mV (CSE) on the 18^{th} and 21^{st} day of the experiment respectively. The curve showed an indication that there was no corrosion of the embedded steel inside the concrete within the last 9 days of test duration. The curve for the 70% concentration of $NaNO_2$ indicated an effective inhibition performance throughout the experimental period, but with a little tendency towards active corrosion reactions behaviour from 12^{th} to the 21st day of the experiment.

The test with the 40% concentration addition of $NaNO_2$ also gave a good corrosion inhibition performance as it remained in the passive corrosion reactions state as indicated by the obtained potential values throughout the experimental period. In general, the effectiveness of $NaNO_2$ as corrosion inhibitor here was not significant when the curves with the added inhibitor and the obtained potential values were compared with the curve without added inhibitor. The test duration was probably not long enough to come out with conclusive information in this regard.

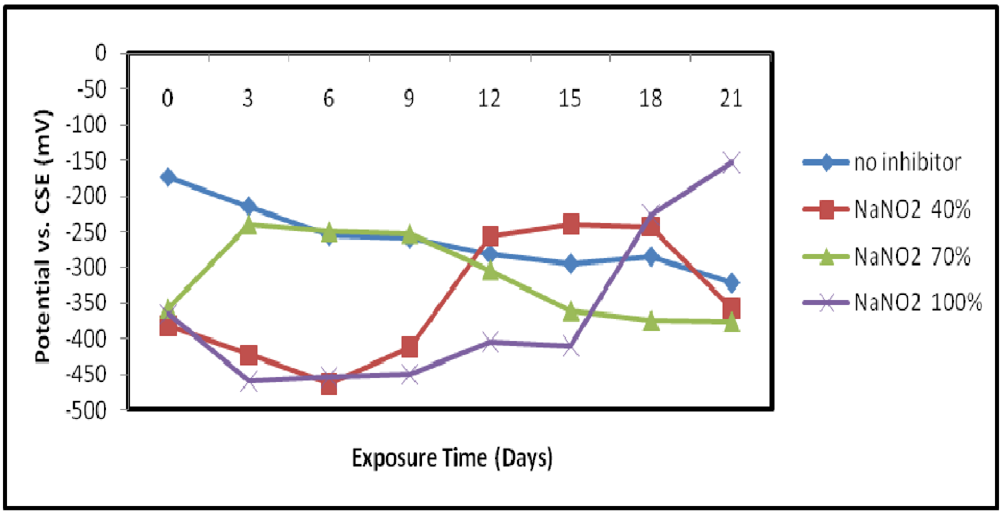

Figure 3: Variation of potential with exposure time for the mild steel specimen embedded in concrete with varied concentrations of $NaNO_2$ addition, partially immersed 0.2M H_2SO_4

Varied Percent Concentrations of Extracts of C. papaya addition

The varied concentrations of 40, 70 and 100% of pawpaw (*carica papaya*) extracts used as inhibitor for the experiments are presented in Fig. 4. The embedded steel specimen in the concrete remained in the passive state of corrosion reactions throughout the experimental period except for the curve of 40% extract addition on the 6th and 12th day. The fluctuation is difficult to explain. However, it could be due to the inability of the extract at that low concentration to maintain stable passivity during that period of the experiment. Potential values of -182 and -278mV were recorded respectively, for the 100 and 70% extract concentrations addition on the last day of the experiment; an indication of absolute corrosion passivity at that period. The test performed with the 40% concentration of the added extract, though remained in the passive state of corrosion reactions for most period of the experiment, gave the least effectiveness in corrosion inhibition performance.

