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Corrosion inhibition effect of *Allium Cepa* extracts on mild steel in H_2SO_4

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ABSTRACT

The effect of allium cepa extract as an inhibitor on mild steel corrosion in 0.5M H_2SO_4 was investigated at ambient temperature. The experiments were performed with gravimetric and potentiostatic polarization measurement methds. Polarization measurement was performed using a potentiostat (Autolab PGSTAT 30 ECO CHIMIE) interfaced with a computer for data acquisition and analysis. Corrosion inhibition of the extract on the steel test specimens in the different concentrations of H_2SO_4 used was achieved, though not very significant. There was increasing inhibition performance with increasing concentration of the extract inhibitor. The 80% onion concentration gave the best inhibition performance. A mixed type inhibitor is indicated with the results of ba and bc. A good correlation of results was obtained for the weight loss and polarization experiments.

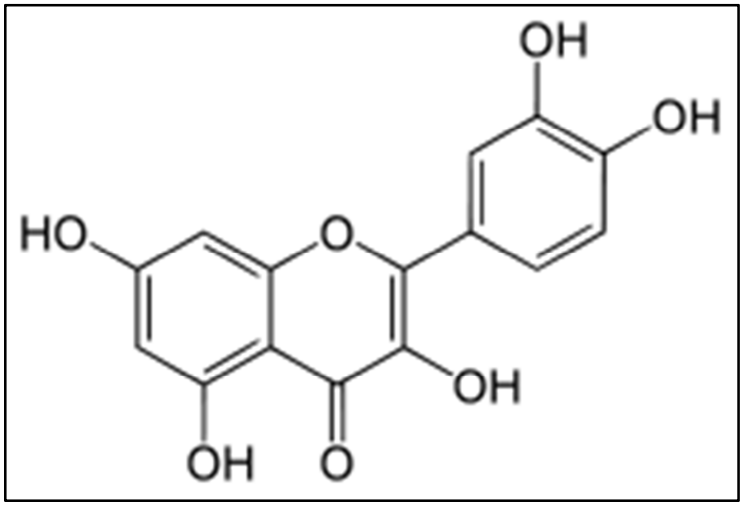
Key words: Corrosion, onion, mild steel, inhibition, sulphuric acid.

INTRODUCTION

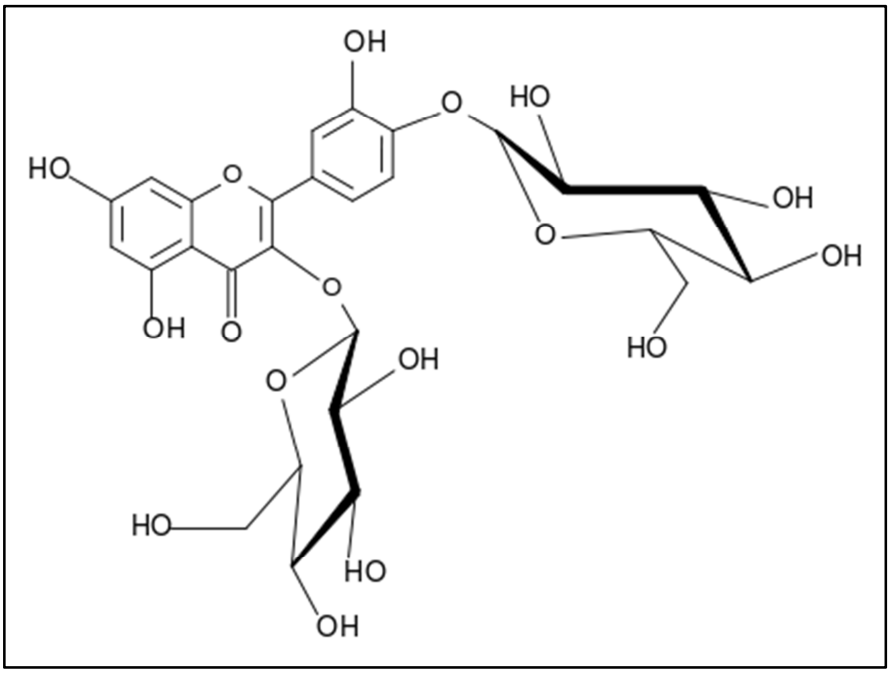
Mild steel is unique among other metallic materials. This is due to its very wide application and its usefulness in domestic, services, construction, marine, industrial and engineering purposes. However, it has a challenge of being subject to corrosive degradation in service. The use of chemical inhibitors is one of the means to mitigate this destructive phenomenon. Chemical inhibitors are chemical compounds that are adsorbed on the metal surfaces to control, prevent and/or minimise the destructive corrosion reactions.

