

Inhibition Effect of Kola Tree and Tobacco Extracts on the Corrosion of Austenitic Stainless Steel in Acid Chloride Environment

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Corrosion and inhibitor protection of austenitic stainless steel (Type 304) specimens immersed in acid chloride solution was investigated at ambient temperature by weight loss method from which the corrosion rates were calculated and inhibition efficiency determined. Extracts of kola plant; the nut, bark and leaf and tobacco leaf in different concentrations were used as ‘green’ inhibitors. This paper reports the results obtained from the various tests performed in the acid chloride environment on the stainless steel during the experiments. The addition of different concentrations of the plants extracts gave some reduction in the active corrosion reactions behavior of the steel specimen in the strong acid chloride. There was a reduction in the weight loss and in the corrosion rate of the test samples, though not very significant. The stainless steel was self-passivated; the passive film was, however, significantly destroyed by the strong reacting species of the test solution. The reduction in weight loss was attributed to the protective film provided on the steel’s surface by the complex chemical constituents of the plants extracts. Effective protection of the austenitic stainless steel was minimally achieved in nearly all the extracts for the greater part of the experimental period.

Keywords: Inhibition, corrosion, austenitic stainless steel, kola tree, tobacco, acid chloride, protection.

1. INTRODUCTION

The use of plant extracts as inhibitors for the corrosion of metals/alloys, has gained very wide interest among researchers in recent time [1-13]. In very many cases, the corrosion inhibitive effect of some plants’ extracts has been attributed to the presence of tannin in their chemical constituents [7]. Also associated with the presence of tannin in the extracts is the bitter taste in the bark and /or leaves of the plants.

Some previous work on extracts of tobacco (genus – *Nicotiana*: family- *Solanaceae*), as an environmental benign corrosion inhibitor [2-7; 14-15] had shown it 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, 5, 6]. Tobacco plants produce ~ 4,000 chemical compounds – including terpenes, alcohols, polyphenols, carboxylic acids, nitrogen – containing compounds (nicotine), and alkaloids [14]. These may exhibit electrochemical activity such as corrosion inhibition [3].

Kola nut tree's chemical composition similarly, 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 [15]. It has been reported in some previous studies [7, 2], that tannin is known to possess corrosion inhibitive properties on metals such as mild steel and aluminium alloy.

With the very complex structural chemical compounds of the extracts of the two plants, a reasonable amount of corrosion inhibition of the austenitic stainless steel in the strong acid chloride environment used in this work is expected.

2. EXPERIMENTAL PROCEDURE

The experimental procedure here follows that of other previous investigations, Loto [7]. The Type 304 austenitic stainless steel used as specimens was obtained locally from Lagos. The nominal percentage composition of the austenitic stainless steels are: 0.157% C, 0.428% Si, 1.39% Mn, 0.025% P, 0.0085% S, 17.96% Cr, 8.4% Ni, 0.228 Mo, 0.051% Al, 0.104% Cu, 0.142% Co, 0.023% Ti, 0.047% Nb, 0.061% V, 0.031% W, <0.003% Pb, 0.023% Mg, 0.0018% B, 0.006% Sn, 0.027% Zn, 0.02% As, <0.002% Bi, 0.005% Ca, 0.028% Ce, 0.012% Zr, 0.0031% La and 70.8% Fe.

The austenitic stainless steel samples were cut into dimension of 25 x 55 x 1.0 mm. A 1.5 mm diameter hole was drilled about 5 mm from the top of the 20 mm edge. The test specimens were finely cleaned with silicon carbide abrasive papers of 240, 320, 400 and 600 grits and kept in a desiccator for further corrosion tests.

2.1. Preparation of test media and the plants extracts

The experiment was performed in acid chloride medium (0.5M H₂SO₄ + 5% NaCl of Analar grade). The separately extracted juices from the nuts and leaves of the kola tree and from tobacco were used as the corrosion inhibitor, in different concentrations. The procedure used as stated below had been previously reported [9].

The kola tree - nuts, bark and leaves and tobacco (*nicotiana*) with each weighing 1Kg were collected. The nuts were pounded and ground to a coarse powder. The leaves were cut, oven dried at 72°C and blended to fine powders using a blending machine. The bark was cut, force-dried in an oven and blended to fine powder as well, while the tobacco (leaves) were first sun-dried for seven days, then

blended to fine powder. The samples, each of 100g, were then separately soaked in different 400 ml containers containing ethanol. These were filtered and the solution was left to evaporate at room temperature for three days to concentrate the juice extracts. Each of the plant extract was stored in clean airtight bottles and refrigerated.

2.2. The test media

150 ml of acid chloride solution (0.5 M sulphuric acid and 5% NaCl) was put into different 250ml beakers. The first beaker contained only the acid chloride test medium; it did not contain any extract solution. 20 ml each of the extracts in different concentrations of 100% (as obtained), 60% and 20% were put separately in the next three beaker containers for each of the extracts.

2.3. Weight loss experiment

Weighed test specimens were totally immersed in each of the test media contained in a 250ml beaker for 21 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 10) were made. All the experiments were performed at ambient temperature(s). The percentage inhibitor efficiency, P, was calculated from relationship:

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

where W_1 and W_2 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 concentrations and the results are presented in Table 1.

2.4. Micrographs

Some optical micrographs of the test specimen before and after immersion in acid chloride were made in the experiments. The representative ones are presented in Figs. 11 and 12.

3. RESULTS AND DISCUSSION

3.1. Weight loss method

The results obtained for the variation of weight loss and corrosion rate with exposure time respectively for the austenitic stainless steel test specimens immersed in 0.5M acid chloride with varied concentrations of added kola tree and tobacco extracts are presented in Figs. 1 to 8. Figs 9

and 10 show the curves of weight loss and corrosion rates made for the combination of the extracts relative to time of exposure.

