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Effect of *Vernonia amygdalina* extract and zinc oxide inhibitor on the corrosion of mild steel reinforcement in concrete in 0.2M H_2SO_4 Environment

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ABSTRACT

The effect of Vernonia Amygdalina- VA(bitter leaf) extract and zinc oxide (ZnO) inhibitors on the corrosion behaviour of embedded steel rebar in concrete immersed in 0.2% H_2SO_4 was investigated by potential measurement, pH and gravimetric methods using the inhibitor concentrations of 25, 50, 75, and 100%. The results were further analysed using the two-factor ANOVA test. Potential measurements were performed using a digital voltmeter and a copper sulphate reference electrode. Compressive strength of each block sample was determined after the experiments. Weight loss values were obtained from the gravimetric method, and the inhibitors' efficiency was computed from the corrosion rate of each of the tested samples. Both inhibitors gave appreciable corrosion inhibition of the embedded steel rebar at 25 and 50% concentrations. ANOVA test confirmed the results at 95% confidence. VA's concentration had greater effect on potential and pH; ZnO showed great significance in potential measurements only.

Keywords: corrosion; inhibition; *Vernonia Amygdalina*; zinc oxide; reinforced concrete; sulphuric acid, rebar.

INTRODUCTION

The significant role and/or importance of reinforced concrete in today's world have generated considerable continuous research effort in searching for ways to mitigate the adverse corrosion effect in concrete. Several chemicals have been used as inhibitors in admixture with concrete in this respect by various research scientists [1-3]. According to Amitha Rani and Bharathi Bai[4], several factors including cost, easy availability and safety to environment and its species need to be considered when choosing an inhibitor. There is a need to develop inhibitors that are sustainable and environmentally friendly (otherwise known as green inhibitors). Studies have been carried out using *Delonixregia* extract for aluminium in acid [5]; aqueous extract of *Rosmarinus officinalis L* for Al/Mg alloy in chloride [6]; natural honey for copper in neutral aqueous solution [7]; *Opuntia* extract for aluminium [8]; *Khillah* extract for 316 steel[9]; *Camellia sinensis* for aluminium in H_2SO_4[10] and *Carica papaya* leaves extract for mild steel in H_2SO_4,[11].

Further investigations for plant extracts use as inhibitors also include the use of *Azadirachta indica* leaves extract for mild steel in H_2SO_4[12]; *Raphia hookeri* exudates gum-halide mixtures for aluminium in acid [13]; and Guar gum for carbon steel in sulphuric acid[14] to mention but a few. *Vernonia Amygdalina* extract has also been used as green inhibitor for mild steel in 0.5M HCl and 0.5M H_2SO_4,[15]; mild steel reinforcement in concrete in 3.5M NaCl [16];aluminium in 0.5M HCl [17]; Al–Si alloy in 0.5M caustic soda solution [18]; and for aluminium in 1M HCl

[19].Zinc oxide (ZnO) has also been reported to inhibit corrosion on exposure to sea water or 3% chloride solution. In this situation ZnO acted as an anodic inhibitor. Other studies which have been carried out using ZnO inhibitor include: a comparison of the action of ZnO and $Ca(NO_2)_2$ as rebar corrosion inhibitors [20]

In a study by Oboh[21], it was revealed that VA leaf has high protein(33.3%), fat (10.1%), crude fibre (29.2%), ash (11.7%), mineral (Na, K, Ca, Mg, Zn, &Fe), phytate (1015.4 mg/100 g) and tannin (0.6%) content, while it contains low cyanide(1.1 mg/kg). Bitter leaf is known [22] to contain tannin, among others, which has been variously associated with corrosion inhibition in aqueous and acidic environments. Likewise, in a study [23], it was revealed that the addition of ZnO in concrete manufacturing improves the processing time and the resistance of concrete against water. Zinc oxide is known to have high refractive index, high thermal conductivity, binding, antibacterial and UV-protection properties[24].

This study aims at investigating the effect of *Vernonia amygdalina* (bitter leaf extract) as an organic corrosion inhibitor and Zinc oxide as an inorganic 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. The chemical constituents of bitter leaf, especially saponnin and tannin, as well as the fine particles of ZnO are expected to exhibit electrochemical activity of strong adsorption to the embedded mild steel surface and thus enhancing its corrosion resistance in corrosive environments.

