



Research Article

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## Corrosion inhibition effect of *Allium sativum* extracts on mild steel in HCl and H<sub>2</sub>SO<sub>4</sub>

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### ABSTRACT

The effect of *Allium sativum* (garlic) extract as a 'green' inhibitor on mild steel corrosion in 0.5M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub> was studied at ambient temperature. Weight loss/corrosion rate and potentiostatic polarization measurement techniques were used for the experimental work. Potentiostatic polarization measurement was performed using a potentiostat (Autolab PGSTAT 30 ECO CHIMIE) interfaced with a computer for data acquisition and analysis. Results obtained showed effective corrosion-inhibition of the extract on the mild steel test-specimens in the different concentrations of HCl and H<sub>2</sub>SO<sub>4</sub> used. There was increasing inhibition performance with increasing concentration of inhibitor. The best inhibition performance was achieved with the 100% (as extracted) garlic concentration. In 0.5M HCl, 100% garlic gave the optimal performance with weight loss at 8 days of the experiment of -0.15g, polarization resistance value of 2.78E+03Ω, corrosion rate, CR, of 9.47E - 02 mm/yr and current density (I<sub>corr</sub>) value of 9.46E-02 A/cm<sup>2</sup>. A similar result was observed in 0.5M H<sub>2</sub>SO<sub>4</sub> where 100% garlic gave the best results of -0.145g weight loss, polarization resistance value of 2.79E+03Ω; corrosion rate, CR, value of 9.46E-02 mm/yr and current density of 9.20E-06 mm/yr. Results of ba and bc indicate a mixed type inhibitor.

**Key words:** Corrosion, *Allium Sativum*, mild steel, inhibition, sulphuric acid, hydrochloric acid.

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### INTRODUCTION

Mild steel is apparently one of the most versatile metallic materials that is widely used in construction, manufacturing, marine and diverse areas of other industrial and engineering purposes. However, the versatility of mild steel and hence its engineering performance is continually being threatened as it is subject to corrosive environmental degradation in service. One of the means to mitigate this destructive phenomenon which can be disastrous and with economic and technological consequences is the use of chemical inhibitors. These are chemical compounds that are adsorbed on the metal surfaces to minimize, control and/or prevent corrosion destructive processes and reactions.

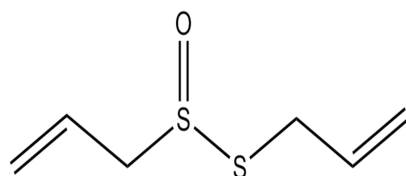
In very recent time, the use of plant extracts as inhibitors for the corrosion of metals/alloys, has gained very wide interest among researchers [1-12]. In many cases, the corrosion inhibitive effect of some plants' extracts has been attributed to the presence of tannin in their chemical constituents [7-9]. Also associated with the presence of tannin in the extracts is the bitter taste in the bark and /or leaves of the plants. Extracts of plants used as inhibitors are environment friendly and this generates further additional interest in research in this area.

In this present work, extract of garlic, *Allium Sativum*, was investigated. Garlic is of the Genus *Onions*; Class: *Equisetopsida* in the family of *Amaryllidaceae*. Garlic has been cultivated for thousands of years and is used throughout the world for its aromatic, spice and health giving properties. It is known to consist of calcium, Vitamin C, Vitamin B-6, Iron and Magnesium. It also contains protein, carbohydrates, potassium and sodium. With the major

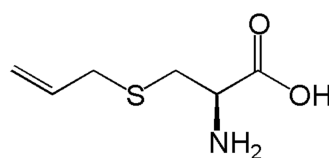
chemical constituents, garlic contains 0.1-0.36% of a volatile oil. These volatile compounds are generally considered to be responsible for most of the pharmacological properties of garlic. Garlic contains at least 33 sulphur compounds like aliin, allicin(diallylthiosulphinate or diallyl disulphide), ajoene, allylpropl, diallyl trisulphide, sallylcysteine, vinylthiines, S-allylmercaptocystein, and others. Besides sulphur compounds garlic contains 17 amino acids and their glycosides, arginine and others. Minerals such as selenium and enzymes like allinase, peroxidases and myrosinase. Garlic contains a higher concentration of sulphur compounds than any other *Allium* species. The sulphur compounds are responsible both for garlic's pungent odour and many of its medicinal effects. The odour is formed by the action of the enzyme allinase on the sulphur compound aliin. 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 retard the growth of chemically induced and transplantable tumors[13].

Garlic sulphur-containing compounds are 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-allylmercaptocysteine (SAMC) and S-methyl cysteine, and gamma-glutamyl cysteine derivatives, all as previously mentioned above. Oil-soluble sulphur compounds are odorous, whereas water-soluble compounds are odourless. Moreover, water-soluble compounds are more stable and safer than oil-soluble compounds. Garlic was also found to contain unique non-sulphur compounds, such as allixin and saponins and recent studies have revealed the important contribution of these compounds to garlic's health benefits [14].

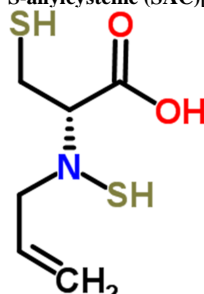
With the complex structural chemical compounds of the extract of garlic such as shown below (i-iii), a reasonable amount of exhibition of electrochemical corrosion activities of inhibition of the mild steel in the very corrosive acid environments used in this work is expected. Such a positive result will be economically and technologically beneficial.



(i) Allicin [15]



(ii) S-allylcysteine (SAC)[16]



(iii) S-allylmercaptocysteine (SAMC)(17)

## EXPERIMENTAL SECTION

### 2.1. Preparation of specimens

The mild steel specimen used as test specimens was obtained from a local rolling mill in Nigeria. It has a per cent nominal composition as shown in Table 1. The cylindrical steel 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. A total number of 24 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  $\mu$ m. 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 24 samples for the corrosion polarization experiments were cleaned in the same manner as those for the weight loss experiment except that they were mounted in resin to ensure that only the surface of the samples were exposed to the corrosive medium. Before mounting, copper wire was spot welded to each of the samples.

**Table 1: Summary of per cent nominal composition of mild steel**

C	Si	S	P	Mn	Ni	Cr	Mo	V	Cu	Sn	Al
0.171	0.209	0.04	0.025	0.55	0.141	0.067	0.011	0.002	0.252	0.01	0.003
Zn	Nb	Ti	W	Pb	B	Ca	Ce	Zr	Bi	Co	Fe
0.003	0.012	0.0004	0.004	0.0004	0.001	0.0007	0.008	0.002	0.001	0.009	98.48

### 2.2. Preparation of Garlic (*allium sativum*) Extracts and Test Media

The experiment was performed in (i) hydrochloric acid medium, 0.5M HCl and (ii) sulphuric acid medium, 0.5M H<sub>2</sub>SO<sub>4</sub> both of AnalaR grade. 0.5M HCl was prepared by diluting 41.39 cm<sup>3</sup> of concentrated HCl in 1 liter of distilled water while 0.5M H<sub>2</sub>SO<sub>4</sub> was prepared by diluting 44.44cm<sup>3</sup> of concentrated H<sub>2</sub>SO<sub>4</sub> in 1 liter of distilled water. Garlic was obtained from the neighbourhood of the Covenant University, Ota, Nigeria. 1Kg of the garlic was chopped into pieces and soaked with 2.5litres 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. While for preparing 40% concentration requires taking 40ml of the garlic extract and 60ml of any of the acidic medium. 100ml of the stock inhibitor solution was used as 100% *allium sativum* inhibitor concentration. The same procedure was followed to obtain 60% and 80% inhibitor concentrations. The HCl and H<sub>2</sub>SO<sub>4</sub> acidic media were separately used in turns for the preparation of percent concentrations of the extract inhibitors.

