

Full Length Research Paper

Effect of neem leaf (*Azadirachita indica*) extract on the corrosion inhibition of mild steel in dilute acids

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The corrosion inhibition performance of Neem leaf (*Azadirachita indica*) extract on the corrosion of mild steel test specimen immersed in 0.5 M HCl and H₂SO₄ acids respectively at the ambient temperature of 30°C and elevated temperature of 80°C was investigated. The experimental work was performed by the use of weight loss method and the potential measurement technique. From the weight loss values, corrosion rates were determined by calculation. In the results obtained, the leaf extract, in sulphuric acid medium, gave its best corrosion inhibition performance at 0.50 g/l extract concentration at 30°C. A more appreciable corrosion inhibition performance was achieved in the dilute hydrochloric acid at 0.25 g/l extract concentration and also at 30°C.

Key words: Neem extract, corrosion, inhibition, corrosion rate, mild steel, weight loss, sulphuric and hydrochloric acids.

INTRODUCTION

The use of plant extracts as inhibitors for the corrosion of metals/alloys, has gained very wide interest among researchers in recent time (Loto et al., 2005; Okafor, 2007, Davis, et al, 2003., Fraunhofer et al., 1995; Davis et al., 2001; Fraunhofer, 2000; Loto, 2003). In very many cases, the corrosion inhibitive effect of some plants' extracts has been attributed to the presence of tannin in their chemical constituents (Loto, 2003). Also associated with the presence of tannin in the extracts is the bitter taste in the bark and/or leaves of the plants. The use of Neem (*Azadirachita indica*) leaves in this investigation is another further effort in making a contribution to this current interest in corrosion inhibition properties of plants. The unusual biological properties of the Neem tree had been well known in the Indian subcontinent for many centuries but only attracted the interest of scientists in the past 40 to 50 years (Hello indya.com, 2011). Neem is bitter in taste. The bitterness is due to an array of complex compounds called "triterpenes" or more specifically, "limonoids" (Hello indiya.com, 2011). Nearly

100 protolimonoids, limonoids, or tetranotriterpenoids, pentanortriterpenoids, hexanortriterpenoids and some nonterpenoid constituents have been isolated from various parts of the Neem tree (Jones et al., 1984) and still, more are being isolated. The most important bioactive principal constituent is azadirachtin. The chemistry of the Neem tree leaves has widely been investigated (Hello indya.com, 2011; Siddiqui et al., 1984). Neem bark and leaves are known to possess diverse and multifarious therapeutic uses for the treatment of many ailments/diseases. Fresh leaves of Neem tree are also known (Hello indya.com, 2011) to contain among others, the following physico-chemical compounds: calcium (510 mg/100 g), phosphorus (80 mg/100 g), iron (17 mg/100 g), thiamine (0.04 mg/100 g), niacin (1.40 mg/100 g), vitamin C (218 mg/100 g), carotene (1,998 µg/100 g), tyrosine (31.50 mg/100 g), alanine (6.40 mg/100 g), proline (4.00 mg/100 g), glutamine (1.00 mg/100 g), glutamic acid (73.30 mg/100 g), aspartic acid (15.50 mg/100 g), carbohydrates (22.9%), minerals (3.4%), proteins (7.1%), fibre (6.25%) moisture (59.4%), and calorific value 1290 Kcal/Kg. In addition to azadirachtin mentioned earlier, there are many other active compounds found in the Neem tree.

The other most common are: nimbin, nimbidin,

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Table 1. Inhibitor efficiency.

Test medium (0.5 M)	Temperature (°C)	Neem leaf extract concentration (g/l)	Corrosion rate (mm/year)	Extract inhibitor efficiency (%)
HCl	30	-	20.75	-
	80	-	43.37	-
	30	0.25	15.06	27.42
	80	0.25	37.93	12.54
	30	0.50	15.07	27.37
	80	0.50	38.51	10.98
H ₂ SO ₄	30	-	48.87	-
	80	-	85.92	-
	30	0.25	49.35	-9.82
	80	0.25	4.86	12.87
	30	0.50	37.10	24.08
	80	0.50	71.08	17.27

nimbidol, sodium nimbinat, geduin, salanin and quercetin – all which possess significant pharmaceutical applications (www.neem foundation.org, 2011). The Neem tree is widely distributed in India and many other Asian countries, West Indies, West Africa and in East Africa. With the type of its highly complex structural compounds, it is expected that a good corrosion inhibition property will be exhibited by this tree – the leaves and the bark in particular. In this work, the corrosion inhibition performance of the Neem leaves solution extract on the corrosion of mild steel test specimens in 0.5 M HCl and H₂SO₄ has been studied at both the ambient temperature of 30°C and at the elevated temperature of 80°C. These acids were selected for investigation because of their known and very strong corrosive action. A positive result from this investigation could lead, later to the identification of the specific compound(s)/active constituents in the leaves that exhibit(s) the corrosion inhibition. This could be economically and technologically beneficial.