EXPERIMENTAL SECTION

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. The samples were filtered after five days, 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 Zinc Oxide solution

200g of ZnO was obtained. From this, four different percentage concentrations of 25, 50, 75 and 100% ZnO solutions were prepared using distilled water.

2.3 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 120mm and 12mm 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 rods are to be kept in a desiccator but for the purpose of this experiment, they were not because the rods were used just after cleaning.

2.4 Preparation of concrete and the test environment

The concrete blocks used for the experiment were made of Portland cement, Sand, Gravel and Water. They were prepared in the ratio 1:2:3 (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 water cement (W/C) ratio was 0.44. Four different concentrations of 25%, 50%, 75% and 100% of each inhibitor were used, along with the control experiments. 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 30mm 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 0.2M H_2SO_4 solution of AnalaR grade.0.2M Sulphuric acid was prepared by diluting 110ml of concentrated Sulphuric acid in 9,890ml of distilled water which was used as corrosion medium for reinforced concrete samples with and without inhibitor.

2.5 Potential and pH measurements
The procedure used followed the previously reported experimental work [22, 25 - 26]. Potential measurements were taken using a digital voltmeter connected to a copper-copper sulphate electrode as shown in Figure 1. The readings were taken at three different points on each concrete block directly over the embedded steel rebar.

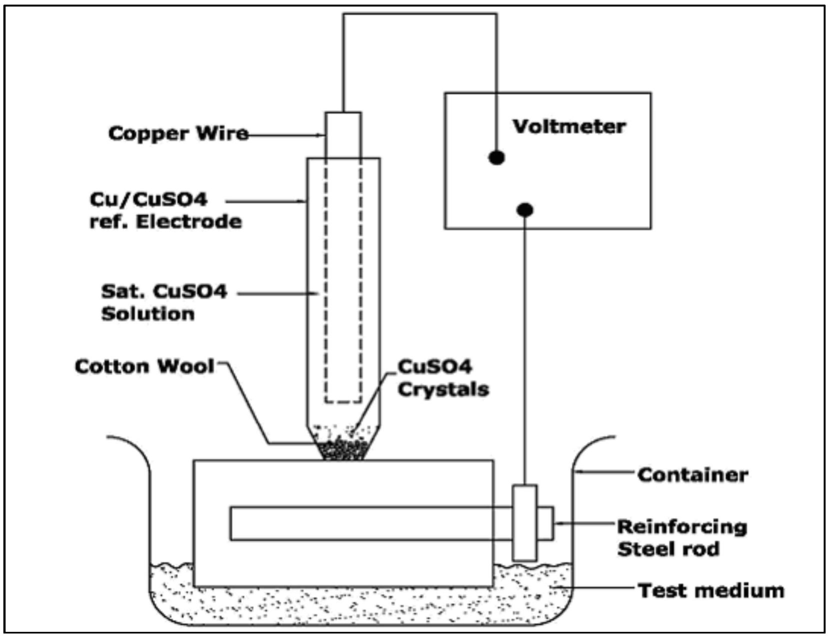

Figure 1: Schematic representation of experimental set up

The average of the three readings was found and computed as the potential readings 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.

2.6 Compressive Strengths
At the completion of the experimental period, compressive strength test was carried out on each block sample after weighing, with the aid of a compressive strength testing machine.

2.7 Weight loss measurements
Weight loss measurements were taken as described by Loto et al. [25].The coupons were retrieved from their corrodent at intervals of 30 minutes progressively for 150 minutes, scrubbed with bristle brushing distilled water and then immersed in ethanol for 2 minutes to remove the corrosion product, dried in acetone and weighed. The weight loss was computed as the difference between the weight at a given time and the initial weight of the test coupon. Corrosion rate and inhibition efficiencies were calculated with the following equations [19]:

$$\%I.E = \left[1 - \frac{CR_{inh}}{CR_{BL}}\right] \times 100. \quad (1)$$

$$CR(= gh^{-1}cm^{-2}) = \Delta W/AT. \quad (2)$$

Where CR_{inh} and CR_{BL} are the corrosion rate of mild steel in presence and absence of the inhibitors, respectively. A is area of coupon in cm^2, T is the period of immersion in hours and $\Delta W = W_1 - W_2$; where $W_1$is the initial weight of mild steel and $W_2$is its final weight.