### 2.3. Weight loss experiment

Weighed test specimens were totally immersed in each of the test media contained in a 200ml 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 and 0.5M sulphuric acid test media in which some had the *allium sativum* extract added. Test specimens were taken out of the test media 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.

$$C. R. (mm /y) = 87.6 \times (W / DAT) \quad (1)$$

Where:

W = weight loss in milligrams

D = metal density in g /cm<sup>3</sup>

A = exposed area of sample in cm<sup>2</sup>

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:

$$P = 100[1 - W2/W1]$$

Where:

W1 and W2 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), Figures 7 and 8.

### 2.4. Potentiostatic polarization experiments

Potentiostatic polarization experiments were performed on the mounted specimens in turns by immersing them in each of the acid test media with and without garlic extract inhibitor. For test, 1 cm<sup>2</sup> 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 separately conducted in different percent concentrations of the HCl and H<sub>2</sub>SO<sub>4</sub> in garlic extract. All the chemicals used were of the analytic reagent grade (AR). The polarization cell was connected to a potentiostat (Autolab PGSTAT 30 ECO CHIMIE) and interfaced with a computer for data acquisition and analysis. Two different experiments were performed for each of the samples under the same conditions for reproducibility of results. A scan rate of 1 mV/s was maintained throughout the experiment.

## 2.5. 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 [18]. Surface coverage was calculated from the formula in equation 2.

$$\phi = (CR_{\text{blank}} - CR_{\text{inh}}) / CR_{\text{blank}} \quad (2)$$

Where:

$\phi$  is surface coverage;  $CR_{\text{blank}}$  is corrosion rate without inhibitor, and  $CR_{\text{inh}}$  is the corrosion with inhibitor [19]

## RESULTS AND DISCUSSION

### 4.1 Weight loss method

Results obtained from the experiments described above are separately presented in this section in turns for both the tests in HCl and H<sub>2</sub>SO<sub>4</sub> acidic test media with the addition of different concentrations of *allium sativum* extract.

#### 4.1.1 Weight loss of mild steel in 0.5M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub> + Concentrations of garlic extract

Presented in Figures 1 and 2 are the results obtained for the weight loss experiments performed with the different concentrations of the extract used as the inhibitor in 0.5M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub> acidic media respectively.

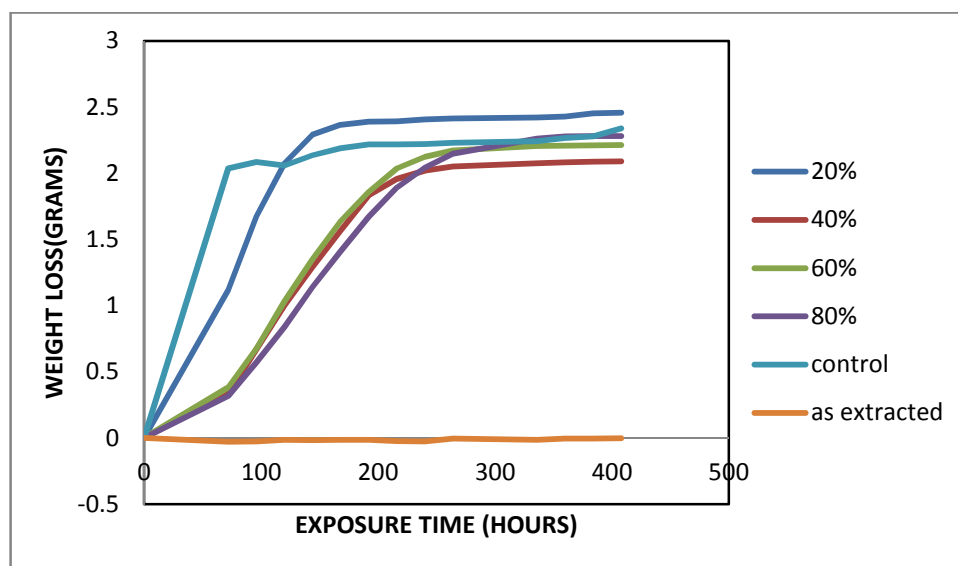
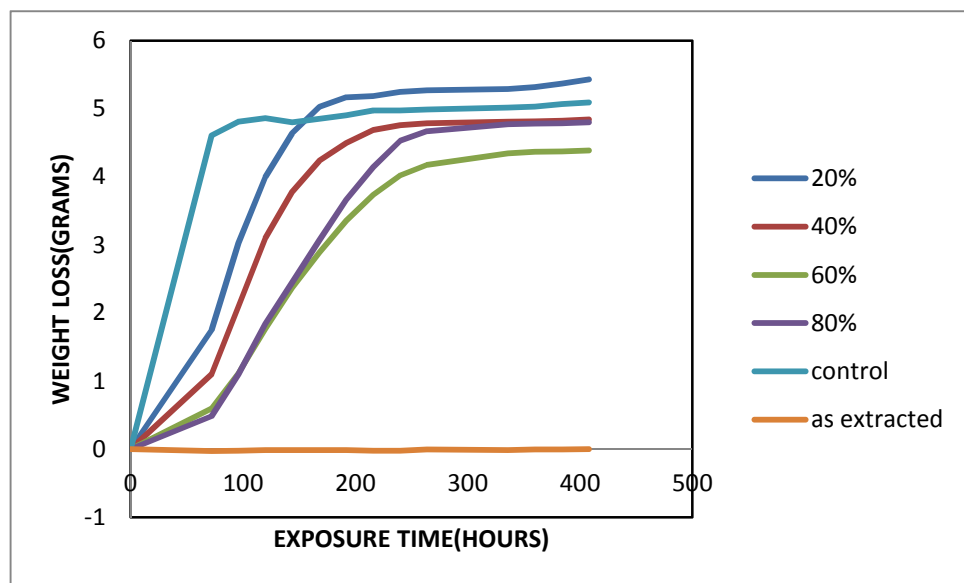


Figure 1: Plot of weight loss with exposure time for mild steel immersed in 0.5M HCl in addition of different concentrations of garlic extract

It is clear that the mild steel sample immersed in the solution with 20% inhibitor concentration lost the most weight within the 20 days duration of the experiment with a weight loss of 2.239g as at the 192 hours ( 8 days) of the experiment. The mild steel sample immersed in the solution with 40% of inhibitor concentration showed improved effect in inhibiting the corrosion of mild steel achieving a total weight loss of 2.0903g. The tests performed with the 60% and 80% extract inhibitor concentrations, similarly had improved corrosion inhibiting values with reduced weight loss of 1.859 and 1.6673g as at 192 hours 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 inhibiting value achieving a negative corrosion weight loss value of -0.15g. This indicates absolute/perfect inhibition within

the experimental conditions used. The value for the control experiment (without inhibitor addition) is 2.219g as at the 192 hours of the experiment..



**Figure2:** Plot of weight loss with exposure time for mild steel immersed in 0.5M H<sub>2</sub>SO<sub>4</sub> in addition of different concentrations of garlic extract

The results obtained for the experiments of the weight loss with exposure time for mild steel immersed in 0.5M H<sub>2</sub>SO<sub>4</sub> in addition of different concentrations of garlic extract presented in Figure 2, showed similar trend of inhibition, as in Figure 1 in the HCl test medium. However, the weight loss values here tend to be more severe due to the very strong nature of sulphuric acid at the concentration of 0.5 M used. It is clear that the mild steel sample immersed in the solution with 20% inhibitor concentration lost the most weight within the 192 hours (8 days) with a weight loss of 5.1167; and a total weight loss of 5.4298g in 20 days for the duration of the experiment. The mild steel sample immersed in the solution with 40%, 60% and 80% of inhibitor concentration showed improved corrosion inhibition values of 4.494, 3.356 and 3.659g, respectively as at 192 hours (8 days) of the experiment. At the same period of the experiment, (192 hours; 8 days) the 100% extract in the acid recorded a negative value of corrosion inhibition of -0.145g; and a total weight loss of -0.001g in 20 days of the experiment. Again, this appeared clearly a very good corrosion inhibition of the mild steel in this strong acid at that concentration. The value for the control experiment (without inhibitor addition) is 4.903g as at the 192 hours of the experiment..