Experimental procedure

The experimental procedure here follows that of other previous investigations (Loto CA 2003). The nominal per cent composition of the mild steel used in this work was: 0.19 C, 0.25 Si, 0.64 Mn, 0.05 S, 0.06 P, 0.09 Ni, 0.08 Cr, 0.02 Mo, and 0.27 Cu, the rest being Fe. The bar was cut into various rectangular pieces of dimensions 2.90 x 14.50 x 20 mm. The test specimens were descaled using a wire brush; ground with silicon carbide abrasive paper of 240, 320 and 400 grits; polished to 1 micron, thoroughly cleaned and rinsed in ultrasonic cleaner, and dried and kept in a desiccator for further tests. Selected specimens were, in turn spot welded to a connecting insulated flexible wires and mounted in araldite resin. They were subsequently used for potential measurement.

Preparation of test media and neem leaf extract

The Neem leaf extract used as inhibitor was obtained by oven

drying the fresh leaves at 1150°C for 2 h. The dried leaves were ground into powder; and a small amount of 20 g was put into 250 ml of 0.5 M HCl and 0.5 M H₂SO₄ in a beaker, in turns. These were boiled for 2 h and left overnight. The solutions were then filtered with filter papers. Two different concentrations of Neem leaf extract were made from these: the 0.25 g/l and the 0.5 g/l for the hydrochloric and sulphuric acid test media respectively. The acids were of AnalaR grade.

Weight loss experiment

Weighed test specimens were totally immersed in each of the test media contained in a 250 ml beaker for 25 days. Experiments were performed with acid test media in which some had the solution extract added. Test specimens were taken out of the test media every 5 days, washed with distilled water, rinsed with methanol, air-dried, and re-weighed. Plots of weight loss versus the exposure time and of calculated corrosion rate versus time of exposure (Figures 1 to 8) were made. All the experiments were performed at a temperature of 30 and at 80°C respectively. The percentage inhibitor efficiency, P, was calculated from relationship:

$$P = 100 (1 - W_2) / (W_1) \quad (1)$$

Where W₁ and W₂ are the corrosion rates in the absence and presence, respectively, of a predetermined concentration of inhibitor. The percent inhibitor efficiency was calculated for all the inhibitors as at the 25th day of the experiment, and the results are presented in Table 1.

Potential measurements

Potential measurements were performed on the mounted specimens in turns by immersing them in each of the acid test media with and without inhibitor (plant extract). The potential was recorded at 5 – day intervals using a digital voltmeter and saturated calomel reference electrode.

RESULTS AND DISCUSSION

The results obtained for the variation of weight loss with

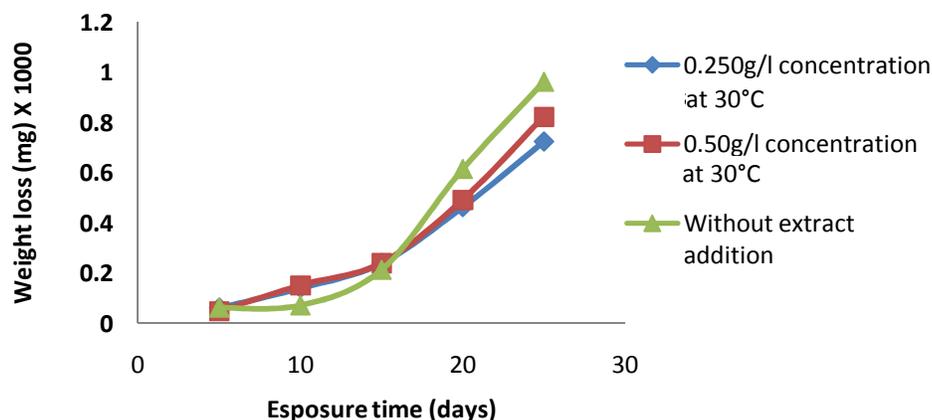


Figure 1. Variation of weight loss with exposure time for the mild steel test specimen immersed in 0.5 M HCl at 30°C with and without Neem's leaf extracts addition.

