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Electrode Potential Monitoring of Effect of Plants Extracts Addition on the Electrochemical Corrosion Behaviour of Mild Steel Reinforcement in Concrete

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The corrosion and protection of a mild steel reinforcement in concrete, partially immersed in 5% sodium chloride solution, was investigated at ambient temperature by potential monitoring technique. The work was carried out using a digital voltmeter and a copper sulphate electrode (CSE) as the reference electrode. Extracts of kola plant and tobacco in different concentrations were used as 'green' inhibitors. This paper reports the observed electrochemical response from the electrode potential monitoring of the reinforcing mild steel during the experiments. A reduction in the active corrosion reactions behaviour of the embedded mild steel in sodium chloride solution was obtained with the addition of different concentrations of the plants extracts. This behavior was attributed to the protective film provided on the steel's surface in the concrete by the complex chemical compounds of the plants extracts, which prevented and/or reduced the chloride ions penetration through the film to the steel surface. Effective protection of the embedded steel was achieved in nearly all the extracts for the greater part of the experimental period. However, the most effective results were obtained from the tobacco extract and from the combination of other individual extracts concentrations by synergistic effect.

Keywords: Inhibition, corrosion, steel, kola, tobacco, concrete, sodium chloride, protection.

1. INTRODUCTION

The importance of steel reinforced concrete as one of the most widely used materials of construction throughout the world has necessitated very wide interest in this subject by many researchers worldwide. Many authors (1-8) have worked on and/or reviewed this research subject at different times. This work is done to contribute to the already existing knowledge in this research field.

One unique aspect of the present work is that it makes use of very environment friendly ‘green’ inhibitors from natural sources – plant extracts as addition to the concrete mix. It makes use of kola tree parts and tobacco. It is anticipated that the extracts of different parts of kola tree – the leaves, nuts and the bark; and tobacco will possess chemical properties through their various chemical constituents/composition that could provide inhibitive film on the embedded rebar. The film will then serve as a barrier for the steel – concrete environment interfacial reaction(s) and hence stop or minimise the corrosion reactions on the steel surface. Kola is a genus of trees native to the tropical rainforests of Africa, classified in the family *Malvaceae*, subfamily *Sterculioideae* (or treated in the separate family *Sterculiaceae*).

Some previous work on extracts of tobacco (genus – *Nicotiana*: family- *Solanaceae*), as an environmental benign corrosion inhibitor (9-13) had shown it to be effective in preventing the corrosion of steel and aluminium in saline environments; and in fact, exhibiting a greater corrosion inhibition effect than chromates (10-12). Tobacco plants produce ~ 4,000 chemical compounds – including terpenes, alcohols, polyphenols, carboxylic acids, nitrogen – containing compounds (nicotine), and alkaloids (13). These may exhibit electrochemical activity, such as corrosion inhibition (9).

Similarly, 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 (14). As reported in some previous studies (15-16), tannin is known to possess corrosion inhibitive properties on metals – particularly, mild steel.

Considering the very complex structural chemical compounds of the extracts of the two plants used, a reasonable amount of corrosion inhibition on the metal used is not unexpected. The 5% NaCl solution used in this work simulates the marine and other saline environments where corrosion of reinforced concrete structures remains prominent.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of the extracts

Fresh leaves, nuts and bark of kola tree were obtained and oven dried at 110°C for two hours. The dried materials were then separately ground into powder and put in different containers. Ethanol was added to each container. The resulting solutions were boiled for two hours and then left overnight to settle while it cooled down. Each was filtered with filter papers after about a day and a half. From each of these solutions, two different concentrations of 30 and 40% respectively were made for further use as inhibitors –mixed with concrete.

2.2. Preparation of concrete block samples

Preparation of concrete block samples follows the same process as previously reported (1, 5, 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.

Forty two (42) blocks of concrete comprising two specimens each were cast with different plant extracts concentration. Two different concentrations of 30% and $0% each of the extracts were used. The sets were prepared with the plant extracts percent concentration as presented below:

1. 5% sodium chloride and no extracts addition
2. Kola nut-K, 30%
3. Kola nut-K, 40%
4. Kola leaves -KL, 30%
5. Kola leaves- KL, 40%
6. Kola bark - KB, 30%
7. Kola bark - KB, 40%
8. Tobacco - T, 30%
9. Tobacco - T, 40%
10. Kola nut- K + Kola leaves- KL, 30%
11. Kola nut- K + Kola leaves- KL, 40%
12. Kola nut- K + Kola bark- KB, 30%
13. Kola nut- K + Kola bark- KB, 40%
14. Kola nut- K +Tobacco- T, 30%
15. Kola nut- K + Tobacco- T, 40%
16. Kola leaves- KL + Kola bark- KB, 30%
17. Kola leaves- KL + Kola bark- KB, 40%
18. Kola leaves- KL + Tobacco- T, 30%
19. Kola leaves- KL + Tobacco- T, 40%
20. Kola bark- KB + Tobacco- T, 30%
21. Kola bark- KB + Tobacco- T, 40%.

Set 1, above served as the control test sample. 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 used was of AnalaR grade.