#### 4.1.2. Corrosion rate of mild steel immersed in 0.5M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub> in different concentrations of garlic extract

Figures 3 and 4 show the corrosion rate with exposure time for the experiments whose weight loss measurement are just reported above in Figures 1 and 2 respectively, that is, separately in 0.5 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> with *allium sativum* extract as the inhibitor.

The highest corrosion rate, apart from the control (without added inhibitor) was recorded with the test specimen immersed in 20% inhibitor concentration. In the first 192 hours (8 days) of the experiment it achieved a corrosion rate inhibition value of 23.044 mm/yr. The inhibition values progressively improved with the increase in inhibitor concentration, achieving values of 17.91 and 16.11mm/yr for 60 and 80% inhibitor concentration respectively. The extract used as 100%, that is, as-received extract, had the least corrosion rate with a corrosion rate value of -0.141 mm/yr at the same period of the experiment. In general the corrosion rate values decreased with the increase in the time of exposure after about 120 hour (5 days) of the experiment. The control experiment, as expected, recorded 21.37 mm/yr corrosion rate at the same period of the experiment.

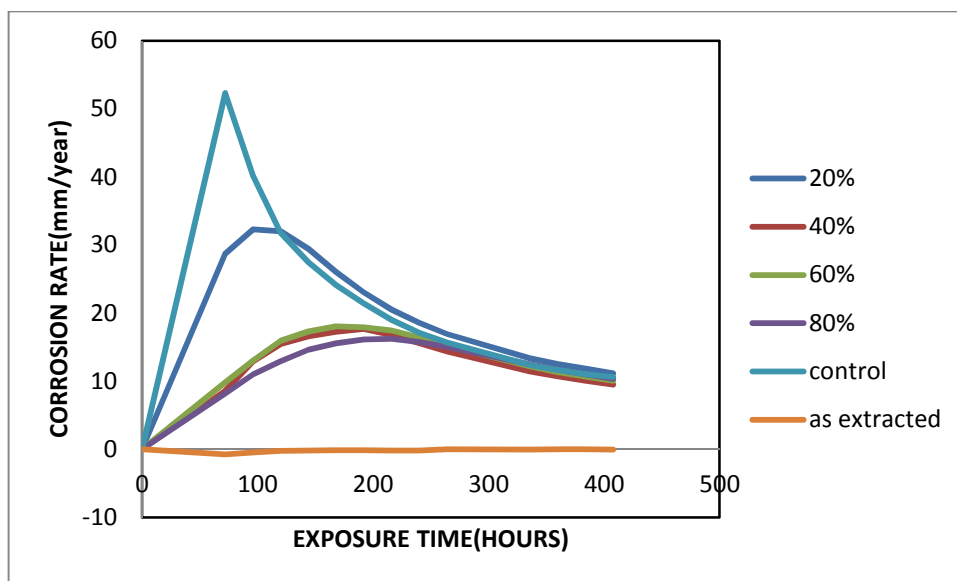


Figure 3: Variation of corrosion rate with exposure time for mild steel immersed in 0.5M HCL in addition of different concentrations of garlic extract

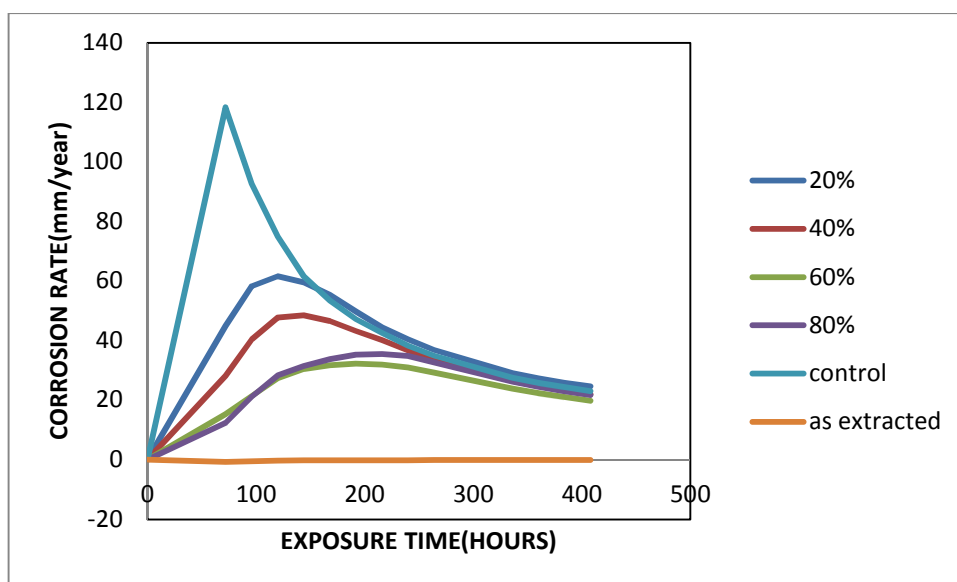


Figure 4: Variation of corrosion rate with exposure time for mild steel immersed in 0.5M H<sub>2</sub>SO<sub>4</sub> in addition of different concentrations of garlic extract

In Figure 4, the specimen immersed in 20% inhibitor concentration, except the control (without inhibitor addition) had the highest corrosion rate value of 49.7 mm/yr at 192 hours (8 days) of the experiment. The corrosion rate values decreased steadily with the increase in extract inhibitor concentration achieving 43.29, 32.33, 32.26 mm/yr for 40, 60 and 80% inhibitor concentrations respectively. The 100% (as received *allium sativum* extract) had the least corrosion rate value of -0.162 mm/yr and thus indicating excellent inhibition characteristic.

#### 4.1.3. Surface coverage of mild steel immersed in 0.5M HCL and 0.5M H<sub>2</sub>SO<sub>4</sub> in different concentrations of garlic extract.

Curves of the surface coverage of the garlic extract concentrations for corrosion inhibition of mild steel in the acidic test media are presented in Figures 5 and 6 for the HCL and H<sub>2</sub>SO<sub>4</sub> respectively. A significant observation recorded in the both Figures 5 and 6 are that the surface coverage started high at about 72 hours (3 days) of the experiment. Except for the 100% extract, the surface coverage curves decreased progressively with the time of exposure before maintaining an almost steady state at lower values of surface coverage at about 240 hours (10 days) of the experiment. The test with the 100% garlic extract maintained a very high and steady surface coverage value of 1.007 throughout the whole experiment indicating very effective protection and adsorption of the inhibiting molecules on

the surface of the test electrode in the strong acidic concentration. On the other hand, the test with 20% extract inhibitor achieved a negative value of -0.084 of surface coverage. This indicates very poor surface coverage performance. The active adsorbing molecules within the inhibitor concentration would have presumably been insufficient to be effective.