3.2. The Kola nut solution extract

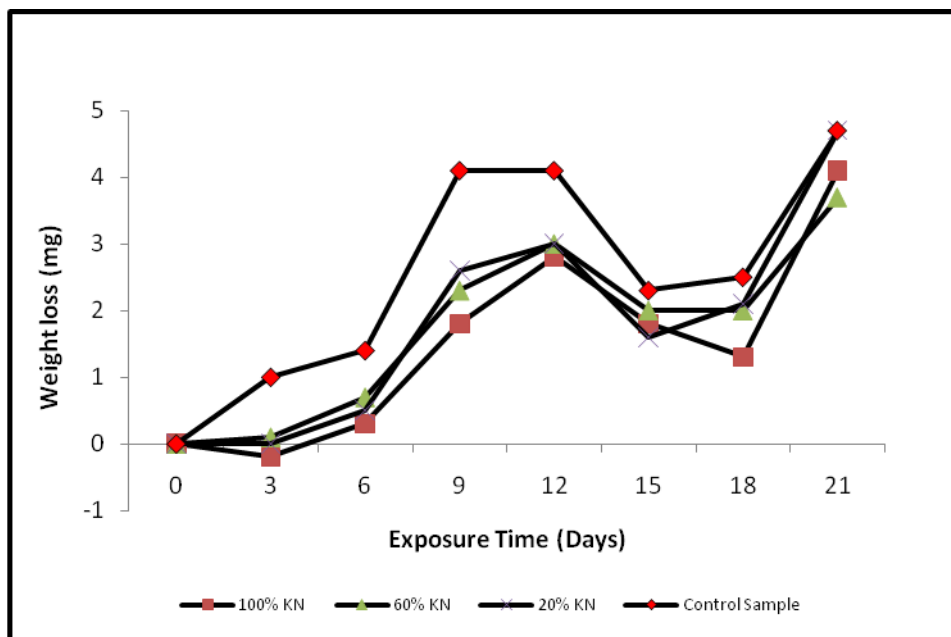


Figure 1. Variation of weight loss with exposure time for the austenitic stainless steel specimen immersed in acid chloride, with varied percent concentrations of added kola nut extracts. (KN = kola nut extract)

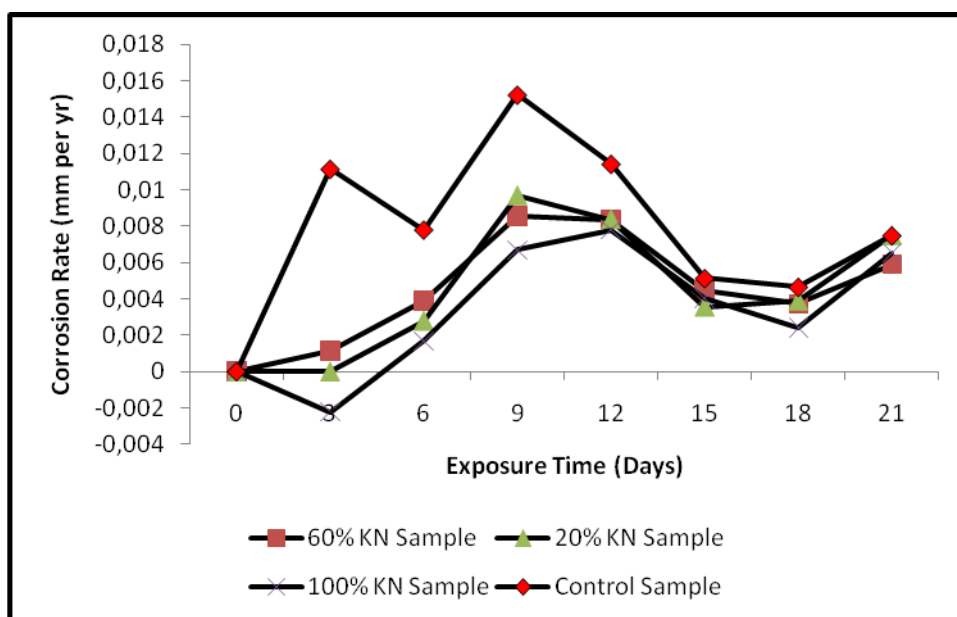


Figure 2. Variation of corrosion rate with exposure time for the austenitic stainless steel specimen immersed in acid chloride, with varied percent concentrations of added kola nut extracts. (KN = kola nut extract)

The results obtained for the variation of weight loss with exposure time for the austenitic stainless steel test specimen immersed in 0.5M acid chloride with varied concentrations of added kola nut juice extracts (20%, 60%, 100% concentrations) are presented in Fig.1.

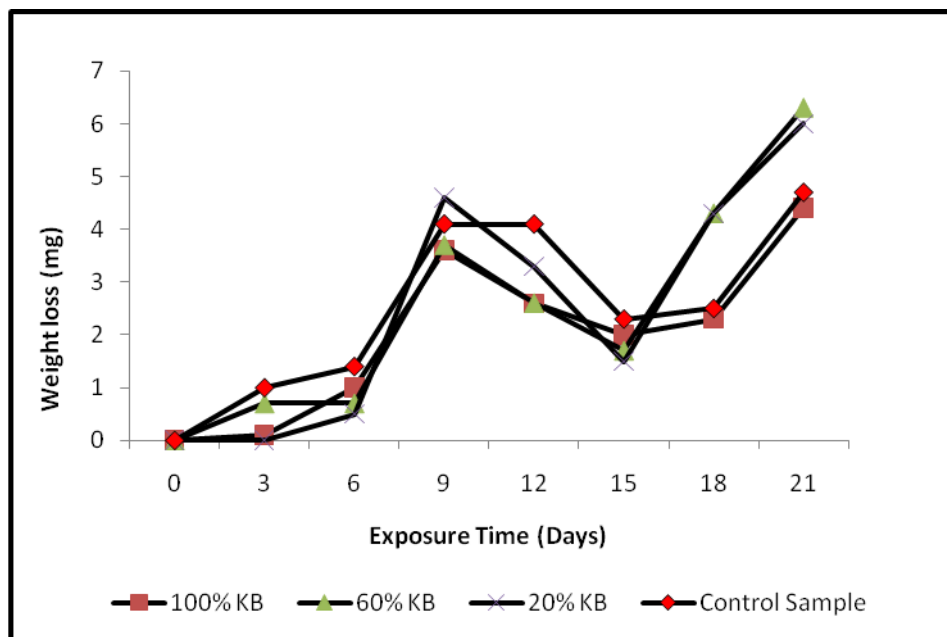


Figure 3. Variation of weight loss with exposure time for the austenitic stainless steel specimen immersed in acid chloride, with varied percent concentrations of added kola bark extracts. (KB = kola bark extract)

