

PLANTS EXTRACTS CORROSION INHIBITION OF ALUMINIUM ALLOY IN H₂SO₄

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ABSTRACT

Effects of tobacco (*Nicotiana*) and Kola tree (*Cola acuminata*) extracts on the corrosion inhibition of an aluminium alloy 2S (1200) grade specimens immersed in 0.5M sulphuric acid was investigated at ambient temperature by gravimetric and metallographic methods. Extracts of kola plant and tobacco in different concentrations were used as 'green' inhibitors. This paper reports the results obtained from the weight loss method, calculated corrosion rates, inhibitor efficiencies and the optical microscopy metallographic observations. Addition of different concentrations of the plants extracts gave clear reduction in weight loss and in the corrosion rate of the test samples. This apparent corrosion inhibition was associated with the protective film provided on the aluminium alloy's surface by the complex chemical constituents of the plants extracts.

Keywords: Inhibition, corrosion, aluminium alloy, kola tree, tobacco, sulphuric acid.

INTRODUCTION

Corrosion phenomena, control and prevention are unavoidable major scientific issues that must be addressed daily as far as there are increasing needs of metallic materials in all facets of technological development. Chemical inhibitors have been very effective in addressing this among other corrosion protection methods. In very recent time, however, there has been the need to look at some other environment friendly substances, especially from natural sources that could be used to inhibit/reduce incessant corrosion problems apart from the synthesized inorganic and other organic chemicals, some which are toxic to the environment. Many scientific researchers have responded to this need and it has generated increased research studies into the use of plant extracts (Loto, 2005; Okafor, 2007; Davis and Fraunhofer, 2003; Fraunhofer, 1995; Davis *et al.*, 2001; Fraunhofer, 2000 and Loto, 2003). Very encouraging results have been obtained in this regard. Attempt at making a contribution to this growing research area has necessitated the present investigation. Parts of the plants that have been used include leaves, bark, fruit and the roots. In very many cases, the corrosion inhibitive effect of some of the 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 present investigation is focused on the use of kola tree (nut, leaves) and tobacco. Extracts of tobacco (genus – *Nicotiana*: family- *Solanaceae*), as an environmental benign corrosion inhibitor had been

shown(3 - 6, 8) to be effective in preventing the corrosion of steel and aluminium in saline environments; and in fact, exhibiting a greater corrosion inhibition effect than chromates (4 – 6). Tobacco plants produce ~ 4,000 chemical compounds – including terpenes, alcohols, polyphenols, carboxylic acids, nitrogen – containing compounds (nicotine), and alkaloids (WHO-IARC, 1985). These constituents may be effective in showing corrosion inhibition performance, particularly as in the present investigation likewise, kola nut tree's chemical composition consists of caffeine (2.0 - 3.5%), theobromine (1.0 – 2.5%), theophylline, phenolics – such as phobaphens, epicachins, D- catechin, tannic acid (tannin), sugar – cellulose, and water (Wikipedia, 2011). As reported in some previous studies (Okafor, 2007; Loto, 2003), tannin is known to possess corrosion inhibitive properties on metals – particularly, mild steel. The other chemical composition in kola tree extracts may have the capacity also to exhibit electrochemical activity such as corrosion inhibition for aluminum alloy in H₂SO₄. In this work, a positive result is anticipated that could be beneficial technologically and economically.

MATERIALS AND METHODS

Preparation of specimen

The aluminum alloy test specimen used was of the 2S (1200) grade and had a nominal percent composition of: 0.60%Fe, 0.30% Si, 0.05% Mn the rest being Al. The cylindrical steel bar was cut into various pieces of different lengths and the specimens were de-scaled by wire brushing. They were then ground with silicon

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carbide abrasive paper of 240, 320, 400, and 600 and polished with 1.0 μ diamond paste. They were thoroughly cleaned, rinsed in ultrasonic cleaner, dried, and kept in desiccators for further weight loss tests.

Test media

The experiments were performed in 0.5M H₂SO₄ of AnalaR grade. The extracted juices used as the corrosion inhibitor were separately extracted from the leaves of kola tree and tobacco and were prepared in different concentrations.