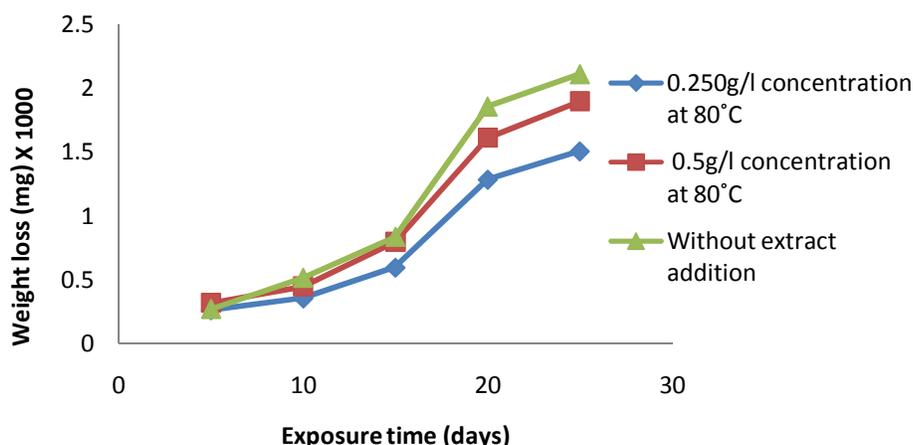


Figure 2. Variation of weight loss with exposure time for the mild steel test specimen immersed in 0.5 M HCl at 80°C with and without Neem's leaf extracts addition.

exposure time and for their calculated corrosion rates also with exposure time, for the mild steel test specimen immersed in the two test media - 0.5 M HCl and 0.5 M H₂SO₄ at 30 and 80°C are presented in Figures 1 to 8. The recorded values obtained for the tests performed without any extract addition, are also presented in each of the figures. An increase in weight loss of the test specimens with exposure time was recorded for the two concentrations of the plant extract addition at 30°C for both tests, Figure 1. More loss of weight for the test specimens was, however, observed in the test in which there was no Neem extract addition.

HCl test medium

The addition of 0.25 and 0.5 g/l of the extract to 0.5 M

HCl test medium at 30°C, Figure 1, did not give much significant difference in the weight loss of the mild steel test specimens. However, though very close results in terms of weight loss values, there appeared to be marginal better corrosion inhibition performance with the lower extract concentration of 0.25 g/l in the 25 days of the experiment except the first 5 days. These results also reflected in the calculated corrosion rates. The concentration effect in these results seems difficult to explain as 0.50 g/l could not be said to be more than the inhibitor optimum limit at this stage of the work/report. At the elevated temperature of 80°C, Figure 2, the weight loss for the two concentrations of 0.25 and 0.50 g/l increased very significantly. This was not unexpected, as every rise in temperature increases corrosion reactions through increased atomic/molecular vibrations/agitations and diffusional movement(s). At 0.25 g/l the weight loss

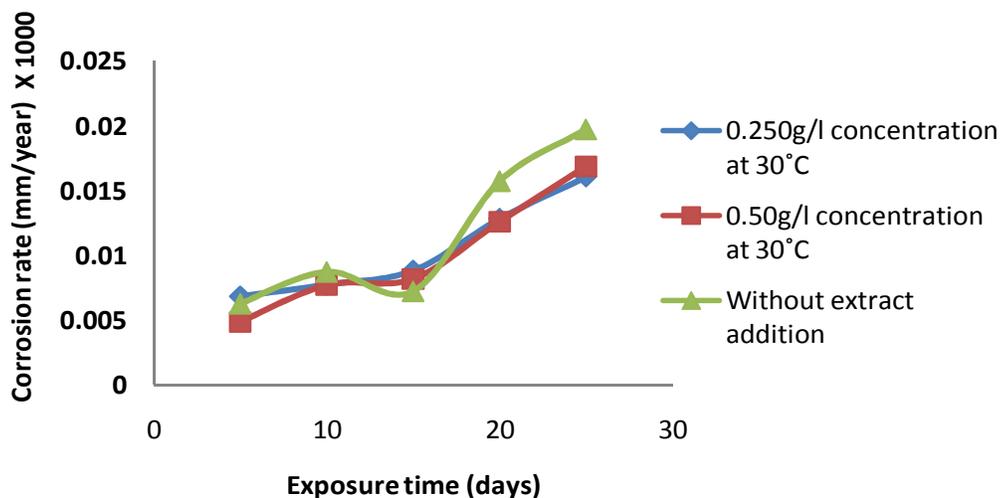


Figure 3. Variation of corrosion rate with exposure time for the mild steel test specimen immersed in 0.5 M HCl at 30°C with and without Neem's leaf extracts addition.

