The Effectiveness of *Vernonia amygdalina* and *Allium cepa* Extract Mixture as Corrosion Inhibitor on Mild Steel in Hydrochloric Acid Solution

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ABSTRACT

A combination of bitter leaf (*Vernonia amygdalina*) and white onion (*Allium cepa*) extract is more effective together as an inhibitor on mild steel in hydrochloric acid solution than if they were used separately. In this study, series of weight loss experiments were carried out. Hydrochloric acid and varying concentrations of inhibitors were tested with mild steel coupons. The experimental set-up was left to stand for four (4) days with 24 hours periodic washing, drying and weighing of the metal plates. Increase in the concentration of the leaves extract reduces the rate of corrosion of the mild steel in the corrosion medium. Analyses of the experimental results were done using a quadratic model to determine the optimum inhibition efficiency as well the corresponding concentration and time; a surface plot was used to illustrate these optimum conditions. The surface plot of the mixture of *Allium cepa* and *Vernonia amygdalina* extract shows that maximum inhibition efficiency can be achieved at 94.94% after 20.4hrs and 49.5ml concentration which is higher than the maximum inhibition efficiency of *Allium cepa* (93.4%) and *Vernonia amygdalina* (88.52%) extract used individually.

Keywords— *Allium cepa*, corrosion inhibitor, inhibition efficiency, mild steel, *Vernonia amygdalina*.

I. INTRODUCTION

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometime applied to plastics, wood and concrete degradation, but generally refers to metals [3]. Corrosion, being the breaking down of a metal as a result of various chemical reactions layer by layer until it loses its mechanical strength and cracks, is common knowledge. The effects of corrosion on metals are more than just loss of metal; according to [4], corrosion affects the safe, reliable, and efficient operation of equipment or structures. The effects of corrosion include: reduction of metal thickness leading to loss of mechanical strength and structural failure, loss of operational time of industrial equipments, reduction in the value of goods, contamination of fluids in vessels and pipes, cracks in equipments which may lead to escape of contents, loss of technically important surface properties of metallic components.

It has been of great importance to discover the methods with which industries could prevent corrosion of equipments, as corrosion is capable of changing the physical and chemical structure of the metals. Total elimination is almost impossible, but ways (corrosion controls) have been developed to prevent or slow down this effect on metals. There are several ways of preventing corrosion and the rates at which it can propagate with a view of improving the lifetime of metallic and alloy materials. The use of inhibitors for the control of corrosion of metals and alloys which are in contact with aggressive environment is one of the acceptable practices of reducing and/or preventing corrosion [3]. A corrosion inhibitor is a substance (or a combination of substances) added in small concentration to treat the surface of a metal exposed to a corrosive environment that diminishes the properties of the metal. Organic inhibitors have been developed, but there have been some growing concerns about its application, for example, chromates are good inhibitors but are highly toxic and environmentally unfriendly. Plant extracts - also referred to as green inhibitors - are better promoted because they are inexpensive, biodegradable, renewable, ecologically acceptable, environmentally friendly and readily available. They contain many organic compounds and molecules which have appreciable high inhibition efficiency. These organic compounds possess polar atoms such as O, P, S, or N, and have triple or conjugated double
bonds with aromatic rings in their molecular structures which are adsorbed on the metal surface, form protective films, and obey various adsorption isotherms [8].

*Allium cepa* (white onion) is a plant that can be found in everyday household kitchen. It is cheap, fairly abundant to be accessed, safe, and environmentally friendly [14]. Research has been conducted on *Allium cepa* and its properties, and the findings have proven that the compounds in the onion skin (quercetin) can inhibit corrosion. Using weight loss technique, the efficiency of onion as a corrosion inhibitor was found to be dependent on its concentration [1]. *Vernonia amygdalina* (bitter leaf), a member of the Asteraceae family is a small shrub that grows in the tropics of Africa. The leaves may be consumed either as a vegetable (macerated leaves in soups) or aqueous extracts as treatment of various illnesses [2]. Research has also found *Vernonia amygdalina* extract to be an effective corrosion inhibitor.