Extraction of plants extracts

The nuts and leaves of the Kola tree (*Cola acuminata*) and Tobacco (*Nicotiana*) were cut separately into pieces which were then oven dried at 105°C for two hours, cooled, and trimmed to be uniformly 0.70kg each. They were separately ground into powder, and soaked in different containers containing ethanol for five days in order to extract the juice by leaching. Each of the different juice extracts in each container was filtered at the end of the soaking period. The solutions were distilled at 79°C to remove the ethanol from the juice extracts and concentrate the inhibiting chemical(s). Each of the juice extracts (the respective distillates) was stored in a clean bottle and covered properly.

Preparation of the test media and juice extracts

100ml of 0.5M H₂SO₄ was measured into different beakers. In addition to the original extract which was taken as 100% concentration, other different percent concentrations of 80 (tobacco extract alone), 60 and 30 by dilution from the original extracts were made of which 10ml of each of the extracts - the tobacco, kola leaf, and kola nut extracts, was separately added to the acid in each of the beakers. This was repeated for every concentration of the extracts made. One beaker was left plain, that is, contained only the test medium, the H₂SO₄; this served as the control experiment.

Weight loss experiment

Weighed test specimens were totally immersed in each of the test media contained in a 250ml beaker for 24 days. Experiments were performed with acid chloride test medium in which some had the solution extract added. Test specimens were taken out of the test media every 3 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 (Figs. 1 to 6) were made. Corrosion rates were calculated from the recorded weight loss values from this formula:

$$\text{mm/yr} = 87.6W/DAT \dots \dots \dots (1)$$

where W is the weight loss in milligrams, D is the density in g/cm², A is the area in cm², and T is the time of exposure in hours.

The percentage inhibitor efficiency, P, was calculated from relationship:

$$P = 100 (1 - W_2) / (W_1) \dots \dots \dots (2), \text{ where:}$$

W₁ and W₂ are the corrosion rates in the absence and presence, respectively, of a predetermined concentration of inhibitor. The per cent inhibitor efficiency was calculated for all the inhibitors for every 3 days of the experiment, and the results are presented in Table 1. All the experiments were performed at ambient temperature(s).

Micrographs

Some optical micrographs of the test specimen before and after immersion in sulphuric acid were made in the experiments. The representative micrographs are presented in figure 7 (a-d).

RESULTS AND DISCUSSION

Weight loss method

The results obtained for the variation of weight loss and corrosion rate with exposure time respectively for the aluminum alloy test specimens immersed in 0.5 M sulphuric acid with varied concentrations of added kola tree (leaves and nuts) and tobacco extracts are presented in figures 1 to 6.

The Kola tree leaves extract

As presented in figure 1, the test medium with 100 % concentration of kola leaves extract addition on the last day of the experiment, recorded the highest values of weight loss throughout the experimental period. Weight loss values that ranged from 157.80mg on the 3rd day to 452.60 mg on the 24th day of the experiment were recorded. This concentration of the leaves extract appeared to accelerate corrosion as it showed no corrosion inhibition performance. In fact, better corrosion weight loss values were obtained with the test environment without extract addition except on the 18th day when both achieved the same weight loss value of 335.80mg. However, the extracts with 30% concentration of the added kola leaves extract, recorded the lowest weight loss values of 70.70; 156.50 and 321mg on the 12th, 15th and 24th day of the experiment. The 60% extract concentration, similarly recorded low weight loss values that ranged from 70.70 on the 12th day, 221.80 on the 15th to 321 mg on the 24th day of the experiment. The strong acidic test medium contributed to the high weight loss values achieved. Clearly, the order of increasing percent corrosion inhibition performance was: 30 > 60 > 100. Only the 30 and 60% extract concentrations addition performed well when compared with the test medium which contained no extract addition.