Green inhibitors are the plant extracts that are used for corrosion inhibition of metals/ alloys in different test environments. Many researchers have recently shown interest in the use of these extracts for corrosion inhibitive control [1-12]. Corrosion inhibitive effect of plants' extracts has been attributed, in many cases, to the various complex chemical constituents of the extracts such as tannin and polyphenols among others [7-9]. These extracts of plants used as inhibitors are environment friendly.

Extract of onion (*Allium cepa)* is investigated in this work. *Allium cepa* are known [13] to contain on analysis, vitamin C, vitamin B_6, folic acid and small quantities of other nutrients. Phenolics and flavonoids are other chemical compounds found in onions [14]. These have been described to include quercetin and its glycosides quercetin 3, 4'-diglucoside and quercetin-4'-glucoside [15].



Quercetin (a polyphenol) - a typical flavonoid [15]



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

The complex chemical compositions contained in *Allium cepa* is expected to provide effective corrosion inhibition of the mild steel in the tested environment. This work aims at obtaining positive result that will be of economic and technological benefit.

MATERIALS AND METHODS

2.1. *Preparation of specimens*

Preparation of the experimental specimens has been previously described [17]. The mild steel specimen used as test specimens was locally obtained from a rolling mill in Nigeria. Table 1 shows the per cent nominal composition of the metal. 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 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 in test solution to further prevent 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. Copper wire was spot welded to each of the samples which were thereafter mounted in resin to ensure that only the surface of the samples were exposed to the corrosive medium.

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 Medium*

The experiment was performed in sulphuric acid medium, 0.5M H_2SO_4 of AnalaR grade. Onion was obtained from a local market near the Covenant University, Ota, Nigeria. 1.25Kg of the onion was chopped into pieces together with bark and soaked in 2.5litres 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 H_2SO_4.

2.3. *Weight loss experiment*

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 sulphuric acid test media in which the *allium cepa* extract was added except for the control experiment. 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 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 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 H_2SO_4 in the 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

3.1 **Weight loss method**

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

3.1.1 *Weight loss of mild steel in 0.5M H_2SO_4 + Different concentrations of onion extract*

Results obtained for the weight loss experiments performed with the different concentrations of the *allium cepa* extract in 0.5M H_2SO_4 are presented in Fig. 1.The mild steel sample immersed in the solution with 20% inhibitor concentration lost the most weight as at the 120 hours (5 days) of the experiment with a weight loss of 5.0978g.

The value for the control experiment (without inhibitor addition) is 4.6059 in the first 3 days of the experiment and thus recorded the highest weight loss within this period. However, that changed into the lowest weight loss values as at 10 days with values ranging between 4.9731g and 5.0909g as at 408 hours (17 days) of the experiment.