Mild steel is a medium carbon steel with a carbon content of 0.2-0.5%, and is often used as piping material [7]. It is widely employed in most industries due to its low cost and wide availability for the fabrication of various vessels and piping systems [5]. It can corrode in both acidic and non-acidic media [6], but this paper discusses its corrosion in acidic media.

This study is to determine the effectiveness of the combination of *Vernonia amygdalina* and *Allium cepa* extract as a corrosion inhibitor on mild steel, using 2.0M hydrochloric acid as medium. The inhibition efficiencies of *Vernonia amygdalina* and *Allium cepa* extract will be determined at different concentrations and time; the concentration and time at which optimum inhibition efficiency will be achieved is also determined.

### II. MATERIALS AND METHODS

#### Raw Materials, Reagents and Equipment

Bitter leaves and white onion bulbs were purchased from an open market in Owerri, Imo state, Nigeria. Hydrochloric acid and acetone used were purchased in a reagent store in Owerri. The 4 x 3 x 0.04cm mild steel coupons used were fabricated by the Mechanical Engineering Department of the Federal University of Technology, Owerri; with composition (wt%) Mn (0.42), P (0.02), C (0.25), Si (0.02), Ni (0.01), Cr (0.03), Fe (99.25). Experiments were carried out in the Chemical Engineering laboratory of the Federal University of Technology, Owerri. The equipment used for the experiment include: beakers, blender, desiccators, electric oven, retort stand, weighing balance, stop watch, measuring cylinders and thread.

**Preparation of Plant Extracts**

700g of onions was rinsed, chopped and blended. Distilled water was added, and it left to stand for some time; the ground mix was then squeezed to obtain the liquid extract, and then filtered using muslin. 750ml of the extract was stored. 1000g of bitter leaf was washed thoroughly with distilled water, and the first extract obtained was used; 750 ml was collected and stored. To obtain the mixture of both extracts, 250ml of each was added to separate conical flask to obtain 500ml, and later stored in a plastic bottle.

#### Weight Loss Measurement Experimental Procedures

1600ml of HCl with molar concentration 2M was prepared, after which 100ml was poured into sixteen separate beakers. The beakers were labeled in the order of the varying inhibitor volume they were to contain. The inhibitor was poured into fifteen beakers in the varying volumetric order of 50ml, 40ml, 30ml, 20ml, and 10ml, the remaining beaker was blank (beaker without any extract). The metal coupons were taken from the desiccators and were initially weighed with a digital weighing balance after which they were put into the solution by suspending the metals with threads. The experiment was carried out using the individual extracts, white onion and bitter leaf extract, and also with a mixture of the extracts. They were first left for twenty four hours after which, they were removed dried and weighed to check for weight loss. The metal specimen was then dropped back and the experiment carried out all over again; this experiment went on for 4 days after which readings were compiled and analysis made. It should be noted that this experiment was carried out at room temperature, and the time used for washing, drying and weighing was not put into consideration.

**Determination of Weight Loss and Percentage Inhibition Efficiency (I.E.%)**

The weight loss was calculated for each metal coupon after each day from the experimentally determined weight with and without an inhibitor. It was calculated by subtracting the weight of the coupon after each day from its initial weight for both the blank solution and the inhibitor solutions.

The percentage inhibition efficiency can be calculated using the equation below:

\[
\%IE = \frac{W_0 - W_i}{W_0} \times 100
\]

Where,

*W₀* = weight loss without inhibitor,

*Wᵢ* = weight loss with inhibitor

### III. RESULTS AND DISCUSSIONS

#### Weight Loss of Mild steel Coupons

Table 1 shows the weight loss of mild steel calculated from the experimental weight data. The weight loss increased with time in both the blank solution and the
inhibitor solutions. Under the experimental conditions investigated in this study, the weight loss results did not follow a particular trend for the different extract concentrations. However, in general, the weight loss decreased as the concentration of the *Vernonia amygdalina* and *Allium cepa* extract increased from 10ml to 50ml; while for the combination of both extracts, as the concentration increased, the weight loss varied after the third and fourth day.