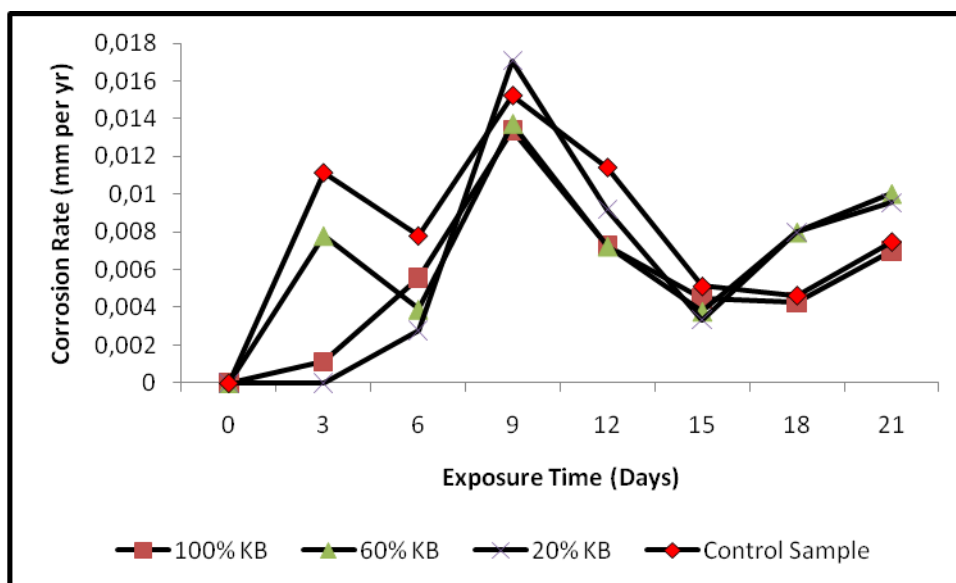


Figure 4. Variation of corrosion rate with exposure time for the austenitic stainless steel specimen immersed in acid chloride, with varied percent concentrations of added kola bark extracts. (KB = kola bark extract)

The acid test medium with 20% concentration extract addition had the least corrosion inhibition effect of the immersed specimens with a weight loss value of 0.0047g. The added 60% concentration of the same extract gave a slightly better corrosion inhibition performance, achieving just 0.0037g weight loss value at the end of the 21st day of the experiment. This was the lowest recorded value. The acid test medium with the added 100% concentration of the same extracts and at the same duration of the experiment recorded a weight loss a value of 0.0041g but a value of 0.0015g on the 18th day of the experiment.

The corresponding corrosion rate vs. the exposure time results in Fig. 2 gave a good correlation with the results in Fig.1. The test medium with added 60% concentration of solution extract gave the least corrosion rate at the end of the 21 days with a value of 0.0059 mm/yr. The test medium with 20% concentration of solution extract addition gave the highest overall corrosion rate with a corrosion rate of 0.0075 mm/yr. The test medium with added 100% concentration of solution extract gave the least corrosion rate, which ranged between 0.0024 mm/yr on the 18th to 0.0061mm/yr on the 21st day.

The weight loss and the recorded corrosion rates did not increase proportionally with time. This could be associated with haphazard corrosion reactions fluctuating phenomenal pattern of austenitic stainless steel in interfacial reaction with acid chloride test environment. The strong reacting species of Cl^- and SO_4^- were breaking down the chromium enhanced passive film on the test electrode surface and its self- healing property was building it back. It was a continuous surface film random depassivation and repassivation reacting phenomenon. This situation made it difficult to really know the depth of the actual inhibition performance of the used plants' extracts. What seemed to be better results were shown as as at the 18th of the experiments. This explanatory observation also applies to all the extracts as will be discussed further in sequence.

3.3. Kola bark solution extract

The results obtained for the variation of weight loss with exposure time for the austenitic stainless steel test specimen immersed in 0.5M acid chloride with varied concentrations of added kola bark extract (20%, 60%, 100% concentrations) are presented in Fig. 3. The acid test medium with 20% concentration extract addition had the least corrosion inhibition effect of the immersed specimen with a weight loss value of 0.006g. The weight loss recorded at the end of the experimental period for the corrosive acid medium with added 60% concentration of solution extract achieved a weight loss value of 0.0063g at the end of the 21 days. The lowest recorded value was that of the addition of 100% concentration of solution extract, having achieved a weight loss value of 0.0044g on the 21st day. The trend of inhibition of the solution extract for austenitic stainless steel shows that the optimum value lies between 100% and 60% of its concentration.

The corresponding corrosion rate vs. the exposure time curves are presented in Fig. 4. The results obtained here gave a good correlation with the results in Fig. 3. The test medium with added 100% concentration of solution extract gave the least corrosion rate at the end of the 21 days with a value of 0.007 mm/yr; its value on the 15th and 18th day was 0.0041 mm/yr. The test medium with 60% concentration of solution extract addition gave a fairly good value of 0.004mm/yr on the 15th day but

jumped to the highest overall corrosion rate with a corrosion rate of 0.01 mm/yr on the 21st day of the experiment. The same trend of haphazard fluctuating results as in kola nut above was expectedly also obtained here due to the test electrodes' ability to continuously repair its broken surface film as caused by the penetrating reacting species. This phenomenon made it difficult to have a clear pattern of each extract corrosion inhibition performance.

3.4. Kola leaf solution extract

Figs.5 and 6 show the results obtained for the variation of weight loss and of corrosion rate with exposure time, respectively, for the austenitic stainless steel test specimen immersed in 0.5M acid chloride with varied concentrations of added kola leaf solution extract.

