*Int. J. Electrochem. Sci.*, 8 **(2013)** xx - yy

International Journal of
ELECTROCHEMICAL
SCIENCE
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# Inhibition Effect of *Vernonia amygdalina* Extract on the Corrosion of Mild Steel Reinforcement in Concrete in 3.5M NaCl Environment

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*Received:* 6 June 2013 / *Accepted:* 1 xxx 2013 / *Published:* 1 xxx 2013

The inhibition effect of *Vernonia amygdalina* (bitter leaf) extract on the corrosion behaviour of embedded mild steel rebar in concrete has been investigated by electrochemical potential measurement, pH and gravimetric (weight loss) methods. The results were further analysed using the two-factor ANOVA test. The experiments were performed using bitter leaf extract as a green inhibitor in 3.5% sodium chloride solution. Inhibitor extracts concentrations of 25, 50 75, and 100% were prepared from the fresh leaves of *Vernonia amygdalina* with distilled water. The voltage (potential) measurements were recorded with a digital voltmeter and a copper-copper sulphate electrode as the reference electrode. The pH of the test medium was measured by a pH meter. Compressive strength of each of the block samples was determined after the experiments. Weight loss values were obtained from the weight loss method (gravimetric) and the inhibitor efficiency was computed from the corrosion rate of each of the tested samples. Results showed that varied concentration of *Vernonia amygdalina* and the test exposure time significantly affect both the corrosion potential of embedded steel rebar in concrete and the pH of the medium. The outcome of the ANOVA test confirmed the results at 95 % confidence, and further showed that concentration of *Vernonia amygdalina* had greater effect on potential measurements, whereas, exposure time had greater effect on pH measurements. *Vernonia amygdalina* extract gave good corrosion inhibition performance of the embedded steel rebar in concrete at 25%, 50% and 75% concentrations in NaCl test medium. The highest inhibition efficiency of 90.08 % was achieved at 25% concentration, the lowest inhibitor concentration used.

**Keywords:** Inhibition; Corrosion; bitter leaf*;* Reinforced Concrete; Sodium Chloride

## 1. INTRODUCTION

The importance and use of reinforced concrete in our world today cannot be over emphasized. Its area of application ranges from small buildings, to tall ones, bridges etc. and it is exposed to various environments depending on the use it is being applied to. Corrosion has posed to be more of a nuisance than good. Corrosion of steel reinforcing bars is a problem in many structures. The significant role and /or importance of reinforced concrete in today's world, has generated considerable continuous research effort in searching for ways to mitigate the adverse corrosion effect in concrete [1]. For steel embedded in concrete, corrosion results in the formation of rust which has two to four times the volume of the original steel and none of the good mechanical properties. More so, corrosion produces pits or holes in the surface of reinforcing steel, reducing strength capacity as a result of the reduced cross-sectional area [2]. As a result, the effect of various predetermined constant concentration of some inhibitors on the electrochemical corrosion of mild steel reinforcement in concrete in environments (such as sodium chloride and sulphuric acid environments) is emphasized.

Various research works have been performed in recent time on the use of plant extracts either as corrosion inhibitor or as additives in electroplating [3-12]. The research interest has been necessitated by the fact that the present corrosion inhibitors in market for the protection of steel reinforcement in concrete exposed to chloride attack or other corrosive environments are toxic to the environment and thus compromise safety and sustainability drives. There is, therefore, the need to develop inhibitors that are eco-friendly and sustainable. Studies such as mentioned above include the use of *Bambusa Arundinacea*is for reinforced concrete [13]; extracts of kola plant and tobacco for mild steel reinforced concrete [14]; *Vernonia amygdalina* for mild steel in 0.4M $HNO_3$ [15] and extracts of green tea for mild steel in dilute sulphuric acid [16]. It is however, noteworthy that results of these studies show that extracts of plant materials are at the top of the list of non – chromates that have been used as corrosion inhibitors to replace environmentally hazardous chromates. They are non- toxic, environmentally friendly and readily available.

This investigation aims at studying the effect of *Vernonia amygdalina* (bitter leaf extract) as an organic corrosion inhibitor on the corrosion of mild steel embedded in concrete by electrochemical and gravimetric methods and by further statistically analysing the results using Analysis of Variance (ANOVA) test. In a study [17], it was revealed that Vernonia amygdalina leaf has high protein (33.3%), fat (10.1%), crude fibre (29.2%), ash (11.7%), minerals (Na, K, Ca, Mg, Zn & Fe), phytate (1015.4mg/100g) and tannin (0.6%) content, while it contains low cyanide (1.1mg/kg). Bitter leaf is known [18] to contain tannin, among others, which has been variously associated with corrosion inhibition in aqueous and acidic environments. Though the concrete environment is, in general alkaline and thus making the embedded steel passive, the use of NaCl test environment is hazardous to the surface film passivity on the steel surface. The experiment was performed using bitter leaf as a green inhibitor in 3.5% sodium chloride. The sodium chloride addition accelerates the corrosion of the embedded steel by providing increased chloride ions ($Cl^-$) in the solution and around the reinforcing steel rebar. The chemical constituents of bitter leaf, especially saponnin and tannin, are expected to exhibit electrochemical activity of strong adsorption to the embedded mild steel surface and thus enhancing its corrosion resistance in corrosive environments. The results obtained could be of economic/technological benefit.