The rebars 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 5% sodium chloride solution.

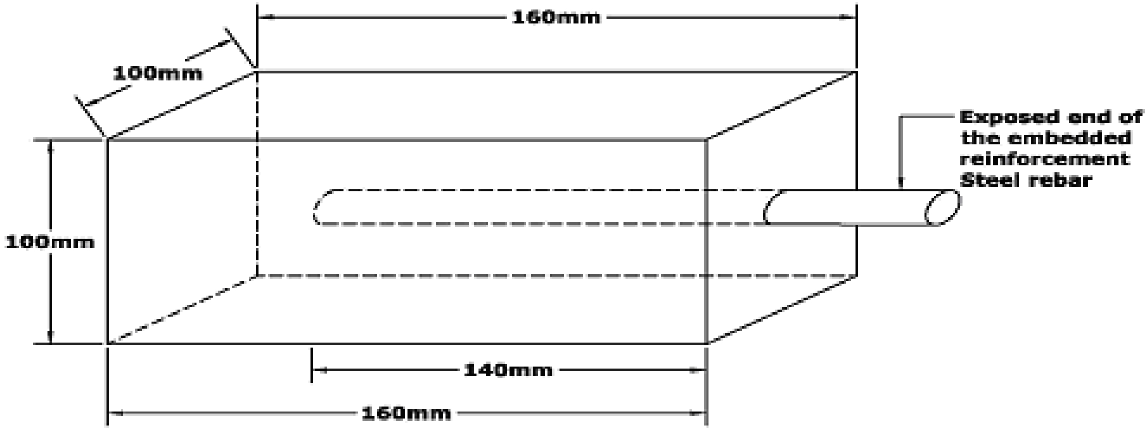

Figure 1. A sample block (not to scale).

2.3. Potential measurement

Each concrete block was partially immersed in 5% sodium chloride solution such that the medium level was just below the exposed reinforcing steel but not making any 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 5 –day intervals. All the experiments were performed under free corrosion potential and at ambient temperature.

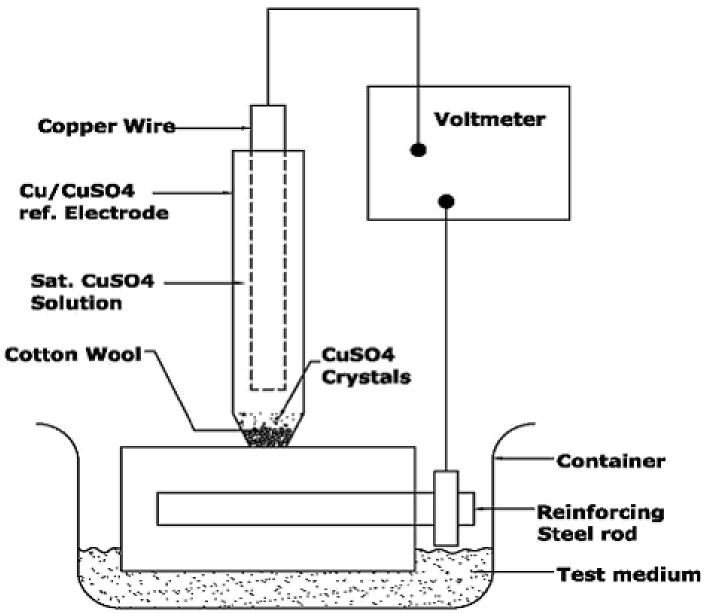

Figure 2. Schematic representation of experimental set up.

3. RESULTS AND DISCUSSION

3.1. The kola nuts, leaves and bark

The results obtained for the two different concentrations of 30% and 40% of the extracts of kola nuts, leaves, and barks, separately mixed with the concrete test samples are presented in the curves of Figs.3. All the curves show the variation of potentials (mV) with exposure time (days) for the steel reinforced concrete samples partially immersed in 5% sodium chloride solution. In general, a fairly good result was obtained for each of the different extracts used and for each of the concentrations.

The performance of the 30% concentration was not much different from that of 40% for all the kola tree components' extracts. For the kola nuts alone, the 40% concentration seems to give a marginal better performance.

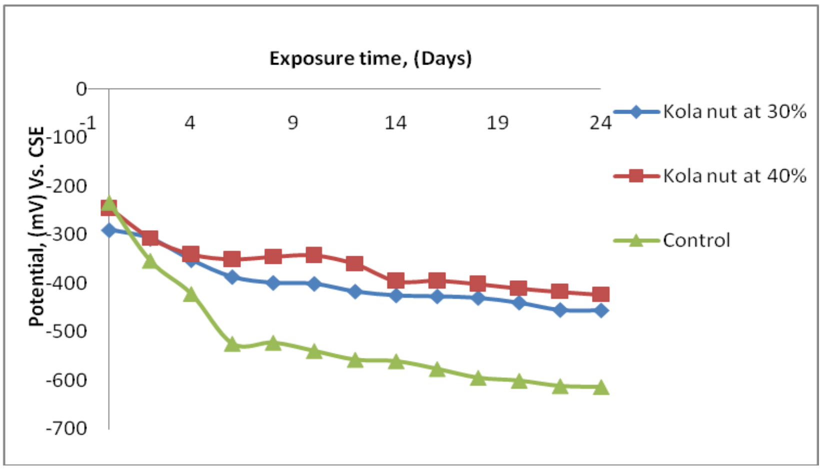

Figure 3. Variation of potential with time for mild steel reinforcement in concrete mixed with 30 and 40% concentrations of kola nuts extracts and partially immersed in 5% NaCl solution.