RESULTS AND DISCUSSION

3.1 Potential Measurement

The results obtained for the four different concentrations of 25, 50, 75 and 100% of *Vernonia Amygdalina* mixed with the concrete test samples and ZnO mixed with the concrete test samples respectively are presented in the curves of Figures 2–6. At this concentration, both VA extract and ZnO inhibitor could not be described as being protective.

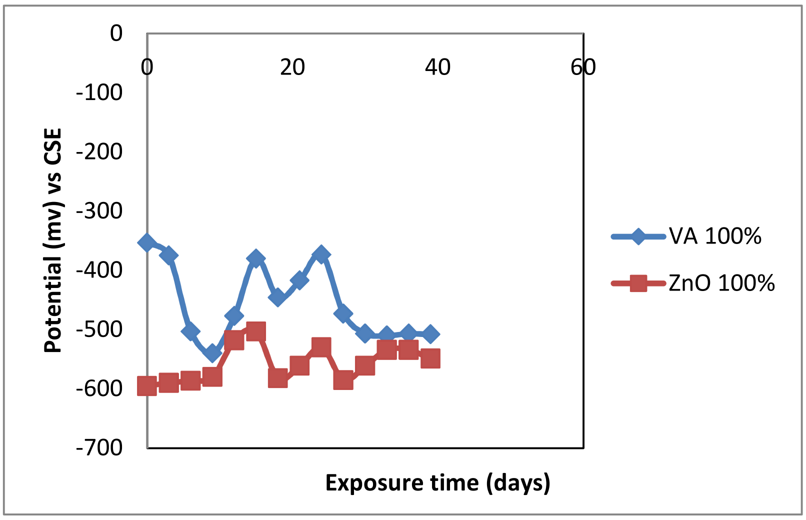

Figure 2: Variation of potential with time for mild steel reinforcement in concrete mixed with 100% concentration ZnO inhibitor partially immersed in 0.2M H_2SO_4 solution and 100% VA partially immersed in 0.2M H_2SO_4 solution

In comparison, the concentration at 75% ZnO and 75% VA showed better corrosion inhibition performance than that of 100% ZnO and 100% VA. A comparison of the performance of both inhibitors at 50% concentration with 75 and 100% concentrations showed more passive corrosion reactions.

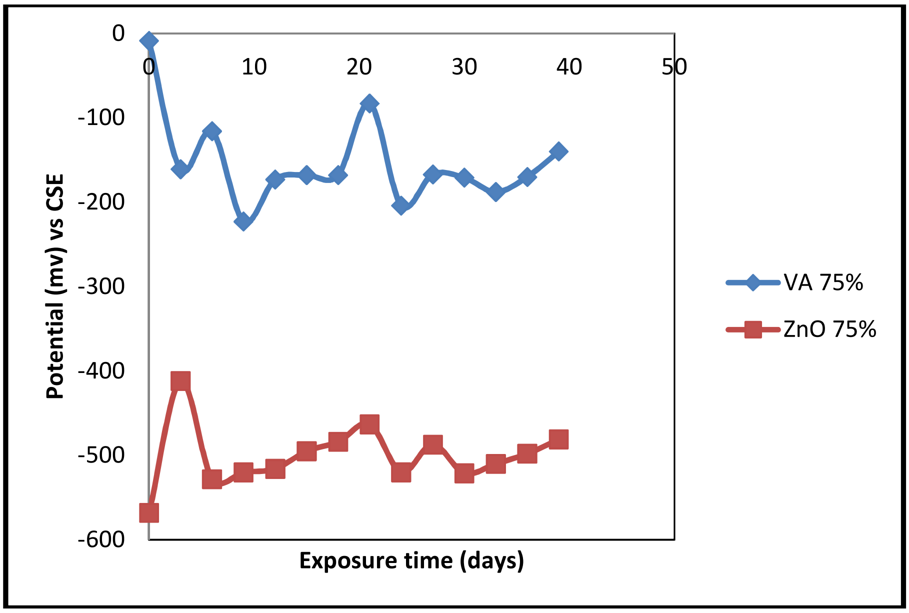

Figure 3: Variation of potential with time for mild steel reinforcement in concrete mixed with 75% concentration ZnO inhibitor partially immersed in 0.2M H_2SO_4 solution and 75% VA partially immersed in 0.2M H_2SO_4 solution