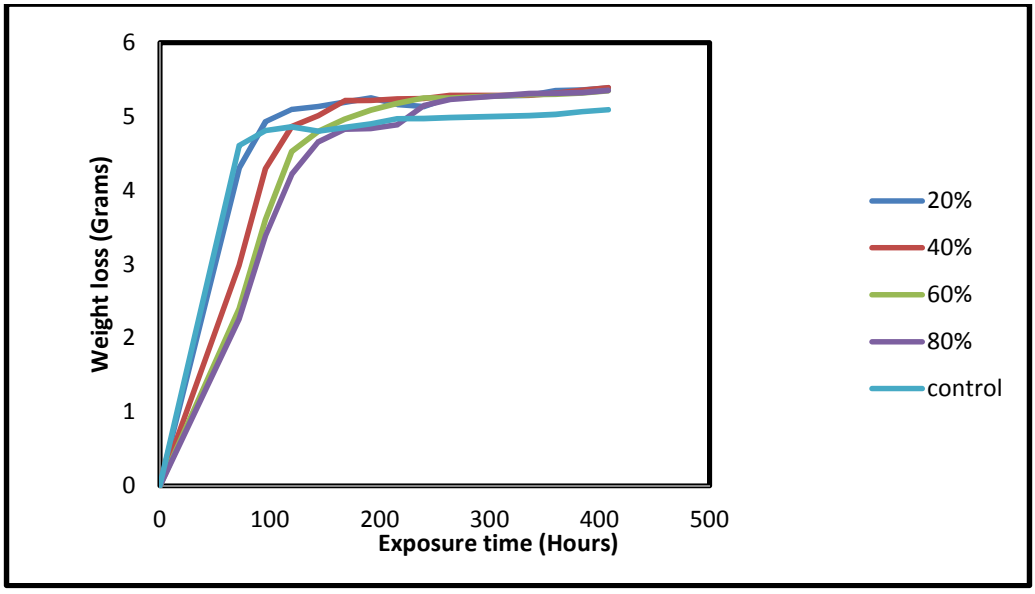


Figure 1: Plot of weight loss with exposure time for mild steel immersed in 0.5M H_2SO_4 in addition of different concentrations of onion extract

The mild steel sample immersed in the solution with 40%, 60% and 80% of inhibitor concentrations showed corrosion inhibition values of 5.349 (360 Hrs), 5.254 (240 Hours) and 5.314g at 360 hours (15 days) of the

experiment respectively. Thus with these values, except in the first three days, *allium cepa* did not perform very well as an extract inhibitor in 0.5 M H_2SO_4.

3.1.2. *Corrosion rate of mild steel immersed in 0.5M H_2SO_4 in different concentrations of onion extract*
Presented in Figures 2 are the corrosion rates with exposure time for the experiments whose weight loss measurements have just been reported above in Figure 1

In Figure 2, the specimen immersed in 0.5M H_2SO4, recorded corrosion rate values that decreased with time. As at 192 hours (8 days) of the experiment, the 20% extract concentration apart from the control had the highest corrosion rate value of 92.584 mm//yr. The corrosion rate values decreased steadily with the increase in extract inhibitor concentration achieving 50.269, 49.041, 46.611 mm/yr for 40, 60 and 80% inhibitor concentrations respectively.

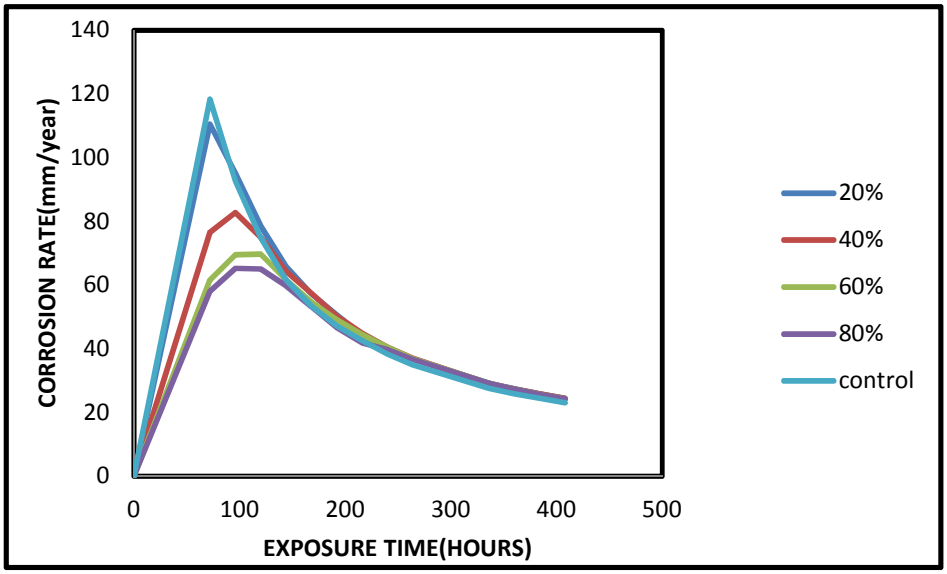


Figure 2: Variation of corrosion rate with exposure time for mild steel immersed in 0.5M H_2SO_4 in addition of different concentrations of onion extract

