Effect of *Allium Sativum* Extracts on the Corrosion and Inhibition of α-Brass in HCl


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**Abstract**

An investigation of the effect of *allium sativum* (garlic) extract as a ‘green’ inhibitor on the corrosion and inhibition of α-brass in 0.5M HCl was performed at ambient temperature. Weight loss and corrosion rate and potentiodynamic polarization measurement techniques were used for the experimental work. Potentiodynamic polarization measurement was performed using a potentiostat (Autolab PGSTAT 30 ECO CHIMIE) interfaced with a computer for data acquisition and analysis. This work reports the gravimetric and electrochemical response of the study. The obtained results showed effective corrosion inhibition of the garlic extract on the test-specimens in the different concentrations of the test medium. Though there was inconsistent increasing inhibition performance with increasing concentration of inhibitor, the overall performance was not effective at other concentrations other than the 100%’s. The only appreciable corrosion inhibition performance was achieved with the 100% (as extracted) garlic concentration. In 0.5M HCl, and as at 360 hours (15 days) of the experiment, 100% garlic gave the optimal performance with weight loss of -0.020g, polarization resistance value of 6.88E+03 Ω, corrosion rate, CR, of 3.44E – 02 mm/yr and current density (Icorr) value of 3.74E-06 A/cm². A mixed type inhibitor was indicated by the results of ba and bc.

**Keywords:** Corrosion, *Allium Sativum*, α-Brass, Inhibition, Hydrochloric acid.

**1. Introduction**

A member of the copper-zinc alloys, alpha brass is versatile as a metallic material and its applications in manufacturing, marine and other diverse areas of industrial and engineering applications and for different purposes is widely acclaimed and valued. This alloy is, however, like many others, subject to adverse corrosive environmental degradation challenges in service and this threatens its engineering performance. Chemical inhibitors are chemical compounds that are adsorbed on the metal surfaces to minimize, control and/or prevent corrosion destructive processes and reactions. These inhibitors have long been used as effective means to mitigate this destructive phenomenon which can be disastrous. In very recent time, there has been wide interest among researchers [1-12] in the use of plant extracts as inhibitors for the corrosion of metals/alloys. In addition, plant extracts have also been used as effective additives in electroplating...
processes [13-14]. In many cases, the corrosion inhibitive effect of some plants’ extracts has been attributed to the presence of tannin and polyphenols in their complex chemical constituents. Extracts of plants used as inhibitors are environment friendly. Extract of garlic, *Allium Sativum*, was used in this work as the green inhibitor. Garlic is of the Genus *Onions*; Class: *Equisetopsida* in the family of *Amaryllidaceae*. It is known to consist of Calcium, Vitamin C, Vitamin B-6, Iron and Magnesium. It also contains protein, carbohydrates, potassium and sodium among many others. Garlic also contains 0.1-0.36% of a volatile oil. As previously reviewed [15], garlic contains at least 33 sulphur compounds like alliin, allicin (diallyl thiousulphinate or diallyl disulphide), ajoene, allylpropl, diallyl trisulphide, sallylcysteine, vinylthiines, S-allylmercaptocystein, and others. Besides sulphur compounds garlic contains 17 amino acids and their glycosides, arginine and others. Garlic also contains minerals such as selenium and enzymes like *alliase*, *peroxidases*, *myrosinase*, and others. Garlic contains a higher concentration of sulphur compounds than any other *Allium* species. The two major compounds in aged garlic, S-allylcysteine and S-allylmercapto-L-cysteine, had the highest radical scavenging activity. In addition, some organosulphur compounds derived from garlic, including S-allylcysteine, have been found to have significant medical value [16]. Alliin has been found to affect immune responses in blood [17]. Sulphur-containing compounds in *allium sativum* can also be further classified as oil- and water-soluble compounds. Oil-soluble compounds include sulphides, such as diallyl sulphide (DAS), diallyl disulphide (DADS), diallyl trisulphide and allyl methyl trisulphide, dithiins, and ajoene. Water-soluble compounds include cysteine derivatives, such as S-allyl cysteine (SAC), S-allyl mercaptocystein (SAMC), S-methyl cysteine, and gamma-glutamyl cysteine derivatives. [18]. With the complex structural chemical compounds of the extract of garlic such as shown below (i-iv), an appreciable amount of electrochemical corrosion activities of inhibition of the mild steel in the very corrosive HCl environments used in this work is anticipated. The expected benefit could have technological and economic advantage.