## 2. METHODS

### *2.1. Preparation of the Plant Extracts*

Fresh leaves of *Vernonia amygdalina* were obtained and air dried. The dried material was machine ground into powder and known weights were placed in different containers. Ethanol was added to each container and the powdered leaves were allowed to soak. After five (5) days, the samples were filtered, and the filtrates were distilled using the distillation equipment in order to leave the samples ethanol free. Stock solutions were prepared from the inhibitor. From the stock solution obtained, inhibitor test concentrations of 25, 50 75, and 100% were prepared by diluting with distilled water.

### *2.2. Preparation of mild steel rebar*

The steel rebar with chemical composition of: 0.3%C, 0.25 %Si, 1.5%Mn, 0.04%P, 0.64%S, 0.25%Cu, 0.1%Cr, 0.11%Ni, and the rest Fe, was used for the reinforcement. The rebar was cut into several pieces each with a length of 120 mm and 12 mm diameter. The weight of each piece was taken and recorded. An abrasive paper was used to remove any mill scale and rust stains on the steel specimens before being cleaned with ethanol. Ideally, the prepared steel rebar samples are to be kept in a desiccator but for the purpose of this experiment, they were not because they were used just after cleaning.

### *2.3. Preparation of Concrete and the test environment*

The preparation of the concrete block samples followed the previous procedures [14-15]. The concrete blocks used for the experiment were made of Portland cement, sand, gravel and water. They were prepared in the ratio 1:2:4 (C: S: G) – cement, sand, gravel. Each concrete block, embedded with a reinforcing steel rebar, was 100 mm long, 100 mm wide and 120 mm thick. The formulation for the reinforced concrete specimens used, in Kg/m3, was: Cement 320; Water 140; Sand 700 and Gravel 110. The water cement (W/C) ratio was 0.44. Four different concentrations of 25%, 50%, 75% and 100% of the extract were used, along with the control experiment. Each steel rebar was placed symmetrically across the length of the block in which it was embedded and had a concrete cover of 50 mm (Fig.1). Only about 90 mm was embedded in each concrete block. The remaining 30 mm protruded at one end of the concrete block, and was coated to prevent atmospheric corrosion. This part was also used for electrical connection. The test medium used for the investigation was 5% sodium chloride solution, of AnalaR grade.

3.5% of NaCl was prepared by diluting 35 grams of NaCl in 10,000 ml (10 L) of distilled water which was used as corrosion medium for reinforced concrete samples with inhibitors and without inhibitor**.**

*2.4. Potential and pH measurements*

Potential measurements were taken using a digital voltmeter connected to a copper-copper sulphate electrode as shown in Fig.1. The readings were taken at three different points on each concrete block directly over the embedded steel rebar. The average of the three readings was found and computed as the potential reading for the embedded rebar in 3 –day intervals. All the experiments were performed at ambient temperature and under free corrosion potential.

The pH of the media was measured by placing a small amount of the medium in the cup of the pH meter, with the probes positioned in the sample solution.

*2.5. Compressive Strengths*

At the completion of the experimental period, compressive strength test was carried out on each block sample after weighing, using a compressive strength test machine.

*2.6. Weight loss method*

The metal samples were separately weighed before embedding in concrete and labelled at the protruding end after embedding each of the samples. After the corrosion experiments, the concretes were broken down completely and each of the samples re-weighed. Weight loss was obtained by computing the difference between the initial and final weights of the samples.

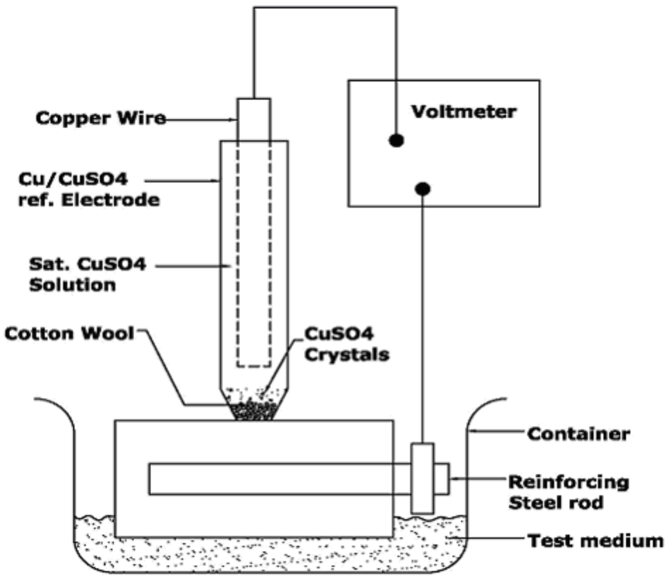


**Figure 1**. Schematic representation of experimental set up

The results obtained were used to compute the corrosion rate and inhibitor efficiency. The corrosion rate (R) was calculated from the formula:

$$R = \left[\frac{87.6W}{DAT}\right] \quad \ldots\ldots\ldots\ldots(1)$$

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. The percentage inhibitor efficiency, P, was calculated from the 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.