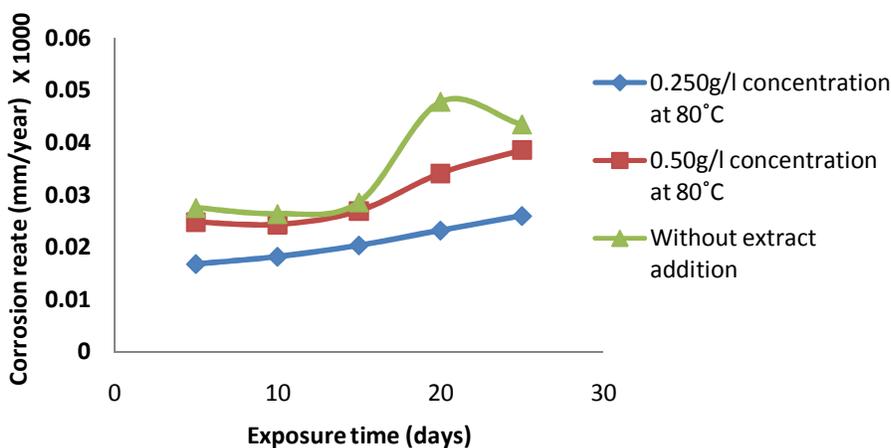


Figure 4. Variation of corrosion rate with exposure time for the mild steel test specimen immersed in 0.5 M HCl at 80°C with and without Neem's leaf extracts addition.

ranged between 260.5 mg (0.265 g) to 1,506.3 mg (1.506 g/l) from the first day to the 25th day of the experiment. At 0.50 g/l, the range was between 318.2 (0.318) to 1,897 mg (1.897 g) at the same period of the experiment. Again, the corrosion inhibition performance of the 0.25 g/l concentration of the extract was better than the 0.50 g/l concentration. When these results are compared with the recorded weight loss and corrosion rates obtained from the test without extract addition (weight loss of 2,111.7 mg (2.11 g)) as at the 25th day of the experiment, it could be said that there was some amount of corrosion inhibition by the addition of the Neem leaf extract and hence some degree of protection. The variation of corrosion rate with exposure time calculated for the test specimens immersed in 0.5 M HCl for the two

concentrations of 0.25 g and 0.50g/l of the Neem extract are presented in Figures 3 and 4. The corrosion rate, in all the figures, increased with the exposure time though not drastically. The strength of the acid medium used and its reaction with mild steel in particular could account for this increasing phenomenon. The corrosion products generated and deposited on the specimens tend to slow down the corrosion rate as the exposure time increased.

The corrosion rate was much higher with the test at the elevated temperature of 80°C for the two different concentrations of Neem extract used. It recorded the corrosion rates of 25.93 and 38.51 mm/year respectively as at the end of the experiment. At 30°C, the corrosion rate was much lower for the two concentrations of the extract – 16.06 and 16.89 mm/year respectively. The

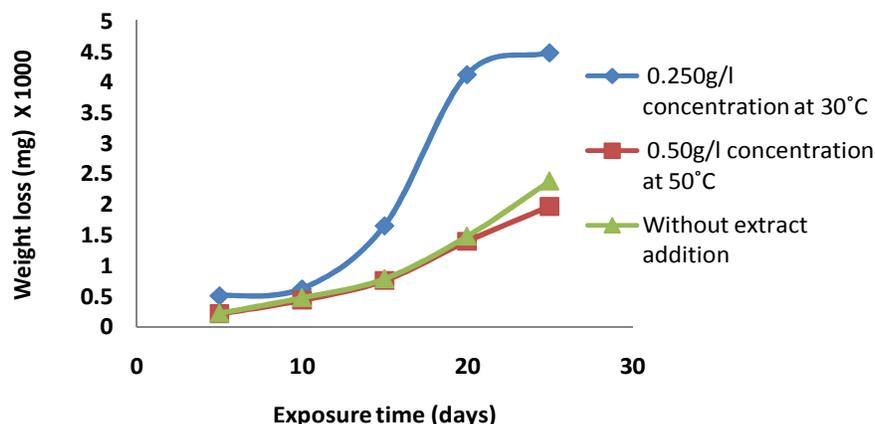


Figure 5. Variation of weight loss with exposure time for the mild steel test specimen immersed in 0.5 M H₂SO₄ at 30°C with and without Neem's leaf extracts addition.