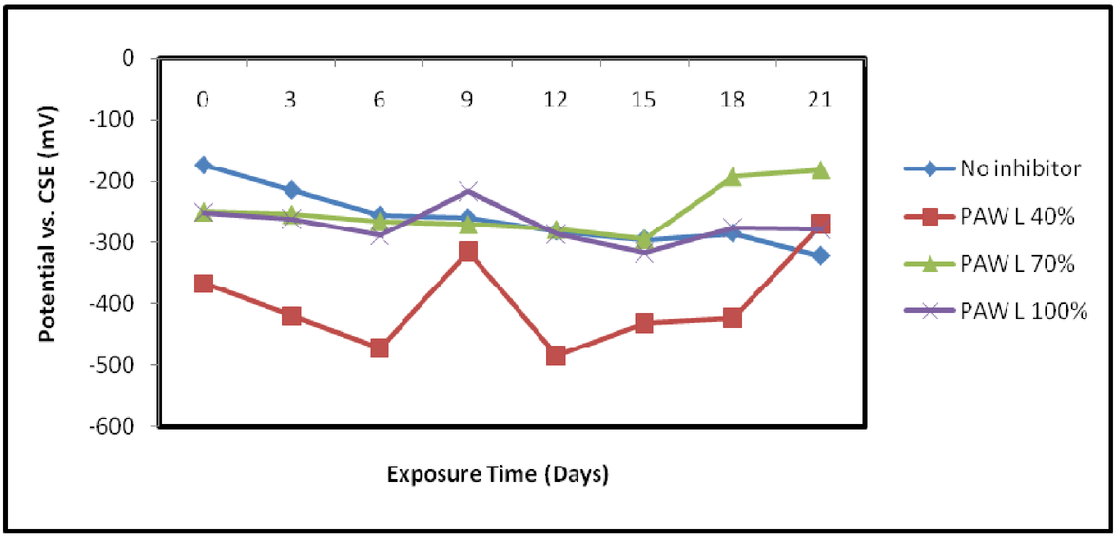

Figure 4: Variation of potential with exposure time for the mild steel specimen embedded in concrete with varied concentrations of pawpaw extracts addition partially immersed in H_2SO_4

Obviously, extract of pawpaw (*carica papaya*) was concentration sensitive/dependent; its effective corrosion inhibition improves with increase in extract concentration. The overall performance was very good particularly at very high concentrations. The effective performance can be associated with the very complex chemical composition of the extract as mentioned in the introduction. These could react with the alkaline environment of the concrete to form a strongly adherent passive film on the embedded steel surface that hindered the penetration of the sulphate ions ($SO_4^{=}$) to initiate, perpetrate and sustain continuous active corrosion reactions at the concrete matrix environment/steel's interface.

Combination of sodium nitrite and pawpaw (c. papaya) extracts

The results obtained for the combination of different concentrations of $NaNO_2$ and extracts of pawpaw addition to the concrete are presented in Fig. 5. An apparent synergism of results is shown here. The 100% concentration of the combined inhibitors achieved the potential values with increasing active corrosion reactions from the beginning of the experiment to the 12th day after which it maintained stable passive reactions to the end of the experiment with a value of -284mV on the 21st day. The 70% concentration addition remained in the passive corrosion reactions state throughout the experimental period, though the performance was low in the first 18 days of the experiment. The inhibitive performance of the 40% concentration addition was significant as the curve remained in the passive corrosion reactions state from the 12th day to end of the experimental period and with best passive potential values ranging from -214mV at the 12th day to -211mV on the last day of the experiment. There was apparent corrosion reactions synergism in these combined concentrations with best result achieved with the 40% concentration addition and least with the 100% concentration addition.