## 3. RESULTS AND DISCUSSION

### *3.1. Potential Measurement*

The results obtained for the four different concentrations of 25, 50, 75 and 100% of the extracts of bitter leaf mixed with the concrete test samples are presented in the curves of Figs. 3 – 7. At the concentration of 100%, Fig. 2, the passive corrosion reactions lasted for only 5 days at the potential voltage of -400 mV. Curiously, a spike of another passive corrosion reaction was obtained after 23 days achieving a potential of -250 mV. For most part of the experiment, using this concentration, the corrosion reactions remained in active state that ranged between -500 and -650mV. Obviously, at this concentration the extract could not be described as being protective.

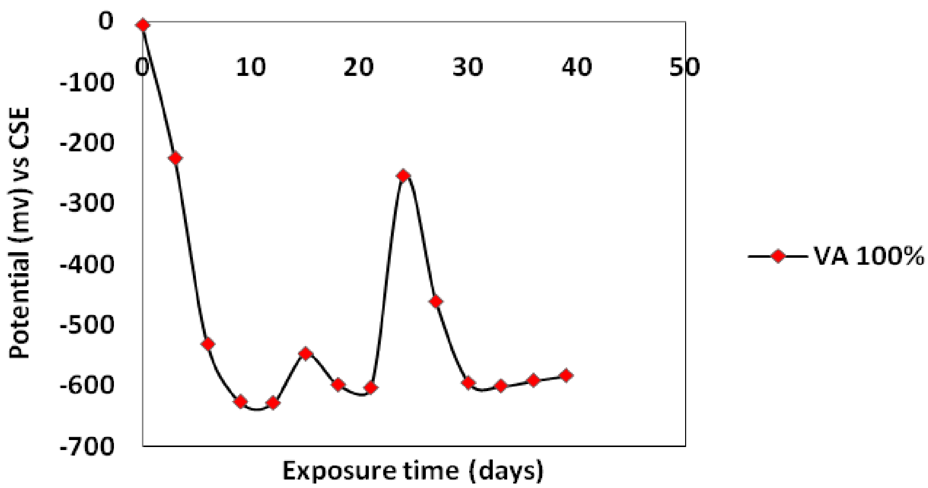


**Figure 2**. Variation of potential with time for mild steel reinforcement in concrete mixed with 100% concentration bitter leaf (VA) extract and partially immersed in 3.5% NaCl solution.

At the extract concentration of 75%, Fig. 3, a fluctuating and fairly passive corrosion reaction that ranged between -400 and -470 mV was achieved. This indicates some stability in the corrosion protection of the extract throughout the experimental period. However, this passive condition could not be described as strong as the potential voltage values seem to be on the borderline of passive and active corrosion reactions. The active corrosion reaction apparently indicates a tendency towards corrosion taking place on the metallic sample's surface. In comparison, the extract concentration at 75% showed a better corrosion inhibition performance than that of the 100%.

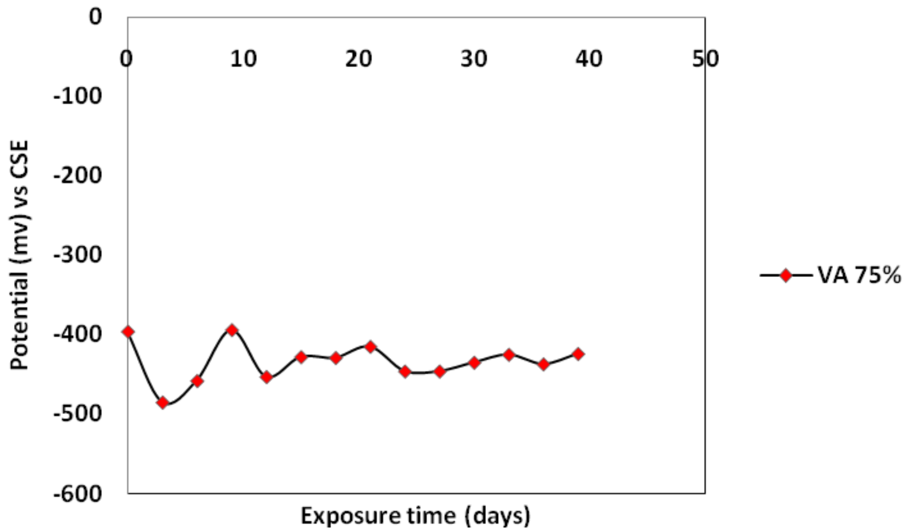


**Figure 3**. Variation of potential with time for mild steel reinforcement in concrete mixed with 75% concentration bitter leaf (VA) extract and partially immersed in 3.5% NaCl solution.