The results obtained for the corresponding corrosion rate versus the exposure time, figure 2, followed the same

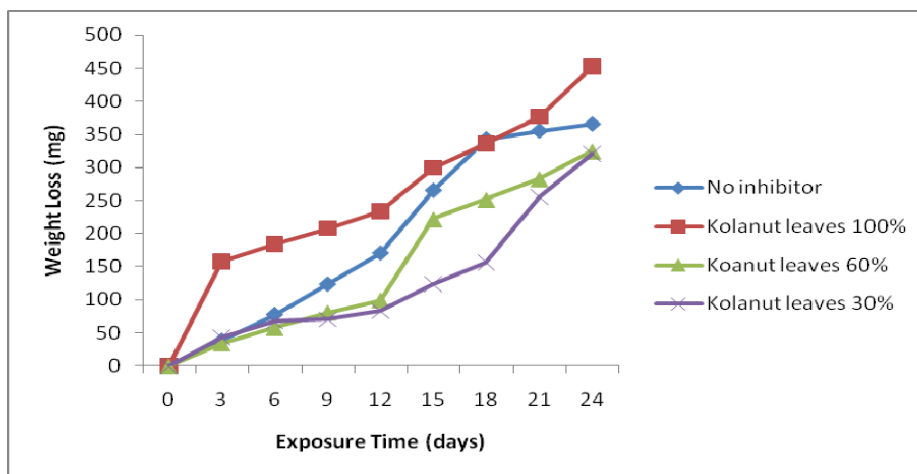


Fig. 1. Variation of weight loss with exposure time for the aluminium alloy specimen immersed in 0.5 M H₂SO₄ with varied concentrations of added kola tree leaves extract.

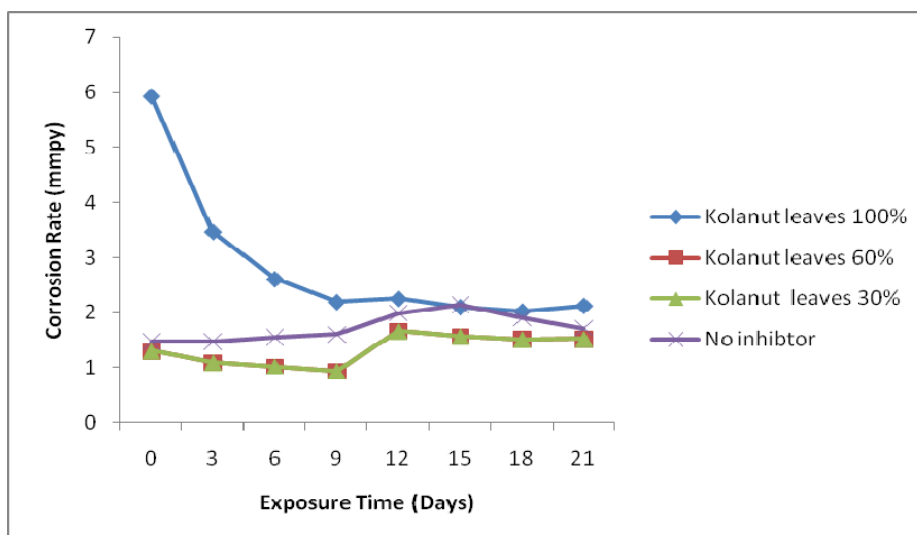


Fig. 2. Variation of corrosion rate with exposure time for the aluminium alloy specimen immersed in 0.5 M H₂SO₄ with varied concentrations of added kola tree leaves extract.

trend of corrosion inhibition performance. The lowest corrosion rate values were obtained for the kola leaves extract at the concentrations of 30 and 60%. The recorded corrosion rate values throughout the experimental period remained the same; and these ranged from 1.303 at the beginning to 1.523 mm/yr on the 21st day of the experiment. The test medium with 100% concentration of added leaves extract, recorded the highest corrosion rate values that ranged between 5.96 at the beginning to 2.12 mm/yr at the end of the experiment. The 30 and 60% extract concentrations addition had lower corrosion rate values than the test without extracts addition; but it was not so the 100% concentration addition. Characteristically, all inhibitors have different optimum concentrations of effective performance in different environments and for different metallic alloys.

No doubt, the constituents of kola leaf extract exhibited a reasonable degree of electrochemical corrosion inhibition activity that was concentration dependent and /or sensitive – this is usually very characteristic of inhibitors in general. The observed corrosion inhibition performance here could be attributed to the presence of tannin and the synergistic effect of combination of other constituents that were mentioned above in the introduction.