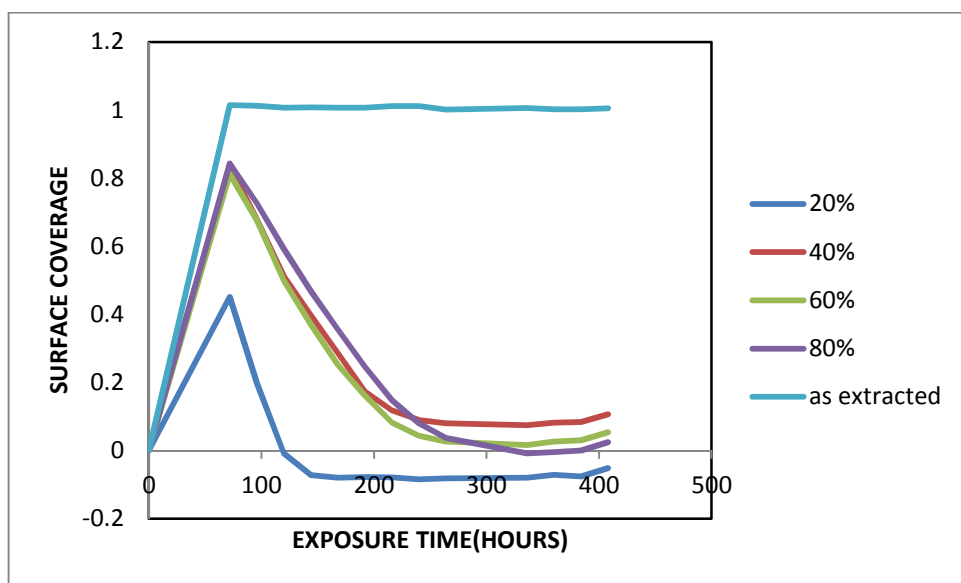


Figure 5: Curves of surface coverage with exposure time for mild steel immersed in 0.5M HCL in addition of different concentrations of garlic extract

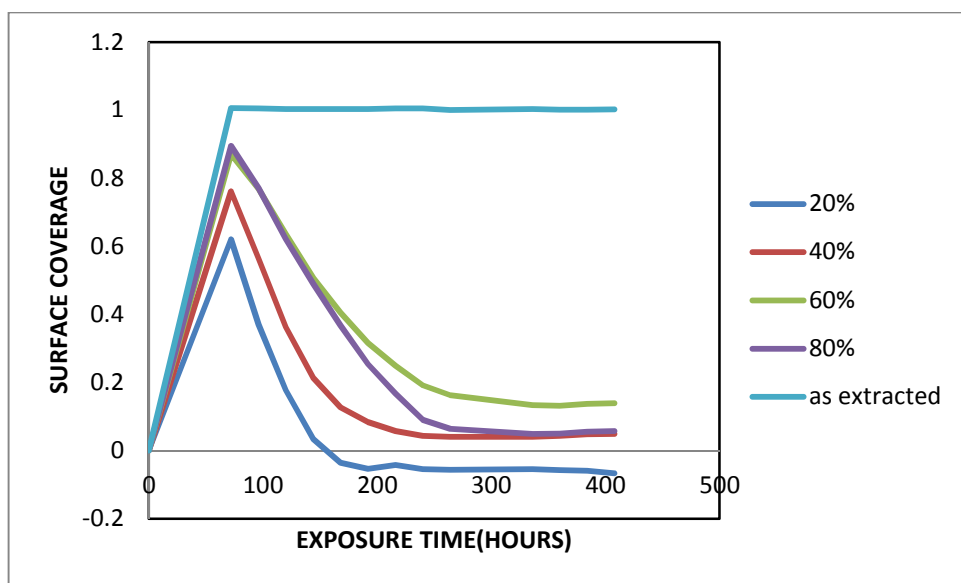


Figure 6: Curves of surface coverage with exposure time for mild steel immersed in 0.5M H<sub>2</sub>SO<sub>4</sub> in addition of different concentrations of garlic extract

In Figure 6, the curves of surface coverage with exposure time for mild steel immersed in 0.5M H<sub>2</sub>SO<sub>4</sub> in addition of different concentrations of garlic extract follow the same trend with that of Figure 5 in HCl test environment. The test with the 20% inhibitor concentration also achieved negative values of surface coverage after 144 hours (6 days). As at 240 hours (10 days) of the experiment, all other inhibitor concentrations performed with the positive values of surface coverage: 0.043, 0.192, and 0.090 for 40, 60, and 80% inhibitor concentrations respectively. It is important to note in Figure 6, that the experiment performed with the 100% extract inhibitor concentration has the highest magnitude of surface coverage achieving a value of 1.005 and hence better inhibition corrosion protection necessitated by sufficient test electrode surface adsorbed molecules of the complex chemicals in the inhibitor compounds.



#### 4.1.4. Inhibition efficiency of mild steel immersed in 0.5M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub> in different concentrations of garlic extract

The results obtained for the corrosion inhibition efficiency of mild steel immersed in 0.5M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub> test environments at different concentrations of *allium sativum* extract are presented in Figures 7 and 8 respectively. In general, the per cent inhibition efficiency decreased from the initial high values with the exposure time and thus becoming very 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.

Results presented in Figure 7, clearly show that except for the 20% inhibitor concentration which recorded a negative value of -7.81%, all other per cent additions of 40, 60, 80 and 100 recorded positive inhibition values ranging from 25.16 to 35.54% for 60 and 80% inhibitor concentration respectively as at 168 hours (7 days) of the experiment. The inhibition efficiency values decreased with time to low values achieving -5.14, 10.63, 5.36, and 100.52 % for 20, 40, 60, 80 and 100% respectively. The result obtained with the 20% inhibitor concentration was an indication that instead of corrosion inhibition expected, the concentration increased the corrosion reactions. This is one of the characteristics of the inhibitors. The available molecules in the inhibitor were not enough for the corrosion inhibition effectiveness in the strong acid environment. The highest inhibition efficiency was achieved with the 100% (as- extracted) inhibitor concentration. This conferred very good and effective protection throughout the experimental period.

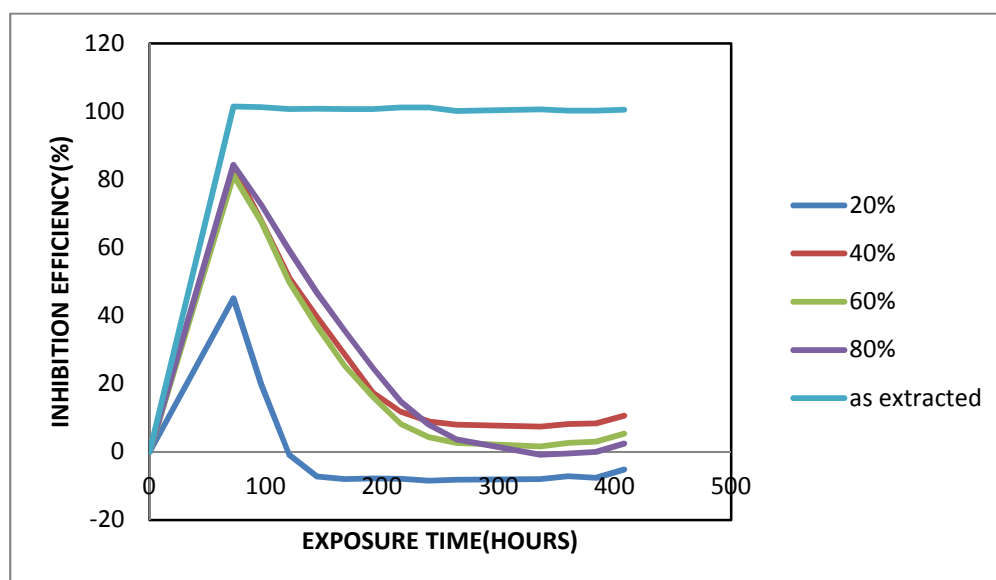


Figure 7: Curves of inhibition efficiency with exposure time for mild steel immersed in 0.5M HCl in addition of different concentrations of garlic extract

The results obtained in H<sub>2</sub>SO<sub>4</sub>, Figure 8, followed the same trend as in Figure 7 except that the values are obviously different due to different acidic environments used. After 144 hours (6 days), the 20% inhibitor concentration began to record negative values of inhibition efficiency ranging from -3.62% at 168 hours (7 days) to -6.66% at 408 hours (17 days) of the experiment. As at 144 hours (6) of the experiment, per cent inhibition values of 3.34, 21.32, 50.69, 48.96 100.34 recorded for inhibitor concentrations of 20, 40, 60, 80, and 100% respectively. As at 408 hours (17 days), the inhibition efficiency has decreased for each of the inhibitor concentrations, achieving 5.76 for 40 and 80%; 13.89 for 60%; and 100.24 for 100% (as- extracted) respectively. The results confirm the effectiveness of the *allium sativum* extract in corrosion inhibition of mild steel in strong acidic media of HCl and H<sub>2</sub>SO<sub>4</sub>.



