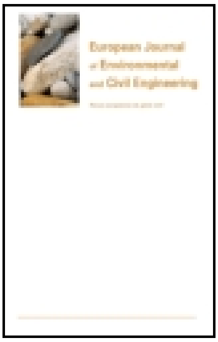

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Inhibition effect of Vernonia amygdalina extract on the corrosion of mild steel reinforcement in concrete in 0.2M H_2SO_4 Environment

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Inhibition effect of *Vernonia amygdalina* extract on the corrosion of mild steel reinforcement in concrete in 0.2 M H_2SO_4 Environment

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Inhibition effect of *Vernonia amygdalina* (bitter leaf) extract on the corrosion behaviour of embedded mild steel rebar in concrete immersed in 0.2% H_2SO_4 solution was investigated by potential measurement, pH and gravimetric methods using the extracts concentrations of 25, 50, 75, and 100%. The results were further analysed using the two-factor ANOVA test. Potential measurement was performed using a digital voltmeter and a copper/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 inhibitor efficiency was computed from the corrosion rate of each of the tested samples. Results showed that varied concentration of *V. 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 extracts gave appreciable corrosion inhibition performance of the embedded steel rebar at 25 and 50% concentrations with the weight loss of 500 (0.5 g) and 400 mg (0.4 g) and corrosion rates values of 0.000240 and 0.000180 mm/yr, respectively. The highest inhibition efficiency (60.68%) was achieved at 50 and 39.94% at 25% concentrations, respectively. The 100 and 75% concentrations gave negative inhibitor values of −51.52 and −20.11%. The ANOVA test confirmed the results at 95% confidence, and further showed that concentration of *V. amygdalina* had greater effect on potential and pH measurements.

Keywords: corrosion; inhibition; *Vernonia amygadalina*; reinforced concrete; sulphuric acid

1. Introduction

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. Several chemicals have been used as inhibitors in admixture with concrete in this respect by various research scientists (De Schutter & Luo, 2004; Loto, Omotosho, & Popoola, 2011; Omotosho, Loto, Ajayi, & Okeniyi, 20ll; Rakanta, Zafeiropoulou, & Batis, 2013).

According to Amitha Rani and Bharathi Bai (2011), 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

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carried out using *Delonix regia* extract for aluminium in acid (Abiola, Oforka, Ebenso, & Nwinuka, 2007); aqueous extract of *Rosmarinus officinalis* L for Al/Mg alloy in chloride (Kliskic, Radoservic, Gudic, & Katalinic, 2000); natural honey for copper in neutral aqueous solution (El-Etre, 1998); *opuntia* extract for aluminium (El-Etre, 2003); *khillah* extract for Sx 316 steel (El-Etre, 2006) and *Carica papaya* leaves extract for mild steel in H_2SO_4 (Ebenso & Ekpe, 1996).

Further investigations for plant extracts use as inhibitors also include the use of *Azadirachta indica* leaves extract for mild steel in H_2SO_4 (Ekpe, Ebenso, & Ibok, 1994); *Raphia hookeri exudates* gum-halide mixtures for aluminium in acid (Umoren & Ebenso, 2008); and *Guar gum* for carbon steel in sulphuric acid (Abdallah, 2004) to mention but a few. *V. amygdalina* extract has also been used as green inhibitor for mild steel in 0.5 M HCl and 0.5 M H_2SO_4 (Loto, 2003); aluminium in 0.5 M HCl (Oluseyi et al., 2012); Al–Si alloy in 0.5 M caustic soda solution (Ayeni et al., 2012); and for aluminium in 1 M HCl (Alinnor & Ukiwe, 2012).

In a study by (Oboh, 2006), it was revealed that *V. amygdalina* 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 (Loto, 1992) to contain tannin, among others, which has been variously associated with corrosion inhibition in aqueous and acidic environments. However, the concrete environment is, in general, alkaline and thus making the embedded steel passive, the use of sulphuric acid test environment is hazardous to the surface film passivity on the steel surface.

This study aims at investigating the effect of *V. 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. 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.

2. Methods

2.1. Preparation of the plant extracts

Fresh leaves of *V. 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 mild steel rebar

The steel rebar with the following 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 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 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.