The weight loss values recorded for the first 15 days of the experiment for all the different percent concentrations of the extracts used could be described as reasonably good with values of 0.019g for the 100% extract and 0.001g for 20 and 60% kola leaf extracts respectively. The weight loss values recorded as at the 21st day of the experiment for each of the different concentrations could not be described as protective. The acid test medium with 100% concentration extract addition achieved a weight loss value of 0.0062g and the medium with added 60% concentration of solution extract achieved a weight loss value of 0.0053g at the end of the 21 days. The addition of 20% concentration of solution extract achieved a weight loss value of 0.0058g at the same period of the experiment.

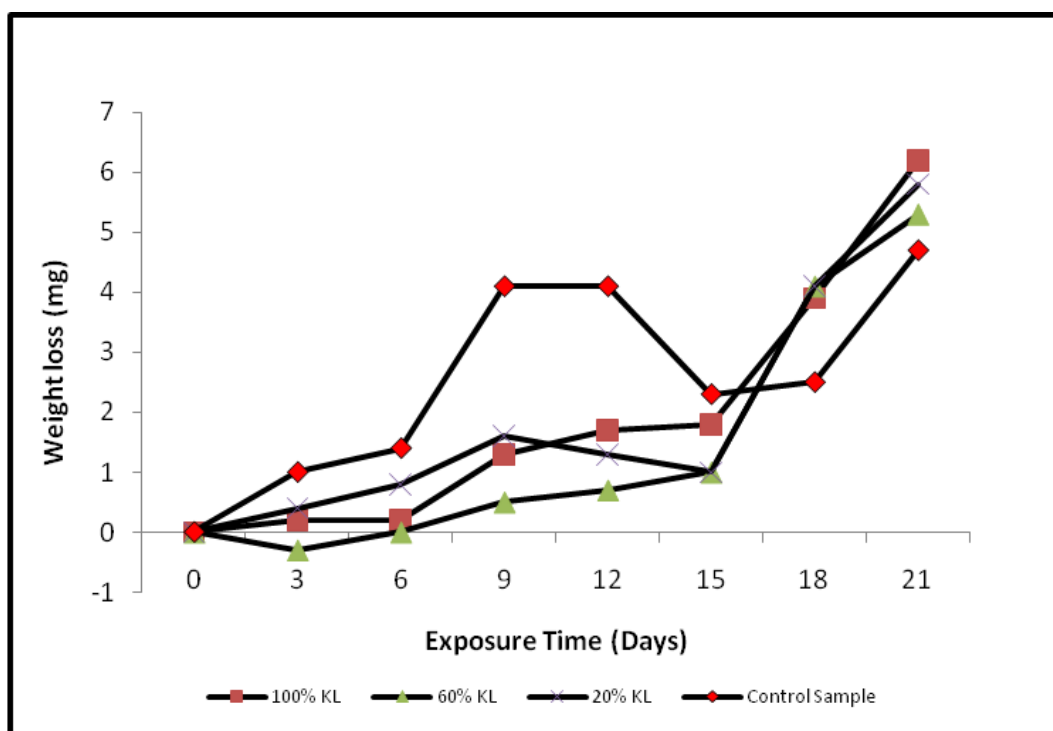


Figure 5. Variation of weight loss with exposure time for the austenitic stainless steel specimen immersed in acid chloride, with varied percent concentrations of added kola leaf extracts. (KL = kola leaf extract)

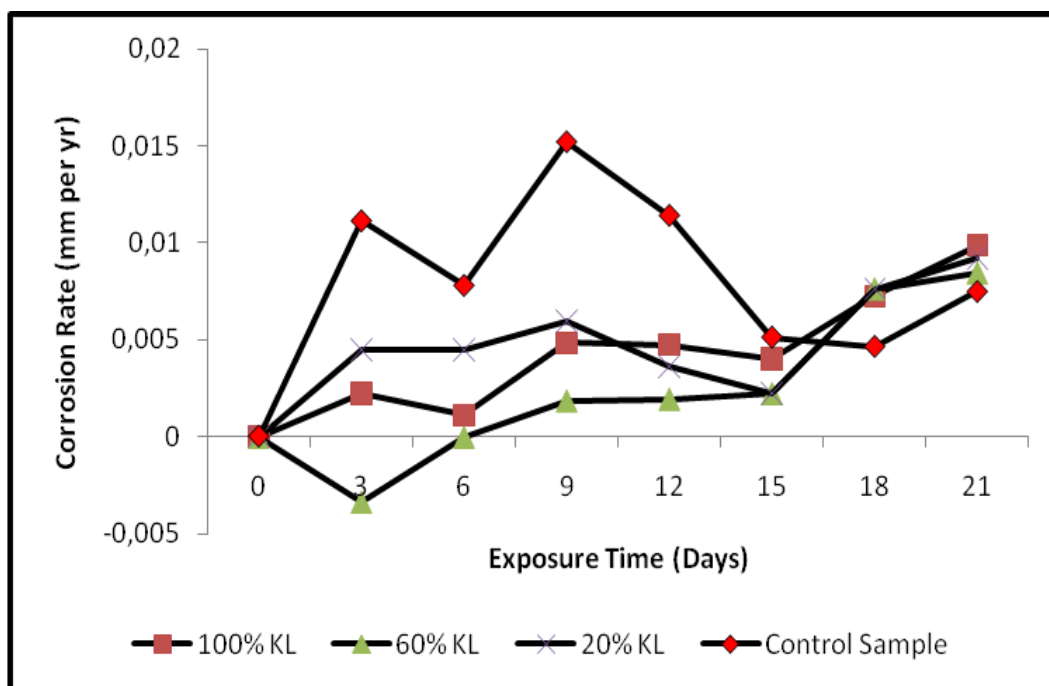


Figure 6. Variation of corrosion rate with exposure time for the austenitic stainless steel specimen immersed in acid chloride, with varied percent concentrations of added kola leaf extracts. (KL = kola leaf extract)

The corresponding corrosion rate versus the exposure time results in Fig. 6 gave a good correlation with the results in Fig. 5. The test medium with added 60% concentration of solution extract gave the least corrosion rate at the end of the 21 days with a value of 0.0084 mm/yr. The test medium with 100% and 20% concentrations of solution extract addition gave the corrosion rate values of 0.004 and 0.0025 mm/yr respectively at the 15th day of experiment. Except for the 60% concentration, the other extract addition recorded relatively higher corrosion rate at the end of the experiment.