**Table 1:** Weight loss of mild steel specimen in different concentrations of the three extracts used at different time interval

<table>
<thead>
<tr>
<th>EXTRACT AND CONCENTRATION (ML)</th>
<th>WEIGHT LOSS (G)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AFTER 24 HRS</td>
<td>AFTER 48 HRS</td>
<td>AFTER 72 HRS</td>
<td>AFTER 96 HRS</td>
<td></td>
</tr>
<tr>
<td>BLANK</td>
<td>0.171</td>
<td>0.285</td>
<td>0.375</td>
<td>0.389</td>
</tr>
<tr>
<td><em>Vernonia amygdalina</em></td>
<td>10</td>
<td>0.066</td>
<td>0.094</td>
<td>0.100</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.060</td>
<td>0.082</td>
<td>0.086</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.038</td>
<td>0.055</td>
<td>0.058</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.031</td>
<td>0.047</td>
<td>0.050</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.029</td>
<td>0.044</td>
<td>0.044</td>
</tr>
<tr>
<td><em>Allium cepa</em></td>
<td>10</td>
<td>0.046</td>
<td>0.058</td>
<td>0.065</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.036</td>
<td>0.046</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.035</td>
<td>0.043</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.035</td>
<td>0.041</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.016</td>
<td>0.020</td>
<td>0.022</td>
</tr>
<tr>
<td><em>Vernonia amygdalina</em> + <em>Allium cepa</em></td>
<td>10</td>
<td>0.018</td>
<td>0.028</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.015</td>
<td>0.024</td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.010</td>
<td>0.019</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.009</td>
<td>0.017</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.008</td>
<td>0.016</td>
<td>0.022</td>
</tr>
</tbody>
</table>

**Percentage Inhibition Efficiency**

The percentage inhibition efficiency of the plant extracts used – *Vernonia amygdalina*, *Allium cepa* and a mixture of both *Vernonia amygdalina* and *Allium cepa* were calculated and tabulated for mild steel. Just as in the analysis of the weight loss, the results of the percentage inhibition efficiency did not follow a particular trend for the various concentrations of the extracts used. This is because for the extracts used, optimal inhibition efficiency can be achieved at a particular concentration of the extract and after a particular period of time, and not necessarily at the highest concentration of the extract (50ml). But it should be noted that inhibition efficiency increases with inhibitor concentration.

Statistical modeling and analysis was done to determine the optimum inhibition efficiency achievable and at what time and concentration the optimum inhibition will be obtained. The knowledge of the optimum inhibition efficiency is vital because at this point, corrosion inhibition is at its peak, and this in turn helps to safeguard the lifespan of the metal in real life application.

**Table 2:** Calculated and tabulated results of %I.E. at various concentrations of the three extracts used on mild steel at different time intervals