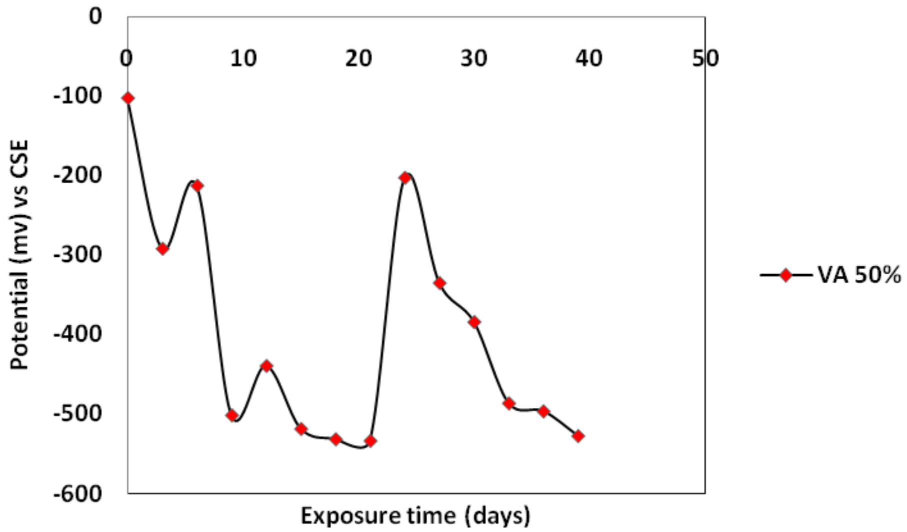


**Figure 4**. Variation of potential with time for mild steel reinforcement in concrete mixed with 50% concentration bitter leaf (VA) extract and partially immersed in 3.5% NaCl solution.

There was a mixed result for the extract at 50% concentration, Fig. 4. The first 8 days of the experiment could be described as inhibitive for a potential range of -100 to -400 mV. From about the $8^{th}$ to the $20^{th}$ day, however, the achieved potentials (-500 to – 550 mV) had moved into active corrosion reactions, indicating a tendency towards corrosion. From the $24^{th}$ to the $33^{rd}$ day of the experiment, the corrosion reaction again was in the passive state with the potentials in the range of 200 – 450 mV. It is difficult to explain this corrosion behaviour. Plausibly, however, it could be associated with the chemistry of the concrete environment and the rate of ingress of NaCl through the concrete matrix to break down the passive film provided by the extract constituents and the alkaline concrete environment.

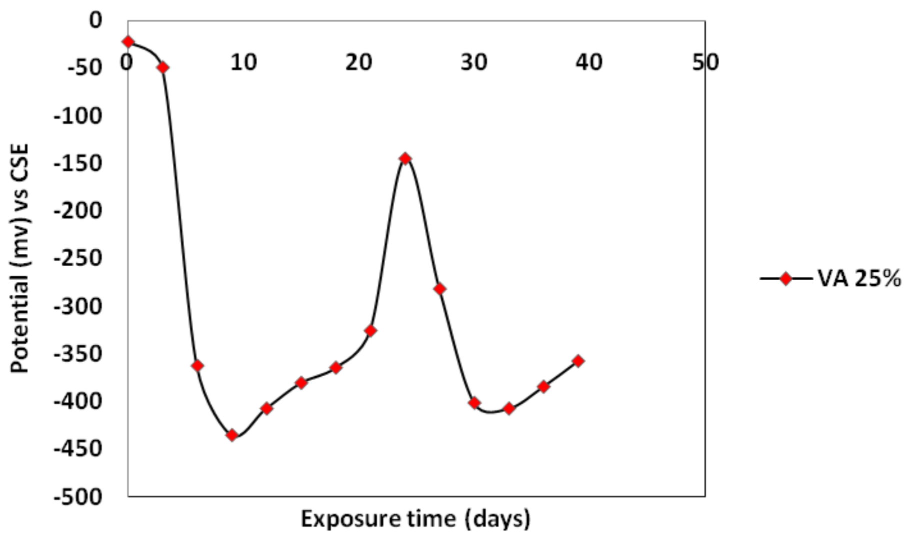


**Figure 5**. Variation of potential with time for mild steel reinforcement in concrete mixed with 25% concentration bitter leaf (VA) extract and partially immersed in 3.5% NaCl solution

In Fig, 5, the *Vernonia amygdalina* extract at 25% concentration, exhibited corrosion inhibition performance throughout the experimental period with the potentials that ranged from -25 mV at the beginning to -310 mV on the last day of the experiment; except for some few voltage fluctuations where potential values of -400 to -430 mV were recorded. This concentration gave the best corrosion inhibition performance among the other extract concentrations used. It could be described in this experiment to be the optimum value for the extract inhibition performance in the tested environment.