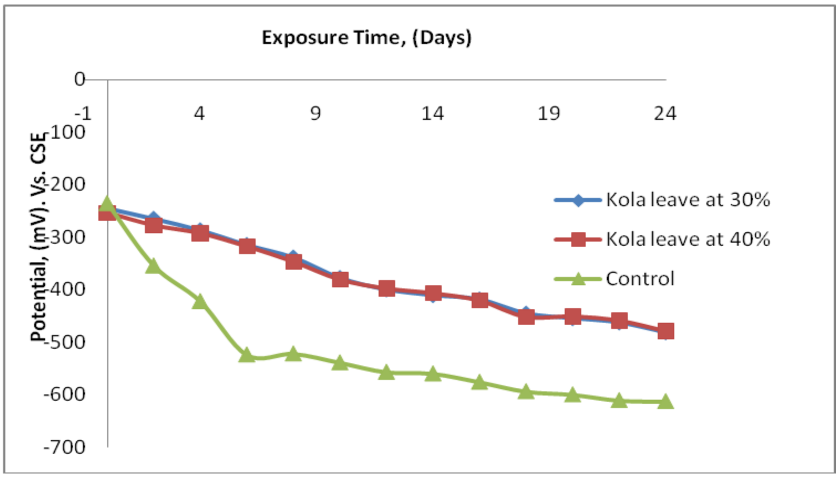

Figure 4. Variation of potential with time for mild steel reinforcement in concrete mixed with 30 and 40% concentrations of kola leaves extracts and partially immersed in 5% NaCl solution.

This could be associated with the increased concentration of the passive film forming species within the kola nut constituents, particularly tannin which has been known to be an effective 'green' inhibitor (15). Other constituents such as epicatechin, D-catechins, theophylline and theobromine could be, or act as inhibiting passive film formers on the steel substrate and surface. The formed film would act as a barrier between the steel and corrosive environment interface and thus preventing and/or stifling corrosion reactions.

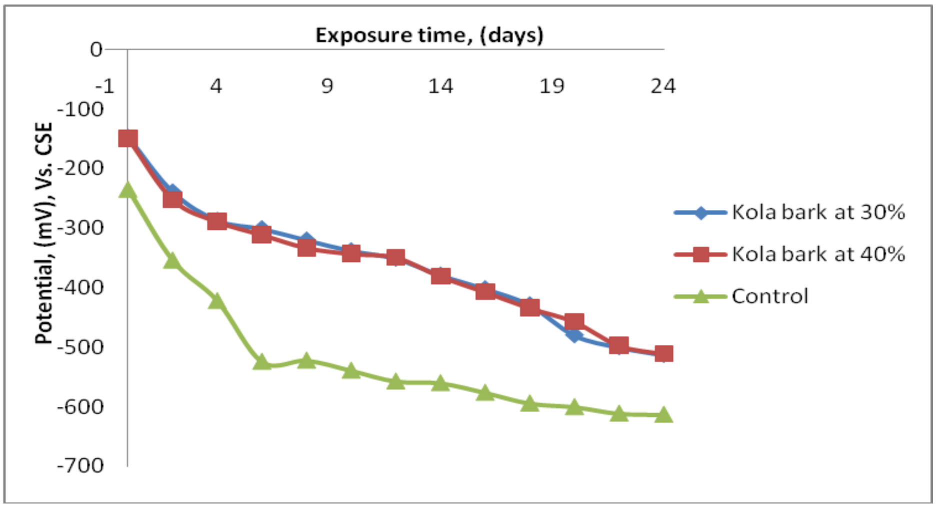

Figure 5. Variation of potential with time for mild steel reinforcement in concrete mixed with 30 and 40% concentrations of kola bark extracts and partially immersed in 5% NaCl solution.

The same trend of corrosion inhibition performance as above was observed for the 30 and 40% concentrations of extracts of the kola tree leaves, Fig.4. Though very close potential readings were obtained throughout the experimental period, there appears to be a better marginal corrosion inhibition performance for the 30% concentration of the leaf extracts in the first 10 days of the experiment. The rest 14 days of the experiment recorded fluctuating voltage readings in which neither of the two extract concentrations was prevalent or dominant. This phenomenon seems difficult to explain. However, it could be due to the closeness of the per cent concentrations of the extracts. Nevertheless, it is apparent that the leaves extracts recorded potential readings that showed it to be very fairly protective throughout the experimental period. After 14 days of the experiment, the inhibitor's protection appeared to be weak as increasing negative values of potential ≥ -420mV were being recorded.