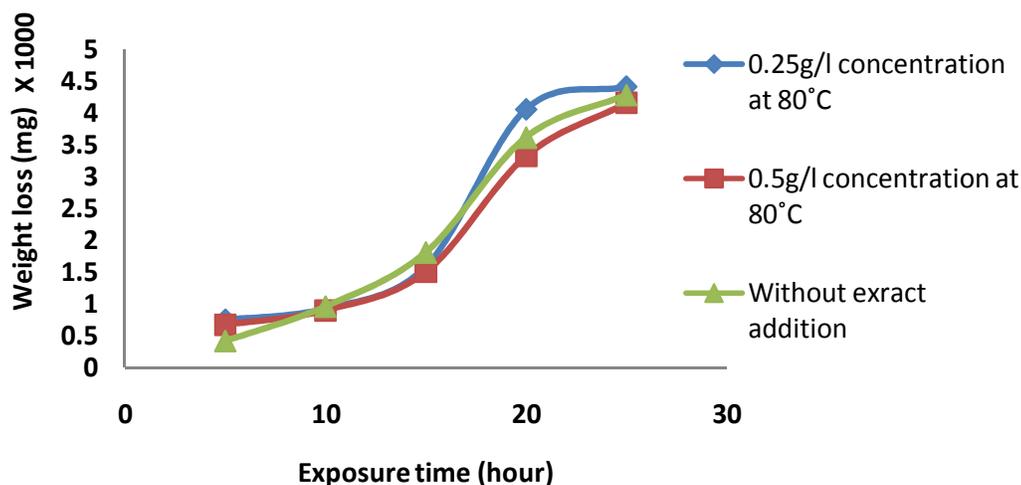


Figure 6. Variation of weight loss with exposure time for the mild steel test specimen immersed in 0.5 M H₂SO₄ at 80°C with and without Neem's leaf extracts addition.

effect of temperature on corrosion rate here is apparent. A comparison of the above corrosion rate results with the test without Neem leaf extract addition as inhibitor, gave very much higher values of corrosion rate at both the temperatures of 30 and 80°C (19.75 and 43.37 mm/year respectively).

H₂SO₄ test medium

The curves of variation of weight loss and also of corrosion rate with exposure time for the mild steel specimens immersed in 0.5 M H₂SO₄ with and without Neem leaf extract addition, at the concentrations of 0.25 and 0.50g/l and at 30 and 80°C, respectively, are presented in Figures 5 to 8. Weight loss in H₂SO₄ at 30

and 80°C at 0.25 and 0.50 g/l extract concentration was far more than what obtained in the HCl test medium under the same experimental operating parameters. The weight loss at an extract concentration of 0.25 g/l at 30°C achieved 4,477 mg (4.477 g) in the 25 days of the experiment. The corrosion rate also ranged from 35.01 at the beginning to 59.35 mm/year at the end of the experiment. There was no apparent corrosion reactions inhibition at this extract concentration when compared with the test without added Neem leaf extract. At 80°C, the same trend of high weight loss and increased corrosion rate of 74.86 mm/year was achieved. The concentration of 0.50 g/l in H₂SO₄ test medium gave a good corrosion inhibition performance for about 15 days of the experiment. The results obtained were far better than those obtained from the test without added Neem

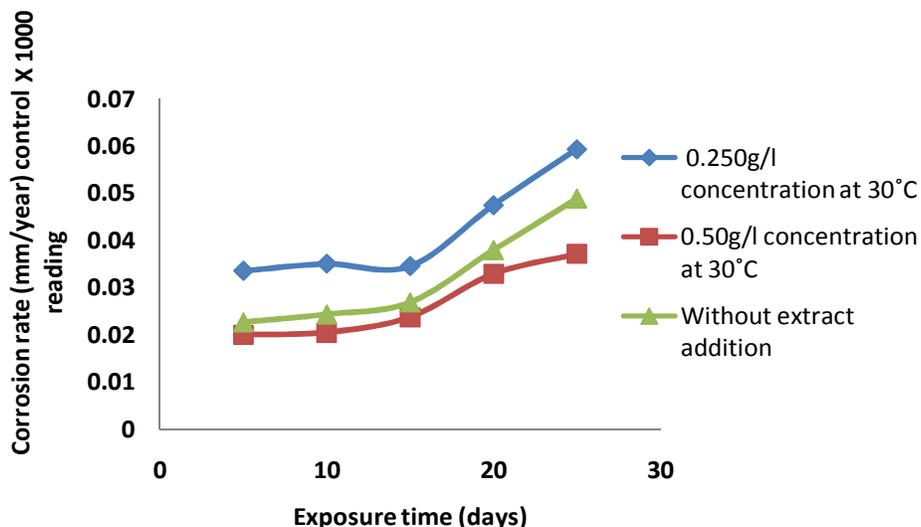


Figure 7. Variation of corrosion rate with exposure time for the mild steel test specimen immersed in 0.5 M H_2SO_4 at 30°C with and without Neem's leaf extracts addition.