The Kola nut extracts

The curves for the variation of weight loss and corrosion rate with exposure time for the aluminum alloy test specimen immersed in 0.5M H₂SO₄ with varied concentrations of added kola nut (fruit) extract are presented in figures 3 and 4 respectively. In figure 3, the trend of weight loss values obtained with respect to

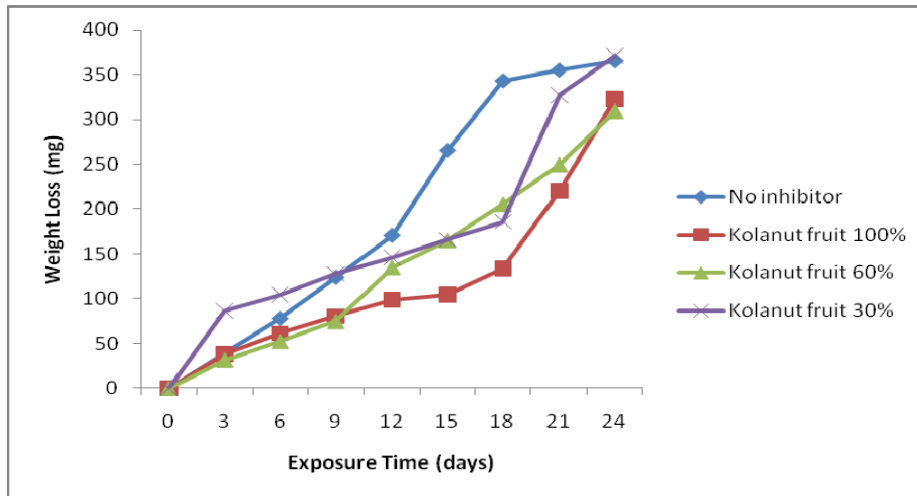


Fig. 3. Variation of weight loss with exposure time for the test specimens immersed in 0.5M H₂SO₄ with varied concentrations of added kola tree nuts extract.

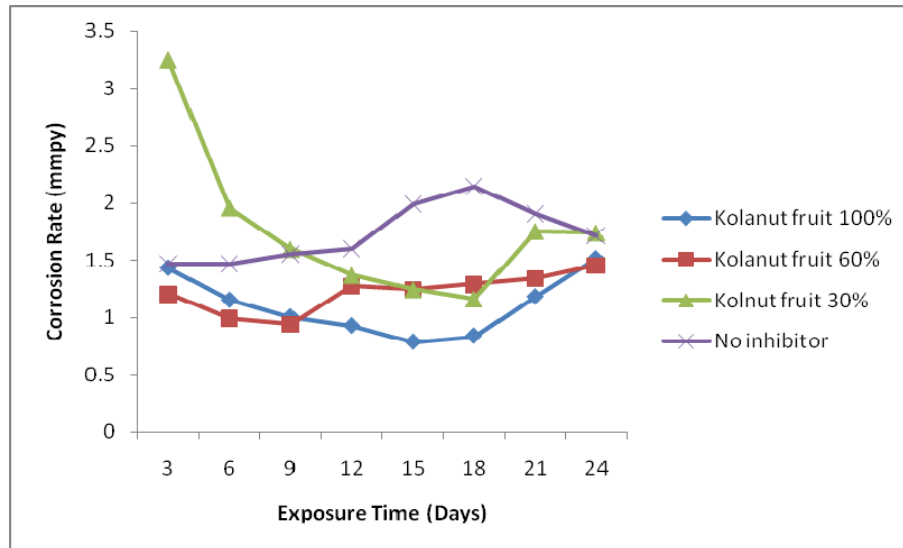


Fig. 4. Variation of corrosion rate with exposure time for the test specimens immersed in 0.5M H₂SO₄ with varied concentrations of added kola nuts extract.