In Fig.5, extracts from the bark of the kola tree gave very good corrosion inhibiting performance for the protection of the embedded steel in the concrete for the first 12 days of the experiment in particular for the two concentrations of 30 and 40% used. In this period of work, the recorded potential voltage were between -197mV and 351mV vs. CSE. These fell within the accepted values of protection. The rest results were good till the rest period of the experiment except in the last two days when the readings achieved potential values of between -457 to -513 mV vs. CSE. In all, when compared with the samples without extract additions to the concrete matrix, the results obtained towards the last days of the experiment, though high in negative potential values, showed some amounts of protection.

3.2. The tobacco extracts

As presented in Fig.6, the results obtained for the addition of 30 and 40% concentrations of tobacco extracts to the steel reinforced concrete showed very good results throughout the whole period of the experiment.

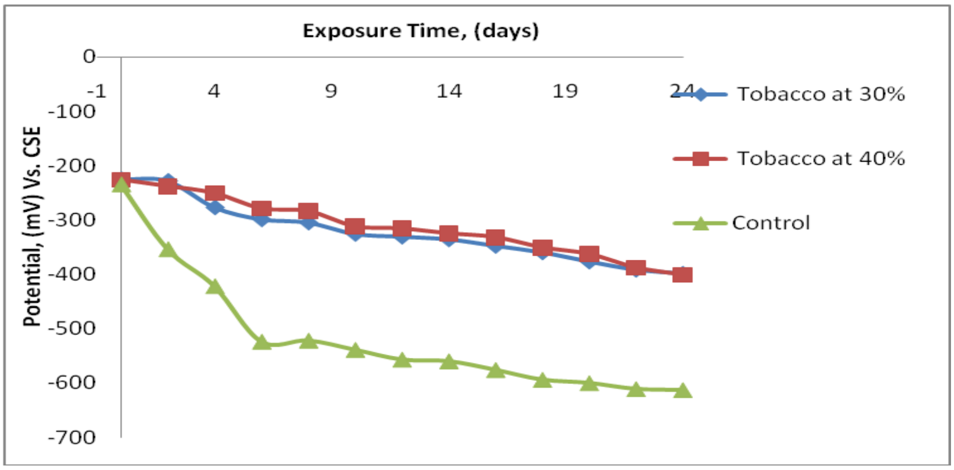

Figure 6. Variation of potential with time for mild steel reinforcement in concrete mixed with 30 and 40% concentrations of tobacco extracts and partially immersed in 5% NaCl solution.

Potential values of between -225mV to -392mV vs. CSE were achieved from the first day to the last day of the experiment. The two different concentrations of 30 and 40% of tobacco extracts used did not show appreciable better comparative performance in potential values between both of them. Considering the very complex structural compounds and the multifarious constituent composition of tobacco which consists of about 4,000 chemical compounds, the results obtained were not unexpected. As previously mentioned, tobacco is known to consist among others, chemical compounds such as terpenes, polyphenols, carboxylic acids, nitrogen containing compounds (nicotine) and alkaloids (13). The synergistic action/reaction of these compounds within the concrete matrix and on the surface of the embedded steel could hinder the chloride ion species, promote more stable passive film formation on the surface of the embedded steel and hence inhibit and stifle corrosion reactions at the embedded steel’s concrete environment interface.

3.3. Effect of combined extracts – synergism

3.3.1. The combination of kola nuts, leaves and bark extracts

The results obtained from the various combinations of the individual extracts reported and discussed above, are presented in Figures 7 to 12.

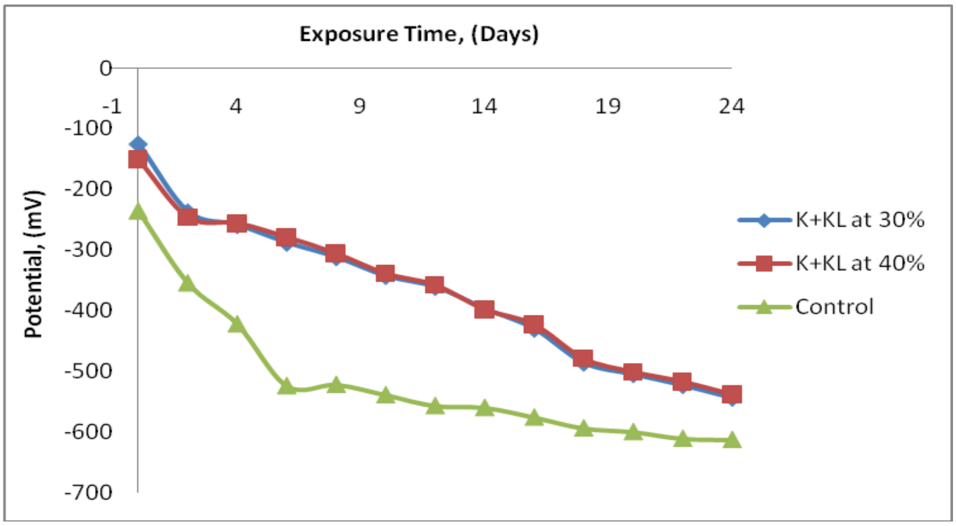

Figure 7. Variation of potential with time for mild steel reinforcement in concrete mixed with 30 and 40% concentrations of kola nuts and kola leaves extracts and partially immersed in 5% NaCl solution.