3.5. Tobacco leaf solution extract

The results obtained for the variation of weight loss with exposure time for the austenitic stainless steel test specimen immersed in 0.5M acid chloride with varied concentration of added tobacco extract (20%, 60%, 100% concentrations) are presented in Fig. 7. The corresponding corrosion rate vs. the exposure time curves are presented in Fig. 8.

The weight loss recorded as at the 15th day of the experiment for the corrosive acid medium with added 60 and 100% concentrations of solution extract achieved the same weight loss value of 0.0018g while the 20% concentration of solution extract addition, recorded a value of 0.0024 at the same period of the experiment. After the 15th day of the experiment, the stainless steel alone in the test period apparently recorded lower corrosion weight loss values than those with the added extract concentrations. On the 21st day of experiment, weight loss values of 0.0061g, 0.0057 and 0.0059 were obtained respectively for the 100, 60 and 20% tobacco extract concentrations addition used.

A plausible explanation for the above results could be given. As the corrosion reactions continued, there was probably a stifling corrosion reactions caused by the weakened test medium due to corrosion deposits. At this stage, the stainless steel specimen was most likely able to stabilize its self generated passive film while the green inhibitors were also weakened due to the test environment contamination by corrosion deposits.

The corresponding corrosion rate versus the exposure time results in Fig. 8 gave a good correlation with the results in Fig. 7.

The recorded corrosion rate value on the 15th day of the experiment for 20, 60 and 100% concentrations of the extracts addition were the same at a value of 0.0042mm/yr. The test medium with added 60% concentration of solution extract gave the least corrosion rate at the end of the 21 days of the experiment with a value of 0.00907 mm/yr. The test medium with 20% concentration of solution extract addition gave the highest overall corrosion rate with a corrosion rate of 0.00939 mm/yr at the same period of experimental time. The 100% extract concentration addition gave a corrosion rate value of 0.0098 at the same period of the experiment.

3.6. The combination of kola nut, bark and leaf and tobacco extracts

The results obtained for the variation of weight loss with exposure time for the austenitic stainless steel test specimens immersed in 0.5M acid chloride with the additions of varied concentrations (20%, 60%, and 100%) of combinations of kola nut, bark, leaf and tobacco leaf extracts are presented in Fig. 9.

The corresponding corrosion rate curves are presented in Fig. 10. The test medium with 20% concentration extract addition had the least corrosion inhibition effect with a weight loss value of 0.0065g on the 21st day of the experiment. The weight loss recorded at the end of the experimental period for the corrosive acid medium with added 60% concentration of solution extract achieved a weight loss value of 0.0058g. The addition of 100% concentration of solution extract achieved a weight loss value of 0.0061g on the 21st day. However, the lowest weight loss values that ranged between 0.0002 and 0.0010 were obtained for all the percent concentrations on the 18th day of the experiment.

The corrosion rate results in Fig. 10 correlated with the results in Fig. 9. The test medium with added 60% concentration of solution extract gave the least corrosion rate at the end of the 21 days with a value of 0.0092 mm/yr.

The test medium with 20% concentration of solution extract addition gave the highest overall corrosion rate with a corrosion rate of 0.0103 mm/yr. However, the best corrosion rate values of 0, 0.0025, 0.0040 and 0.0020 mm/yr respectively were obtained on the 3rd, 12th, 15th and 18th day of the experiments. The apparent synergism here was that lower corrosion rate values were obtained on the different days of the experiment mentioned above in this combined extract concentrations than those previously reported above.

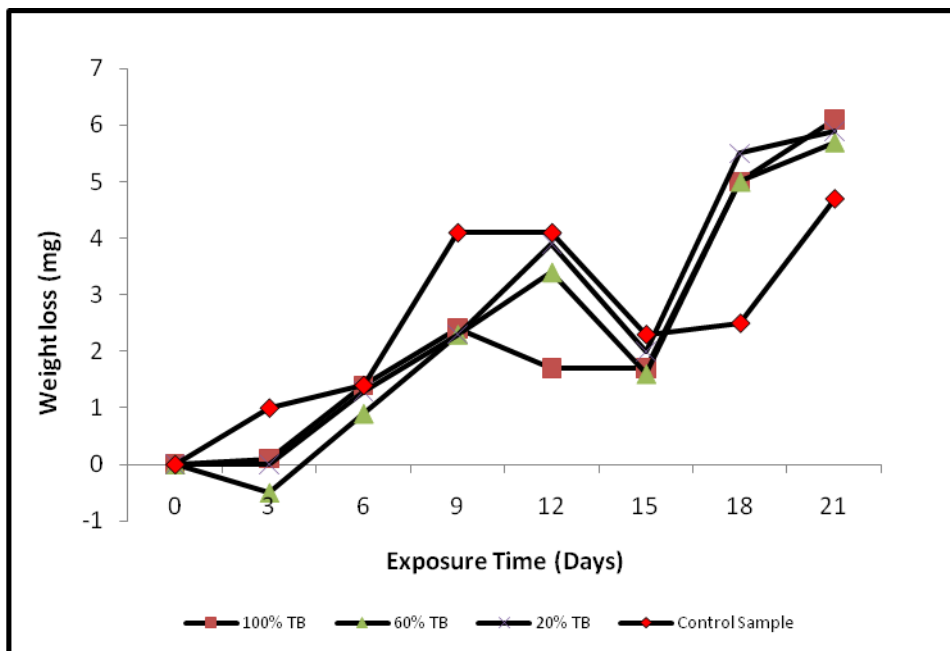


Figure 7. Variation of weight loss with exposure time for austenitic stainless steel test specimen immersed in acid chloride, with varied per cent concentration of added tobacco leaf extracts. (TB = tobacco leaf)