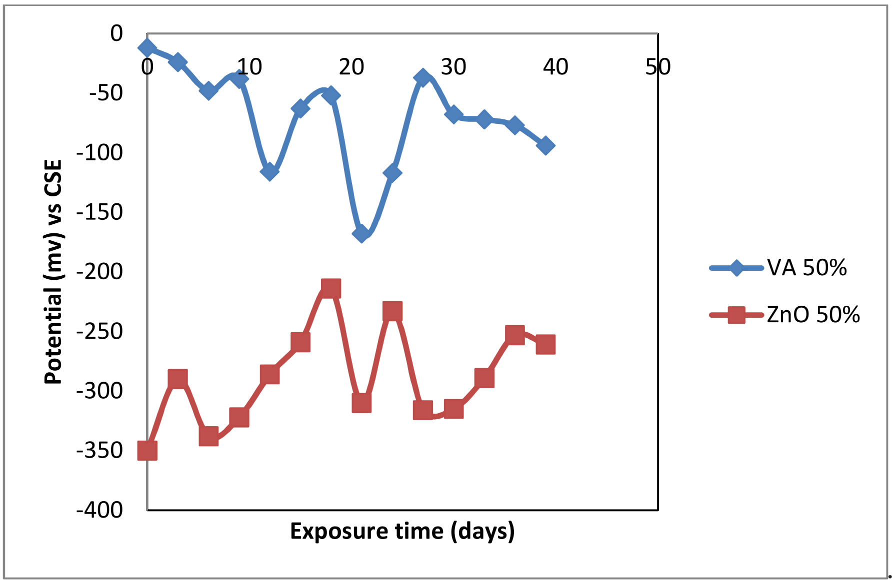

Figure 4: Variation of potential with time for mild steel reinforcement in concrete mixed with 50% concentration ZnO inhibitor partially immersed in 0.2M H_2SO_4 solution and 50% VA partially immersed in 0.2M H_2SO_4 solution

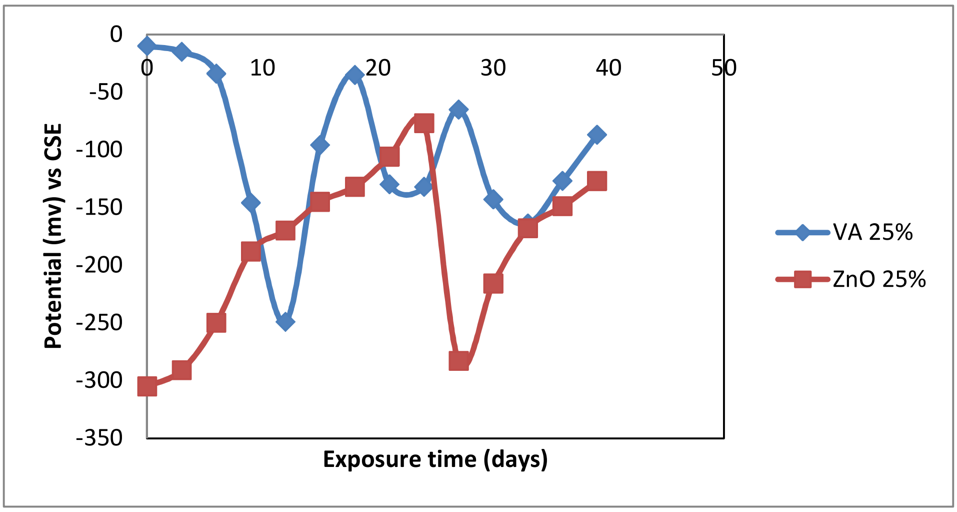

Figure 5: Variation of potential with time for mild steel reinforcement in concrete mixed with 25% concentration ZnO inhibitor partially immersed in 0.2M H_2SO_4 solution and 25% VA partially immersed in 0.2M H_2SO_4 solution

At 50% concentration, ZnO and *Vernonia Amygdalina* inhibitors could be described as more protective. The optimum value for the ZnO inhibitor performance was obtained with 25% concentration whereas the optimum value for the extract inhibition performance was obtained with 50% VA concentration. Figures 6 and 7 provides the overall zinc oxide and *Vernonia Amygdalina* corrosion inhibition performance profile respectively for the mild steel embedded in concrete and partially immersed in 0.2M H_2SO_4test medium.