<table>
<thead>
<tr>
<th>EXTRACT AND CONCENTRATION (ML)</th>
<th>INHIBITION EFFICIENCY (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AFTER 24 HRS</td>
<td>AFTER 48 HRS</td>
<td>AFTER 72 HRS</td>
<td>AFTER 96 HRS</td>
<td></td>
</tr>
<tr>
<td><em>Vernonia amygdalina</em></td>
<td>10</td>
<td>61.404</td>
<td>67.018</td>
<td>73.333</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>64.912</td>
<td>71.228</td>
<td>77.067</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>77.778</td>
<td>80.702</td>
<td>84.533</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>81.871</td>
<td>83.509</td>
<td>86.667</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>83.041</td>
<td>84.561</td>
<td>88.267</td>
</tr>
<tr>
<td><em>Allium cepa</em></td>
<td>10</td>
<td>73.099</td>
<td>79.649</td>
<td>82.667</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>78.947</td>
<td>83.860</td>
<td>86.133</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>79.532</td>
<td>84.912</td>
<td>87.467</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>79.532</td>
<td>85.614</td>
<td>88.000</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>90.643</td>
<td>92.982</td>
<td>94.133</td>
</tr>
<tr>
<td><em>Vernonia amygdalina</em> + <em>Allium cepa</em></td>
<td>10</td>
<td>89.474</td>
<td>90.175</td>
<td>88.267</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>91.228</td>
<td>91.579</td>
<td>91.733</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>94.152</td>
<td>93.333</td>
<td>93.867</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>94.737</td>
<td>94.035</td>
<td>93.067</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>95.322</td>
<td>94.386</td>
<td>94.133</td>
</tr>
</tbody>
</table>
**Model Equation and Analyses**

Model equations were developed for the different extracts using MATLAB 8.2 software. The Inhibition efficiency was set as the output variable; time and extract concentration were set as the input variables. For all three extracts used, a quadratic model was developed, and is given below:

\[ F(x,y) = p_{00} + p_{10}x + p_{01}y + p_{20}x^2 + p_{11}xy + p_{02}y^2 \]

\( x = \) concentration; \( y = \) time.

**For Vernonia amygdalina**:

Coefficients (with 95% confidence bounds); Probability value (pval):

- \( p_{00} = 42.3903 \) (33.24, 51.54); \( 1.0106 \times 10^{-7} \)
- \( p_{10} = 1.0809 \) (0.6616, 1.5); \( 7.434 \times 10^{-5} \)
- \( p_{01} = 0.4178 \) (0.1799, 0.6557); \( 0.00208 \)
- \( p_{20} = -0.007949 \) (-0.01424, -0.00165); \( 0.1486 \)
- \( p_{11} = -0.001978 \) (-0.00475, 0.00079); \( 0.0169 \)
- \( p_{02} = -0.002108 \) (-0.00393, -0.00027); \( 0.0268 \)

Goodness of fit:

\( \text{SSE:} \) 67.49, \( R\text{-square:} \) 0.9458,

Adjusted \( R\text{-square:} \) 0.9265, \( \text{RMSE:} \) 2.196

**For Allium cepa**:

Coefficients (with 95% confidence bounds); Probability value (pval):

- \( p_{00} = 64.624 \) (56.19, 73.06); \( 1.5149 \times 10^{-10} \)
- \( p_{10} = 0.1048 \) (-0.2818, 0.4913); \( 0.570 \)
- \( p_{01} = 0.4202 \) (0.2009, 0.6395); \( 0.0011 \)
- \( p_{20} = 0.004471 \) (-0.00133, 0.00102); \( 0.2154 \)

FIGURE 1: Variation of Inhibition Efficiency with Inhibitor Concentration for mild steel coupons in 2.0M HCl solution at different time periods,

- (a) In *Vernonia amygdalina* extract
- (b) In *Allium cepa* extract
- (c) In the mixture of *Vernonia amygdalina* and *Allium cepa* extract

**Figure 2a**: Surface plot of Inhibition Efficiency vs. concentration (ml) and time (hrs) for mild steel in *Vernonia amygdalina* extract

**For Allium cepa**:

Coefficients (with 95% confidence bounds); Probability value (pval):

- \( p_{00} = 64.624 \) (56.19, 73.06); \( 1.5148 \times 10^{-10} \)
- \( p_{10} = 0.1048 \) (-0.2818, 0.4913); \( 0.5702 \)
- \( p_{01} = 0.4202 \) (0.2009, 0.6395); \( 0.0011 \)
- \( p_{20} = 0.004471 \) (-0.00133, 0.00102); \( 0.2154 \)
p11 = -0.001548 (-0.004106, 0.001011); 0.1206285316751
p02 = -0.002315 (-0.004001, -0.0006301); 0.01061734322