(i) **Alliin (S-Allyl-L-cysteine sulfoxide)** [19]  
alliin was the first natural product found to have both carbon- and sulphur-centered stereochemistry [20].

(ii) **Diallyl trisulphide** [21]

(iii) **Vinylthiins** (3-vinyl-4*H*-1, 2-dithiin and 2-vinyl-4*H*-1, 3-dithiin) [22]

**Vinylthiins**, more precisely named 3-vinyl-4*H*-1, 2-dithiin and 2-vinyl-4*H*-1, 3-dithiin, are organosulphur phytochemicals formed in the breakdown of *allicin* from crushed garlic (*Allium sativum*). Vinylthiins are Diels-Alder dimers of thioacrolein, H$_2$C=CHCH=S, formed in turn by decomposition of allicin [23].
3-vinyl-4H-1, 2-dithiin and 2-vinyl-4H-1, 3-dithiin, are organosulphur phytochemicals formed in the breakdown of allicin from the cysteine sulphoxide alliin [22]. As shown in (iv) in the reaction scheme above, allicin (1) decomposes into 2-propenesulfenic acid (2) and thioacrolein (3). Compound 2 reforms allicin while 3 gives Diels-Alder dimers 3-vinyl-4H-1, 2-dithiin (4) and 2-vinyl-4H-1, 3-dithiin (5) [17, 23]

2. Materials and methods

2.1. Preparation of specimens

The alpha brass specimen used as test specimens was obtained from a local metal market in Nigeria. It has a per cent nominal composition 70%Cu and 30%Zn. The alpha brass specimen used as test specimens was obtained from a local metal market in Nigeria. It has a per cent nominal composition 70%Cu and 30%Zn. The cylindrical brass alloy sample was cut into average size of 20 mm x 20 mm coupons for weight loss measurements and 20 mm x 20 mm coupons for potentiostatic polarization measurements. Test samples used for the weight loss experiment were de-scaled with a wire brush, ground with various grades of emery paper and then polished to 6 μm,. They were further rinsed in distilled water to remove any corrosion products and then cleaned with acetone to degrease. The samples were fully immersed thereafter preventing further exposure to moisture in the atmosphere. Another set of samples for the corrosion polarization experiments were cleaned in the same manner as those for the weight loss experiment. They were subsequently mounted in resin to ensure that only the tested surface of the sample was exposed to the corrosive medium. Before mounting, copper wire was spot welded to each of the samples.

2.2. Preparation of Garlic (Allium sativum) Extracts and Test Media

The experiment was performed in 0.5M HCl medium. The acid was of AnalaR grade. Garlic was obtained from the neighbourhood of the Covenant University, Ota, Nigeria. 1Kg of the garlic was chopped into pieces and soaked with 2.5 litres ethanol for 24 days. At the end of the soaking period, the chopped garlic was filtered to obtain a liquid solution of ethanol and garlic organic matter. The liquid was separated with the use of a rotary evaporator which extracted the ethanol from the liquid solution leaving behind the solution of garlic organic matter. The organic solution was stored in a refrigerator until it was used. The garlic extract (allium sativum) inhibitor test solutions were prepared in the percentage concentrations of 20, 40, 60, 80 and 100 respectively from the stock solution. This entailed taking 20 ml of the extract and 80 ml of the acidic medium to make 20% concentration. 100 ml of the stock inhibitor solution was used as 100% allium sativum inhibitor concentration. The same procedure was followed to obtain 40%, 60% and 80% inhibitor concentrations. The HCl medium was used for the preparation of per cent concentrations of the extract inhibitors.

2.3. Weight loss experiment

As previously reported [15], weighed test specimens were totally immersed in each of the test media contained in a 200 ml beaker for 20 days. Two test coupons were used for each test and the average weights used. Experiments were performed with 0.5M hydrochloric acid test medium in which some had the allium
sativum extract added. Test specimens were taken out of the test medium every 2 days, washed with distilled water, rinsed in methanol, air-dried, and re-weighed and then re-immersed in the test solution for continued tests during the whole experimental period. The plots of accumulated weight loss and of corresponding calculated corrosion rate versus exposure time are respectively presented in Figures 1 to 4. Corrosion rate was calculated from the formula in equation 1.