Fig. 6 provides the overall *Vernonia amygdalina* extract corrosion inhibition performance profile for the mild steel embedded in concrete and partially immersed in 3.5% sodium chloride test medium. Here it could be confirmed again that the best inhibition performance in this work is with the extract with 25% concentration. All the extracts performed better than the control experiment in which there was no extract addition. The general observation/inference here is that the extract of *Vernonia amygdalina* (bitter leaf) could provide reasonable measure of corrosion inhibition of mild steel in concrete in the sodium chloride environment within the all other experimental conditions used, particularly at 25% concentration. Obviously, the chemical constituents of bitter leaf would have acted synergistically to exhibit this electrochemical activity of corrosion inhibition.

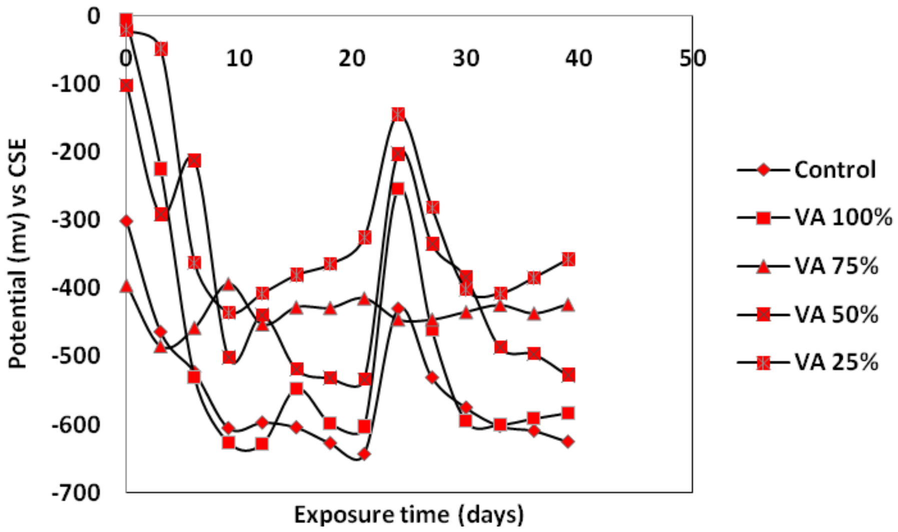


**Figure 6.** Variation of potential with time for mild steel reinforcement in concrete mixed with 25, 50, 75 and 100% concentrations of bitter leaf (VA) extract and partially immersed in 3.5% NaCl solution.

### *3.2. Statistical Analysis*

The scatter plots show that there was an initial abrupt decrease in potential with respect to time; average stability was attained from the 9$^{th}$ day. It can also be deduced that 25%VA exhibited optimal performance while 100%VA showed the least performance in corrosion inhibition.

Two-factor single level experiment ANOVA test (F-test) was used to evaluate the separate and combined effects of concentration of bitter leaf (VA) extracts and exposure time on the corrosion potential of the mild steel reinforcement in 3.5% NaCl solution. The F-test was used to examine the amount of variation within each of the samples relative to the amount of variation between the samples. The Sum of Squares among columns (exposure time) was obtained with the equation [21]:

$$SS_c = \frac{\sum T_c^2}{nr} - \frac{T^2}{N} \quad \text{.......................................... (3)}$$

Sum of Squares among rows (concentration of VA)

$$SS_r = \frac{\sum T_r^2}{nc} - \frac{T^2}{N} \quad \text{.......................................... (4)}$$

Total Sum of Squares

$$SS_{Total} = \sum x^2 - \frac{T^2}{N} \quad \text{.......................................... (5)}$$

The calculation using the ANOVA test is tabulated (Table 1) as shown.

On the basis of the results in Table 1, it can be concluded with 95 % confidence that varied concentration of *Vernonia amygdalina* and exposure time significantly affects the corrosion potential of the test medium (Fig.7). The effect of concentration of inhibitor was much higher.

**Table 1**. Summary of ANOVA analysis for potential measurements

| Source of Variation | SS | Df | MS | F | Significance F |
|---|---|---|---|---|---|
| Exposure Time | 188956.75 | 13 | 14535.13 | 62.95 | 1.91 |
| Concentration of VA | 118983.81 | 4 | 29745.95 | 128.82 | 2.55 |
| Residual | 12007.59 | 52 | 230.92 | | |
| Total | 319948.15 | 69 | | | |