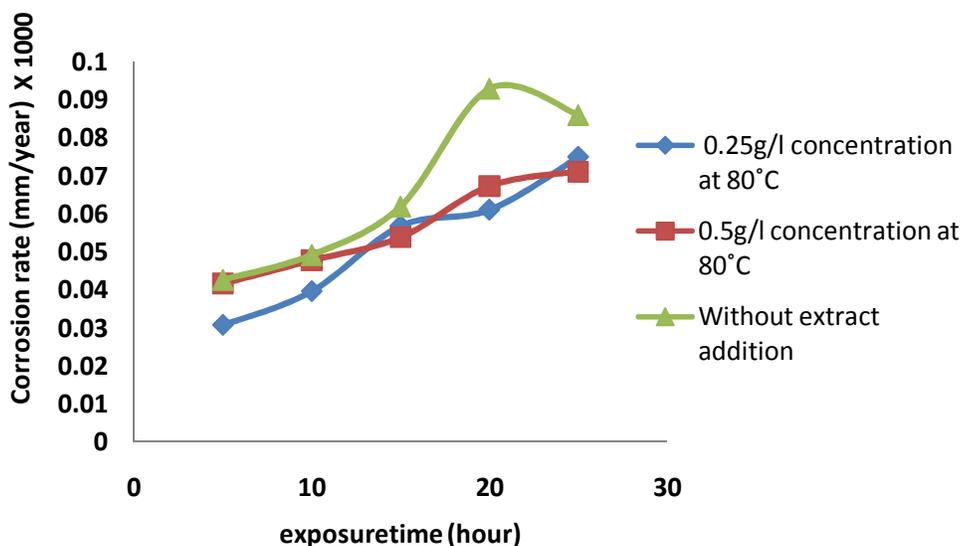


Figure 8. Variation of corrosion rate with exposure time for the mild steel test specimen immersed in 0.5 M H_2SO_4 at 80°C with and without Neem's leaf extracts addition.

leaf extract at both the temperatures of 30 and 80°C respectively, Figures 5 to 8. At 30°C, the final weight loss at the 25th day of the experiment was 1,967.3 mg (1.967 g) and the corrosion rate at the same day was 37.10 mm/year. At 80°C, the weight loss increased significantly to 4,153 mg (4.153 g) because of the elevated temperature. This elevated temperature, increased the kinetics of corrosion reactions as a result of increased atomic/molecular vibrations as explained earlier. In consequence, there will be increase in weight loss and higher corrosion rate values. Sulphuric acid is a very

strong and aggressive inorganic acid that always has devastating corrosive effect on mild steel in particular. The strength/concentration of the two acids used was high at 0.5 M. The inhibiting chemical film from the complex chemical constituents/compounds in the Neem leaf extract, could not maintain stability in this acid environments. These could have contributed to the weak corrosion inhibition performance in these two test media. The calculated inhibitor efficiency, Table 1, was, therefore, low.

In general, inhibitors possess specificity characteristics,

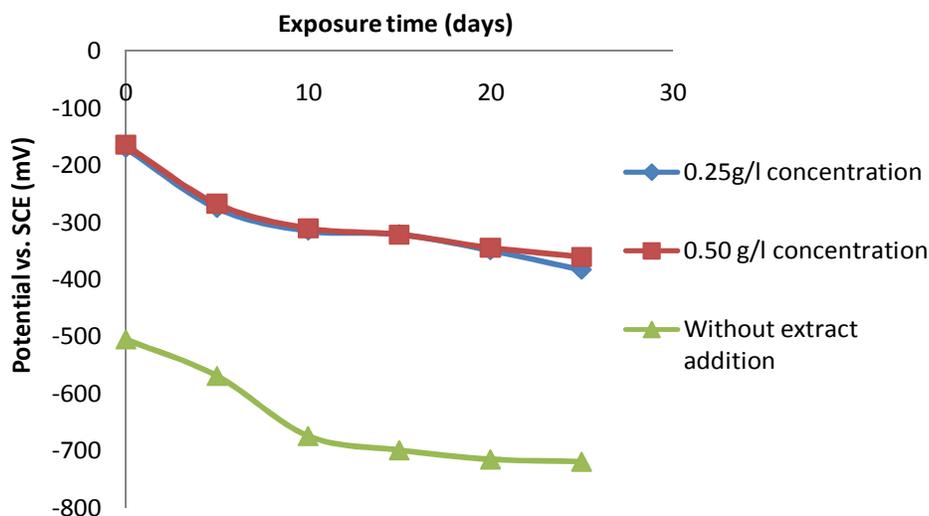


Figure 9. Variation of potential (vs. SCE) with exposure time (days) for the mild steel test specimen immersed in 0.5 M HCl at 30°C with and without Neem's leaf extracts addition.