As at 144 hrs (6 days) of the experiment the 80% extract inhibitor concentration has the lowest corrosion rate value of 59.8400 m/yr. At the same period the control test recorded corrosion rate value of 61.6731 mm/yr.

3.1.3. Surface coverage of mild steel immersed in 0.5M H_2SO_4 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 H_2SO_4. A clear observation recorded in Figure 3 is that the surface coverage started high at about 72 hours (3 days) of the experiment. In the Figure 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. The test with the 20% inhibitor concentration achieved negative values of surface coverage after 96 hours (4 days). As at 120 hours (5 days) of the experiment, all other inhibitor concentrations performed with the positive values of surface coverage: 0.001, 0.068, and 0.131 for 40, 60, and 80% inhibitor concentrations respectively after which they maintained negative values throughout the experimental period.

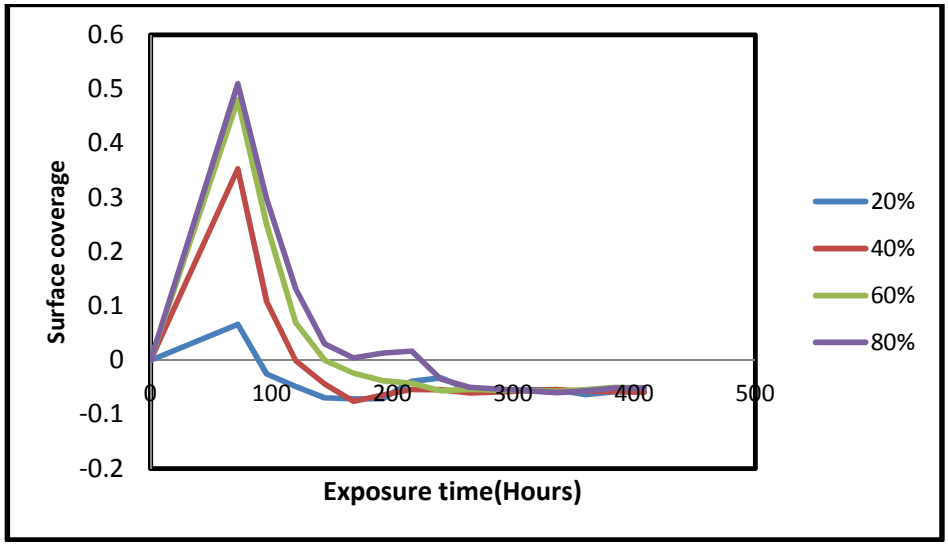


Figure 3: Curves of surface coverage with exposure time for mild steel immersed in 0.5M H_2SO_4 in addition of different concentrations of onion extract