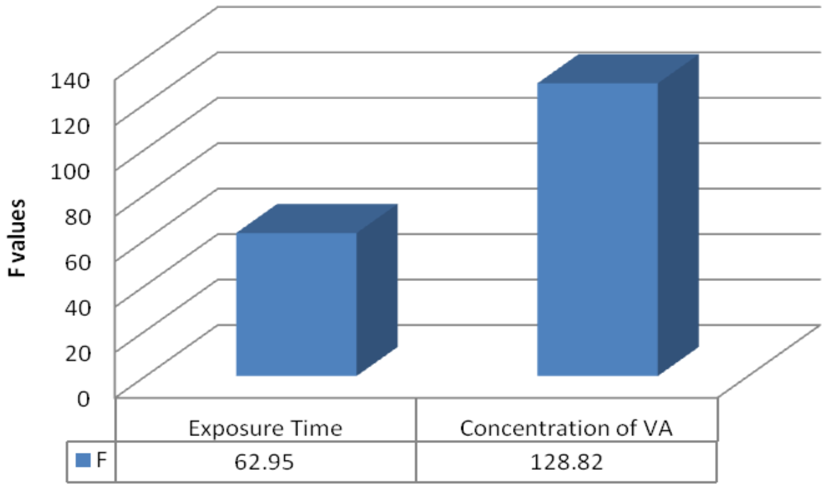


**Figure 7.** Influence of exposure time and VA concentration on corrosion potential

### *3.3. Effect of pH*

The results obtained for the different concentrations (25, 50, 75 and 100%) of the *Vernonia amygdalina* extracts are presented in Table 2. The reinforced concrete blocks recorded pH values which its acidity decreased from 10.17 from the beginning of the experiment to 8.95 at the end in a period of 39 days. Similar trends were recorded for all the different per cent concentrations of inhibitor addition.

*Vernonia Amygdalina* at 25% concentration addition, the acidity reduced from 10.63 – 9.04. At 50% concentration, it reduced from 10.52 – 9.10; and at 100%, from 10.64 – 9.11. This decrease in acidity could be due to the reactions between the concrete constituents, *vernonia amygdalina*, the NaCl test environment and the reactions at the steel/environment interface for the steel reinforced concrete blocks.

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

**Table 2**. pH Readings of NaCl Medium

| Day | Control | VA 100% | VA 75% | VA 50% | VA 25% |
|---|---|---|---|---|---|
| 0 | 10.17 | 10.64 | 8.85 | 10.52 | 10.63 |
| 3 | 8.65 | 9.63 | 9.43 | 9.57 | 9.46 |
| 6 | 10.05 | 10.79 | 9.06 | 10.6 | 10.22 |
| 9 | 9.02 | 9.63 | 9.44 | 9.5 | 9.37 |
| 12 | 8.7 | 8.61 | 9.16 | 9.25 | 9.08 |
| 15 | 8.61 | 8.64 | 8.67 | 9.1 | 8.99 |
| 18 | 8.89 | 9.28 | 9.45 | 9.64 | 9.45 |
| 21 | 9.18 | 9.46 | 8.67 | 9.45 | 9.3 |
| 24 | 8.73 | 8.7 | 9.10 | 8.9 | 8.8 |
| 27 | 9.38 | 9.61 | 9.41 | 9.58 | 9.39 |
| 30 | 8.6 | 8.75 | 9.04 | 8.75 | 8.57 |
| 33 | 8.45 | 9.2 | 9.06 | 9.29 | 9.12 |
| 36 | 9.23 | 9.42 | 9.1 | 9.46 | 9.32 |
| 39 | 8.95 | 9.11 | 9.41 | 9.10 | 9.04 |

The scatter plot of pH values against exposure time show an almost linear relationship between the variables at all VA concentration levels. This shows that at varied concentration of VA inhibitor in solution, there are fluctuations in pH as exposure time varies. The effect of these variables on the pH of the solution was further confirmed with the ANOVA test using equations (i) – (iii) [21] as stated earlier. The results are displayed in Table 3.

**Table 3**. Summary of ANOVA analysis for pH measurements

| Source of Variation | SS | Df | MS | F | Significance F |
|---|---|---|---|---|---|
| Exposure Time | 12.439 | 13 | 0.96 | 9.37 | 1.91 |
| Concentration of VA | 1.866 | 4 | 0.47 | 4.57 | 2.55 |
| Residual | 5.31 | 52 | 0.10 | | |
| Total | 19.615 | 69 | | | |

On the basis of the results shown in Table 3, it can be concluded with 95 % confidence that the concentration of *Vernonia amygdalina* and exposure time significantly affects the pH of the test environment (Fig.13). Unlike the ANOVA test result for potential measurement, the effect of exposure time is greater on pH than the effect of inhibitor concentration.

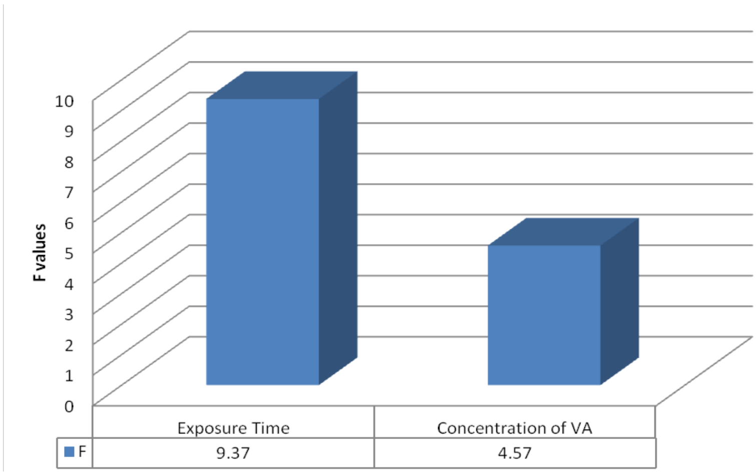


**Figure 13.** Influence of exposure time and VA concentration on pH of test environment

### *3.4. Compressive Strengths of Test Samples*

The table of results of the compressive strength is presented in Table 4.