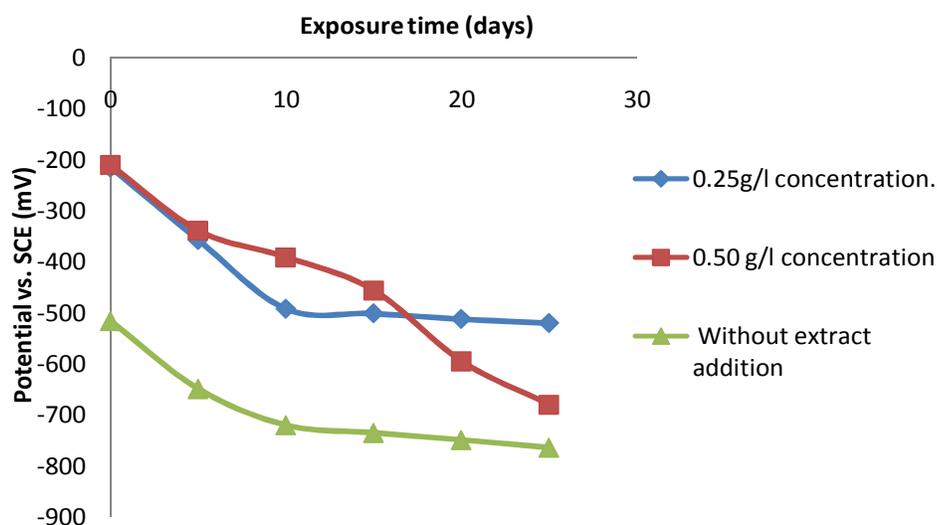


Figure 10. Variation of potential (vs. SCE) with exposure time (days) for the mild steel test specimen immersed in 0.5 M HCl at 80°C with and without Neem's leaf extracts addition.

and always perform best at the optimum level. Below and above this level, they will accelerate corrosion. Series of further work may need to be done on this plant's extracts – leaves and bark in particular and in different test environments under varied conditions in order to bring out the best of them.

Potential measurement and the neem extract inhibitor efficiency

The curves for the variation of potential versus saturated

calomel electrode (SCE) with exposure time for the test specimens immersed in 0.5 M hydrochloric acid (HCl) with and without the addition of the leaf extract are presented in Figures 9 and 10. The tests were performed under the same conditions of 30 and 80°C and at the two different extract concentrations of 0.25 g and 0.50g/l, respectively. Similar curves for the tests performed in the 0.5 M sulphuric acid (H₂SO₄) are presented in Figures 11 and 12. The results obtained in both cases were in agreement with those obtained by the weight-loss method. In Figures 9 and 10, a potential range of between -165 and -383 mV recorded for tests performed

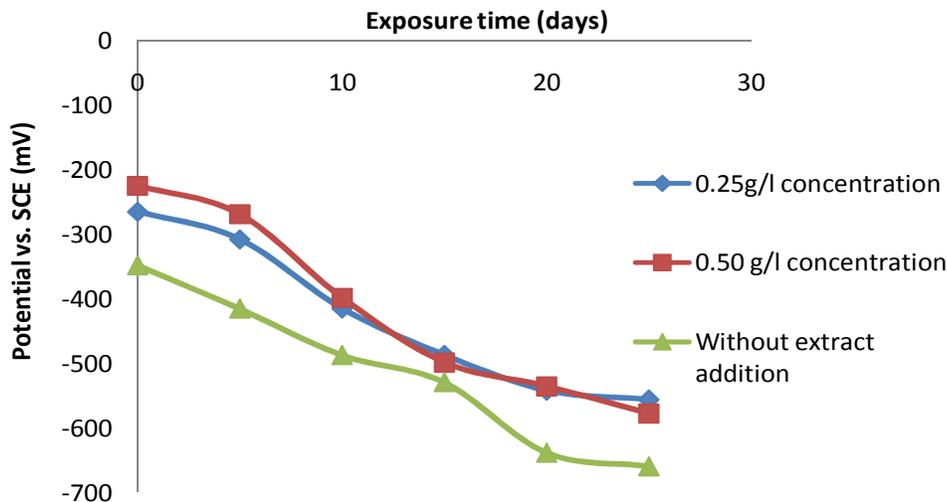


Figure 11. Variation of potential (vs. SCE) with exposure time (days) for the mild steel test specimen immersed in 0.5 M H₂SO₄ at 30 °C with and without Neem's leaf extracts addition.