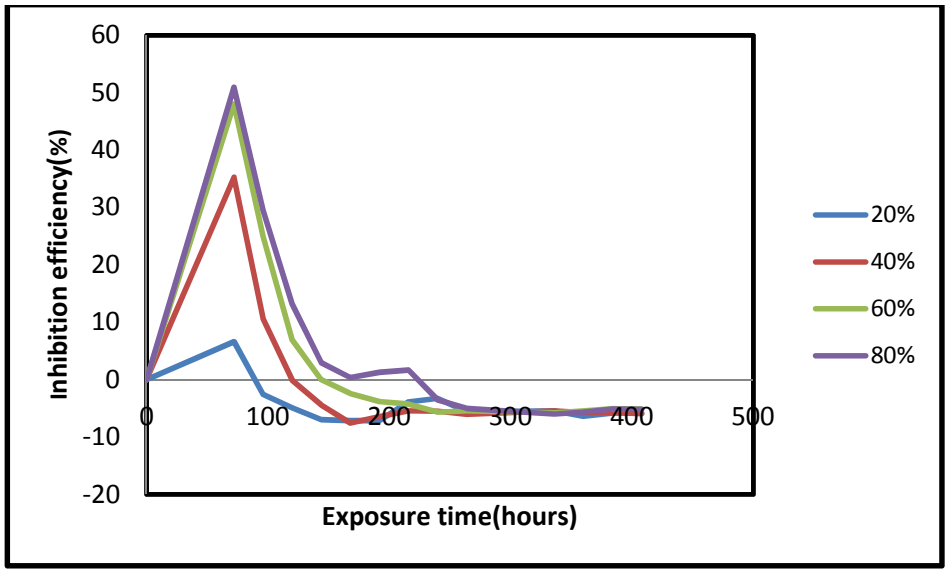


Figure 4: Curves of inhibition efficiency with exposure time for mild steel immersed in 0.5M H_2SO_4 in addition of different concentrations of onion extract

3.1.4. *Inhibition efficiency of mild steel immersed in 0.5M H2SO4 in different concentrations of onion extract*

The results obtained for the corrosion inhibition efficiency of mild steel immersed in 0.5M H_2SO_4 test environments at different concentrations of *allium cepa* extract are presented in Figures 4. In general, the per cent inhibition efficiency (I.E.) decreased from the initial high values with the exposure time. Results in Figure 4, clearly show that all the per cent inhibitor concentrations decreased in inhibitor efficiency with the inhibitor concentration. Within 4 days of the experiment the 20, 40 and 60% have all recorded negative values. The results obtained with these inhibitor concentrations, was an indication that instead of corrosion inhibition expected, the concentrations increased the corrosion reactions just after 4 days of the experiment. The 20% extract concentration was minimally effective only for about 72 hours (3 days) of the experiment, achieving 6.61% inhibitor efficiency value after which it remained in negative values throughout. As at 120 hours (5 days) of the experiment, per cent inhibition values of -4.902, -0.134, 6.877 and 13.141 were recorded for inhibitor concentrations of 20, 40, 60 and 80 respectively. As at 240 hours (10 days) of the experiment the inhibition efficiency has decreased for each of the inhibitor

concentrations, with all achieving negative values indicating lack of inhibition at that period and throughout the experimental duration.

3.2. Electrochemical Corrosion Polarization Measurement

The results obtained for the electrochemical corrosion polarization measurement for the mild steel separately immersed in H_2SO_4 test media using onion (*allium cepa*) extract as green inhibitor are presented in Figures 5 to 8.

3.2.1. *Mild steel in H_2SO_4 with various concentrations of Allium Cepa (onion) extract*

The corrosion polarisation curves for the mild steel test specimens in H_2SO_4 using separately different concentrations of onion (*allium cepa*) extract as inhibitor are present in Figures 5 to 8. The results for the experiments are summarised in Table 2. As indicated in the Table 2, the control experiment showed the highest corrosion intensity as indicated in the Table 2. The corrosion rate is 1.116E+01 mm/yr; current density (Icorr), 1.13E-03 A/cm^2; open corrosion potential (Ecorr value of -0.419 and polarisation resistance, Rp, 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. It has an open corrosion potential (Ecorr) value of -0.414V, the corrosion rate (CR) value was 6.63E+00 mm/yr; while the corrosion polarisation resistance, Rp, value recorded was 3.98E + 01Ω and a value of 6.45E-04 A/cm^2 was recorded for corrosion current density (Icorr).

The results for 40, 60 and 80% inhibitor concentrations as presented in Figures 5 to 9 and summarised in Table 2, showed progressive improvement in corrosion resistance values than that of 20%'s. This is clearly indicated by the decreasing corrosion rates, increasing polarisation resistance and decreasing current density, Icorr, values. The values of the Tafel slope (ba and bc) indicate that the onion extract inhibits both cathodic and anodic reactions and thus confirms that the inhibitor is a mixed corrosion inhibitor. Also, these results are very much in agreement with the results obtained for the weight loss measurements described above.