**Table 4**. Compressive strengths of test samples

| Concentration | Compressive Strength (KN) |
|---|---|
| Control | 150 |
| VA 100% | 140 |
| VA 75% | 150 |
| VA 50% | 100 |
| VA 25% | 105 |

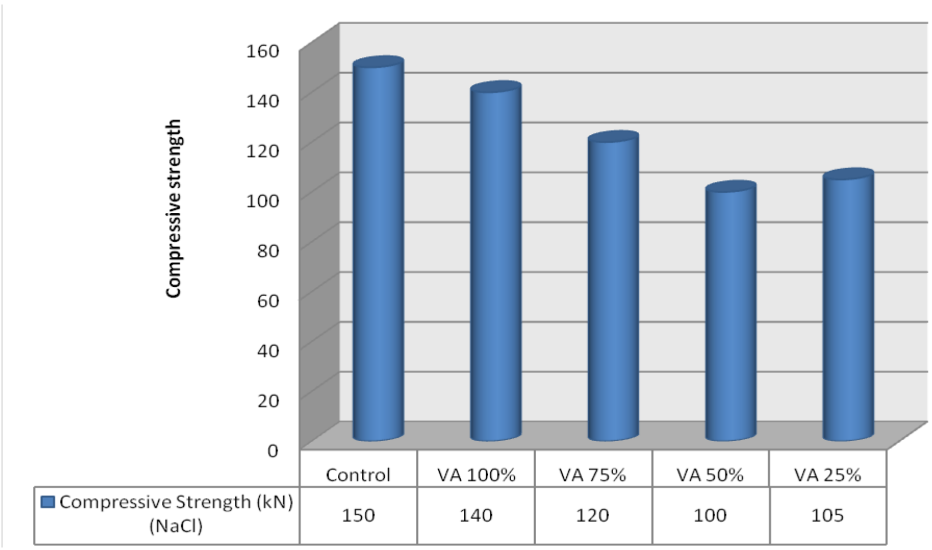


**Figure 14.** Influence of concentration of *Vernonia amygdalina* on compressive strength of test samples

Compressive strength of concrete is very important, as it is used more often in compression than in any other way. It was therefore, necessary to investigate the effect of inhibitor concentration on compressive strength. Lower concentration of *Vernonia amygdalina* in the test environment yielded lower compressive strength of the samples (Fig.14). This signifies that higher VA concentration has a positive effect on the compressive strengths of the samples

### *3.5. Weight Loss, Corrosion Rate and Inhibitor Efficiency*

The table of results for the weight loss, corrosion rate and the inhibitor efficiency is presented in Table 5. The results presented in Table 5 bear a very close relationship with the results of potential measurement. The extract at 25% concentration had the lowest weight loss (0.1g); a corrosion rate of 4.5 x 10-5 mm/yr and with an inhibitor efficiency of 90.08%. This value was followed with extract of 50% concentration with a weight loss value of 0.3 g; a corrosion rate of 13.9 x 10-5 mm/yr and an inhibitor efficiency of 69.70. The 75 and 100% extract concentrations showed relatively very low values of inhibitor efficiency. The lowest inhibitor efficiency of – 53.19 was recorded with the 100% extract concentration. This has a tendency of accelerating corrosion instead of inhibiting it. This phenomenon is a characteristic of inhibitor when the appropriate concentration value is not used.

**Table 5**. Weight loss, Corrosion rate and Inhibitor Efficiency in sodium chloride medium

| Extract Concentration | Initial Weight (g) | Final Weight (g) | Weight Loss (g) | Corrosion Rate (mm/yr) | Inhibitor Efficiency (%) |
|---|---|---|---|---|---|
| Control | 124 | 122.5 | 1.5 | 0.000610 | |
| VA 100% | 115 | 113.4 | 1.6 | 0.000702 | -53.19 |
| VA 75% | 111 | 110.1 | 0.9 | 0.000409 | 10.73 |
| VA 50% | 109 | 108.7 | 0.3 | 0.000139 | 69.70 |
| VA 25% | 111 | 110.9 | 0.1 | 0.000045 | 90.08 |

The variation of weight loss based VA concentration is shown in Fig.16. The least weight loss, 0.1, was obtained at VA concentration of 25%. As VA concentration increased, weight loss also increased. Since the weight loss of the control test was 1.5, this signifies that corrosion inhibition was more effective with lower concentration of *Vernonia amygdalina*.

Fig. 17 shows clearly the concentrations of *Vernonia amygdalina* with the highest and lowest efficiency. The highest efficiency is 90.08% obtainable with 25%VA while the lowest efficiency is -53.19% obtainable with 100%VA.