Goodness of fit:
SSE: 57.36, R-square: 0.9071,
Adjusted R-square: 0.8603, RMSE: 2.024

Figure 2b: Surface plot of Inhibition Efficiency vs. concentration (ml) and time (hrs) for mild steel in *Allium cepa* extract

*For Vernonia amygdalina and Allium cepa mixture:*

Coefficients (with 95% confidence bounds); Probability value (pval):

\[ p00 = 86.16 \text{ (83.29, 89.02); 1.009369620678836e-18} \]
\[ p10 = 0.3905 \text{ (0.2591, 0.5219); 1.722785052287884e-05} \]
\[ p01 = -0.005686 \text{ (-0.08022, 0.06885); 0.872360921739148} \]
\[ p20 = -0.004203 \text{ (-0.006175, -0.002232); 0.796420479274} \]
\[ p11 = -0.0001066 \text{ (-0.0009759, 0.0007628); 4.345800e-04} \]
\[ p02 = -6.884e-05 \text{ (-0.0006416, 0.0005039); 0.8003299210} \]

Goodness of fit:
SSE: 6.625, R-square: 0.9267,
Adjusted R-square: 0.9006, RMSE: 0.6879.

The *Vernonia amygdalina* extract model was a quadratic model with \( R^2 \) value 0.9458, which shows that only 5.42% of the total variation on the inhibition efficiency could not be explained by the model. The surface plot showed its optimum inhibition efficiency at 88.52%; achieved by keeping the concentration at 49.25ml and time at 75.84hrs. The *Allium cepa* extract model was also a quadratic model with \( R^2 \) value 0.9071. The surface plot showed its optimum inhibition efficiency at 93.4%; achieved by keeping the concentration at 49.25ml and time at 72.67hrs. The mixture of *Vernonia amygdalina* and *Allium cepa* extract model was also a second-order polynomial (quadratic) model with \( R^2 \) value 0.9267, showing an acceptable correlation with the experimental data. The surface plot showed its optimum inhibition efficiency at 94.94%; achieved by keeping the concentration at 49.25ml and time at 20.4hrs.

The probability value (pval) of the coefficients was determined by analysis of the data using MATLAB 8.2. It is asserted that terms of a model having coefficients with pval > 0.05 are of less significance to the model equation. For the *Vernonia amygdalina* model, the \( x^2 \) term (pval = 0.1486) had no significant effect on the model equation. For the *Allium cepa* model, the x term (pval = 0.5703), \( x^2 \) term (pval = 0.2154), and xy term (pval = 0.1206) had no significant effect to the model equation. As for the mixture of *Vernonia amygdalina* and *Allium cepa* extract model, the Y term (pval = 0.8724), \( x^2 \) term (pval = 0.7964), and \( y^2 \) term (pval = 0.8003) had no significant effect to the model equation.

From the surface plots, done using MATLAB 8.2 curve fitting toolbox, it is observed that the mixture of *Vernonia amygdalina* and *Allium cepa* extracts give a
higher optimum inhibition efficiency for mild steel in hydrochloric acid, than if used separately.

Previous studies showed that temperature affects the efficiency of inhibitors [12][13], thus there is need for further study on the effects of temperature on the inhibition properties of the leaves (Vernonia amygdalina and Allium cepa) extract in hydrochloric acid.

IV. CONCLUSION

The present study shows that extract of Vernonia amygdalina and Allium cepa exhibit good inhibitive property on mild steel in hydrochloric acid. The study further shows that a mixture of Vernonia amygdalina and Allium cepa extract is a better inhibitor for the corrosion of mild steel in 2M HCl than if used separately. From the surface plots, the mixture of Vernonia amygdalina and Allium cepa extract gave the highest optimum inhibition efficiency of 94.94% at a concentration of 49.25ml after 20.4hrs.

REFERENCES