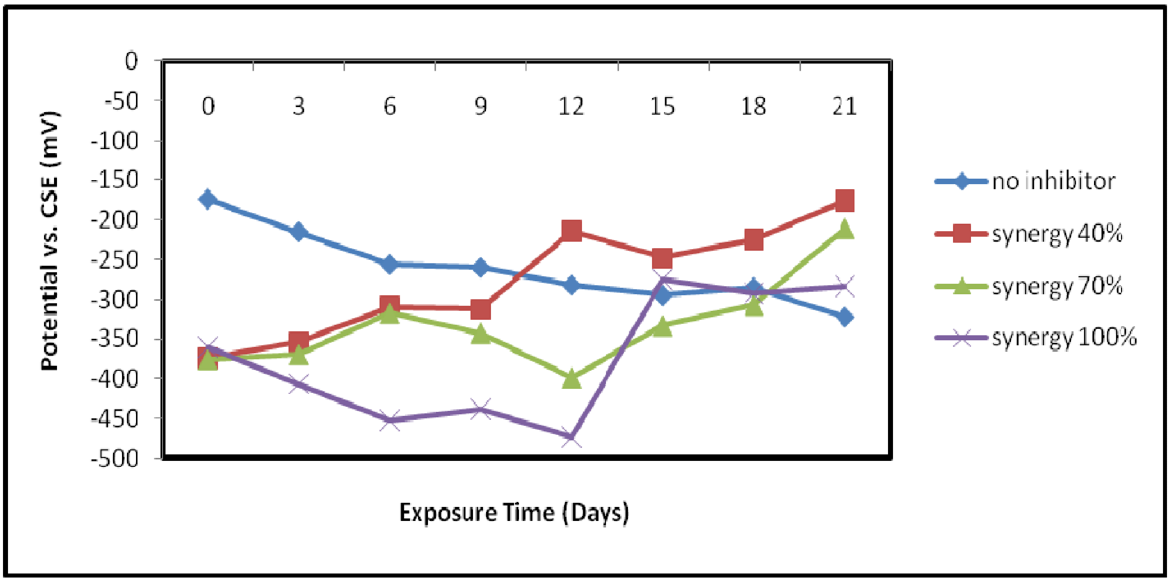

Figure 5: Variation of potential with exposure time for the mild steel specimen embedded in concrete with varied combined concentrations of $NaNO_2$ and pawpaw extracts addition partially in immersed in H_2SO_4

A very noticeable and interesting observation here was that $NaNO_2$, an inorganic chemical compound inhibitor synergised with pawpaw extract with very complex multifarious constituents to for an adherent protective film on the embedded steel surface to effectively hinder sulphate ions ($SO_4^{=}$) from initiating active corrosion reactions in the combined concentrations of the inhibitors during the most period of the experiment.

Comparison of the inhibitors' corrosion inhibition effectiveness

The results obtained for the comparison of the inhibitors effectiveness at each of the different concentrations of 100, 70 and 40% respectively are presented in Figs. 6 to 8.

In Fig. 6, 40% concentration each of $NaNO_2$ and extracts of pawpaw (c. papaya) inhibitors were compared. Based on the potential values recorded, there inhibition performance or effectiveness was relatively low in general when compared with the test without added inhibitor to the concrete. However, from the 12th day to the 18th day of the experiment, the better effectiveness of corrosion inhibition in terms of potential values achieved for the sodium nitrite was observed with potential values of -256 and -242mV respectively on the days mentioned above. The curve for the pawpaw extract picked up on the 21st day of the experiment and achieving appreciable passive potential value of -269mV. The acid seemed very strong for the inhibitors to make impressive inhibition early in the experimental tests.

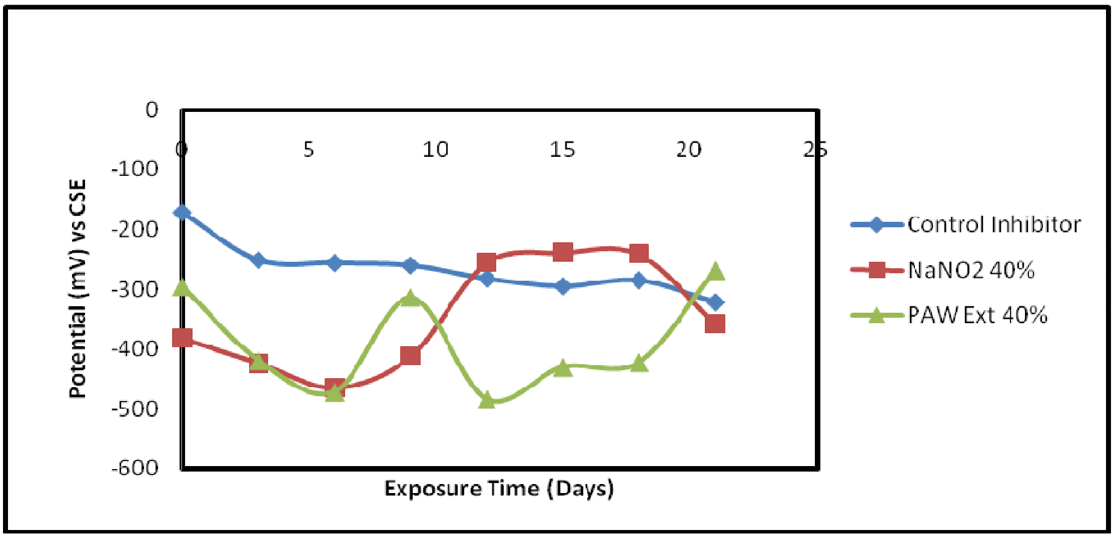

Figure 6: Variation of potential with exposure time for the mild steel specimen embedded in concrete with 40% concentration of each of the $NaNO_2$ and pawpaw extracts addition partially in immersed in H_2SO_4