percent concentrations of added extract was different from the one obtained in figure 1 for the leaf extract values. Lowest weight loss values of 32, 104.60, 220 and 322.30 mg were recorded for the 100% extract concentration of kola nuts on the 3rd, 15th, 21st and 24th day of the experiment respectively. The 60% extract concentration addition recorded almost the same weight loss values as the 100%'s up to the 9th day of the experiment. Weight loss values of 165.70 and 205.60mg were subsequently obtained and recorded on the 15th and 18th day respectively. The corrosion inhibition performance with the use of this 60% concentration as indicated by the weight loss values was less than that of the 100% concentration of the nuts extract. The lowest corrosion inhibition performance was recorded when the 30% concentration of the extract was used; with weight

loss values of 86.50, 185.70 and 370.60 mg recorded on the 3rd, 18th and 24th day of the experiment respectively. All the per cent extract concentrations used had lower weight loss values than the test performed without added extracts. Apparently some degree of corrosion inhibition was exhibited by the extracts addition. However, why the trend of this nuts extract differed in corrosion inhibition characteristic/ performance is difficult to explain, except again for differences in chemical constituents and the inhibitors characteristic behavior.

The corresponding corrosion rate values obtained are presented in figure 4. The lowest corrosion rate values were obtained for the 100% extract concentration addition. Values of 0.927, 0.785, 0.837 and 1.453 mm/yr were recorded on the 12th, 18th, 21st and 24th day of the

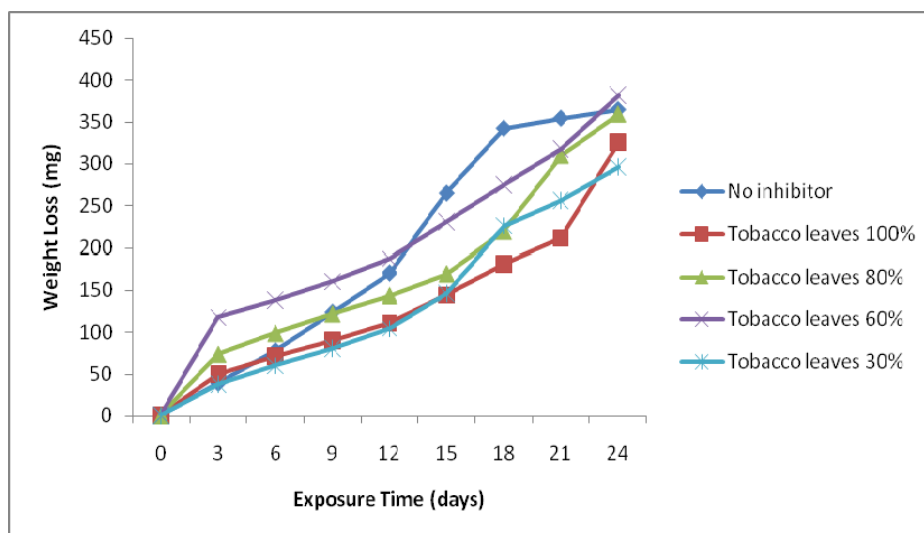


Fig. 5. Variation of weight loss with exposure time for the test specimen immersed in 0.5M H_2SO_4 with varied concentrations of added tobacco leaves extracts.