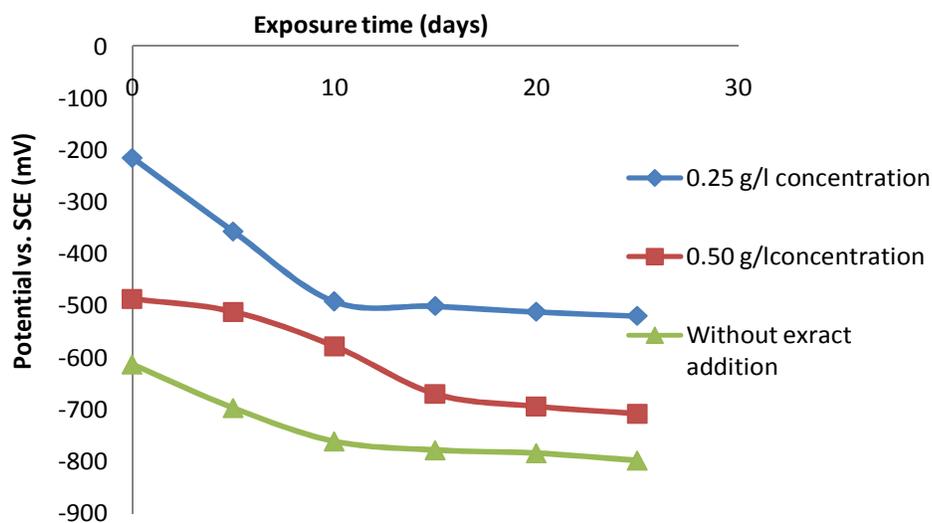


Figure 12. Variation of potential (vs. SCE) with exposure time (days) for the mild steel test specimen immersed in 0.5 M H₂SO₄ at 80 °C with and without Neem's leaf extracts addition.

with leaf extract concentrations of 0.25 g and 0.5 g/l at 30°C showed more passive corrosion reactions which could be associated with inhibitive action of the extract at that temperature. The other results gave more negative potential values that ranged. This is an indication of lack of significant corrosion inhibition performance. In Figures 11 and 12, it is apparent that in the 0.5 M H₂SO₄ the leaf extract did not provide much significant corrosion inhibition for the steel, except at the 30 °C and at the 0.50 g/l concentration where potential values ranging between -225 and -398 mV in the first 10 days of the experiment were achieved. At the temperature of 80°C, the leaf

extract did not provide any obvious inhibition. It is important to mention, however, that sulphuric acid is a very strong acid and its reaction on mild steel is very aggressive. Just like the results in the weight loss method, sulphuric acid at the concentration used seemed to be too strong for the amount of extract concentrations used in this experiment. It can, therefore, be considered inappropriate to effect corrosion inhibition particularly at an elevated temperature such as 80°C. The best results in the HCl test medium were obtained with 0.25 and 0.5g/l concentrations of Neem leaf extract at 30°C. The best corrosion result in H₂SO₄ is with 0.50 g/l at 30°C. All

the results at the elevated temperature of 80°C did not show any corrosion inhibition performance. The calculated percentage inhibitor efficiency is presented in Table 1. The percentage inhibitor efficiency for the 0.25 g/l concentration at 30°C in the HCl is 27.42; and that of 0.50 g/l under the same test conditions is 27.37. It should be expected that the latter higher extract concentration should have more improved inhibitor efficiency. The reason why this result goes against expectation is difficult to explain. However, it was almost the same inhibitor efficiency values. The best result obtained for the test in 0.5M sulphuric acid was with the 0.50 g/l concentration of the leaf extract at 30°C with the percent inhibitor efficiency of 24.08. From these results, it can be inferred that the leaf extract solution behaves as an inhibitor by attaching its polar molecules to the test specimen's surface in the test environment.

In the HCl test medium, it seems the attachment/adsorption was more fairly adherent and not quickly susceptible to depassivation to create a fresh bare surface for active corrosion reactions/anodic dissolution to occur. The inhibition efficiency was observed to be indirectly proportional to temperature as the inhibition fell as the test temperature rose. It seems then that the inhibition was brought about by the physical adsorption of the reactive constituents of the extract to the test metal's surface. Thus as the temperature increased, the increasing atomic/molecular vibrations and agitation weakened the interfacial bond between the extract's active molecular constituents and the metal surface. Subsequent research work on this extract will concentrate on more variable concentrations, lower and variable temperatures far below 80°C and the use of Neem bark in addition to the leaf extract.

Conclusion

In this work, the highest valuable results for corrosion inhibition performance in the HCl test medium were achieved at the Neem leaf's extract concentration of 0.25 and 0.5 g/l respectively at 30°C. In the sulphuric acid test medium, the highest appreciable result was achieved at 0.50 g/l at 30°C. At the elevated temperature of 80°C, the

performance of the extract in the two test media was weak after about 10 days; as the inhibitor efficiency was also low. The two acids test media – HCl and H₂SO₄, at the concentration of 0.5 M were clearly too strong to maintain stable inhibiting film adsorption on the metal specimens' surface, particularly at the elevated temperature(s) with the concentrations of the Neem extract used.

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