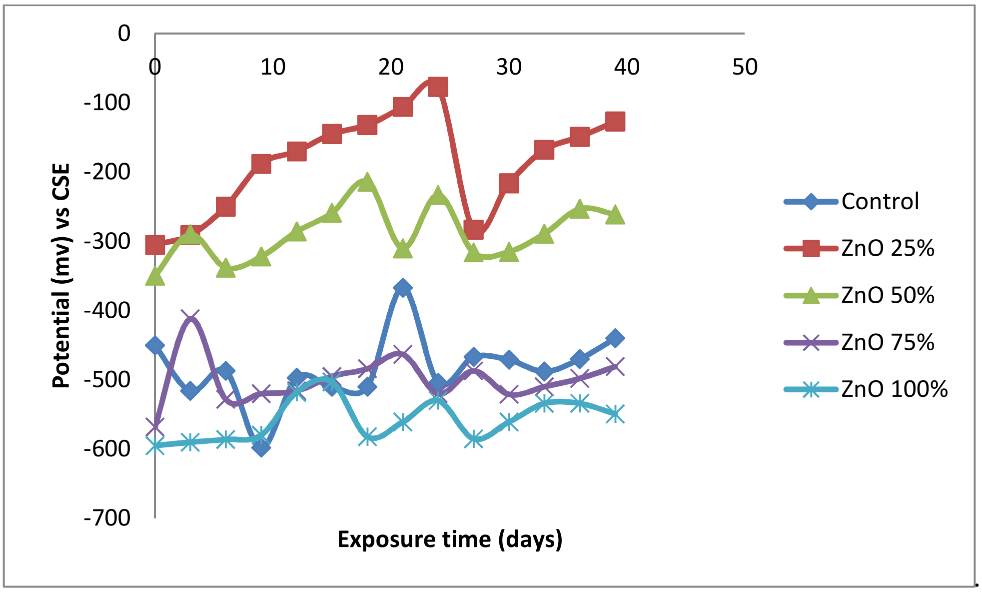

Figure 6:Variation of potential with time for mild steel reinforcement in concrete mixed with 25, 50, 75 and 100% concentrations ZnO and partially immersed in 0.2M H_2SO_4 solution

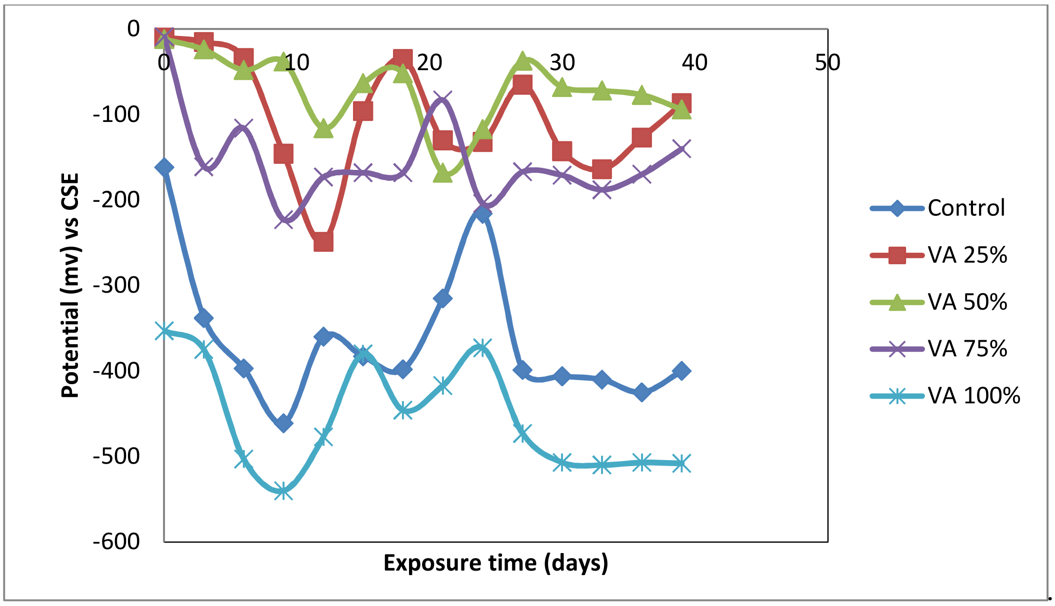

Figure 7: Variation of potential with time for mild steel reinforcement in concrete mixed with 25, 50, 75 and 100% concentrations *Vernonia Amygdalina* and partially immersed in 0.2M H_2SO_4solution

3.2 pH Measurements

The results obtained for the different concentrations (25, 50, 75 and 100%) of the VA extracts and ZnO inhibitors are presented in Tables1 and 2. The reinforced concrete blocks recorded pH values in which its acidity decreased from 3.07 from the beginning of the experiment to 2.44 at the end in a period of 39 days. Similar trends were recorded for all the different per cent concentrations of inhibitor addition. This decrease in acidity could be due to the reactions between the concrete constituents, *Vernonia Amygdalina*, the H_2SO_4testenvironment and the reactions at the steel/environment interface for the steel-reinforced concrete blocks.