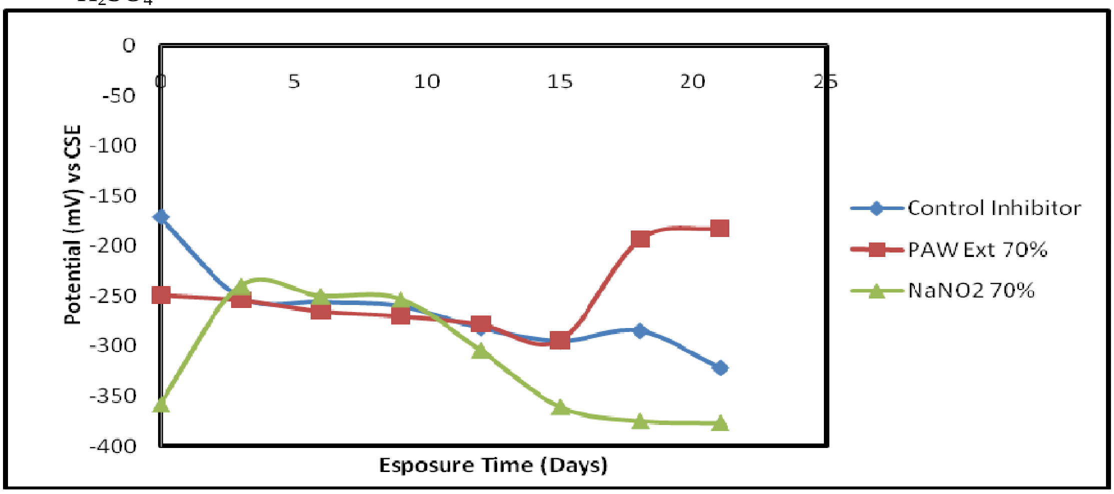

Figure 7: Variation of potential with exposure time for the mild steel specimen embedded in concrete with 70% concentration of each of the $NaNO_2$ and pawpaw extracts addition partially in immersed in H_2SO_4

Fig. 7 shows the curves obtained when 70% concentration of each of the inhibitors was used as addition to the steel reinforced concrete. Here, the pawpaw extract, remained in the passive state of corrosion reactions throughout the experimental duration, and recorded the overall best passive potential value of -193 and -182mV on the 18th and 21st day respectively. The $NaNO_2$ inhibitor also performed fairly well but with a tendency towards active corrosion reactions from the 9th day achieving a potential value of -377mV on the 21st day of the experiment. Averagely, their corrosion inhibition performance was not better than the protection given by the concrete alkaline environment until the 15th day when the pawpaw extract gave an increased significant passive potential corrosion reactions behaviour.