\[
\text{C. R. (mm/yr) } = 87.6 \times \frac{W}{DAT}
\]

Where: \(W\) = weight loss in milligrams; \(D\) = metal density in g/cm\(^3\); \(A\) = exposed area of sample in cm\(^2\); \(T\) = time of exposure of the in hours metal sample

The percentage inhibitor efficiency, \(P\), for each of the corrosion rate results obtained for every experimental reading was calculated from the relationship:

\[
P = 100 \left[1 - \frac{W_2}{W_1}\right]
\]

Where: \(W_1\) and \(W_2\) are, respectively, the corrosion rates in the absence and presence of the predetermined concentration of the allium sativum extract inhibitor. The results obtained are used to plot the curve(s) of % inhibition efficiency vs. exposure time (days), Figure 4.

2.4. Surface coverage

Surface coverage is defined as the number of adsorbed molecules on a surface divided by the number of molecules in a filled monolayer on that surface [24]. Surface coverage was calculated from the formula in equation 3.

\[
\psi = \frac{(CR_{\text{blank}} - CR_{\text{inh}})}{CR_{\text{blank}}}
\]

Where: \(\psi\) is surface coverage; \(CR_{\text{blank}}\) is corrosion rate without inhibitor, and \(CR_{\text{inh}}\) is the corrosion with inhibitor [25]

2.5. Potentiostatic polarization experiments

Experiments by potentiostatic polarization were performed on the mounted specimens in turns by immersing them in the acid test medium with and without garlic extract inhibitor. For the test, 1 cm\(^2\) surface area of the specimen was exposed to the test solution at room temperature. The experiments were performed using a polarization cell with a three – electrode system consisting of a reference electrode (silver chloride electrode – SCE), a working electrode (WE); and two carbon rod counter electrodes (CE). The potentiodynamic studies were made at a scan rate of 0.00166 V/s from \(-1.5\) to \(+1.5\) V and the corrosion currents were recorded. The experiments were conducted in different per cent concentrations of the HCl in garlic extract. The polarization cell was connected to a potentiostat (Autolab PGSTAT 30 ECO CHIMIE) and interfaced with a computer for data acquisition and analysis. A scan rate of 1 mV/s was maintained throughout the experiment.

3. Results and Discussions

3.1. Weight loss method

3.1.1 Weight loss of brass in 0.5M HCl + different concentrations of garlic extract

The results obtained for the weight loss experiments performed with the different concentrations of the garlic extract used as the inhibitor in 0.5M HCl are presented in Figure 1. The alpha brass test samples immersed in the 0.5M HCl test medium with 40% inhibitor concentration lost the most weight within the 20
days duration of the experiment with a weight loss of 0.209g as at 360 hours (15 days) of the experiment. At the same period of the experiment, the test sample immersed in the solution with 20% of inhibitor concentration showed improved corrosion inhibiting effect achieving a total weight loss of 0.084g.

Figure 1: Plot of weight loss with exposure time for alpha brass specimen immersed in 0.5M HCl in addition of different concentrations of garlic extract.

The tests performed with the 60% and 80% extract inhibitor concentrations, similarly had improved corrosion inhibiting values with reduced weight loss of 0.1245g and 0.1429g as at the 15th day of the experiment respectively. The tests performed with the as-received extract which was used as 100% inhibitor concentration gave an excellent result of corrosion inhibition. It achieved a negative corrosion weight loss value of -0.020g. This indicates absolute/perfect inhibition within the experimental conditions used. The value for the control experiment (without inhibitor addition) is 0.033g during the same period of the experiment. These results indicate minimal corrosion of alpha brass in HCl and does not conform to a particular trend of inhibition performance in terms of corrosion weight loss values obtained.

3.1.2. Corrosion rate of brass immersed in 0.5 M HCl + different concentrations of garlic extract

Presented in Figure 2 are the results of corrosion rate obtained from the calculations of weight loss values for the specimen immersed in HCl plus different separate concentrations of garlic extract. The highest corrosion rate value of 0.986 mm/year was recorded for the 40% inhibitor concentration. The corrosion inhibition values for all the other inhibitor concentrations range between 0.669 and 0.587 mm/yr for 20, 60 and 80% inhibitor concentrations respectively.