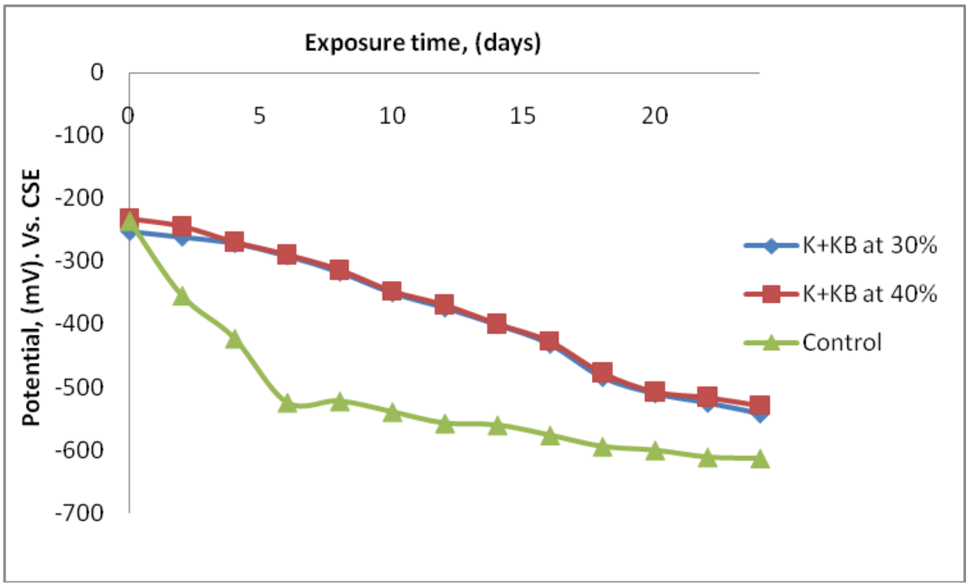

Figure 8. Variation of potential with time for mild steel reinforcement in concrete mixed with 30 and 40% concentrations of kola nuts and kola bark extracts and partially immersed in 5% NaCl solution.

The results obtained for the combination of 30 and 40% concentrations of kola nuts and kola leaves are presented in Fig.7. The results obtained in this combination for the two concentrations of the extracts showed a very much improved results than either the nuts or leaves' extracts alone. Up to the 16^{th} day of the experiment, the recorded readings were still less than -400mV vs. CSE. In fact, it could be said that a near total inhibition and hence protection was achieved in the first 14 days of the experiment. These results could be explained to be due to the synergistic effect of reactions between the reacting species of the nuts and leaves' extracts. Again, the results for the 30 and 40% extracts concentrations did not show much comparative better results than each other; though the 40% concentration seems to have very marginal effective corrosion inhibition performance.

Similar results as above were obtained by the combination of kola nuts and kola bark extracts, Fig.8. A potential range of -232 mV to 374 mV vs. CSE was achieved in the first 12 days of the experiment. This range indicates a protective measure due to the combined extracts inhibitive action. The corrosion inhibition performance to the end of the experiment was also fairly good when compared with the results in which there was no extracts addition. In addition, the results obtained here were far better than those obtained either for Kola nuts or kola bark extracts alone. This is another demonstration of the positive effect of synergism in the combined extracts.

The results obtained for the combination of extracts of 30 and 40% concentrations of kola tree leaves and kola tree bark are presented in Fig.9.

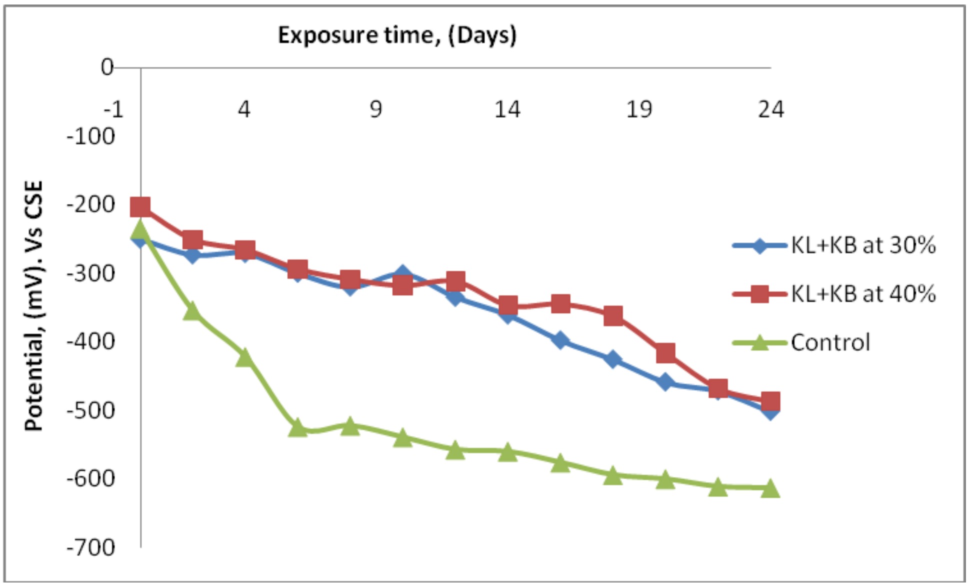

Figure 9. Variation of potential with time for mild steel reinforcement in concrete mixed with 30 and 40% concentrations of kola leaves and kola bark extracts and partially immersed in 5% NaCl solution.