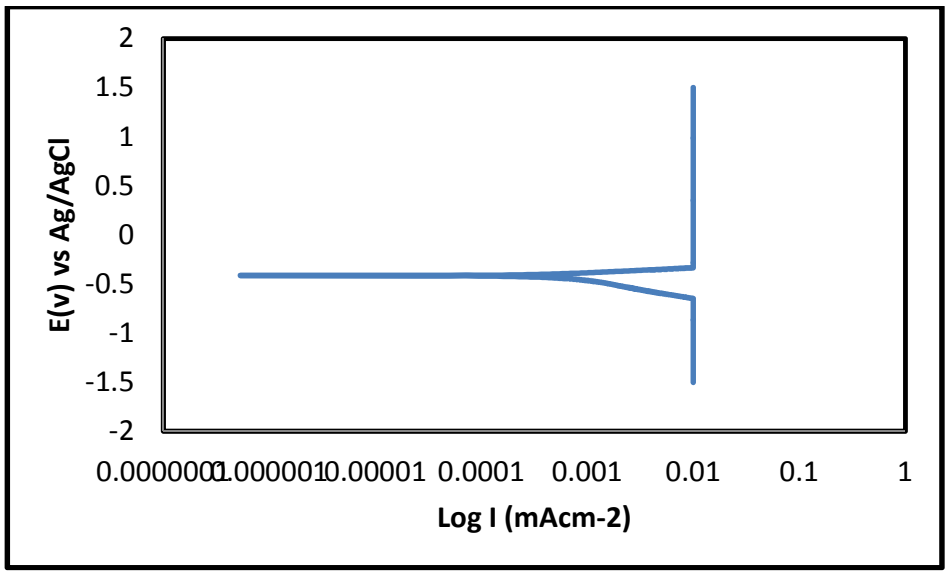


Figure 5: Polarization curve of mild steel in H_2SO_4 +20% onion extract

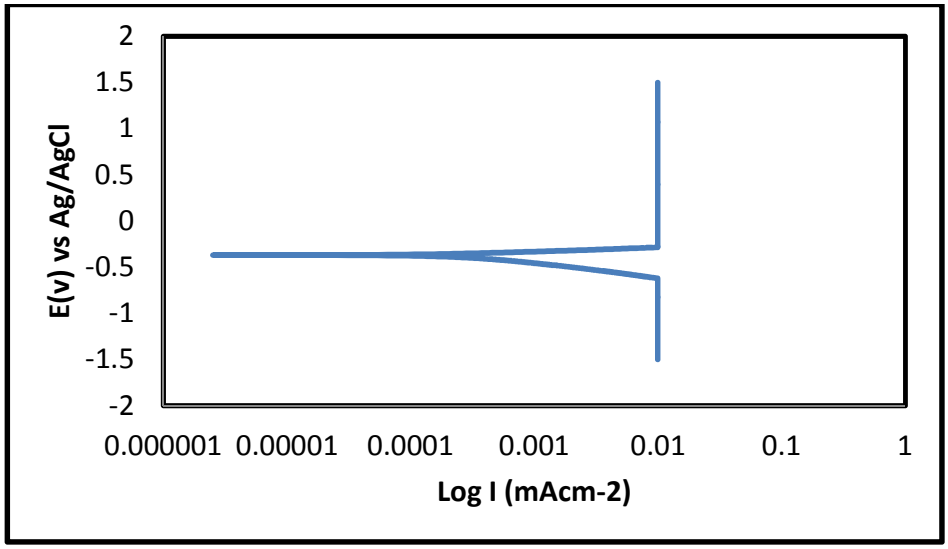


Figure 6: Polarization curve of mild steel in H_2SO_4 +40% onion extract

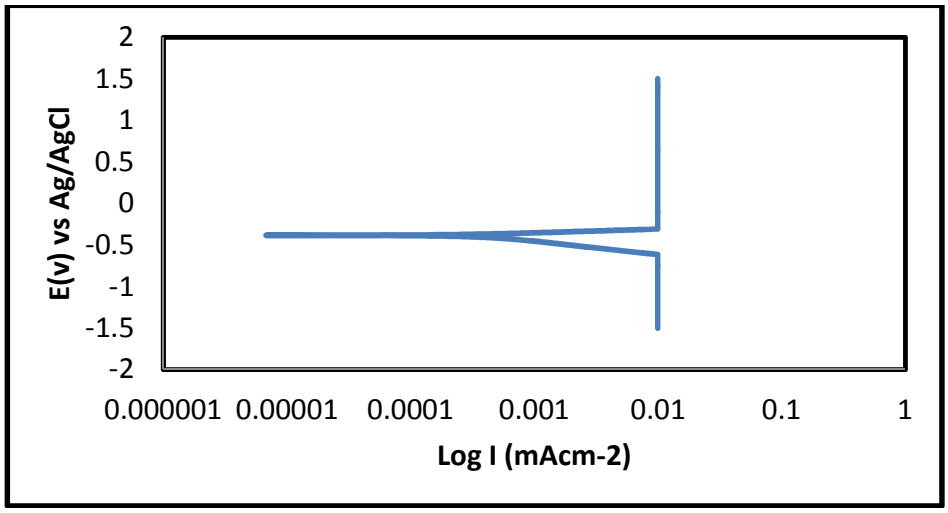


Figure 7: Polarization curve of mild steel in H_2SO_4 +60% onion extract

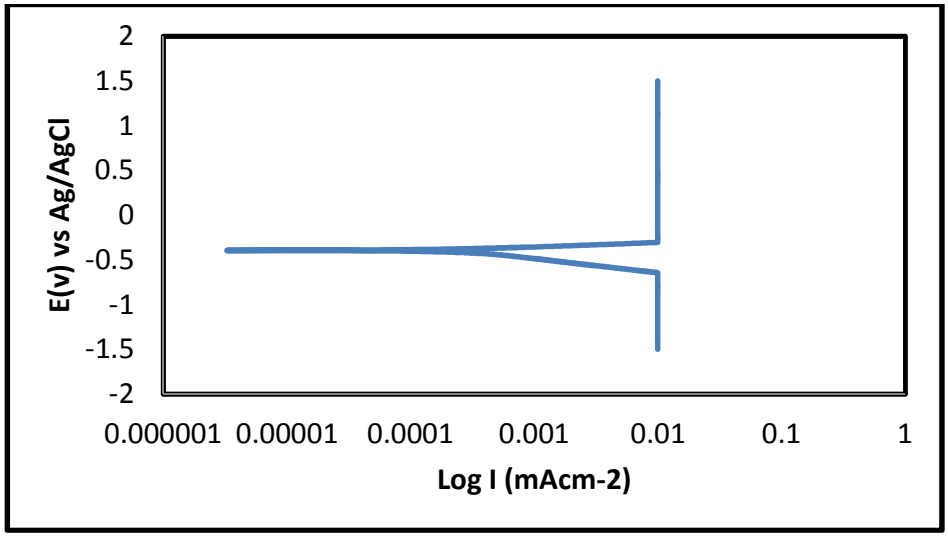


Figure 8: Polarization curve of mild steel in H_2SO_4 +80% onion extract

Table 2: Polarizaton results for the mild steel specimen immersed in H_2SO_4 with various concentrations of 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	5.34E+00	-6.68E+00	-0.419	1.13E-03	1.116E+01	2.27E+01
20	1.26E+01	-5.58E+00	-0.414	6.45E-04	6.63E+00	3.98E+01
40	1.70E+01	-7.65E+00	-0.369	3.13E-04	3.22E+00	8.21E+01
60	1.14E-01	-6.44E+00	-0.384	4.98E-04	5.12E+00	5.16E+01
80	1.90E+01	-6.56E+00	-0.394	3.54E-04	3.64E+00	7.25E+01

The potentiodynamic curves for the unihibited mild steel specimens in H_2SO_4 are respectively presented in Figure 9.