Table 1: pH readings of mixed bitter leaf extract with 0.2M H_2SO_4

Day	Control	VA 100%	VA 75%	VA 50%	VA 25%
0	3.07	1.93	1.79	2.3	2.11
3	1.95	1.87	1.77	1.73	1.8
6	3.24	2.38	1.75	2.64	2.71
9	2.52	1.59	1.54	2.45	2.66
12	1.93	1.8	1.66	1.68	1.78
15	2.35	2.3	2.13	1.74	1.92
18	2.12	2.51	2.3	1.78	2.05
21	2.33	2.1	1.9	2.2	2.27
24	1.98	1.74	1.5	1.78	2.11
27	2.45	1.43	1.39	1.77	1.89
30	1.57	1.47	1.06	1.57	1.82
33	1.95	1.42	1.14	1.63	1.99
36	2.19	1.57	1.32	1.88	1.82
39	2.44	1.65	1.51	2.13	2.06

A different trend was observed with ZnO inhibitor. For each concentration, there was increasing acidity.

Table 2: pH readings of mixed ZnO with 0.2M H_2SO_4

Day	Control	ZnO 100%	ZnO 75%	ZnO 50%	ZnO 25%
0	3.07	1.54	1.52	1.57	1.54
3	1.95	1.80	1.85	1.95	2.10
6	3.24	2.29	1.84	2.29	2.09
9	2.52	2.27	2.09	2.00	1.88
12	1.93	1.72	1.67	1.86	1.65
15	2.35	1.83	1.82	1.98	1.71
18	2.12	2.00	1.79	2.27	1.87
21	2.33	1.77	1.75	2.35	1.55
24	1.98	1.92	1.98	1.64	1.66
27	2.45	1.66	1.67	1.65	1.66
30	1.57	1.79	1.78	1.79	1.82
33	1.95	1.77	1.79	1.87	1.90
36	2.19	1.68	1.79	1.70	1.57
39	2.44	1.93	1.75	1.94	1.78

Statistical Analysis

Two-factor single level experiment ANOVA test (F-test) was used to evaluate the separate and combined effects of VA concentration and exposure time, ZnO concentration and exposure time respectively on the corrosion potential of the mild steel reinforcement in 0.2M H_2SO_4solution. 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 was obtained [26] with equations(3) – (5).

$$SS_c = \frac{\sum {T_c}^2}{nr} - \frac{T^2}{N} \tag{3}$$

Sum of Squares among rows (concentration of VA):

$$SS_r = \frac{\sum {T_r}^2}{nc} - \frac{T^2}{N} \tag{4}$$

Total Sum of Squares:

$$SS_{Total} = \sum x^2 - \frac{T^2}{N} \tag{5}$$

The calculation using the ANOVA test is tabulated (Tables3, 4, 5 and 6) as shown.

Table 3: Summary of ANOVA analysis for potential measurements in VA inhibitor

Source of Variation	SS	Df	MS	F	Significance F
Exposure Time	129740.47	13	9980.04	4.02	1.91
Concentration of VA	1620359.06	4	405089.77	163.05	2.55
Residual	129191.74	52	2484.46		
Total	1879291.27	69			

Table 4: Summary of ANOVA analysis for pH measurements in VA inhibitor

Source of Variation	SS	Df	MS	F	Significance F
Exposure Time	9.23	13	0.71	2.02	1.91
Concentration of VA	6.76	4	1.69	4.80	2.55
Residual	18.29	52	0.35		
Total	34.28	69			

On the basis of the results shown in Tables 3 and 4, it can be concluded with 95% confidence that the concentration of *Vernonia Amygdalina* and exposure time significantly affects the potential and pH of the test environment. The effect of inhibitor concentration was more significant in both cases.