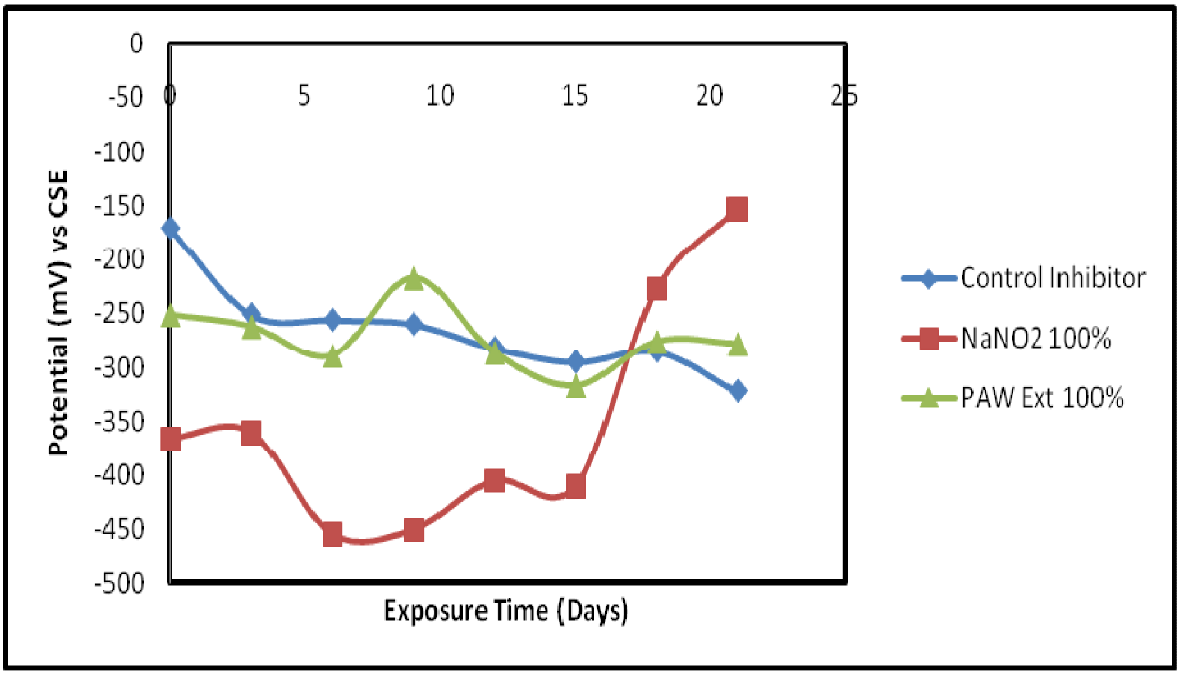

Figure 8: Variation of potential with exposure time for the mild steel specimen embedded in concrete with 100% concentration of each of the $NaNO_2$ and pawpaw extracts addition partially in immersed in H_2SO_4

The addition of sodium nitrite at 100% to the steel reinforced concrete matrix showed better corrosion inhibition performance than the same concentration of pawpaw extract only after the 15th day of the experiment, as presented in Fig. 8. Prior to this point of time, its behaviour was more of active corrosion reactions. Though with some little fluctuations, the addition of pawpaw extract at 100% concentration showed effective corrosion inhibition performance that ranged between -251 at the beginning and -278mV at the end of the experiment. This was an indication that it maintained absolute passivity and no corrosion tendency throughout the experimental period.

Effect of pH

The recorded pH values for the whole duration of the experiment are presented in Table 2. The reinforced concrete blocks recorded pH values which its acidity decreased from 0.97 from the beginning of the experiment to 1.16 at the end in a period of 21 days. Similar trends were recorded for all the different percent concentrations of inhibitor addition.

Sodium nitrite at 40% concentration addition, the acidity reduced from 0.92 – 0.99. At 70% concentration, it reduced from 0.91 – 1.32; and at 100%, from 0.93 – 1.21. This decrease in acidity could be due to the reactions between the concrete constituents, the $NaNO_2$ chemical, the H_2SO_4 test environment and the reactions at the steel/environment interface for the steel reinforced concrete blocks. In addition, since the steel was partially immersed, the carbon dioxide from the atmosphere could have penetrated by diffusion through the concrete pores and reacted with water content of the test medium to form the weak carbonic acid that further reduced the sulphuric acid strength.

Table 2: pH values for the test in H_2SO_4 solution

SAMPLES / DAYS	0	3	6	9	12	15	18	21
Concrete (without inhibitor)	0.97	1	1.02	1.06	1.07	1.13	1.14	1.16
$NaNO_2$ 40%	0.92	0.93	0.95	0.96	0.97	0.98	0.98	0.99
$NaNO_2$ 70%	0.91	0.97	1.03	1.09	1.06	1.09	1.3	1.32
$NaNO_2$ 100%	0.93	0.99	1.04	1.07	1.09	1.1	1.17	1.21
Pawpaw Leaves 40%	0.9	1	1.09	1.07	1.06	1.11	1.22	1.41
Pawpaw Leaves 70%	0.89	0.99	1.09	1.09	1.09	1.13	1.2	1.3
Pawpaw Leaves 100%	0.87	0.91	0.95	0.97	0.98	0.95	1	1.02
Pawpaw L + $NaNO_2$ 40%	0.88	0.93	0.97	1.04	1.02	0.96	0.95	1.02
Pawpaw L + $NaNO_2$ 70%	0.86	0.92	0.98	1.1	1.04	0.97	1.01	1.06
Pawpaw L + $NaNO_2$ 100%	0.87	0.94	1	1.21	1.13	1.03	1.1	1.35

The same trend of reduced/decreased acidity was recorded with the use of pawpaw extracts addition and also with the use of combined inhibitors, for example a reduction from 0.87 to 1.35 at 100% combined concentrations.