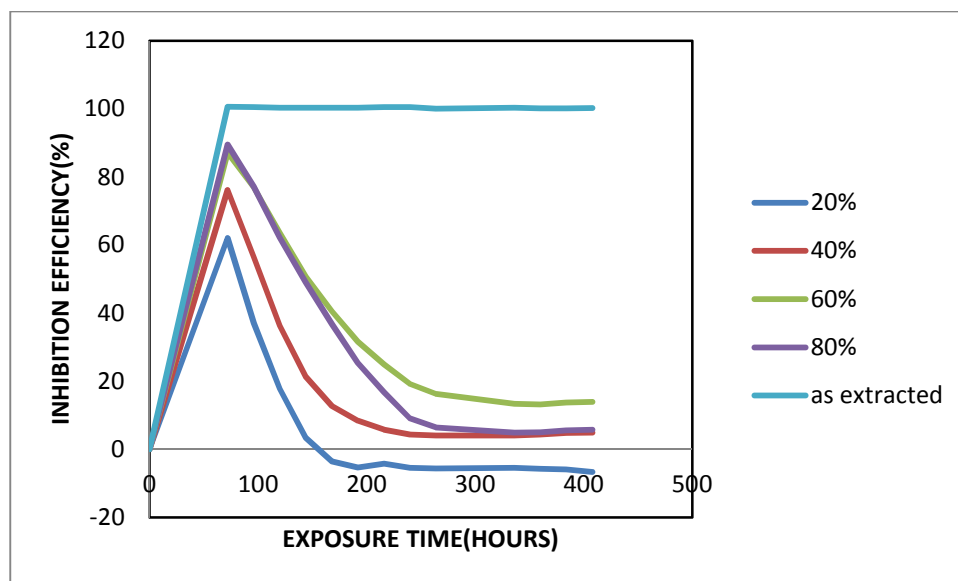


Figure 8: Curves of inhibition efficiency with exposure time for mild steel immersed in 0.5M H<sub>2</sub>SO<sub>4</sub> in addition of different concentrations of garlic extract

#### 4.2. Electrochemical Corrosion Polarization Measurement

The results obtained for the electrochemical corrosion polarization measurement for the mild steel separately immersed in HCl and H<sub>2</sub>SO<sub>4</sub> test media are presented in Figures 9 to 18.

##### 4.2.1. Mild steel in HCl with various concentrations of *Allium Sativum*(garlic) extract

Figures 9 to 13 represent the results obtained for the tests performed in HCl test medium. Table 2 summarises the various parameters of electrochemical corrosion polarization results obtained for the various inhibitor concentrations. The control experiment showed the highest corrosion magnitude as shown in the Table with corrosion rate of 7.68E+ 00 mm/yr; current density ( $I_{corr}$ ), 7.47E-04 A/cm<sup>2</sup> and polarisation resistance,  $R_p$ , 3.44E Ω values respectively. The test with 20% inhibitor concentration recorded the highest corrosion value among the various inhibitor concentrations as shown by the current density, corrosion rate and polarization resistance values among other parameters. With an open corrosion potential ( $E_{corr}$ ) value of -0.428 V, the corrosion rate (CR) value was 4.28E + 00 mm/yr; the open corrosion potential ( $E_{corr}$ ) value was -0.44587 V while the corrosion polarisation resistance,  $R_p$ , value recorded was 6.17E + 01Ω and a value of 4.16E-04 A/cm<sup>2</sup> was recorded for corrosion current density ( $I_{corr}$ ). All these results confirm the very active corrosion reactions on the test electrode/acid interface.

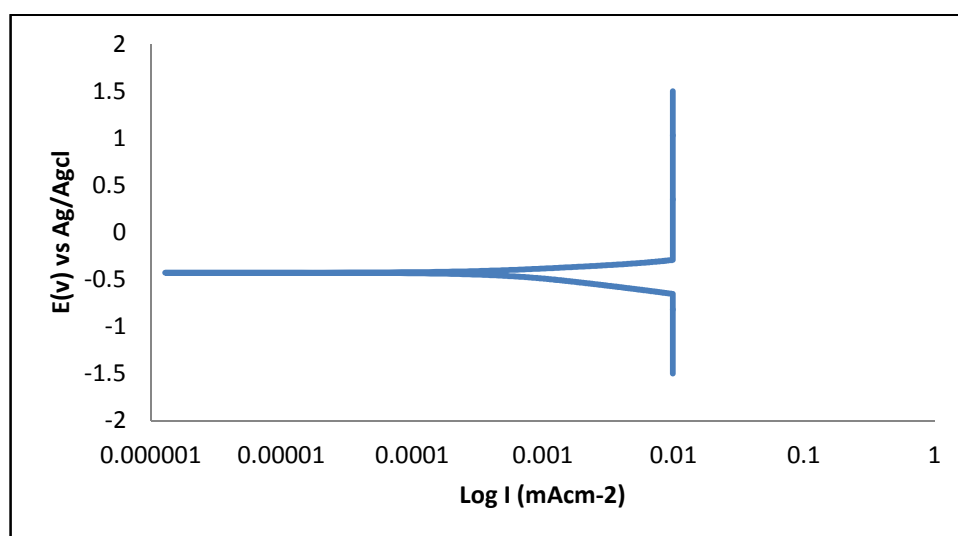


Figure 9: Polarization curve of mild steel in HCl+20% garlic extract

It could be seen from the Table 2 and also in Figures 10 to 13 that other results for 40, 60, 80 and 100% inhibitor concentrations showed very much improvement than that of 20%’s corrosion resistance//protection values. 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 13. The curve profile is very well defined. From Table 2, the  $E_{corr}$  value is  $-0.627$  V; the current density,  $I_{corr}$  is  $9.20E - 06$  A/cm<sub>2</sub>; the corrosion rate, CR, value is  $9.47E - 02$ ; a polarisation resistance,  $R_p$ , value of  $2.78E + 03$   $\Omega$  was recorded for the 100% inhibitor concentration. At this concentration, the corrosion inhibition is very significant. The result obtained here is very much in agreement with the result obtained for the weight loss measurements.

The values of the Tafel slope ( $b_a$  and  $b_c$ ) indicate that the extract inhibits both cathodic and anodic reactions and thus confirms that the inhibitor is a mixed corrosion inhibitor.