Also, the effect of synergism was demonstrated here. A better corrosion inhibition performance was achieved in these results than the results obtained in the use of individual extracts of kola leaves and kola bark alone. A good corrosion inhibition performance was achieved up to the 16^{th} day of the experiment when the combination at 40% concentration gave a potential range value of -345mV vs. CSE. Here, though the results obtained for the per cent concentrations of 30 and40 were close, a clear better performance was shown by the 40% concentration of the extracts.

In all of the above, as previously mentioned, for the combined kola tree components' extracts addition to the concrete matrix, the better corrosion inhibition performance of the various combinations of the extracts than the individual extracts alone could be associated with synergistic effect. The combination of the extracts further presented more complex structural chemical compounds that resulted into formation of more stable passive film on the embedded metal surface. This, in consequence, hindered to a very large extent, the anodic dissolution of the embedded steel in the concrete matrix.

3.3.2. The combination of extracts of kola nuts, leaves and bark with tobacco extracts

The results of the extracts of kola nuts, kola tree leaves and kola tree bark that were separately mixed/combined with the extracts of tobacco in 30 and 40% concentrations are presented in Figs. 11 to 13.

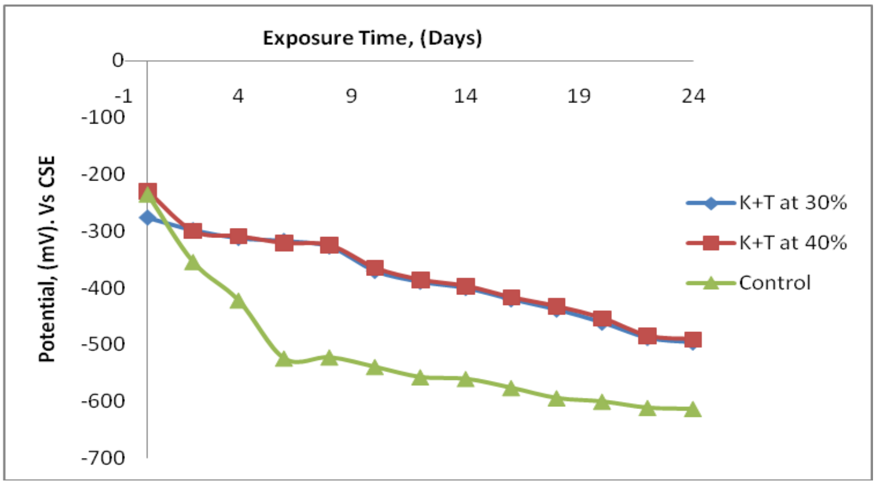

Figure 10. Variation of potential with time for mild steel reinforcement in concrete mixed with 30 and 40% concentrations of kola nuts and tobacco extracts and partially immersed in 5% NaCl solution.

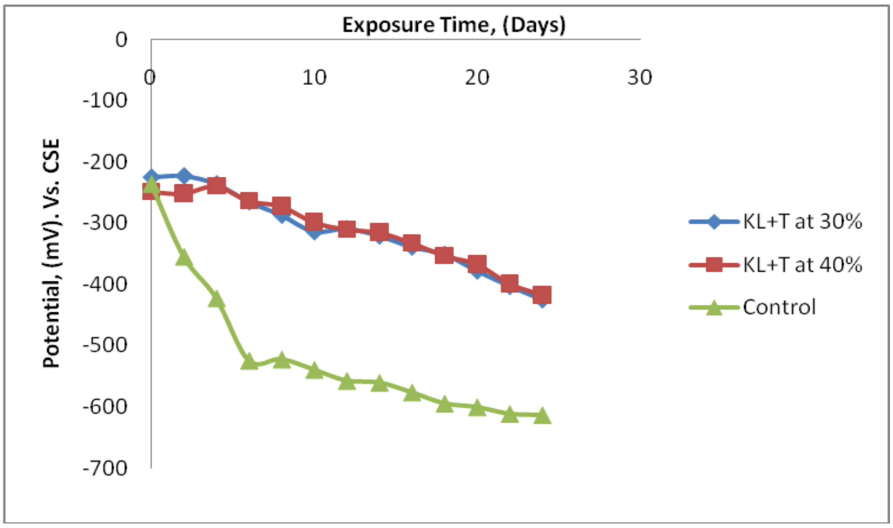

Figure 11. Variation of potential with time for mild steel reinforcement in concrete mixed with 30 and 40% concentrations of kola leaves and tobacco extracts and partially immersed in 5% NaCl solution.

