# Corrosion Inhibition Effect of Allium Cepa Extracts on Mild Steel in HCl

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# Corrosion Inhibition Effect of *Allium Cepa* Extracts on Mild Steel in HCl

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**ABSTRACT**

*A study of the effect of allium cepa extract as an inhibitor on mild steel corrosion in 0.5M HCl was made at ambient temperature. The experiments were performed with the weight loss/corrosion rate and potentiostatic polarization measurement techniques. Polarization measurement was performed using a potentiostat (Autolab PGSTAT 30 ECO CHIMIE) interfaced with a computer for data acquisition and analysis. Effective corrosion inhibition of the extract on the steel test specimens in the different concentrations of HCl used was achieved as indicated with the results obtained. There was increasing inhibition performance with increasing concentration of the extract inhibitor. The best inhibition performances were achieved at the lower exposure times for all the extract concentrations used in the 0.5 M HCl. A good correlation of results was obtained for the gravimetric and polarization experiments. A mixed type inhibitor is indicated with the results of ba and bc.*

**Key words:** Corrosion, onion, mild steel, inhibition, hydrochloric acid.

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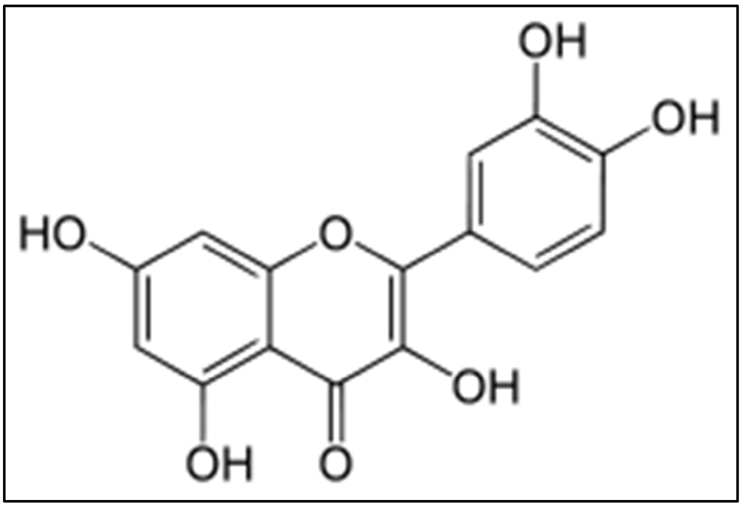
## INTRODUCTION

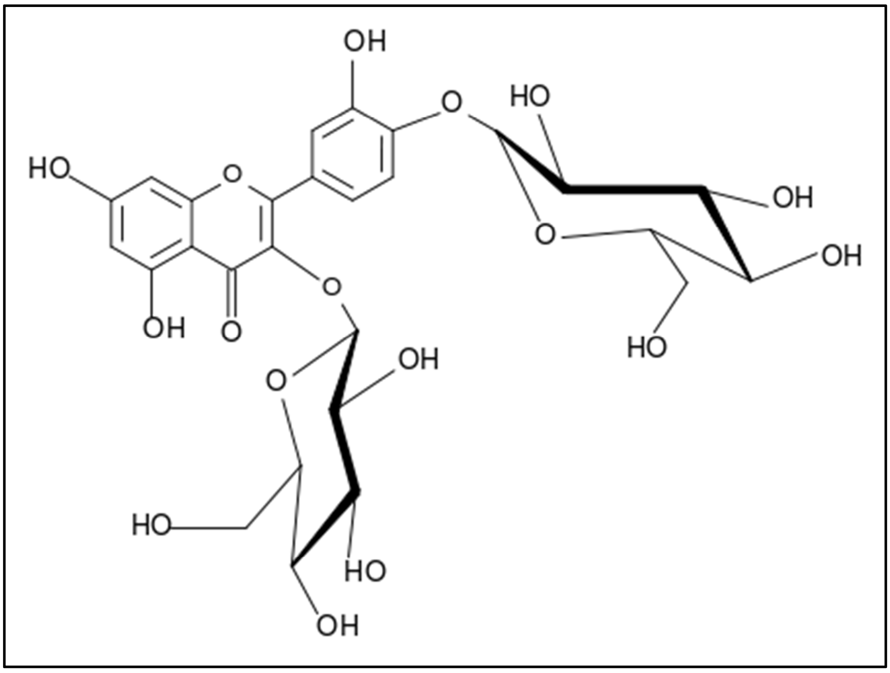
The very wide application of mild steel and its usefulness in domestic, services, construction, marine, industrial and engineering purposes makes it unique among other metallic materials. The challenge, however, is that it is subject to environmental/corrosive degradation in service. Among the means to mitigate this destructive phenomenon is the use of chemical inhibitors – the chemical compounds that are adsorbed on the metal surfaces to control, prevent and/or minimise destructive corrosion reactions processes.