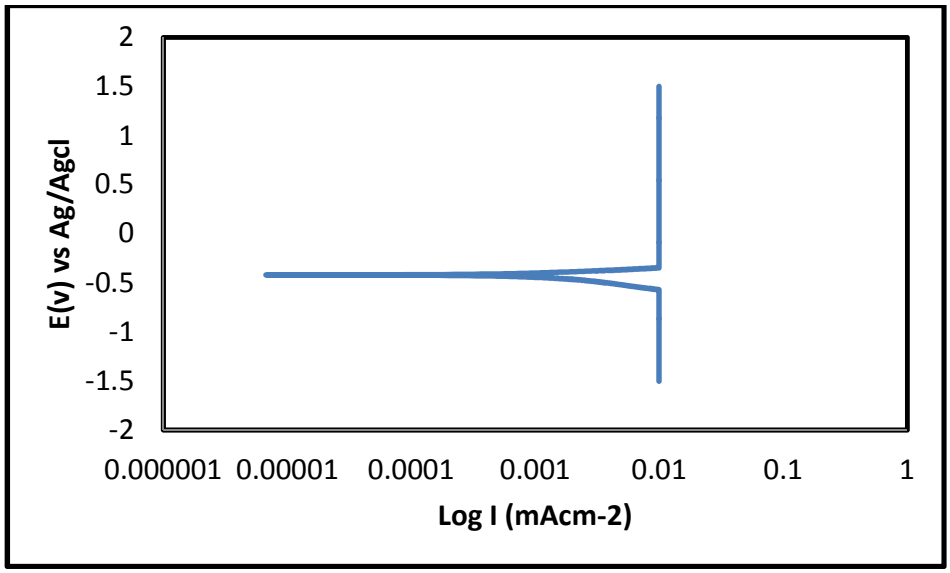


Figure 9: Polarization curve of mild steel in H_2SO_4 without inhibitor addition (Control)

It is apparent, when viewed from the overall corrosion reactions parameter profile, that the mild steel undergoes severe corrosion in 0.5M H_2SO_4 when it is uninhibited by any inhibitor concentration. When the test electrodes were experimented with different concentrations of *allium cepa* (onion) extract concentrations, there was progressive

corrosion inhibition, though not significantly. The inhibition improves, in most cases, with increase in the extract inhibitor concentration.

Summary
It is important to emphasise again that onion (*allium cepa*) has a very complex composition. 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. This 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 [20]. *Allium cepa* consists of phenolics and polyphenols. Polyphenols are known to effectively interact with reactive oxygen species. Polyphenols, particularly, flavonoids, have high complexation affinity to metals [9].

The results of the electrochemical tests which are very much in agreement with the gravimetric tests confirm the effectiveness of the inhibitory properties of onion extract in the acidic test environment. The result of the extract concentrations affected both the anodic and cathodic reactions according to the Tafel slope (ba and bc) values in Tables 2 and thus confirms the extract inhibitor as a mixed type inhibitor. The diverse chemical constituents and complex structural compounds of onion extract clearly exhibited electrochemical activity of effective corrosion inhibition though not significantly. The sulphuric acid test environment at the concentration of 0.5M used seemed to be too strong to achieve improved significant mild steel corrosion inhibition of the extract.

CONCLUSION

The gravimetric and electrochemical results confirm the effectiveness of *allium cepa* (onion) extract as green corrosion inhibitor for mild steel in H_2SO_4 under the experimental conditions in which the investigation was performed.

The inhibition performance, though not very significant 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 corrosion inhibition performance of the onion extract is associated with the very complex composition of diverse chemical compounds such as phenolics and flavonoids with constituents such as quercetin and its glycosides quercetin 3, 4'-diglucoside and quercetin-4'-glucoside.

The best corrosion inhibition was achieved with the 80% onion extract concentration used.

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