The potential values obtained for the combination of extracts of kola nuts and tobacco showed results that were less than that of tobacco alone but better than that of kola nuts alone. Plausibly, the chemical reactions of the complex composition of kola nut and tobacco could not synergize for a better corrosion inhibition performance when combined together. However, the overall corrosion inhibition performance profile was good throughout the experimental period; though with increase in the negative values of potential.

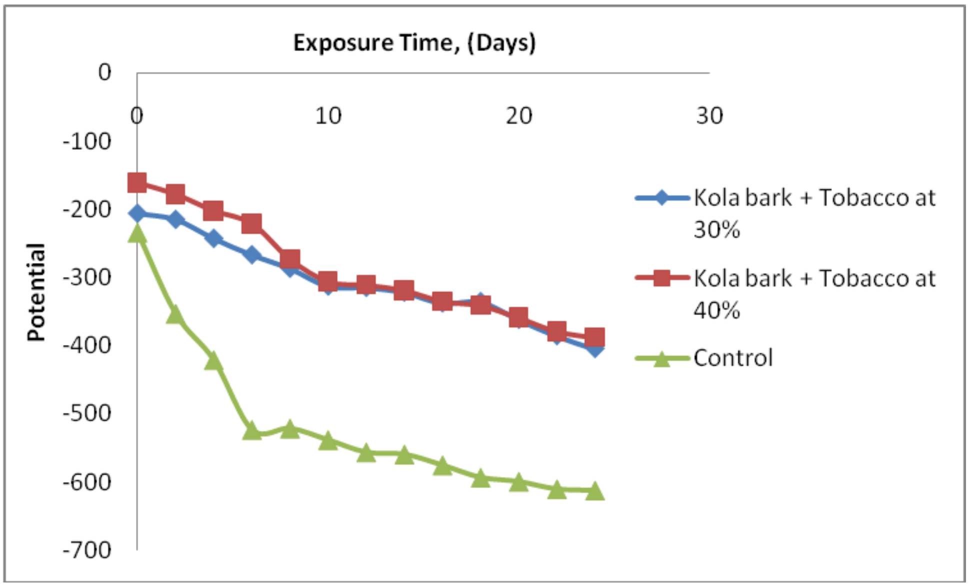

Figure12. Variation of potential with time for mild steel reinforcement in concrete mixed with 30 and 40% concentrations of kola bark and tobacco extracts and partially immersed in 5% NaCl solution.

This is an obvious indication of a tendency towards active corrosion reactions.

The combination of the extracts of kola tree leaves and tobacco, however, gave results where synergistic effect is apparent, Fig.11. The results obtained here showed marginal corrosion inhibition performance than that of tobacco extracts alone, but clearly better than that of kola leaves extracts alone. There was no clear better performance between the two concentrations of the extracts used as the results obtained fluctuated in performance between the concentrations of 30 and 40% throughout the experimental period. The overall results showed effective corrosion inhibition performance throughout, especially up to the 20th day of the experiment.

Fig.12 shows the results obtained for the combination of extracts of kola tree bark and tobacco for corrosion inhibition of embedded steel in concrete immersed in 5% NaCl solution. The potential values recorded throughout the experimental period confirm the results here to be the best of all. A potential range of -161 mV to -386 mV vs. CSE on the 22nd day of the experiment, was clearly better than that of tobacco's alone and that of the kola tree bark extracts alone. The results demonstrated apparent case of synergism. The results obtained for the 40% concentration of extracts were also better than those of the 30% concentration extracts. When compared with the results where there was extracts addition, the better corrosion inhibition performance was obvious.

3.3.3. The tobacco and kola tree nuts, leaves and bark: composition effect

Though various mentions have been made to this in this paper, it is, however, important to write a brief summary here with respect to the composition effect.