Figure 2: Plot of corrosion rate with exposure time for alpha brass immersed in 0.5M HCl in addition of different concentrations of garlic extract.
At these concentrations the corrosion rate values were relatively low and this could be due to the corrosion resistance of the alloy in the acidic test medium rather than the green inhibitor performance at the concentrations used. The control experiment results gave a weight loss of 0.033g and a corrosion rate of 0.153 mm/yr as at the 15th day of the experiment. The extract used as 100% (as-received extract), had the least corrosion rate with a corrosion rate value of -0.095 mm/yr at the same period of the experiment.

3.1.3. Surface coverage of alpha brass immersed in 0.5M HCl in different concentrations of garlic extract.

Curves of the surface coverage of the garlic extract concentrations for corrosion inhibition of alpha brass in the acidic test media are presented in Figure 3. Except for the 100% extract, the surface coverage curves decreased progressively with the time of exposure. This was more pronounced with the inhibitor concentrations of 20, 40 and 80% respectively. It is only the test with the 100% garlic extract maintained positive surface coverage value of 1.622 throughout the whole experiment indicating effective protection and adsorption of the inhibiting molecules on the surface of the test electrode in the strong acidic concentration. The other tests ranging from 20% to 80% extract inhibitor concentration achieved negative values of surface coverage as at 360 hours (15 days) of the experiment. This indicates non- or very low comparative surface coverage performance. The active adsorbing molecules within the inhibitor concentration would have presumably been insufficient to be more effective. However, it should be noted that as at the 120 hours (6 days) of the experiment, all the inhibitor concentrations achieved positive values indicating effective surface coverage. The subsequent loss of the coverage with the exposure time could be due to the interfacial test electrode/ HCl reactions that broke down any probable surface passivity caused by the adsorbed inhibiting molecules.

Figure 3. Plot of surface coverage with exposure time for brass immersed in 0.5M HCl in addition of different concentrations of garlic extract

3.1.4. Inhibition efficiency of brass in 0.5 M HCl using different concentrations of garlic extract

The results obtained for the corrosion inhibition efficiency of alpha brass immersed in 0.5M HCl test environment at different concentrations of allium sativum extract are presented in Figures 4. In general, the per cent inhibition efficiency decreased from the initial high values with the exposure time and thus becoming low at the latter part of the experiment. This could not be unconnected with the weakness of the corroding test medium caused by the contamination of the test environment by the corrosion products in the solution and the reduction in corrosion rate due to the consequent stifling action of the weak environment. The results clearly show the additions of per cent garlic extracts of 20, 40, 60, and 80 recorded negative
inhibition values, except in the first 120 hours (6 days) of the experiment and a spike by the 40% inhibitor concentration between the 168 and 216 hours of the experiment. However, the inhibition efficiency value for the 100% inhibitor concentration remained positive and achieving a per cent value of 162.15. The results obtained for all the inhibitor concentrations were an indication that the garlic extract had little positive effect in corrosion inhibition of the mild steel in this acidic test medium except at the 100% concentration (as extracted) where it achieved a significant positive result and hence effective protection throughout the experimental period.

Figure 4: Percent inhibition efficiency of different concentrations of sativum allium extract addition with exposure time for brass immersed in 0.5M HCl

This is indicated by the per cent I.E value obtained. The available molecules in the other extract (inhibitor) concentrations were considered not adequate for the corrosion inhibition effectiveness in the acid test environment.

3.2. Potentiodynamic Polarization

3.2.1. Brass in HCl with various concentrations of Allium Sativum (garlic) extract.

Figures 5 to 9 show the results obtained for the experiments performed in 0.5M HCl test medium. Table 1 summarises the various parameters of electrochemical corrosion polarization results obtained for the various inhibitor concentrations during the experiments. The results obtained from the different inhibitor concentrations used confirm appreciable active corrosion reactions as indicated by the different corrosion values for the different corrosion parameters as presented in Table 1. The results, in general, particularly with reference to corrosion rates and current density showed that the corrosion magnitude is minimal and thus confirming the positive effect of the extract. As presented in Table 1 and also in Figures 5 to 9 there seems to be progressive improvement in corrosion inhibition with increase in inhibitor concentrations. This is indicated by the decreasing corrosion rates, increasing polarisation resistance and decreasing current density, $I_{corr}$, values among other parameters. The corrosion potentiodynamic polarisation curve for the 100% (as extracted) inhibitor concentration is presented in Figure 9. The $E_{corr}$ value, as obtained from Table 1, is $-0.603 \text{ V}$; the current density, $I_{corr}$ is $3.74 \times 10^{-6} \text{ A/cm}^2$; the corrosion rate, $CR$, value is $3.44 \times 10^{-2}$; a polarisation resistance, $R_p$, value of $6.88 \times 10^3 \text{ \Omega}$ was recorded for the 100% inhibitor concentration. The corrosion inhibition at this concentration is very significant. The results obtained here are very much in agreement with the results obtained for the weight loss measurements. The results showed appreciable though variable corrosion inhibition of the brass specimen with all the extract concentrations used. The
values of the Tafel slope (ba and bc) indicate that the extract inhibits both cathodic and anodic reactions and can therefore be described as indicating a mixed corrosion type inhibition.

