

Synergistic Effect of Tobacco and Kola Tree Extracts on the Corrosion Inhibition of Mild Steel in Acid Chloride

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The corrosion inhibition effect of extracts of kola plant and tobacco in mixed form on the protection of mild steel specimens immersed in acid chloride solution was studied at ambient temperature by gravimetric and potential monitoring methods. The electrode potential monitoring was performed using a digital voltmeter and a saturated calomel electrode (SCE) as the reference electrode. Extracts of kola plant and tobacco in different concentrations and combinations were used as 'green' inhibitors. There was significant reduction in the weight loss and in the corrosion rate of the test samples, particularly at the added extracts concentration of 100%. Some very good inhibitor efficiency values were obtained which suggested good corrosion inhibition performance of the added extracts at the concentrations used. Potential measurement values recorded showed in most cases, a reduction in active corrosion reactions for some combinations of the extracts. This behavior was attributed to the protective film provided on the steel's surface by the complex chemical constituents of the plants extracts. The best corrosion inhibition performance for mild steel was obtained using the combined extracts of kola leaf and tobacco at 100% concentration with an inhibitor efficiency of 91.27%. The combination of kola leaf, nut and tobacco at the same concentration was effective at an inhibitor efficiency of 82.78%.

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

1. INTRODUCTION

In a previous study, the extracts of kola tree and tobacco were investigated in acid chloride under the same test conditions as used in this present work. The results obtained were very encouraging and that necessitated the interest in undertaking the present study to look into the possible reactions synergism of these extracts when used in different combinations at the same previous per cent concentrations. A summary of some of the results are presented in Tables 1 and 2

The use of plant extracts as inhibitors for the corrosion of metals/alloys, has gained very wide interest among researchers in recent time ⁽¹⁻⁷⁾. In very many cases, the corrosion inhibitive effect of some plants' extracts has been attributed to the presence of tannin in their chemical constituents ⁽⁷⁻⁹⁾. 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 ^(2-5, 10) 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 ⁽⁴⁻⁶⁾. Tobacco plants produce ~ 4,000 chemical compounds – including terpenes, alcohols, polyphenols, carboxylic acids, nitrogen – containing compounds (nicotine), and alkaloids ⁽¹⁰⁾. These may exhibit electrochemical activity such as corrosion inhibition ⁽³⁾.

Also, 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 ⁽¹¹⁾. As reported in some previous studies and also mentioned above ⁽²⁻⁷⁾, tannin is known to possess corrosion inhibitive properties on metals – particularly, mild steel.

With the very complex structural chemical compounds of the extracts of the two plants, a reasonable amount of corrosion inhibition of the mild steel in the very corrosive acid chloride environment used in this work is expected. Such a positive result will be economically and technologically beneficial.

2. EXPERIMENTAL PROCEDURE

The experimental procedure here follows that of other previous investigations ⁽⁷⁾. The mild steel specimens were obtained from Metal Samples Inc., Alabama. The nominal composition of the mild steel coupons of grade C1010 was: 0.08 C, 0.34 Mn, 0.012 P, 0.008 S, 0.023 Si, 0.053 Al, 0.03 Cu, 0.002 Sn, 0.0024 N, 0.02 Cr and 0.01 Ni, the rest being iron. The mild steel samples were cut into dimension of 20 x 40 x 1.5 mm. A 1.5 mm diameter hole was drilled about 5 mm from the top of the 20 mm edge. The clean test specimens were ground with silicon carbide abrasive paper of 240, 320, 400 and 600 grits; polished to 1 micron, thoroughly cleaned and rinsed in ultrasonic cleaner, 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.

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, leaves and bark of the kola tree and from tobacco were used as the corrosion inhibitor, in different concentrations.

The nuts, leaves and bark of the kola tree (*Cola acuminata*) and tobacco (*Nicotiana*) leaves 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 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 extracts. Each of the extracts 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. Extracts of kola nuts and kola leaves; kola leaves and tobacco; and of kola nuts, kola leaves and tobacco were added together in three different combinations as mentioned, for three different sets of experiments.

Table 1. Weight Loss for Mild steel in acid chloride with addition of tobacco extract

(A)			(B)			(C)		
100% TB			60% TB			20% TB		
Exp. Time (days)	Milligrams (mg)		Exp. Time (days)	Milligrams (mg)		Exp. Time (days)	Milligrams (mg)	
	Initial wt	Final wt		Initial wt	Final wt		Initial wt	Final wt
0	9057.9	9057.9	0	9040.9	9040.9	0	9011	9011
3	9057.9	9001.1	56.8	9040.9	8908	132.9	9011	8854.2
6	9057.9	8948	109.9	9040.9	8821	219.9	9011	8759.4
9	9057.9	8885.5	172.4	9040.9	8594.3	446.6	9011	8573.9
12	9057.9	8800.9	257	9040.9	8049.8	991.1	9011	8243.4
15	9057.9	8724.6	333.3	9040.9	7431	1609.9	9011	7893.8
18	9057.9	8629.1	428.8	9040.9	6605.3	2435.6	9011	7110.1
21	9057.9	8552.8	505.1	9040.9	5556.39	3484.5	9011	6511.9