2.3. *Preparation of concrete and the test environment*

The Portland cement used in this work that was locally obtained consisted of the following composition: CaO (64%), SiO_2 (23%), Al_2O_3 (4.5%), Fe_2O_3 (2%), and sulphate (3.5%). 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 and 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/m^3, 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. The plant extracts concentrations were separately mixed directly with the concrete, while some portion of the each of the concentrations was also used dissolved in the acid. 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 (Figure 1). Only about 90 mm was embedded in each concrete block. The remaining part protruded at one end of the concrete block and was coated to prevent atmospheric corrosion. A little portion of the coated rebar was put inside the concrete block for the same reason of atmospheric corrosion. This part was also used for electrical connection. The test medium used for the investigation was 0.2 M H_2SO_4 solution of AnalaR grade.

About 0.2 M sulphuric acid was prepared by diluting 110 ml of concentrated sulphuric acid in 9,890 ml of distilled water that was used as corrosion medium for reinforced concrete samples with and without inhibitor.

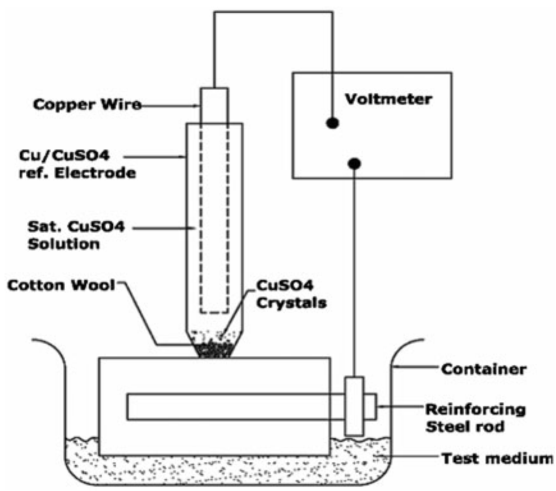

Figure 1. Schematic representation of experimental set-up.

2.4. Potential and pH measurements

Each concrete block sample was partially immersed in the sulphuric acid test medium as shown in Figure 1. 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. The average of the three readings was found and computed as the potential reading for the embedded rebar in 3-day interval. All the experiments were performed at ambient temperature and under free corrosion potential.

The pH of the test medium was measured by placing a small amount of the medium in a cup and using the pH meter.

2.5. 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.

2.6. Weight loss measurements

Weight loss measurements were taken as described by Eddy, Awe and Ebenso (2010). The coupons were retrieved from their corrodent at intervals of 30 min progressively for 150 min, scrubbed with bristle brush in distilled water and then immersed in ethanol for 2 min 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 (Alinnor & Ukiwe, 2012):

$$\% \, I.E = \left[1 - \frac{CR_{\text{inh}}}{CR_{\text{BL}}}\right] \times 100 \tag{1}$$

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

where CR_{inh} and CR_{BL} are the corrosion rate of mild steel in the presence and absence of the inhibitor, 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.

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 Figures 2–6. At the concentration of 100%, Figure 2, there was passive corrosion reaction for only 3 days at the potential voltage of −375 mV. Inquisitively, a point of another passive corrosion reaction was obtained after 15 days achieving a potential of −380 mV. For most part of the experiment, using this concentration, the corrosion reactions remained in active state that ranged between −440 and −540 mV. Obviously, at this concentration, the extract could not be described as being protective.

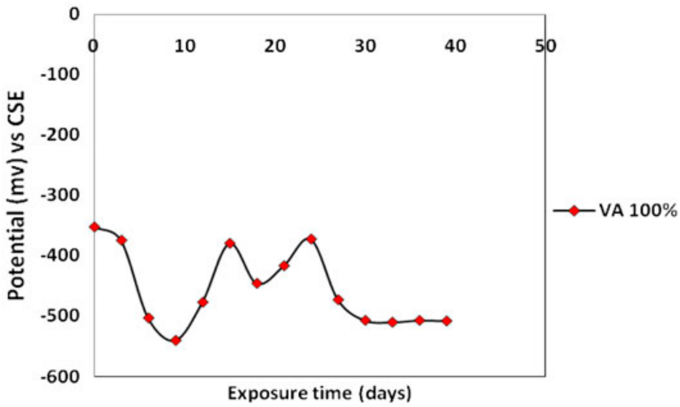

Figure 2. Variation of potential with time for mild steel reinforcement in concrete mixed with 100% concentration bitter leaf (VA) extract and partially immersed in 0.2 M H_2SO_4 solution.