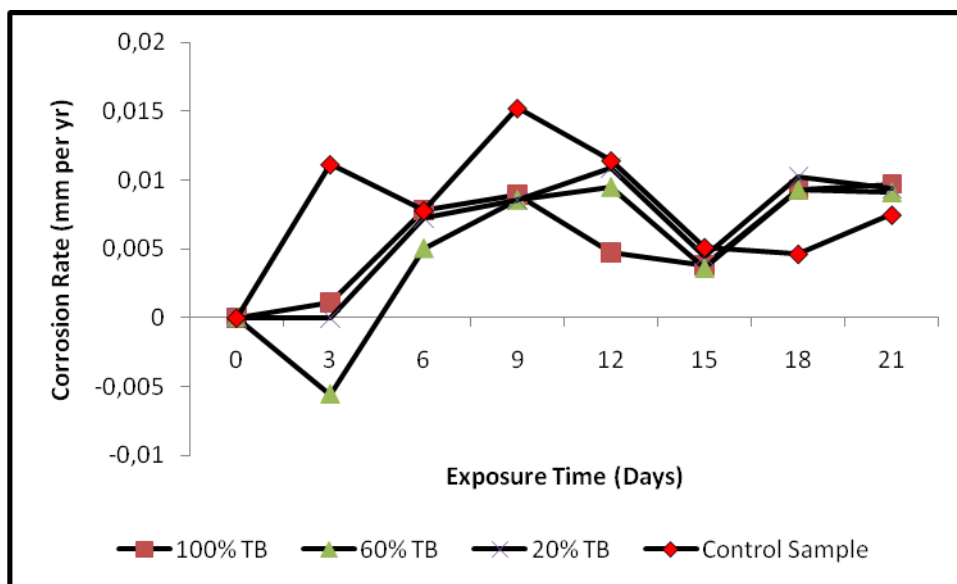


Figure 8. Variation of corrosion rate with exposure time for the austenitic stainless steel specimen immersed in acid chloride, with varied percent concentrations of added tobacco leaf extracts.

It would be grossly misleading if the data of the last day of the experiment alone were to be used in the interpretation of these results.

Austenitic stainless steel has the capacity to withstand corrosion to a large extent at ambient temperature and for a period of exposure in different environments. The curves of weight loss and corresponding corrosion rate showed its characteristic behavior to protect itself by creating a passive

film after the previous one had been penetrated by the Cl^- and SO_4^- reacting species of the test medium. This continuous process accounted for the fluctuating curves obtained for both the weight loss and corrosion rate as presented in the figures; and also, for very low corrosion rate values when compared with those of mild steel⁽⁹⁾.

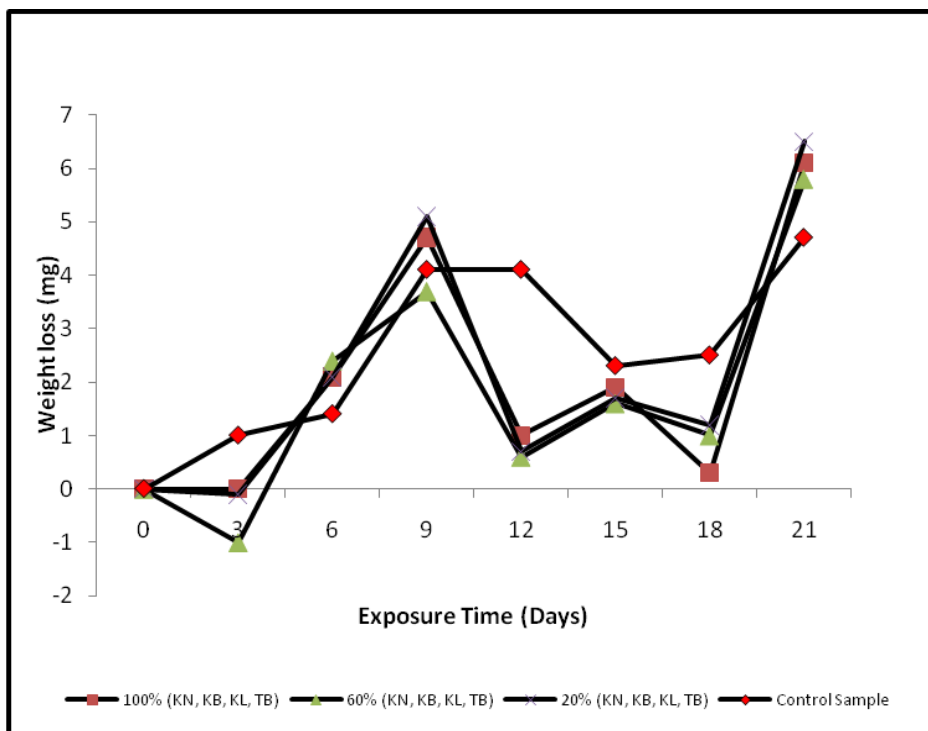


Figure 9. Variation of weight loss with exposure time for austenitic stainless steel in acid chloride in combination with different concentrations of kola nut, bark, leaf and tobacco leaf extracts.