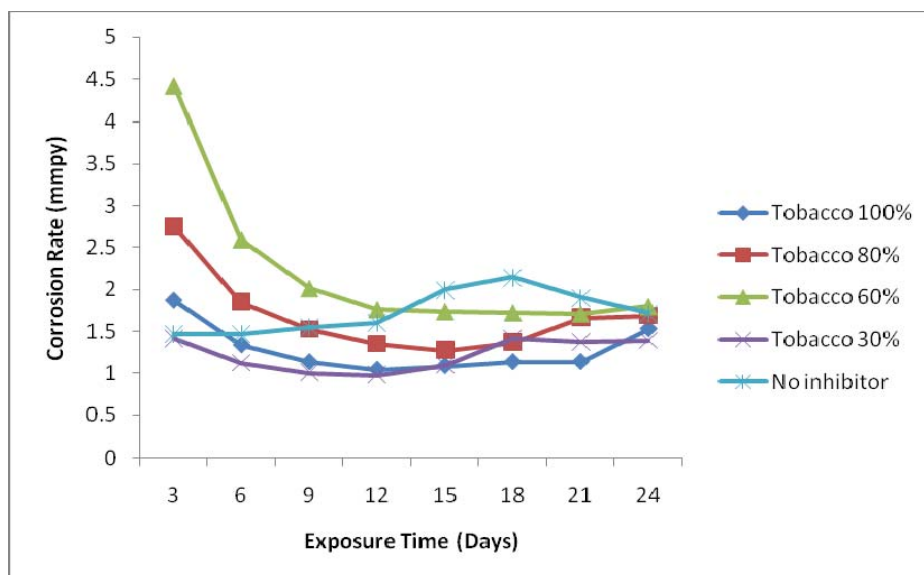


Fig. 6. Variation of corrosion rate with exposure time for the aluminium alloy specimen immersed in 0.5M H_2SO_4 with varied concentrations of added tobacco leaves extracts.

experiment respectively. For the 60% extract concentration addition, the corrosion rate values were slightly higher than the former. The values obtained ranged from 1.202, 0.989, 0.939 to 1.753 and 1.713 from the 3rd to 21st and 24th day of the experiment respectively. With 30% concentration addition, the corrosion rate values were higher than the 60%'s except from the 12th to the 18th day of the experiment when they achieved the same corrosion rate values. Results obtained for the test without extract addition showed it to have the highest corrosion rate with values that ranged from 1.466 (3rd day) to 1.991 (15th day), 2.144 and 1.71 mm/yr on the

18th and 24th day respectively. The corrosion rate values had good correlation with the weight loss values in figure 3.

Tobacco leaves extracts

The results for the variation of weight loss with exposure time for the aluminum specimen immersed in 0.5M H_2SO_4 with varied concentrations of added tobacco extract are presented in figure 5. The corresponding corrosion rate results are similarly presented in figure 6. Here, there were four different percent concentrations used (30, 60, 80, and 100%).