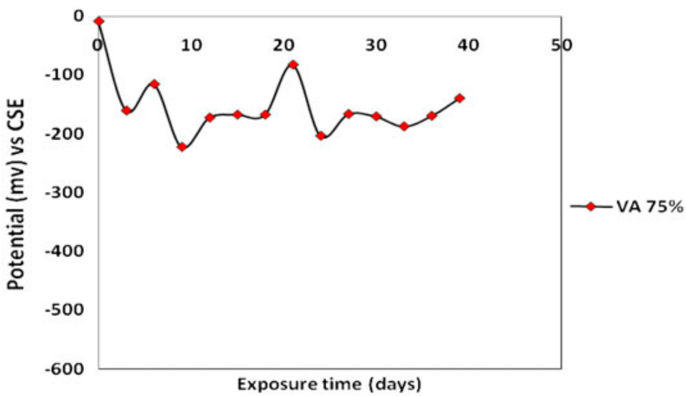

Figure 3. Variation of potential with time for mild steel reinforcement in concrete mixed with 75% concentration bitter leaf (VA) extract and partially immersed in 0.2 M H_2SO_4 solution.

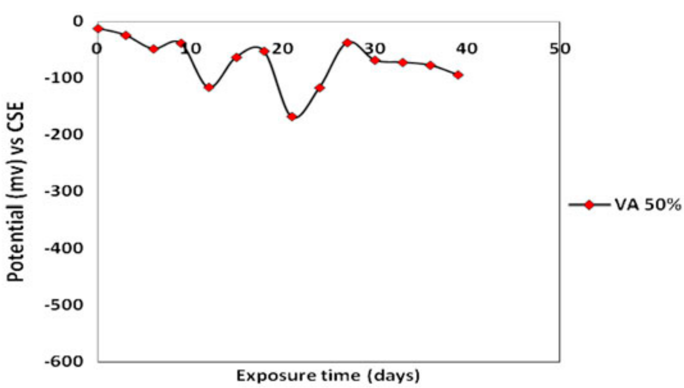

Figure 4. Variation of potential with time for mild steel reinforcement in concrete mixed with 50% concentration bitter leaf (VA) extract and partially immersed in 0.2 M H_2SO_4 solution.

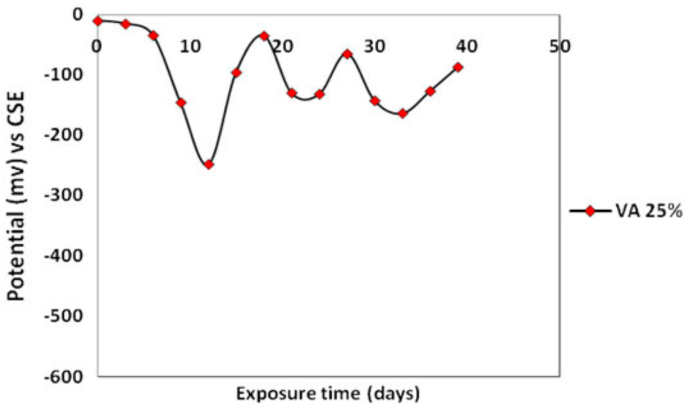

Figure 5. Variation of potential with time for mild steel reinforcement in concrete mixed with 25% concentration bitter leaf (VA) extract and partially immersed in 0.2 M H_2SO_4 solution.

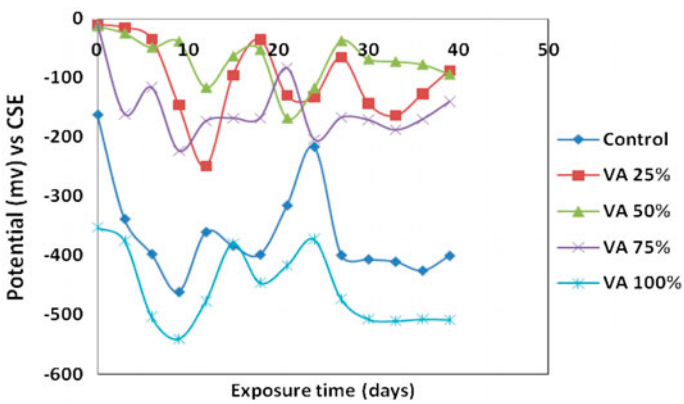

Figure 6. Variation of potential with time for mild steel reinforcement in concrete mixed with 25, 50, 75 and 100% concentrations bitter leaf (VA) extract and partially immersed in 0.2 M H_2SO_4 solution.