Various researchers have recently shown interest in the use of plant extracts which are also referred to as green inhibitors, for corrosion inhibition of metals/ alloys in different test environments [1-12]. In many cases, the corrosion inhibitive effect of some plants' extracts has been attributed to the various complex chemical constituents of the extracts which include tannin among others [7-9]. Extracts of plants used as inhibitors are environment friendly.

This present work investigates extract of onion, *Allium cepa*. *Allium cepa* (onion) are known [13] to contain on analysis, vitamin C, vitamin $B_6$, folic acid and other nutrients though in small quantities. Onions have also been found [14] to contain other chemical compounds such as phenolics and flavonoids. These have been described [15] to include quercetin and its glycosides quercetin 3, 4'-diglucoside and quercetin-4'-glucoside.




**Quercetin (a polyphenol) is a typical flavonoid [15]**




**Chemical structure of quercetin 3, 4'-diglucoside [16]**

The complex chemical compositions contained in *Allium cepa* is expected to exhibit electrochemical activity such as corrosion inhibition of the mild steel in the tested environment. It is anticipated that such an obtained positive result will be economically and technologically beneficial.

## MATERIALS AND METHODS

2.1. *Preparation of specimens*

Preparation of the experimental specimens followed a previous process [17]. 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 Onion (allium cepa) Extracts and Test Media*

The experiment was performed in hydrochloric acid medium, 0.5M HCl of AnalaR grade. 0.5 M Onion was obtained from a local market near the Covenant University, Ota, Nigeria. 1.25 Kg of the onion was chopped into pieces together with bark and soaked in 2.5 litres ethanol for 3 weeks and 3 days. At the end of the soaking period, the chopped onion was filtered to obtain a liquid solution of ethanol and onion 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 onion organic matter. The organic solution was stored in a refrigerator until it was used for the experiments. The onion extract was prepared in various concentrations of 20%, 40%, 60% and 80% with the HCl acidic medium. This entailed taking 20 ml of the extract and 80 ml of the acidic medium to make 20% concentration. The same process was followed in preparing the other per cent extract concentrations.

2.3. *Weight loss experiment*

The procedure had been previously described [17]. 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 the *allium cepa* extract was added except for the control experiments. 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 and 2. Corrosion rate was calculated from the formula in equation 1.

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

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:

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

Where:
W1 and W2 are, respectively, the corrosion rates in the absence and presence of the predetermined concentration of the *allium cepa* extract inhibitor. The results obtained are used to plot the curve(s) of % inhibition efficiency vs. exposure time (days), Figure 4.

2.4. *Potentiostatic polarization experiments*

Potentiodynamic polarization experiments were performed on the mounted specimens in turns by immersing them in each of the acid test media with and without onion extract inhibitor. 1 $cm^2$ surface area of the specimen was exposed to the test solution at room temperature. As had been previously reported [17], 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 per cent concentrations of the HCl and $H_2SO_4$ in onion 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. Throughout the experiment, a scan rate of 1 mV/s was maintained.

**2.5. Surface coverage**

Surface coverage can be 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 equation 2.

$$¢ = (CR_{blank} – CR_{inh}) / CR_{blank} \qquad (2)$$

Where: ¢ is surface coverage; $CR_{blank}$ is corrosion rate without inhibitor, and $CR_{inh}$ is the corrosion with inhibitor [19].

## RESULTS AND DISCUSSION

4.1 **Weight loss method**

Results for the weight loss experiments are separately presented below in turns for both the tests in HCl and $H_2SO_4$ acidic test media with the addition of different concentrations of *allium cepa* extract.