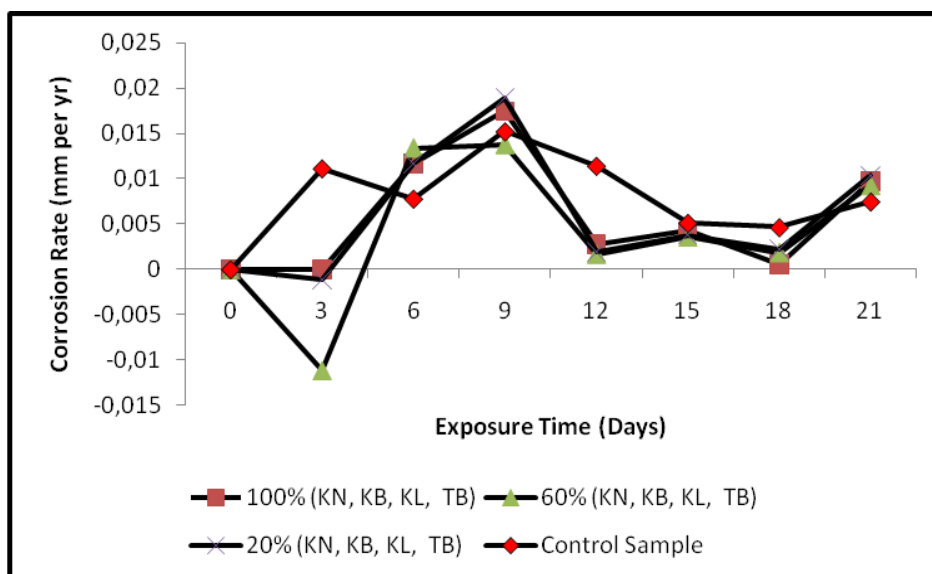


Figure 10. Variation of corrosion rate with exposure time for austenitic stainless steel in acid chloride in combination with different concentrations of kola nut, bark, leaf and tobacco leaf extracts.

3.7. Photomicrographs

Representative micrographs made before and after immersion of the test specimens in acid chloride and also with and without the use of the plants' extracts are presented in Figs. 11 to 12.

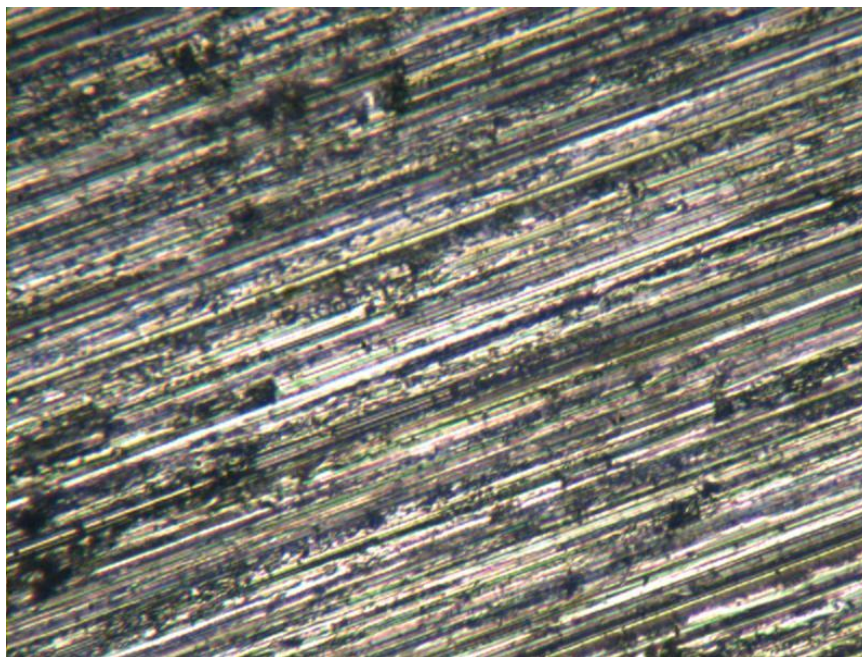
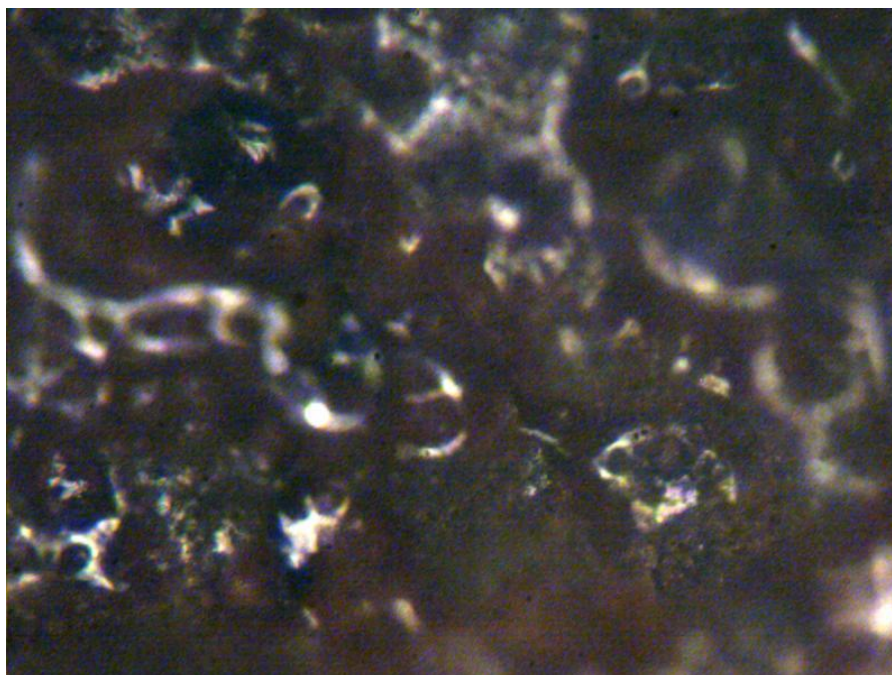
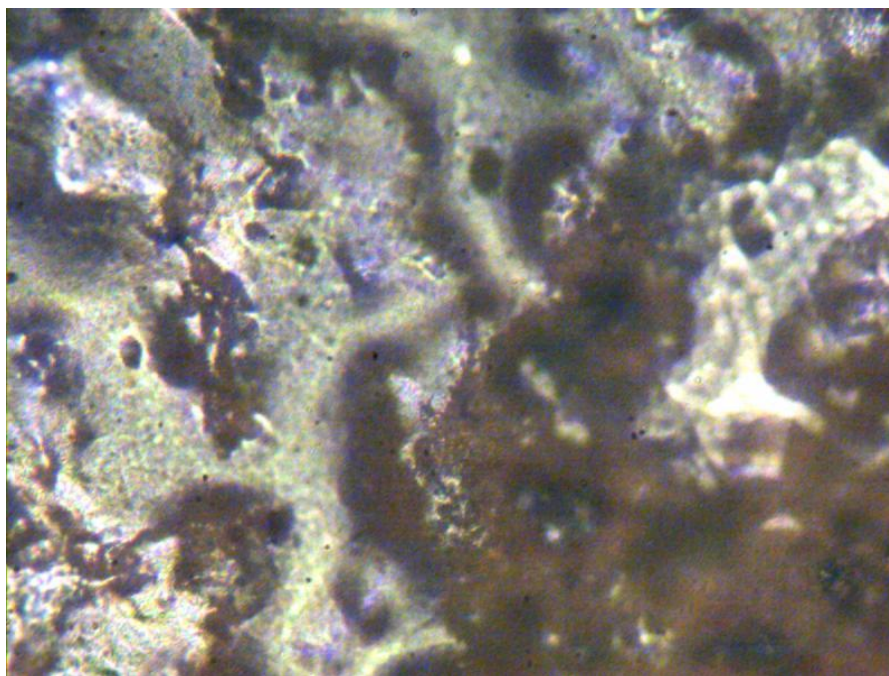