At the extract concentration of 75% (Figure 3), a fluctuating and passive corrosion reaction that ranged between −116 and −223 mV was achieved. This indicates some stability in the corrosion protection of the extract throughout the experimental period. Furthermore, the passive condition could be described as strong since the values were not apparently close to the active corrosion reactions. In comparison, the extract concentration at 75% showed a far better corrosion inhibition performance that of the 100%.

At the extract concentration of 50%, fluctuating but passive corrosion reactions were achieved throughout the experiment for a potential range of −12 to −168 mV. A comparison of the inhibitor performance at 50% concentration with 75 and 100% concentrations showed more passive corrosion reactions, hence, a lesser tendency towards active corrosion. As a result, at 50% concentration, the inhibitor could be described as more protective.

The extract concentration at 25% achieved passive corrosion reactions from the −10 mV on the first day to −87 mV on the last day of the experiment. Although, a closer move towards active corrosion was obtained after the 6th day achieving a potential of −249 mV, passive reactions were subsequently maintained until the end of the experiment. This concentration gave good corrosion inhibition performance, but in comparison with 75 and 50% concentrations, the optimum value for the extract inhibition performance was obtained with 50% concentration.

Figure 6 provides the overall *V. amygdalina* extract corrosion inhibition performance profile for the mild steel embedded in concrete and partially immersed in 0.2 M H_2SO_4 test medium. Here, it could be confirmed again that the best inhibition performance in this work is with the extract with 50% concentration. 25, 50 and 75% extract concentrations performed better than the control experiment in which there was no extract addition. The general observation/inference here is that the extract of *V. amygdalina* (bitter leaf) could provide reasonable measure of corrosion inhibition of mild steel in concrete in the sulphuric acid environment within the all other experimental conditions used, particularly at 50% concentration. Obviously, the chemical constituents of bitter leaf would have acted synergistically to exhibit this electrochemical activity of corrosion inhibition.

3.2. Statistical analysis

Statistical analysis using the ANOVA was performed on the results obtained in this work. ANOVA is a powerful technique for analysing experimental data involving quantitative measurements. It is useful in factorial experiments where several independent sources of variation may be present.

The scatter plots of the potential–time curves show a fluctuating decrease and increase in potential with respect to time; average stability was attained from the 30th day. It can also be deduced that 50%VA and 25%VA exhibited optimal performance, while 75%VA and 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 0.2 M H_2SO_4 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 was obtained with Equations (3)–(5).

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

Sum of squares among rows (concentration of VA):

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

Total sum of squares:

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

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

Table 1. Summary of ANOVA analysis for potential measurements.

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			

On the basis of the results in Table 1, it can be concluded with 95% confidence that varied concentration of *V. amygdalina* and exposure time significantly affect the corrosion potential of the test medium (Figure 7). The effect of VA concentration was highly significant.

3.3. pH measurements

The results obtained for the different concentrations (25, 50, 75 and 100%) of the *V. amygdalina* extracts are presented in Table 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.

V. amygdalina at 25% concentration addition, the acidity reduced from 2.11 to 2.06. At 50% concentration, it reduced from 2.30 to 2.13; at 75% concentration, it reduced from 1.79 to 1.51; and at 100%, from 1.93 to 1.65. This decrease in acidity could be due to the reactions between the concrete constituents, *V. amygdalina*, the H_2SO_4 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 *V. amygdalina* extracts.

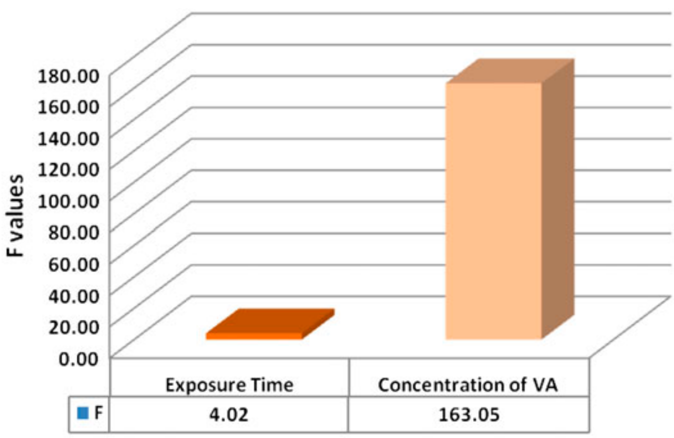

Figure 7. Influence of exposure time and VA concentration on corrosion potential.