Table 5: Summary of ANOVA analysis for potential measurements in ZnO inhibitor

Source of Variation	SS	Df	MS	F	Significance F
Exposure Time	56441.44	13	4341.65	2.40	1.91
Concentration of ZnO	1401282.49	4	350320.62	193.34	2.55
Residual	94219.91	52	1811.92		
Total	1551943.84	69			

On the basis of the results shown in Tables 5 and 6, it can be concluded with 95% confidence that the concentration of Zinc oxide and exposure time significantly affects the potential of the test environment but had no significant effect on the environment's pH.

Table 6: Summary of ANOVA analysis for pH measurements in ZnO inhibitor

Source of Variation	SS	Df	MS	F	Significance F
Exposure Time	1.70	13	0.13	-8.61	1.91
Concentration of ZnO	2.51	4	0.63	-41.30	2.55
Residual	-0.79	52	-0.02		
Total	3.42	69			

3.3 Compressive Strengths of Test Samples
The compressive strength of the samples measured after the corrosion tests are shown in Table 7.

Table 7: Compressive strengths of test samples

Inhibitor Concentration	0	25% VA	50% VA	75% VA	100% VA	25% ZnO	50% ZnO	75% ZnO	100% ZnO
Compressive Strength (Mpa)	18	15	13.5	12	7	16	14	13	10

It was necessary to investigate the effect of inhibitor concentration on compressive strength of concrete due to its relative importance in concrete applications. Lower concentration of VA and ZnO respectively, yielded higher compressive strength. The relatively lower compressive strength obtained with the use of the inhibitors could be associated with the effect of the chemical constituents which most probably acted as contaminant within the concrete matrix and thus weakening its strength.

3.4 Weight Loss and Inhibitor Efficiency
The results for the weight loss, corrosion rate and the inhibitor efficiency are presented in Figures 8, 9, 10 and 11. The results presented in the Figures bear a very close relationship with the results of potential measurement. The 75 and 100% VA inhibitor concentrations showed relatively very low values of inhibitor efficiency. The lowest inhibitor efficiency of – 51.52% was recorded with 100% VA concentration. A slightly different behaviour was observed with ZnO inhibitor. The lowest inhibitor efficiency of – 37.63% was recorded with the 100% ZnO concentration. It was noted that higher concentrations of both inhibitors had a tendency of accelerating corrosion

instead of inhibiting it. This phenomenon is a characteristic of inhibitor when the appropriate concentration value is not used.