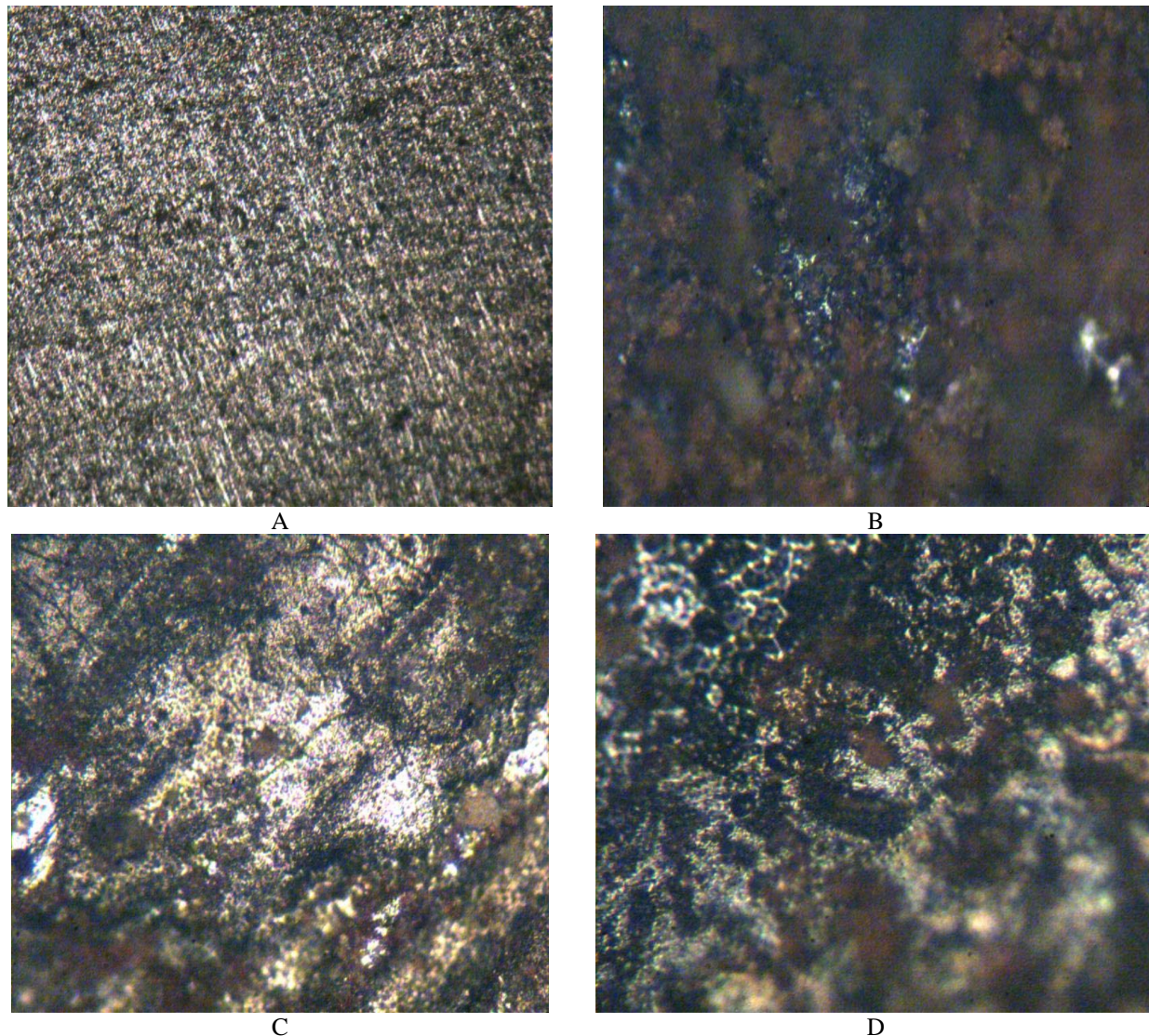


Fig. 7. Micrograph of aluminum test specimens before and after immersion in the test media; A - Before immersion; B- After 24 days of immersion in H_2SO_4 ; C - After 24 days of immersion in H_2SO_4 + extract of Kola tree nuts; and D- After 24 days of immersion in H_2SO_4 + extract of Kola tree leaves

Just like the previous extracts of kola tree parts, the 100% here represents the original extract without dilution. All the different extract concentrations addition recorded weight loss values that increased with time- an indication of active corrosion reactions throughout the experimental period. All the results were very close in weight loss values particularly those with the 100, 30, and 80% extract concentrations addition. The addition of 100% concentration seemed to give averagely, the lowest weight loss value and this was closely followed by the 30% extract concentration addition with weight loss values of 37.5 and 295.9 mg at the beginning and end of the experiment respectively. The 80 and 60% extract concentrations also followed in that order. It did not

follow any particular trend. All the per cent extract concentration additions gave better weight loss values than the blank test, that is, the one without inhibitor addition. The corresponding corrosion rate values also follow the same trend as just described. Corrosion rates values that ranged between 1.87 at the beginning and 1.68 mm/yr at the end of the experiment were recorded for the 100% extract concentration addition. Similarly values of 1.47 and 1.39 mm/yr were recorded at the 3rd day and at the end of the experiment respectively.

Inhibitor efficiency

The results of the inhibitor efficiency obtained by calculations are presented in table 1.

Table 1. Inhibitor Efficiency for Aluminium alloy in H₂SO₄.