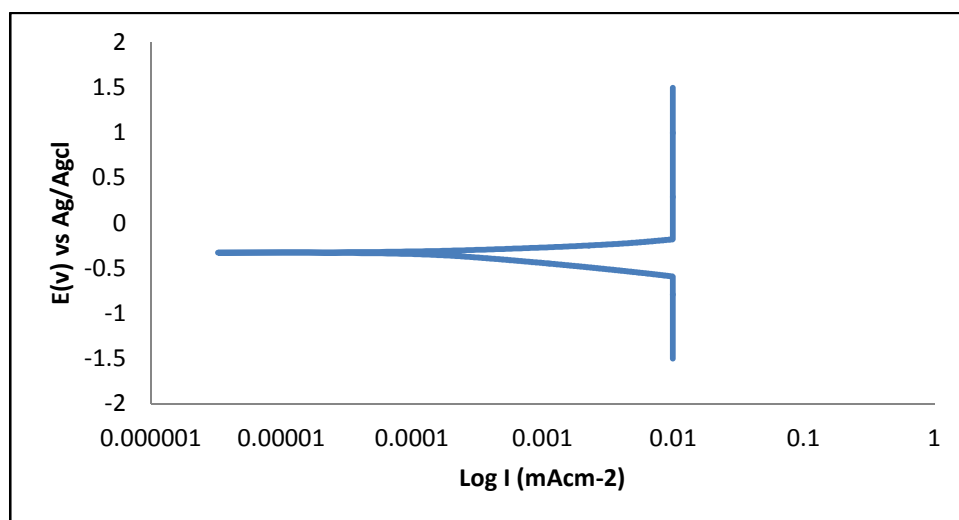


Figure 10: Polarization curve of mild steel in HCL+40% garlic extract

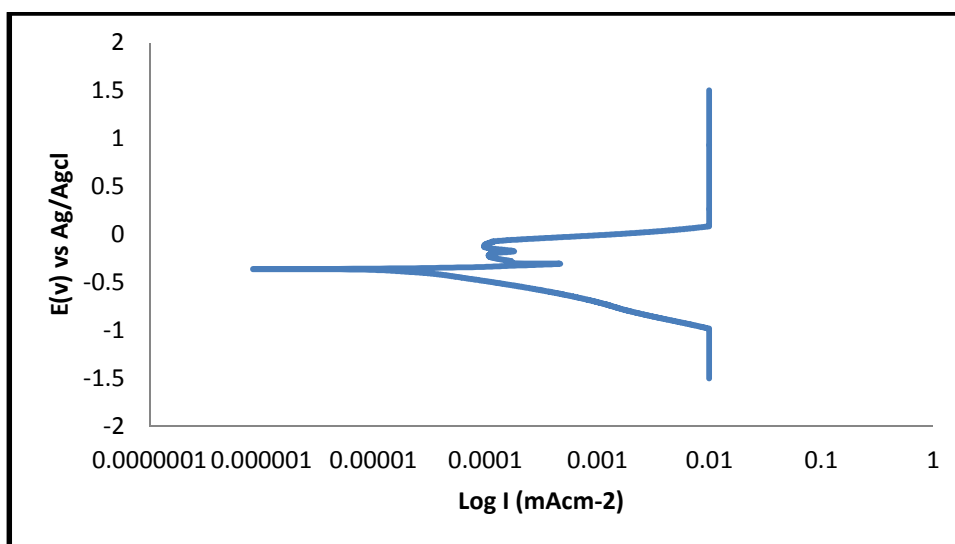


Figure 11: Polarization curve of mild steel in HCL+60% garlic extract

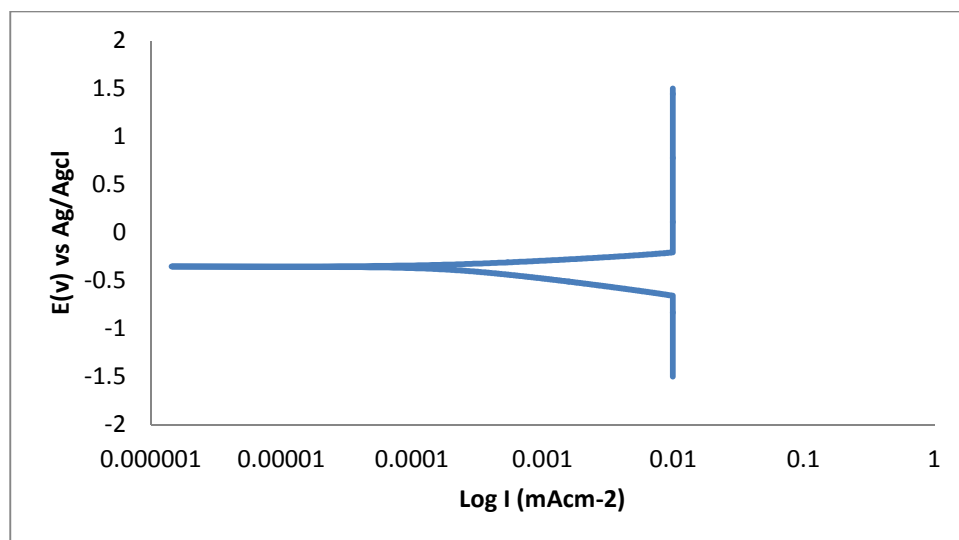


Figure 12: Polarization curve of mild steel in HCL+80% garlic extract

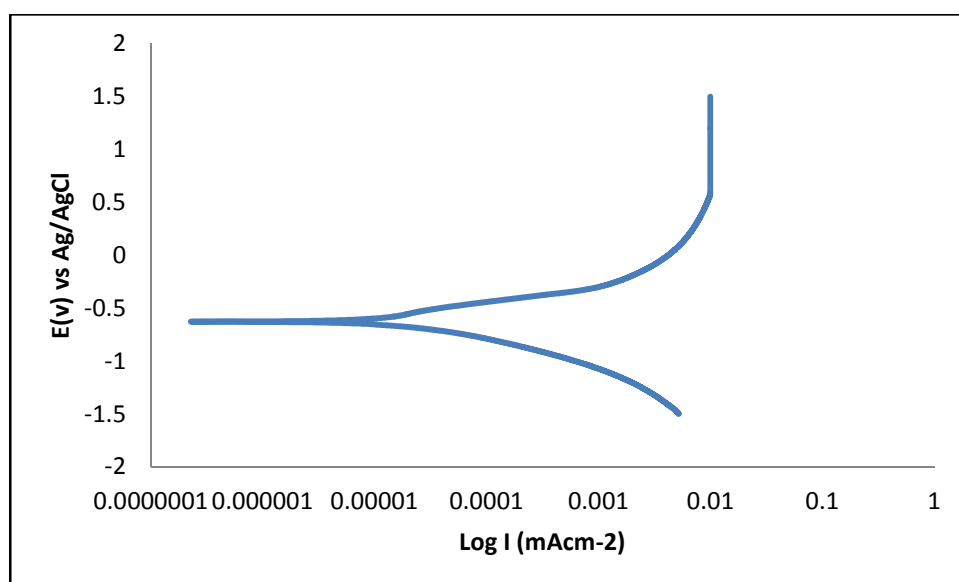


Figure 13: Polarization curve of mild steel in HCl +100% in garlic extract

Table 2: Polarization results for the specimen immersed in HCl using different concentrations of per cent garlic extract

% inhibitor concentrations and Control	ba (V/dec)	bc (V/dec)	E <sub>corr</sub> (V)	I <sub>corr</sub> (A)	Corrosion Rate (CR) (mm/yr)	Polarisation resistance (Ω)
Control	5.34E+100	-6.68E+100	-0.419	1.13E-03	1.116E+01	2.27E+01
20	1.25E+01	-7.19E+00	-0.428	4.16E-04	4.28E+00	6.17E+01
40	1.42E+01	-845E+00	-0.326	1.81E-04	1.86E+00	1.42E+02
60	4.34E-01	-5.95E+00	-0.361	4.84E-05	4.98E-01	5.31E+02
80	1.34E+01	-7.45E+00	-0.355	1.83E-04	1.89E+00	1.40E+02
100 (as extracted)	4.33E+00	-7.58E+00	-0.627	9.220E-06	9.47E-02	2.78E+03