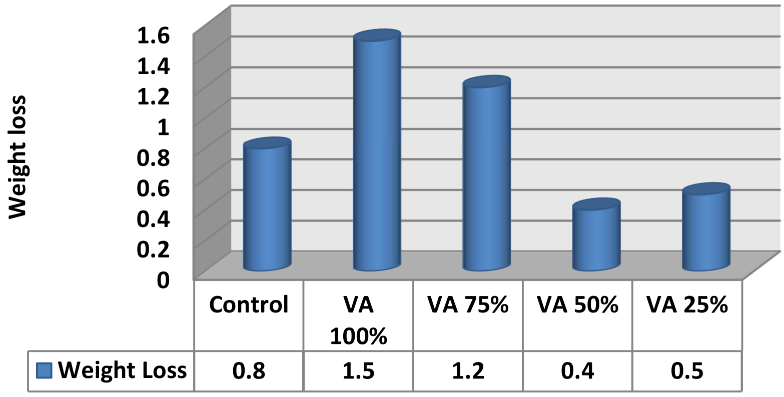

Figure 8: Influence of concentration of VA on weight loss of samples

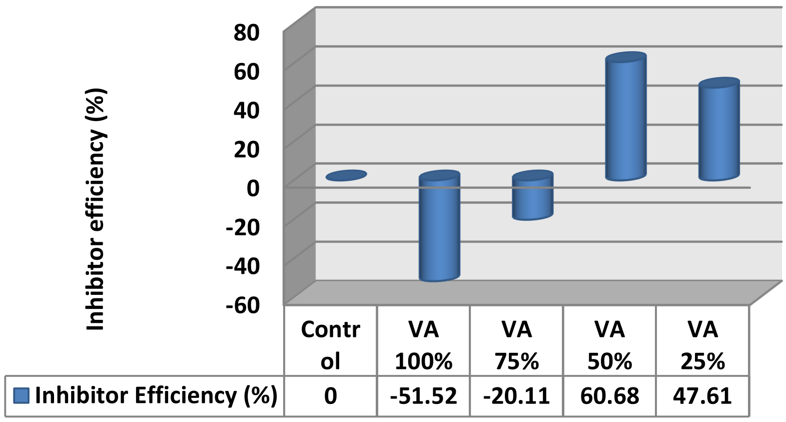

Figure 9: Influence of concentration of VA on Inhibitor Efficiency

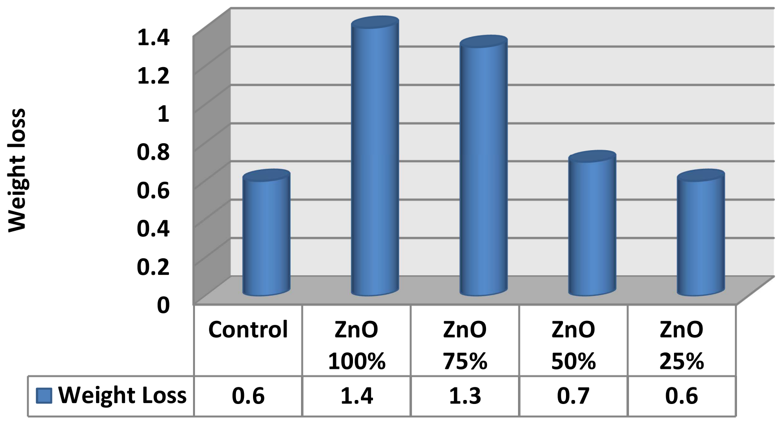

Figure 10: Influence of concentration of ZnO on weight loss of samples

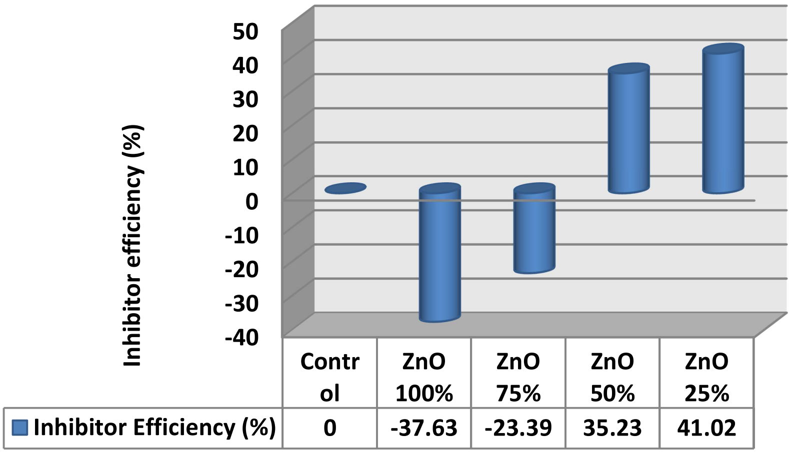

Figure 11: Influence of concentration of ZnO on Inhibitor Efficiency

In summary, the experiments were performed using *Vernonia Amygdalina* and zinc oxide as inhibitors in concrete and 0.2M H_2SO_4 solution test environment. Sulphuric acid is a very strong acid and the ion, SO_4^{2-}, has a very strong tendency to cause severe corrosion/degradation of mild steel even in the concrete environment. There was acceleration of corrosion reactions, on addition of this acid, of the embedded reinforcing steel rebar. The SO_4 ions of the acid broke the passivity of the concrete test environment. The VA and ZnO inhibitors behaved characteristically like chemical inhibitors in that at the optimum level of use (50% VA and 25% ZnO concentrations), a measure of inhibition was provided in spite of the strong acid used.

CONCLUSION

The severity of corrosion on concrete is increased in sulphuric acid environments. From the experimental results obtained and the analysis of the same, the following conclusions can be made:

(1) *Vernonia Amygdalina* (bitter leaf) extract and ZnO performed effectively as inhibitors to the corrosion of the embedded steel rebar in concrete at 25, 50 and 75% concentrations in 0.2 M H_2SO_4 test medium.

(2) The lesser the concentration of both inhibitors used, the more effective was the corrosion inhibition performance achieved in the tests. However, the performance at 25 and 50% concentrations was very close based on the potential and inhibitor efficiency values.

(3) At 95% confidence level, ANOVA test showed that varied concentration of *Vernonia Amygdalina* and Zinc Oxide and their exposure times respectively significantly affects the corrosion potential of embedded steel rebar in concrete with concentration having the greater effect.

(4) 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.

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