ENVIRONMENT	CONCENTRATION	INHIBITOR	INHIBITOR CONCENTRATION	INHIBITOR EFFICIENCY (%)								
				EXPOSURE TIME (DAYS)	3	6	9	12	15	18	21	24
SULPHURIC ACID	0.5M	NONE		NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
SULPHURIC ACID	0.5M	KOLANUT LEAVES EXTRACT	30%	-12.2762	13.18822	42.93785	51.25952	53.30064	54.30657	28.00338	12.05479	
			60%	11.2532	25.60819	34.54399	41.65202	16.33346	26.62774	20.27637	11.09589	
			AS OBTAINED	-303.581	-136.236	-68.2002	-36.8483	-13.1271	1.956204	-6.37338	-24	
SULPHURIC ACID	0.5M	KOLANUT FRUIT EXTRACT	30%	-121.228	-33.4187	-2.90557	14.58699	37.49528	45.78102	7.83982	-1.53425	
			60%	18.15857	32.52241	39.46731	20.73814	37.57073	39.9708	29.55443	15.17808	
			AS OBTAINED	2.557545	21.51088	35.18967	42.17926	60.54319	60.93431	37.95826	11.69863	
SULPHURIC ACID	1M	TOBACCO EXTRACT	30%	4.092072	23.68758	35.35109	39.19156	45.03961	34.16058	27.94698	18.93151	
			60%	-201.023	-76.6965	-29.6207	-9.66608	12.86307	19.73723	10.37789	-4.73973	
			80%	-87.7238	-26.1204	1.856336	15.99297	36.13731	36.05839	12.63395	1.671233	
			AS OBTAINED	-27.6215	8.834827	27.03793	35.03222	45.45455	47.15328	40.35533	10.63014	

The best result obtained for aluminium alloy was provided by kola tree nuts extract at 100% concentration with an efficiency of 60.54 and 60.91% respectively on the 12th and 15th day of the experiment. Kola leaf extract at 30% concentration addition also gave a fairly good corrosion inhibition performance with an inhibitor efficiency of 51.26, 53.80 and 54.31% on the 12th, 15th and 18th day of the experiment respectively.

For the tobacco leaves extract, the best inhibitor efficiency was obtained with the 100% extract concentration (as received) which recorded 45.45 and 47.15% on the 15th and 18th day respectively. Inhibitor efficiency values were generally low on the 24th day of the experiment.

In general, the effective corrosion inhibition performance of kola tree and tobacco extracts could be associated with their complex chemical compounds which include tannin as earlier mentioned. Also, constituents such as epicatechin, D-catechins, theophylline and theobromine contained in the constituents of kola leaf and nut extracts could act as inhibiting passive film formers on the aluminium substrate surface. The film that was formed could act as a barrier between the alloy and corrosive environment interface and thus preventing and/or stifling corrosion reactions of anodic oxidation – (dissolution) and the cathodic reduction processes. Similarly, the very complex structural compounds and the multifarious constituent composition of tobacco would have provided a more stable adherent film on the surface of the aluminium specimen to hinder active corrosion reactions. Thus the penetration of the SO₄²⁻ reacting species through the surface film barrier would be hindered. The

synergistic action/reaction of these compounds on the surface of the test specimens could also hinder the sulphate ion reacting species, promote more stable passive film formation on the surface of the aluminium alloy and hence inhibit and stifle corrosion reactions at the metal / environment interface as mentioned above.

Photomicrographs

Some of the micrographs made before and after immersion of the test specimens in sulphuric acid, with and without the use of the kola tree extracts are presented in figures 7(a-d). There was significant corrosion with corrosion products of the aluminium alloy specimens in the test medium without the added extracts as observed in figure 7(b). Figure 7(c) shows a surface feature with very moderate or minimal corrosive action for the test with the addition of kola nut extract. A similar surface feature though with some pits observed, was obtained as presented in figure 7(d) for the test with added kola tree leaf extract. These micrographs observations bear very close correlation with the results obtained from the weight loss experiments and the calculated corrosion rates.

CONCLUSION

The best corrosion inhibition performance for the aluminium alloy was achieved with the use of kola tree nuts extract at 100% concentration in 0.5M H₂SO₄ with an inhibitor efficiency of 60.91% on the 15th day of the experiment. Kola leaf extract at 30% concentration addition also gave a fairly good corrosion inhibition performance with an inhibitor efficiency of 54.31% on the 18th day of the experiment. The best inhibitor efficiency for the tobacco leaves extract was obtained with the 100%

extract concentration (as received) with an inhibitor of 47.15% on the 18th day. Inhibitor efficiency values were generally low on the 24th day of the experiment. The extracts of kola leaf, kola nut and tobacco at the concentrations used, and under the other working conditions could be said to be effective as environment friendly extracted inhibitors for the aluminum alloy in sulphuric acid which is a very strong acid.

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