4.1.1 *Weight loss of mild steel in 0.5M HCl + Concentrations of onion extract*

Results obtained for the weight loss experiments performed with the different concentrations of the *allium cepa* extract in 0.5M HCl and 0.5M $H_2SO_4$ acidic media are respectively presented in Figures 1 and 2

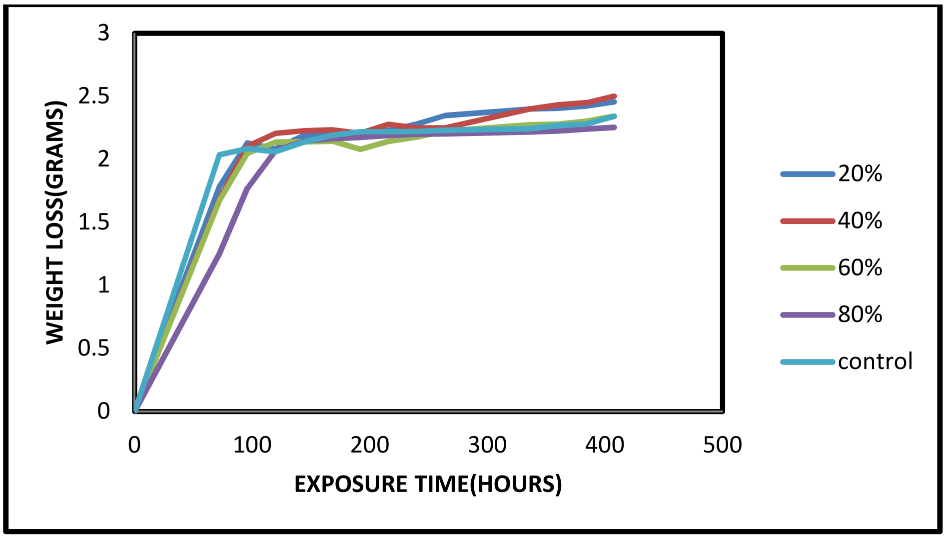



**Figure 1: Plot of weight loss with exposure time for mild steel immersed in 0.5M HCl in addition of different concentrations of onion extract**

Clearly, 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 2.399g as at the 336 hours (14 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 weigtht loss of 2.4477g. The tests performed with the 60% and 80% extract inhibitor concentrations, similarly had improved corrosion inhibiting values with reduced weight loss of 2.1897 and 2.2795g as at 226 and 360 hours of the experiment respectively. The value for the control experiment (without inhibitor addition) is 2.3391g as at the 400 hours (~17 days) of the experiment.

4.1.2. *Corrosion rate of mild steel immersed in 0.5M HCl in different concentrations of onion extract*
Presented in Figure 2 is the corrosion rate with exposure time for the experiments whose weight loss measurements have just been reported above in Figure 1.

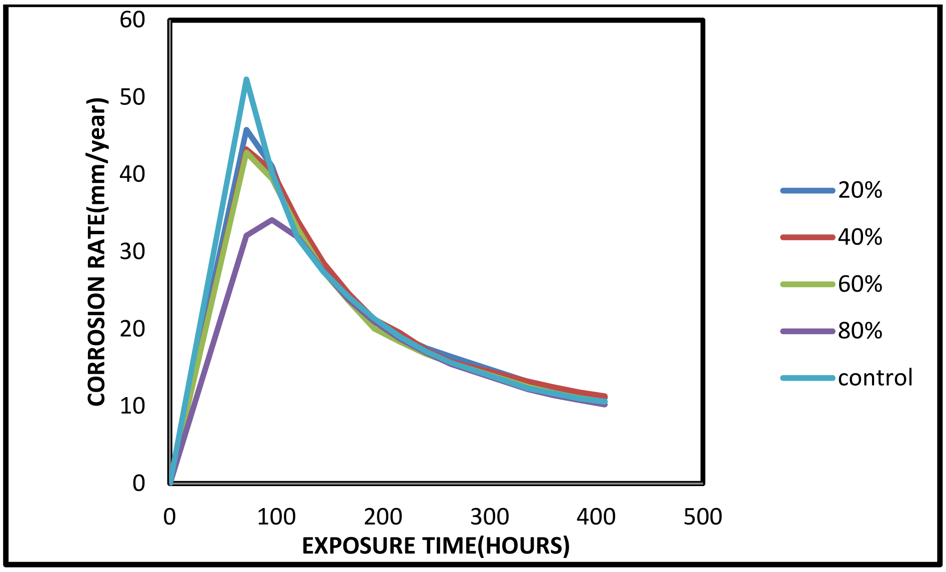



**Figure 2: Variation of corrosion rate with exposure time for mild steel immersed in 0.5M HCL in addition of different concentrations of onion extract**