Figure 11. Photomicrograph of austenitic stainless steel test specimen before immersion in acid chloride.



A



B

Figure 12. Photomicrographs of the austenitic stainless steel test specimens: (A) after 21- day immersion in test medium with 100% kola bark extract addition; (B) after 21- day immersion in test medium with 60% kola leaf and tobacco concentration of extracts.

Pitting corrosion could very clearly be seen on the surfaces of the test specimens in Fig. 12 (a) and (b), indicating the specimens were not adequately inhibited as at the last day of the experiment.

Table 1. Inhibitor Efficiencies for Austenitic Stainless steel in the test medium

Juice Extracts	Concentration of extract	Corrosion rate (mm/yr)	Inhibitor Efficiency (%)	
			21 st Day	15 th Day
Kola nut extract	20%	0.0075	0.00	33.33
	60%	0.0059	21.28	30.00
	100%	0.0065	12.77	23.81
Kola leaf extract	20%	0.0092	-23.40	67.2
	60%	0.0084	-12.77	67.2
	100%	0.0099	-31.91	27.50
Kola bark extract	20%	0.0096	-27.66	66.67
	60%	0.0100	-34.04	50.00
	100%	0.0070	6.38	11.11
Tobacco leaf extract	20%	0.0094	-25.53	8.70
	60%	0.0091	-21.28	11.11
	100%	0.0097	-29.79	11.11
Kola nut + Kola bark + Kola leaf + Tobacco leaf extracts	20%	0.0103	-38.30	31.58
	60%	0.0092	-23.40	35.14
	100%	0.0097	-29.79	19.05

This observation bore a close relationship with the results in Table 1 for inhibitor efficiencies having more negative values at the end of the experiment when the micrographs were made.

The overall corrosion and inhibition profile showed that a fairly good corrosion inhibition was achieved with the use of these extracts up to the 15th day as could even be evidenced with the inhibitor efficiency percent values of all the different extract concentrations. As at the 21st day of the experiment the inhibition performance of the extracts had lost significant effectiveness in most of the different concentrations.

The austenitic stainless steel (Type 304) test specimen used, in general, creates its own passive film on its surface for corrosion resistance. However, in very aggressive environment such as sulphuric acid chloride, this protective barrier could be broken by the penetration of the strong reacting species – Cl^- and SO_4^- to initiate corrosion reactions leading to pitting/general corrosion in most instances. The use of inhibitors as in this work was to further strengthen its corrosion resistance/inhibition performance and this had been achieved to some extent.

Just as it had been previously explained [9], the effective corrosion inhibition performance of kola tree and tobacco extracts could be associated with their complex chemical compounds which include tannin.

Also for kola leaf and nut extracts, constituents such as epicatechin, D-catechins, theophylline and theobromine contained in their constituents could be, or act as inhibiting passive film formers on the steel substrate surface.

The formed film would act as a barrier between the steel and corrosive environment interface and thus preventing and/or stifling corrosion reactions. Similarly, the very complex structural compounds and the multifarious constituent composition of tobacco which consists of about 4,000 chemical compounds would have provided a more stable adherent film on the surface of the steel specimen to hinder active corrosion reactions and hence hindering the penetration of the Cl^- and SO_4^- ions reacting species through the surface film barrier. The synergistic action/reaction of these compounds on the surface of the steel could hinder the chloride ion species, promote more stable passive film formation on the surface of the steel and hence inhibit and stifle corrosion reactions at the steel / environment interface.

3.8. Inhibitor Efficiency

The results of the inhibitor efficiency obtained by calculations are presented in Table 1. The best results obtained were within the first 15 days of the experiment; and by the 21st day, the end of the experiments, the potency of the inhibition performance had dwindled drastically, leaving only kola nut extract – 60 and 100% concentrations with inhibition efficiency percent values of 21.28 and 12.77 respectively; and kola bark (100%) with 6.38% on the positive values. As at the 15th day of the experiment, all the percentage values were on the positive, achieving values up to 67.2% for kola leaf extract (20 and 60% concentrations), and kola bark with a value of 66.67% at 20% concentration. The combined extracts showed some synergistic effect by achieving values of 31.58% and 35.14% especially for the 20 and 60% concentrations.

4. CONCLUSION

The extracts exhibited fairly good corrosion inhibition of the austenitic stainless steel test specimens in the very strong acid chloride test medium up to the 15th and in few cases, to the 18th day of the experiment. Extracts of kola leaf and kola bark gave the best inhibition performance as at the 15th day of the experiment with inhibition efficiency values of 67.2% (20 and 60% concentrations) and 66.67% (20% concentration) respectively. A fairly good synergism was shown with the inhibition efficiency values of 31.58 and 35.14% for the combined contracts of Kola nut + Kola bark (20% concentration) and, Kola leaf + Tobacco leaf (60% concentration) respectively. On the 21st day of the experiment, except the kola bark and kola nut extracts at 100% and 20% concentrations and with positive values of 6.38 and 21.58% respectively, all the other extracts at all concentrations did not show any effective corrosion inhibition performance with the negative values recorded. For the austenitic stainless steel specimen in acid chloride environment and under the experimental working conditions used, the extracts could only be used for a short period of time.

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