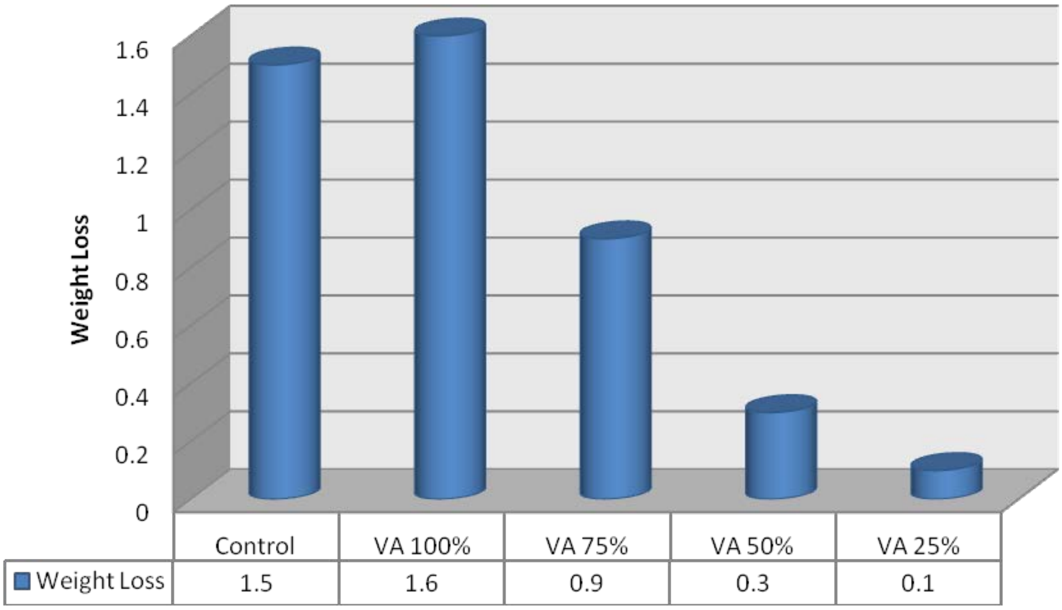


**Figure 16.** Influence of concentration of VernoniaAmygdalina on Weight loss of samples

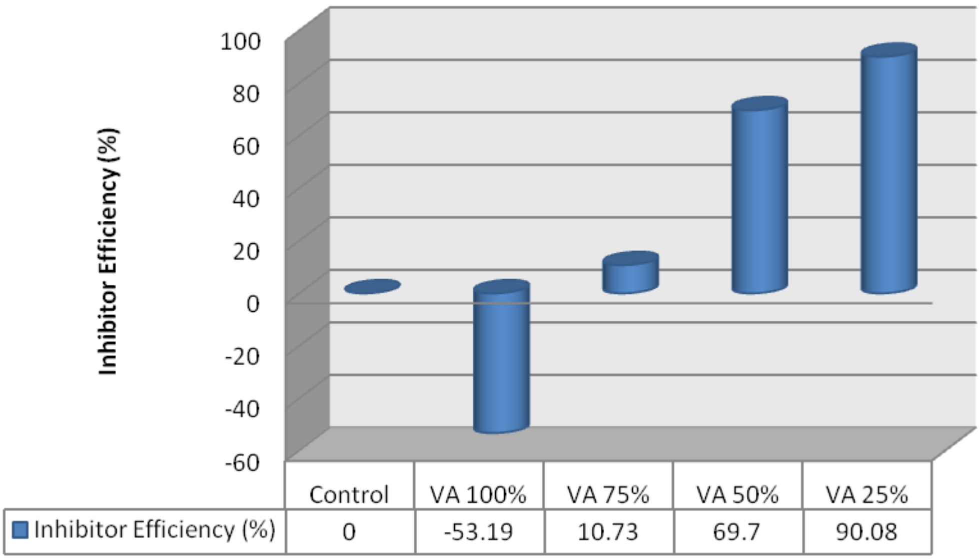


**Figure 17.** Influence of concentration of *Vernonia amygdalina* on Inhibitor Efficiency

## 4. CONCLUSIONS

The severity of corrosion on concrete is increased in sodium chloride such as can be found in sea water environments. From the experimental results obtained and the analysis of the same, the following conclusions can be made:

1. At 95 % confidence level, ANOVA test showed that varied concentration of *Vernonia amygdalina* and exposure time significantly affects the corrosion potential of embedded steel rebar in

concrete with the former having greater effect.

2. At 95 % confidence ANOVA test showed that the concentration of *Vernonia amygdalina* and exposure time significantly affects the pH of the test environment, with the latter having greater effect.

3. *Vernonia amygdalina* (bitter leaf) extract performed effectively as an inhibition agent to the corrosion of the embedded steel rebar in concrete at 25%, 50% and 75% concentrations in NaCl test medium.

4. The lesser the concentration of *Vernonia amygdalina* used the more effective was the corrosion inhibition performance achieved in the tests.

ACKNOWLEDGEMENT
The authors acknowledge the laboratory investigation contribution of Miss Oluwanipinmi O. Oladoyinbo, and also, the Department of Mechanical Engineering, Covenant University, Ota for the provision of research facilities for this work.

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