#### 4.2.2. Mild steel in H<sub>2</sub>SO<sub>4</sub> with various concentrations of *Allium Sativum* (garlic) extract

Figures 14 to 18 represent the corrosion polarisation curves for the mild steel test specimens in H<sub>2</sub>SO<sub>4</sub> using separately different concentrations of garlic extract as inhibitor. The summary of the results for the experiments are presented in Table 3. Just as for the experiment with HCl, the control experiment showed the highest corrosion magnitude as indicated in the Table 3. The corrosion rate is 5.34E+00 mm/yr; current density (I<sub>corr</sub>), 1.13E-03 A/cm<sup>2</sup>; open corrosion potential (E<sub>corr</sub> value of -0.419 and polarisation resistance, R<sub>p</sub>, 2.27E+01 Ω values respectively. The test with 20% inhibitor concentration recorded the highest corrosion value among the various inhibitor concentrations as shown by the current density, corrosion rate and polarization resistance values among other parameters. It has an open corrosion potential (E<sub>corr</sub>) value of -0.403V, the corrosion rate (CR) value was

5.77E+00 + 00 mm/yr; while the corrosion polarisation resistance,  $R_p$ , value recorded was 4.58E + 01 $\Omega$  and a value of 5.62E-04 A/cm<sup>2</sup> was recorded for corrosion current density ( $I_{corr}$ ).

From Table 3 and in Figures 14 to 18, the results for 40, 60, 80 and 100% inhibitor concentrations showed progressive improvement in corrosion resistance values than that of 20%'s. This is indicated, among other parameters, by the decreasing corrosion rates, increasing polarisation resistance and decreasing current density,  $I_{corr}$ , values. The well -defined potentiodynamic polarisation curve for the 100% (as-extracted) inhibitor concentration is presented in Figure 18. The  $E_{corr}$  value is -0.627 V; the current density,  $I_{corr}$  is 9.20E – 06 A/cm<sup>2</sup>; the corrosion rate, CR, value is 9.46E – 02; and the polarisation resistance,  $R_p$ , value of 2.79E + 03  $\Omega$  was recorded for this inhibitor concentration. The corrosion inhibition at this 100% concentration was clearly very significant. The values of the Tafel slope (ba and bc) indicate that the garlic extract inhibits both cathodic and anodic reactions and thus confirms that the inhibitor is a mixed corrosion inhibitor. The results obtained here are also very much in agreement with the results obtained for the weight loss measurements.

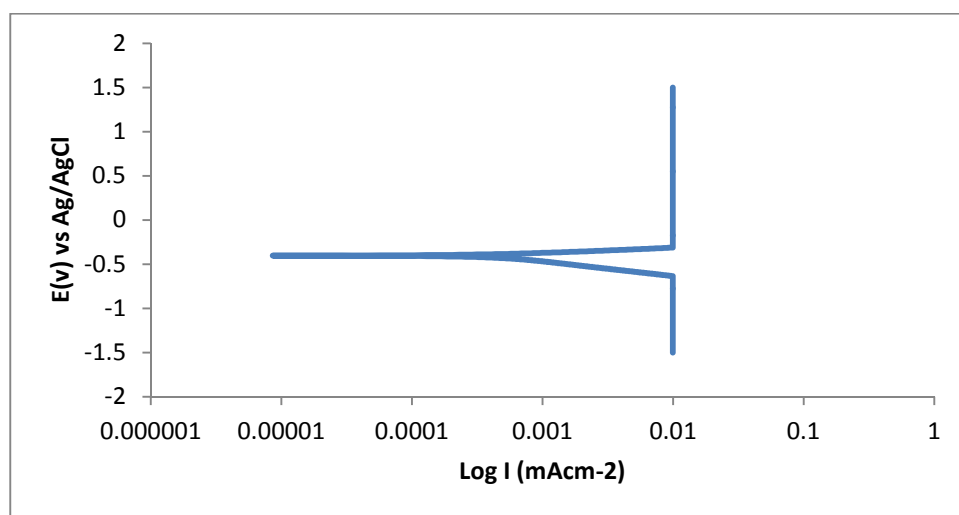


Figure 14: Polarization curve of mild steel in H<sub>2</sub>SO<sub>4</sub> + 20% garlic extract

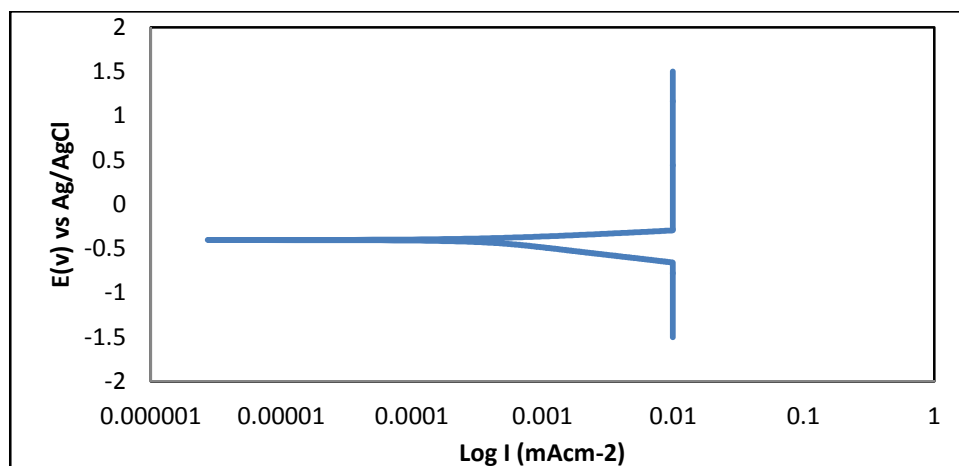
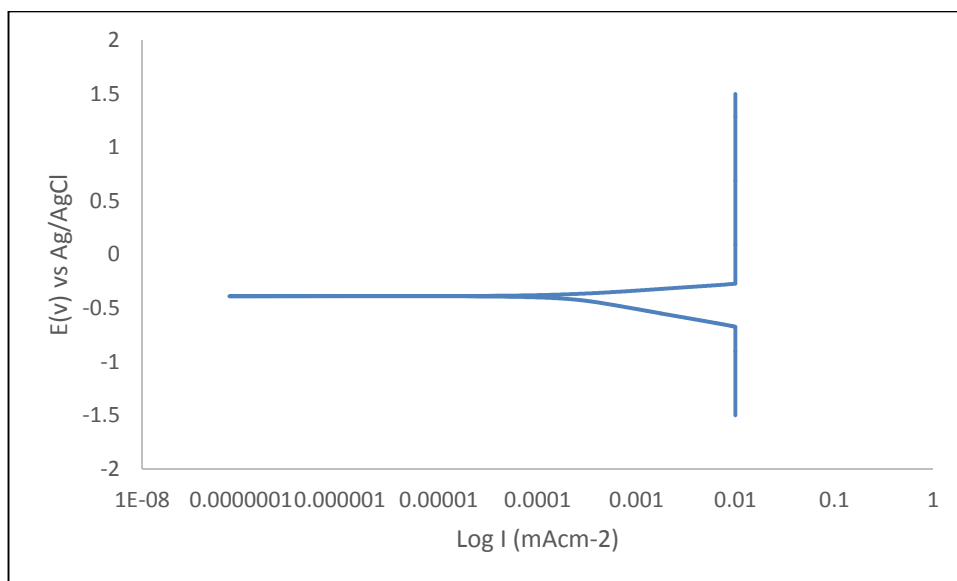
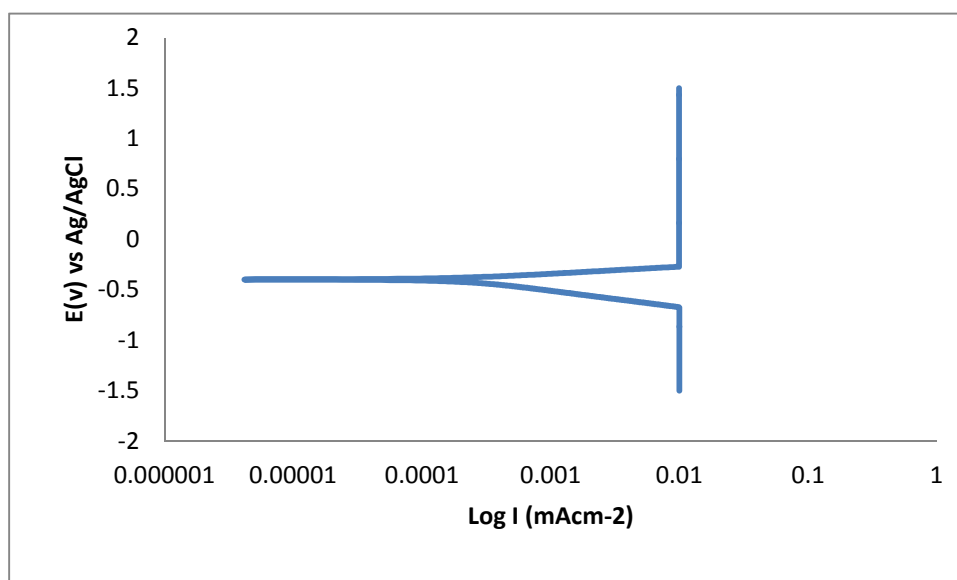