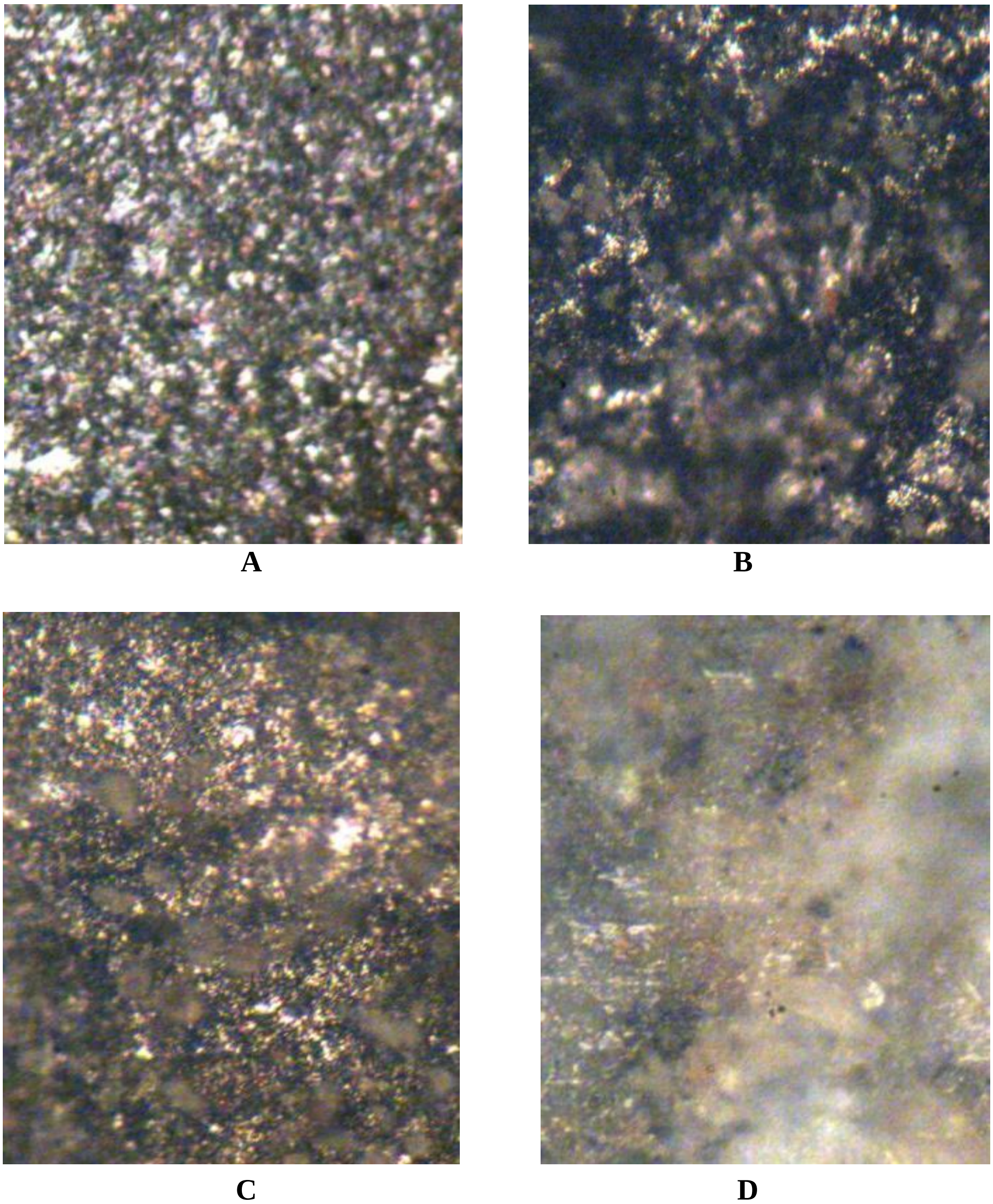

Figure 13. Photomicrographs of the mild steel reinforcement. (a) Before embedding in concrete. (b - d) After the experiments with 40% Kola nut; 40% kola nut bark and 40% tobacco + kola nut extracts concentrations admixed with concrete respectively.

Tobacco alone consists of about 4,000 chemical compounds (9, 13). Similarly, kola nuts, leaves and bark consist of diverse complex composition of which tannin is among. This is a chemical compound that is known to be an effective corrosion inhibitor. It could, therefore, be plausibly explained that the effective corrosion inhibition performance of the extracts for the mild steel reinforcement in concrete can be associated with these complex compounds with diverse chemical compositions.

Tobacco and kola tree components are known to contain polyphenols. Some polyphenols have high complexation affinity to metals, alkaloids and some other biologic macromolecules such as obtained in tobacco and kola tree components/parts. The high complexation affinity to metals could be associated with the effective corrosion inhibition performance. This is because the film generated will be strongly adsorbed to the embedded steel surface.

The surfaces of the photomicrographs in Fig. 13 (a-d) show that some degree of corrosion occurred as presented in Fig.13 (b-d) but could not be described as significant. This observation could be associated with the protective effectiveness of the plants extracts. It also showed a very good correlation with the results obtained with the potential measurements.

In general, the very complex and many chemical compounds and diverse chemical composition of the extracts used, would have provided some degree of stable/passive film on the embedded steel surface that serves as a barrier for corrosion reactions at the concrete matrix environment (containing Cl^- ions) and the steel's interface. The consequence will be that of a stifled corrosion reaction where anodic dissolution of the metal was reduced to the minimal with little or no simultaneous cathodic reactions; and this will result in protection of the embedded steel in concrete.

4. CONCLUSION

Extracts of kola nut, leaves, and bark at 30 and 40% concentrations respectively, were effective for corrosion inhibition of mild steel reinforcement in concrete partially immersed in 5% sodium chloride solution at the ambient temperature.

Under the same conditions of experiments as above, tobacco extracts alone gave the best corrosion inhibition performance for mild steel reinforcement in concrete.

The various combinations of the extracts were equally effective; and in most cases give better but marginal performance in corrosion inhibition of the metal substrate. The overall best result and hence the best corrosion inhibition performance of the steel reinforcement in this work was obtained with the combinations of 30 and 40% concentrations, separately, with kola tree bark and tobacco extracts. It was a clear case of synergism within the reacting species in the chemical composition of the complex structural compounds in the extracts.

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