In Figure 2, the results recorded very high corrosion rates within the first 96 hours (4 days) of the experiment after which the corrosion rates decreased with time to the end. After 120 hours (5) days of the experiment, the curves emanating from the recorded results became muddled together becoming almost indistinguishable for the control; 20, 40, 60 and 80% extract inhibitor concentrations respectively. At this period, the control experiment recorded a corrosion rate of 31.750 mm/yr. However, at between 336 and 360 hours ( 14 and 15 days) of the experiment, the corrosion rate with time achieved the values of 12.346 mm/yr for the control; and 13.207, 13.211, 12.531 and 11.417 mm/yr for the 20, 40,60 and 80% *allium cepa* extract concentrations respectively. 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.

*4.1.3. Surface coverage of mild steel immersed in 0.5M HCL in different concentrations of onion extract.*
Presented in Figure 3 are the curves of the surface coverage of the onion extract concentrations for corrosion inhibition of mild steel in the HCl acidic test medium. A clear observation recorded is that the surface coverage started high at about 72 hours (3 days) of the experiment. The surface coverage curves decreased progressively with the time of exposure before maintaining fluctuating negative and positive values of extreme low surface coverage for the rest of the extract concentrations throughout the experimental period.

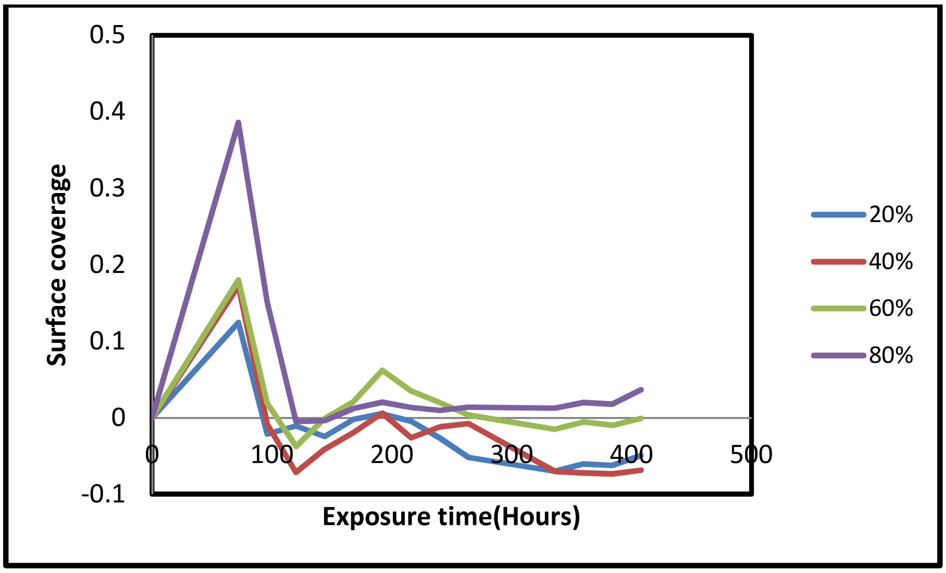



**Figure 3: Curves of surface coverage with exposure time for mild steel immersed in 0.5M HCL in addition of different concentrations of onion extract**