**Figure 5:** Polarization curve of brass in HCl + 20% garlic extract concentration.

**Figure 6:** Polarization curve of brass in HCL + 40% garlic extract concentration.

**Figure 7:** Polarization curve of brass in HCl + 60% garlic extract concentration.
Figure 8: Polarization curve of brass in HCl + 80% garlic extract concentration.

Figure 9: Polarization curve of brass in HCl with 100% of garlic extract concentration.

Table 1: Polarization results for the specimen immersed in HCl using different concentrations of per cent garlic extract

<table>
<thead>
<tr>
<th>Garlics Extracts concentrations</th>
<th>$E_a$ (V/dec)</th>
<th>$E_c$ (V/dec)</th>
<th>$E_{corr}$ (Calc) (V)</th>
<th>$I_{corr}$ (A)</th>
<th>Corrosion rate (mm/year)</th>
<th>Corrosion resistance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-1.61E+00</td>
<td>-5.54E+00</td>
<td>-0.409</td>
<td>6.65E-05</td>
<td>6.13E-01</td>
<td>3.86E+02</td>
</tr>
<tr>
<td>20%</td>
<td>1.14E+01</td>
<td>-6.26E+00</td>
<td>-0.423</td>
<td>2.70E-05</td>
<td>2.48E-01</td>
<td>9.53E+02</td>
</tr>
<tr>
<td>40%</td>
<td>2.38E+01</td>
<td>-4.56E+00</td>
<td>-0.375</td>
<td>4.07E-05</td>
<td>3.75E-01</td>
<td>4.93E+02</td>
</tr>
<tr>
<td>60%</td>
<td>-3.23E+01</td>
<td>-4.38E+00</td>
<td>-0.383</td>
<td>5.321E-05</td>
<td>4.80E-01</td>
<td>8.16E+02</td>
</tr>
<tr>
<td>80%</td>
<td>1.43E+01</td>
<td>-3.38E+00</td>
<td>-0.429</td>
<td>3.15E-05</td>
<td>2.90E-01</td>
<td>8.16E+02</td>
</tr>
<tr>
<td>100% (as extracted)</td>
<td>3.19E+00</td>
<td>-9.683E+00</td>
<td>-0.603</td>
<td>3.74E-06</td>
<td>3.44E-02</td>
<td>6.88E+03</td>
</tr>
</tbody>
</table>

As indicated by the results obtained in this investigation, the overall corrosion reactions parameter profile, obviously show the alpha brass test specimens to undergo corrosion in 0.5M HCl when not inhibited by any inhibitor concentration. However, the corrosion magnitude could not be described as significant. The different concentrations of the garlic extract used as inhibitor showed progressive inhibition which improves in most cases with increase in the extract inhibitor concentration. A significant observation was the near
perfect inhibition achieved with the as-extracted (100%) garlic concentration. There was no corrosion loss observed and all the electrochemical data showed very passive corrosion reactions. From the Table 1, the corrosion current density and the corrosion rate were very low while the polarisation resistance was high.

4. Conclusion

• The results obtained for both gravimetric and electrochemical experiments confirmed the extract of garlic to be an effective green inhibitor for alpha brass in hydrochloric acid under the experimental conditions used for this investigation.
• The garlic extract’s inhibition performance was concentration sensitive in most cases as the result parameters responded positively – either increasing or decreasing with increase in per cent concentration of the extract inhibitor.
• The concentration of 100% (as-extracted) garlic extract gave the best corrosion inhibition.
• The very complex composition of diverse chemical compounds / constituents of the garlic extract inhibitor are associated with its effective corrosion inhibition performance

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References