Table 2. pH readings of mixed bitter leaf extract with 0.2 M H_2SO_4.

Day	Control	VA 100%	VA 75%	VA 50%	VA 25%
0	3.07	1.93	1.79	2.30	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	1.80	1.66	1.64	1.78
15	2.35	2.30	2.13	1.74	1.92
18	2.12	2.51	2.30	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

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 (3)–(5) as stated earlier. The results are displayed in Table 3.

On the basis of the results shown in Table 3, it can be concluded with 95% confidence that the concentration of *V. amygdalina* and exposure time significantly affects the pH of the test environment (Figure 8). The effect of inhibitor concentration on pH was also more significant as was the case in potential measurements.

3.4. Compressive strengths of test samples

The compressive strength of the samples measured after the corrosion tests are shown in Table 4.

It was necessary to investigate the effect of inhibitor concentration on compressive strength of concrete due to its relative importance in concrete applications. The highest compressive strength of 15 MPa was obtained at 25% VA concentration. Lower concentration of *V. amygdalina* yielded higher compressive strength (Figure 9). This signifies that higher VA concentration has a negative effect on the compressive strengths of the samples in 0.2 M H_2SO_4 environment. Similarly, potential measurements showed higher VA concentrations resulting in more active corrosion reactions. The relatively lower compressive strength obtained with the use of bitter leaf extract could be associated

Table 3. Summary of ANOVA analysis for pH measurements.

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			

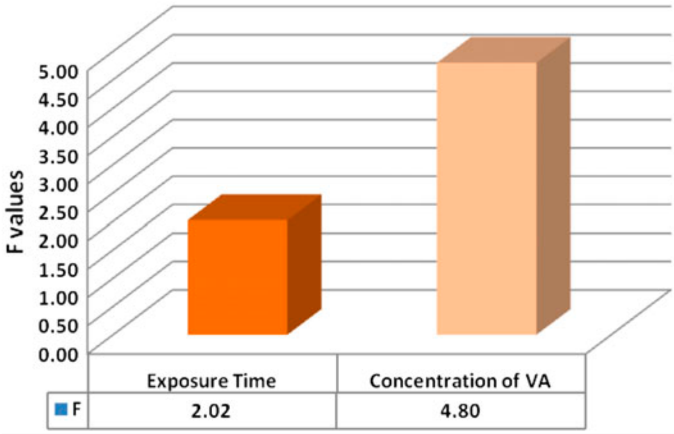

Figure 8. Influence of exposure time and VA concentration on pH of test environment.

Table 4. Compressive strengths of test samples.

Concentration	Compressive strength (MPa)
Control	18
VA 100%	7
VA 75%	12
VA 50%	13.5
VA 25%	15

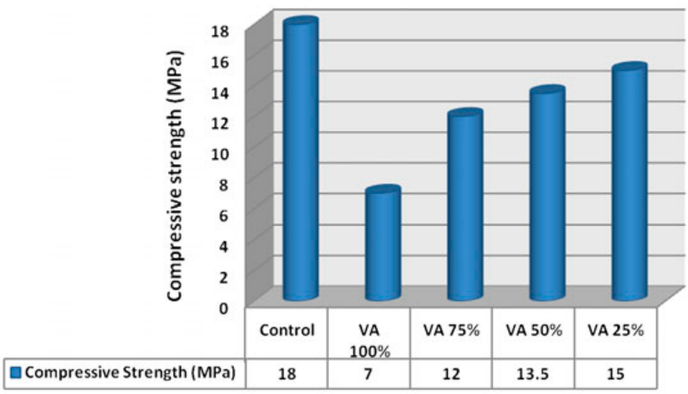

Figure 9. Influence of concentration of *V. amygdalina* on compressive strength of test samples.

with the effect of the chemical constituents of the extracts which most probably acted as contaminant within the concrete matrix and thus weakening its strength.

3.5. Weight loss 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 50% concentration had the

Table 5. Weight loss and inhibition efficiency in 0.2 M H_2SO_4 medium.