Though minimal, one clear correlation of this decreasing acidity with potential readings was that with the decreasing acidity, there was a tendency towards increasing passive potential values, that is, less negative values of potentials, though sometimes with random fluctuations, particularly with some of the concentrations of pawpaw extracts.

Table 3: Compressive strength test

REINFORCED CONCRETE SAMPLES	CRUSHING STRENGTH FOR REINFORCED CONCRETE IN (H_2SO_4) MEDIUM
Concrete (without inhibitor)	125KN
$NaNO_2$ 40%	80KN
$NaNO_2$ 70%	130KN
$NaNO_2$ 100%	140KN
Pawpaw Leaves 40%	70KN
Pawpaw Leaves 70%	130KN
Pawpaw Leaves 100%	150KN
Pawpaw L + $NaNO_2$ 40%	50KN
Pawpaw L + $NaNO_2$ 70%	155KN
Pawpaw L + $NaNO_2$ 100%	160KN

Compressive strength test
The results obtained for the compressive strength test are presented in Table 3. While the concrete sample without inhibitor addition had a compressive strength of 125 KN, the inhibitors with lower percent concentration addition had lower values. The 40% concentration of $NaNO_2$ addition had a compressive strength value of 80 KN while the same per cent concentration of pawpaw extract even had a lower recorded value of 70 KN. From table 3, the trend showed that the compressive strength increased with increase in percent concentrations of each of the two inhibitors used. While the lowest percent concentrations of 40% could be said to be detrimental, to the compressive strength of the concrete samples, highest percent concentration (100%) of the inhibitors addition used, improved the compressive strength significantly, achieving different values of 140 and 150 KN for the sodium nitrite and pawpaw extract respectively. At 70% concentration, the pawpaw extract and the $NaNO_2$ addition recorded the same compressive strength value of 130KN each. The combined inhibitors gave a clearer trend of increasing and hence better compressive strength with increase in the percent concentrations of added inhibitors and thus exhibiting another form of synergism. At 40% concentration, the combined inhibitors had a very poor comparative compressive strength (50KN) with the concrete samples without inhibitor. However, with 70 and 100% concentrations of the added combined inhibitors, the recorded values were 155 and 160 KN respectively.

Conclusion

All the percent concentrations of the pawpaw extracts gave good corrosion inhibition performance of the embedded steel rebar but not in any particular order of concentrations. The sodium nitrite inhibitor also gave effective corrosion inhibition of the embedded steel; and not in any particular order of concentrations.

The combinations of the inhibitors were effective; but did not give an appreciably better performance in corrosion inhibition of the metal substrate. A positive/effective synergy was formed by the combined percent concentrations of an inorganic chemical compound, $NaNO_2$, and the extract from the leaves of a plant, pawpaw *(carica papaya).*

The compressive strength of the tested concrete samples increased in most cases and even recorded a very appreciable value increase (160 KN) with the combination of pawpaw extracts and sodium nitrite at 100% concentration.

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References
1. Craig, R. J., Wood, L. E., Effectiveness of Corrosion Inhibitors and their influence on the Physical Properties of Portland Cement Mortars, Highway Research Record, 1970, No. 328.
2. Griffin, D. F., Corrosion of Metals in Concrete, Detroit M1 A. C. I., !975, 95.
3. Loto, C. A., *Corrosion*, 48 **(**1992) 759-763.
4. Loto, C. A., Okusanya, A., *Corros. Prev. & Control*, 26 (1989) 103 - 109.
5. Berke, N. S., *Matls. Perform*., 10 (1989) 41-42
6. Loto, C. A., Odumbo, E. T., *Corrosion*, 45 (1989) 553 – 557.
7. Loto C. A., *Corros. Prev. & Control*, 50 (2003) 43-49.
8. Slater, J. E., Corrosion of Metals in Association with Concrete, STP 818 (Philadelphia) P.A. - American Society for Testing and Materials, 1983, p 36.
9. Treadaway, K. W. J., Russel, A. D., *Highways and Public Works*, 36 (1968) 40
10. Loto, C. A., Loto, R. T., Popoola, A. P. I, *Int. J. Electrochem. Sci.*, 6 (2011) 3452 - 3465
11. Papaya leaf, http://www.herbalist.com/wiki.details/93/category/11/, 2011/08/17
12. Davis, G. D. and Fraunhofer J.A., *Matls. Perform.*, 2 (2003) 56 – 60.