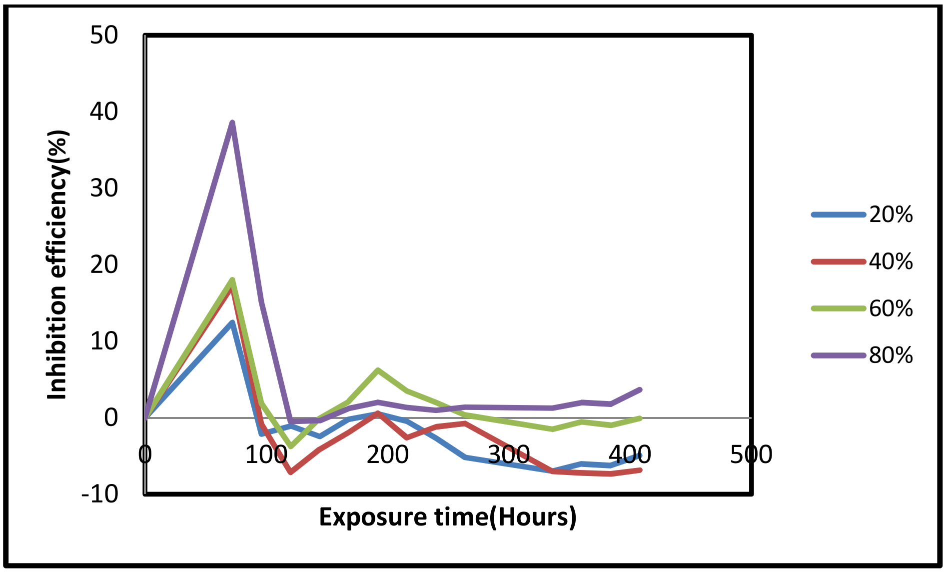



**Figure 4: Curves of inhibition efficiency with exposure time for mild steel immersed in 0.5M HCl in addition of different concentrations of onion extract**

4.1.4. *Inhibition efficiency of mild steel immersed in 0.5M HCl in different concentrations of onion extract*

The results obtained for the corrosion inhibition efficiency of mild steel specimens immersed in 0.5M HCl test environments at different concentrations of *allium cepa* extract is presented in Figure 4. In general, the per cent inhibition efficiency (I.E.) decreased from the initial high values with the exposure time. In Figure 4, the first 4 to 5 days recorded positive inhibition efficiency for 20 to 80% inhibitor extract concentrations. However, while the 20 and 40 % extract concentrations recorded negative values throughout the experimental period the 60 and 80% concentrations maintained positive but low inhibition efficiency values. This indicates increasing inhibitor protective tendency with increase in the extract inhibitor concentration. The very low inhibition values with some little fluctuations, till the end of the experiment could be associated with the weakness of the test medium due to its contamination by the corrosion products in the solution; which also caused reduction in corrosion rate. In addition, the onion extract appears not strong enough to inhibit the steel sample appreciably even at the initial stage of the experiment in the very strong acid. The available molecules in the extract inhibitor were probably not enough for the corrosion inhibition effectiveness in the strong acid environment.

### 4.2. Electrochemical Corrosion Polarization Measurement

The results obtained for the electrochemical corrosion polarization measurement for the mild steel separately immersed in HCl test media using onion (*allium cepa*) extract as green inhibitor are presented in Figures 5 to 9.

4.2.1. *Mild steel in HCl with various concentrations of Allium cepa extract*

The results obtained for the tests performed in HCl test medium are presented in Figures 5 to 9. The various parameters of electrochemical corrosion polarization results obtained for the various inhibitor concentrations are summarized in Table 2. The control experiment showed the highest corrosion magnitude as written in the Table achieving a corrosion rate value of 7.68E+ 00 mm/yr; current density (Icorr), 7.47E-04 A/cm$^2$ and polarisation resistance, Rp, 3.44E Ω values respectively. The tests with 20 and 40% inhibitor concentrations recorded the highest corrosion values among the various inhibitor concentrations as shown by the current density, corrosion rate and polarization resistance values. With an open corrosion potential (Ecorr) values of -0.419V and -4.30 V respectively, the corrosion rate (CR) values were respectively 5.43E + 00 and 5.30E+00 mm/yr; while the corrosion polarisation resistance, Rp, values recorded were 4.86E + 01 and 4.99E+01Ω. The corrosion current density (Icorr) values recorded for both were respectively 5.29E-04 and 5.15E-04 A/cm$^2$. These results indicate the active corrosion reactions on the test electrode/acid interface during the experiments.

From the Table 2 and also in Figures 7 to 9 the other results for 60 and 80% inhibitor concentrations shown in the Table 2 gave appreciable improvement of corrosion resistance//protection values than those of 20 and 40%. Among other parameters, these observations are indicated by the decreasing corrosion rates, increasing polarisation resistance and decreasing current density, Icorr, values. There is obvious agreement with the results obtained here and those of the weight loss measurements. The values of the Tafel slope (ba and bc) indicate that the extract inhibits both cathodic and anodic reactions and thus confirms that the inhibitor is a mixed corrosion type of inhibitor.