Extract concentration	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr)	Inhibitor efficiency (%)
Control	110	109.4	0.6	0.000275	
VA 100%	109	107.5	1.5	0.000694	−51.52
VA 75%	110	108.8	1.2	0.000550	−20.11
VA 50%	109	108.6	0.4	0.000180	60.68
VA 25%	111	110.5	0.5	0.000240	47.61

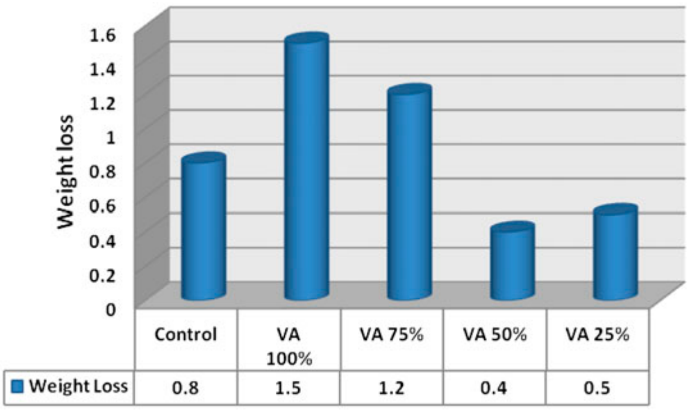

Figure 10. Influence of concentration of *V. amygdalina* on weight loss of samples.

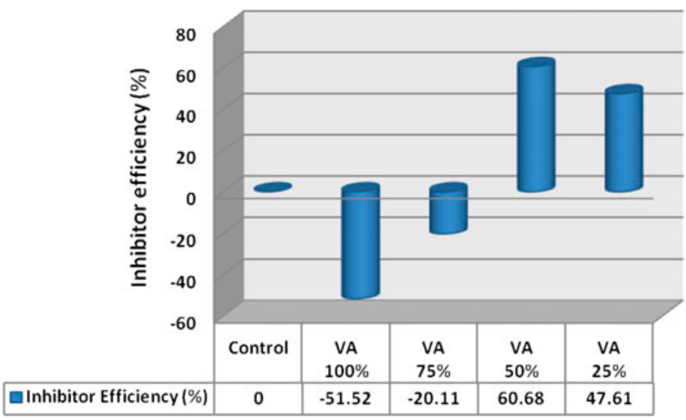

Figure 11. Influence of concentration of *V. amygdalina* on inhibitor efficiency.

lowest weight loss (0.4 g); a corrosion rate of 18.0×10^{-5} mm/yr and with an inhibitor efficiency of 60.68%. This value was followed with extract of 25% concentration with a weight loss value of 0.5 g; a corrosion rate of 24.0×10^{-5} mm/yr and an inhibitor efficiency of 47.61. The 75 and 100% extract concentrations showed relatively very low values of inhibitor efficiency. The lowest inhibitor efficiency of −51.52 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.

The variation of weight loss based VA concentration is shown in Figure 10.

The least weight loss, 0.5, was obtained at VA concentration of 50%. Since the weight loss of the control test was 0.6, this signifies that corrosion inhibition was more effective with lower concentration of *V. amygdalina,* while higher concentration of VA resulted into accelerated corrosion rate.

Figure 11 shows clearly the concentrations of *V. amygdalina* with the highest and lowest inhibitor efficiencies. The highest efficiency is 60.68% obtainable with 50%VA, while the lowest efficiency is −51.52% obtainable with 100%VA.

In summary, the experiment was performed using bitter leaf as a green inhibitor in 0.2 M H_2SO_4 which is a very strong acid. The addition of sulphuric acid accelerates the corrosion of the embedded steel by providing increased sulphate SO_4^- ions in the solution and around the reinforcing steel rebar. The bitter leaf extract behaved characteristically like chemical inhibitors in that at the optimum level of use (50% extract concentration), a measure of inhibition was provided in spite of the strong acid used.

4. Conclusions

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) *V. amygdalina* (bitter leaf) extract performed effectively as an inhibitor 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 *V. amygdalina* 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 *V. amygdalina* and exposure time significantly affects the corrosion potential of embedded steel rebar in concrete with the former having greater effect.
(4) At 95% confidence ANOVA test showed that the concentration of *V. amygdalina* and exposure time significantly affects the pH of the test environment, with the latter having greater effect.

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