Figure 15: Polarization curve of mild steel in H<sub>2</sub>SO<sub>4</sub> + 40% garlic extract

Figure 16: Polarization curve of mild steel in H<sub>2</sub>SO<sub>4</sub> + 60% garlic extractFigure 17: Polarization curve of mild steel in H<sub>2</sub>SO<sub>4</sub> + 80% garlic extractTable 3: Polarization results for the specimen immersed in H<sub>2</sub>SO<sub>4</sub> with different concentrations of per cent garlic extract

% inhibitor concentrations and Control	ba (V/dec)	Bc (V/dec)	E <sub>corr</sub> (V)	I <sub>corr</sub> (A)	Corrosion Rate (CR) (mm/yr)	Polarisation resistance (Ω)
Control	5.34E+00	-6.68E+00	-0.419	1.13E-03	1.1E+01	2.27E+01
20	1.54E+01	-6.08E+00	-0.403	5.62E-04	5.77E+00	4.58E+01
40	1.42E+01	-6.24E+00	-0.402	4.09E-04	4.20E+00	5.29E+01
60	1.59E+01	-6.47E+00	-0.388	2.43E-04	2.50E+00	1.06E+02
80	1.39E+01	-6.76E+00	0.396	2.39E-04	2.46E+00	1.08E+02
100 (as extracted)	4.33E+00	-7.58E+00	-0.607	9.20E-06	9.46E-02	2.79E+03

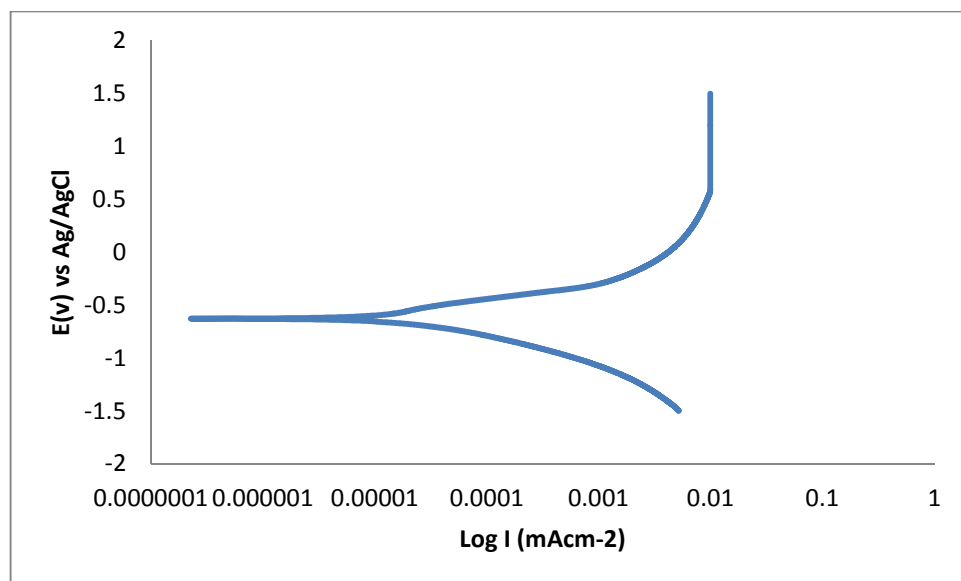


Figure 18: Polarization curve of mild steel in H<sub>2</sub>SO<sub>4</sub> + 100% garlic extract

The overall corrosion reactions parameter profile, clearly show that the mild steel undergoes severe corrosion in 0.5M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub> when not inhibited by any inhibitor concentration. However, the same corrosion test cell with same test electrodes that was experimented with different concentrations of *allium sativum* (garlic) extract concentrations show progressive inhibition which improves in most cases with increase in the extract inhibitor concentration. The improvement of corrosion inhibition that could be described as near perfect inhibition was achieved with the as-extracted (100%) concentration.

### Summary

Garlic has a very complex composition as mentioned in the introduction, which consists among others, of sulphur, (S), nitrogen (N), and oxygen (O). These are heteroatoms that are present in the ring structure of garlic's chemical constituents and are known [20] to have remarkable inhibitory effect and which facilitates their adsorption on the metal surface following the sequence  $O < N < S$ . The inhibition efficiency of an inhibitor which garlic fulfils, therefore, depends not only on the characteristic of the environment in which it acts and the nature of the metal surface. It also depends on the structure of the inhibitor itself which has been described to include the number of adsorption active centres in the molecule, the charge density, the molecular size, the mode of adsorption and the formation of metallic complexes[21].

The results of the electrochemical tests are very much in agreement with the gravimetric tests and the effectiveness of the inhibitory properties of garlic extract in the acidic media of test environments are confirmed. The action of the extract concentrations particularly at 100% concentration of about total inhibition, that affected both the anodic and cathodic reactions according to the Tafel slope ( $b_a$  and  $b_c$ ) values in both Tables 2 and 3 confirms the garlic extract inhibitor to be a mixed type inhibitor as earlier mentioned. The very complex structural compounds and multifarious constituents of garlic extract clearly exhibited electrochemical activity of effective corrosion inhibition particularly at the 100% concentration.

### CONCLUSION

The results both gravimetric and electrochemical confirmed the corrosion inhibition effectiveness of *allium sativum* (garlic) on mild steel in HCl and H<sub>2</sub>SO<sub>4</sub> under the experimental conditions in which the investigation was performed.

In most cases, the inhibition performance was concentration sensitive as all the result parameters such as weight loss, corrosion rate, inhibitor efficiency, surface coverage, polarization resistance and current density responded positively – either increasing or decreasing with increase in per cent concentration of the extract inhibitor.

The best corrosion inhibition was achieved with the 100% (as - extracted) garlic extract concentration while the 20% concentration recorded the lowest/poorest performance.

The effective corrosion inhibition performance of the garlic extract inhibitor is associated with the very complex composition of diverse chemical compounds which consist among others, of sulphur, (S), nitrogen (N), and oxygen (O) hetero atoms.

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