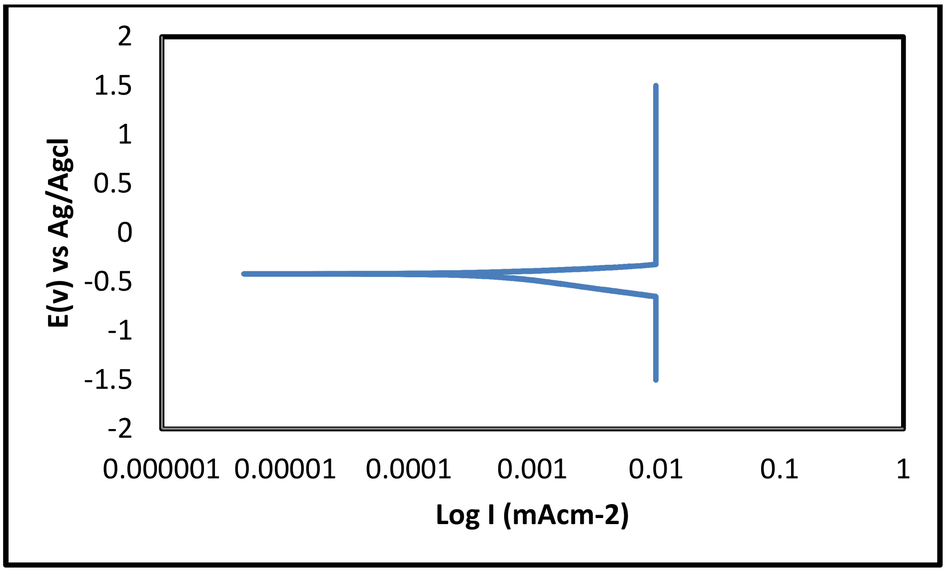



**Figure 5: Polarisation curve of mild steel in HCL+20% onion extract**

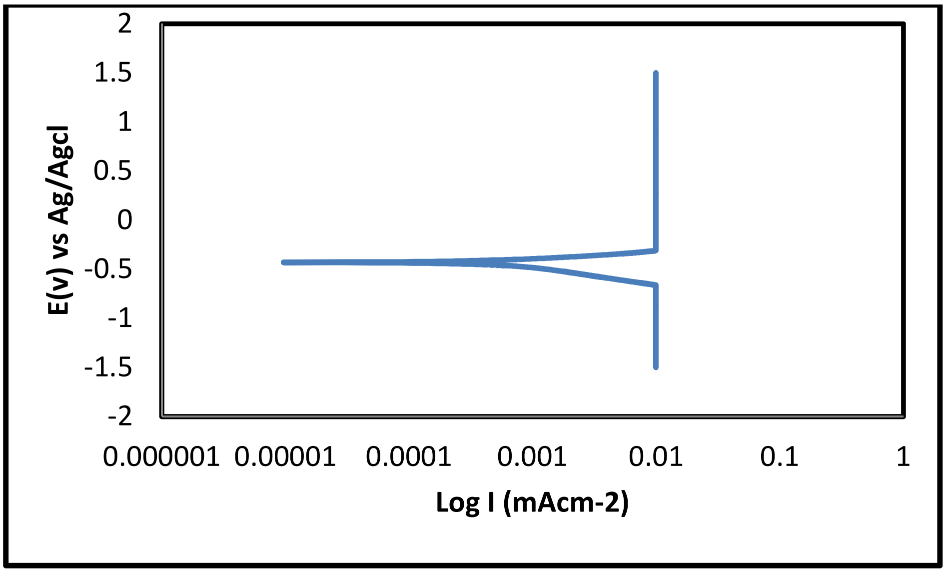



**Figure 6: Polarisation curve of mild steel in HCL+40% onion extract**

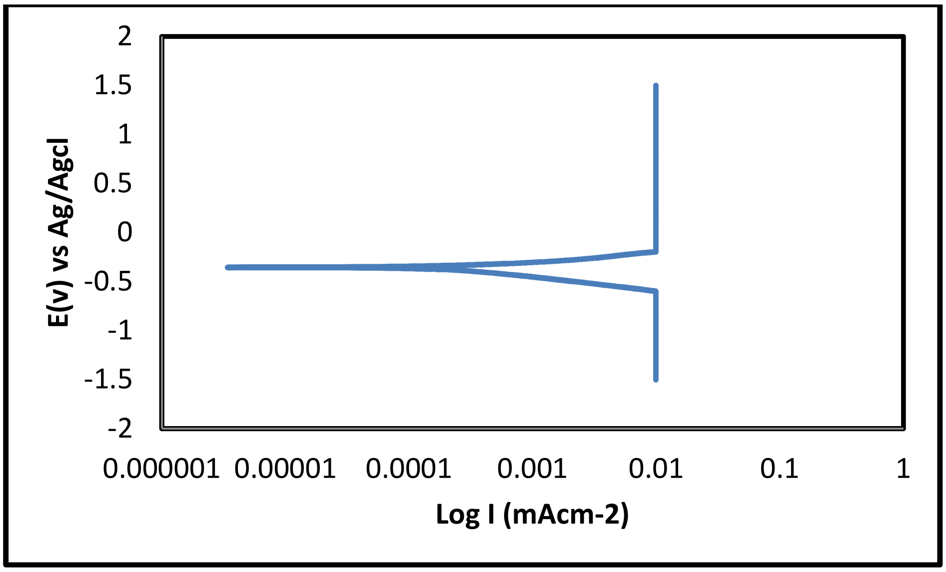



**Figure 7: Polarisation curve of mild steel in HCL+60% onion extract**

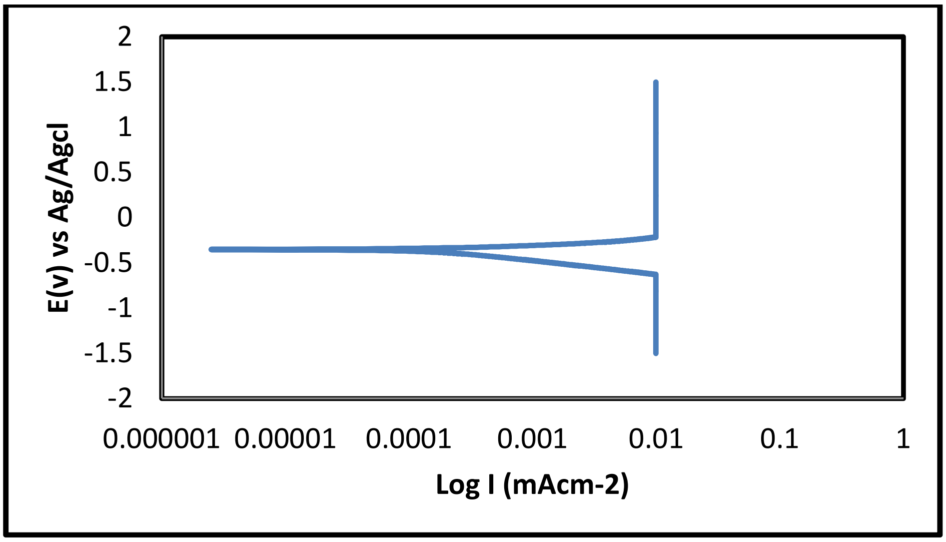



**Figure 8: Polarisation curve of mild steel in HCL+80% onion extract**

**Table 2: Polarisation results for the specimen immersed in HCl using different concentrations of per cent onion extract**

| % inhibitor concentrations and Control | ba (V/dec) | bc (V/dec) | Ecorr (V) | Icorr (A) | Corrosion Rate (CR) (mm/yr) | Polarisation resistance (Ω) |
|---|---|---|---|---|---|---|
| Control | 8.89E+00 | -6.85E+00 | -0.409 | 7.47E-04 | 7.68E+00 | 3.44E+01 |
| 20 | 1.22E+01 | -6.48E+00 | -0.419 | 5.29E-04 | 5.43E+00 | 4.86E+01 |
| 40 | 1.24E+01 | -6.25E+00 | -0.43 | 5.15E-04 | 5.30E+00 | 4.99E+01 |
| 60 | 1.08E+01 | -8.09E+00 | -0.354 | 2.54E-04 | 2.61E-00 | 1.01E+02 |
| 80 | 1.28E+01 | -7.76E+00 | -0.352 | 2.07E-04 | 2.13E+00 | 1.24E+02 |

The potentiodynamic curves for the unihibited mild steel specimens in HCl is presented in Figures 9.

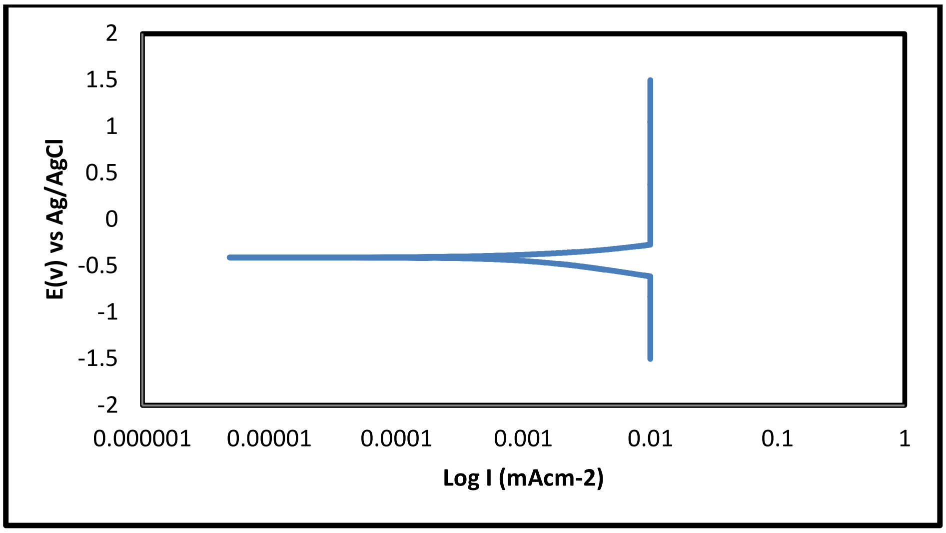



**Figure 9: Polarization curve of mild steel in HCL**

Viewed from the overall corrosion reactions parameter profile, it is apparent that the mild steel undergoes severe corrosion in 0.5M HCl when it is uninhibited by any inhibitor concentration. However, the same corrosion test cell with same test electrodes that was experimented with different concentrations of *allium cepa* (onion) extract concentrations show progressive inhibition, though not significantly, which improves in most cases with increase in the extract inhibitor concentration.

**Summary**

*Allium cepa*, (onion) has a very complex composition as mentioned in the introduction. Onion consists of phenolics and polyphenols. Polyphenols are known to effectively interact with reactive oxygen species. Polyphenols, particularly, flavonoids, have high complexation affinity to metals [20]. The inhibition efficiency of an inhibitor such as the onion extract 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 effectiveness of the inhibitory properties of onion extract in the acidic media of the test environments are confirmed by the results of the electrochemical tests which are very much in agreement with the gravimetric tests. The result of the extract concentrations that affected both the anodic and cathodic reactions according to the Tafel slope (ba and bc) values as presented in Table 2 confirms the onion extract inhibitor to be a mixed type inhibitor. The very complex structural compounds and diverse chemical constituents of onion extract exhibited electrochemical activity of minimal effective corrosion inhibition within the extract concentrations used in the HCl test medium.

## CONCLUSION

The effectiveness of allium cepa (onion) extract as green corrosion inhibitor for mild steel in HCl is confirmed by the gravimetric and electrochemical results.

The results both gravimetric and electrochemical confirmed the corrosion inhibition effectiveness of *allium cepa* (onion) on mild steel in HCl under the experimental conditions in which the investigation was performed.

Though not very significantly, the inhibition performance was concentration sensitive as all the result parameters responded positively – either increasing or decreasing with increase in per cent concentration of the extract inhibitor. The best corrosion inhibition in this work was achieved with the 80% onion extract concentration.

The corrosion inhibition performance of the onion extract inhibitor is associated with the very complex composition of diverse chemical compounds which consist among others, of phenolics and flavonoids with constituents such as quercetin and its glycosides quercetin 3, 4'-diglucoside and quercetin-4'-glucoside.

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