Table 2. Weight Loss for Mild steel in acid chloride with addition of kola leaf extract

(A)			(B)			(C)		
100% KL			60% KL			20% KL		
Exp. Time (days)	Milligrams (mg)		Exp. Time (days)	Milligrams (mg)		Exp. Time (days)	(mg) wt loss	
	Initial wt	Final wt		Initial wt	Final wt		initial wt	final wt
0	8892.3	8892.3	0	8936.1	8936.1	0	8919.7	8919.7
3	8892.3	8653.3	239	8936.1	8373.3	562.8	8919.7	7335.3
6	8892.3	8544.2	348.1	8936.1	8166.2	769.9	8919.7	7033.6
9	8892.3	8370	522.3	8936.1	7854.2	1081.9	8919.7	6408.5
12	8892.3	8144.7	747.6	8936.1	7277.7	1658.4	8919.7	4559.1
15	8892.3	7867.2	1025.1	8936.1	6715.3	2220.8	8919.7	3154.3
18	8892.3	7561.3	1331	8936.1	6001.5	2934.6	8919.7	1115.9
21	8892.3	7221.3	1671	8936.1	5452.5	3483.6	8919.7	0

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 in methanol, air-dried, and re-weighed. Plots of weight loss and of calculated corrosion rate versus exposure time respectively (Figs 1 to 6) were made. All the experiments were performed at ambient temperature(s). The percentage inhibitor efficiency, P, was calculated from relationship:

$$P = 100 (1-W_2)/(W_1) \quad (1): \text{where};$$

W_1 and W_2 are the corrosion rates in the absence and presence, respectively, of a predetermined concentration of inhibitor. The inhibitor efficiency (%) was calculated for all the inhibitors for every 3 days of the experiment; the results are presented in Table 3.

2.4. Potential measurements

Potential measurements were performed on the mounted specimens in turns by immersing them in each of the acid test medium with and without plant extract. The potential was recorded at 3 – day intervals using a digital voltmeter and saturated calomel reference electrode. Plots of variation of potential (vs. SCE) with the exposure time were made, and these are presented in Figs. 7 to 9).

2.5. 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. 10 to 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 mild steel specimens immersed in 0.5M acid chloride with varied concentrations of kola leaf, kola nut and tobacco in combinations are presented in Figs. 1 to 6.

3.1.1. Kola nut and Kola leaf solution extracts

The results obtained for the variation of weight loss with exposure time for the mild steel test specimens immersed in 0.5M acid chloride with addition of varied concentrations of kola nut and kola leaf extracts in different combinations are presented in Fig. 1.

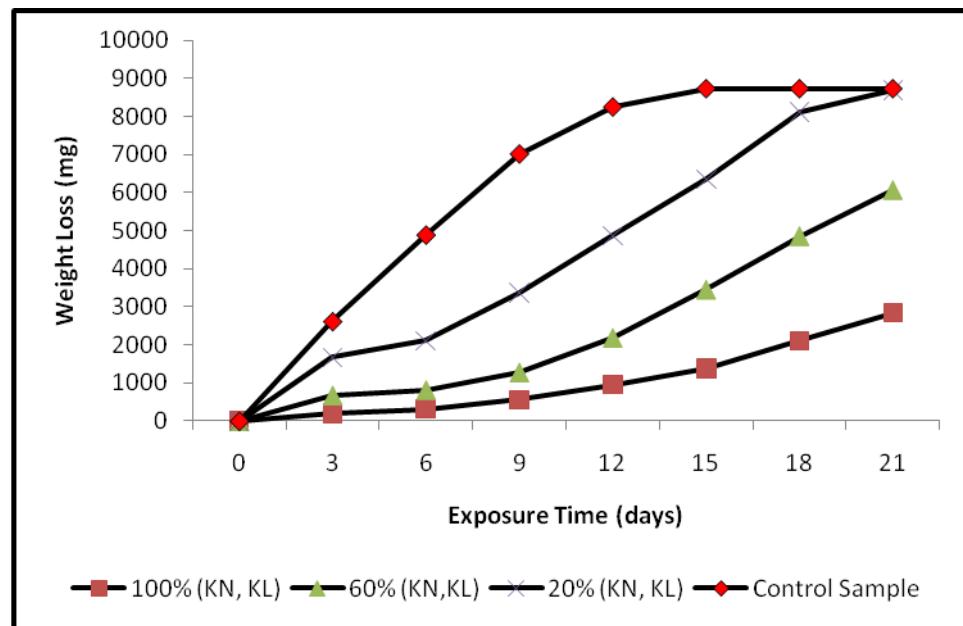


Figure 1: Variation of weight loss with exposure time for the mild steel specimen immersed in acid chloride, with varied percent concentrations of added kola nut and kola leaf extracts. (KN, KL = kola nut and kola leaf extracts respectively)

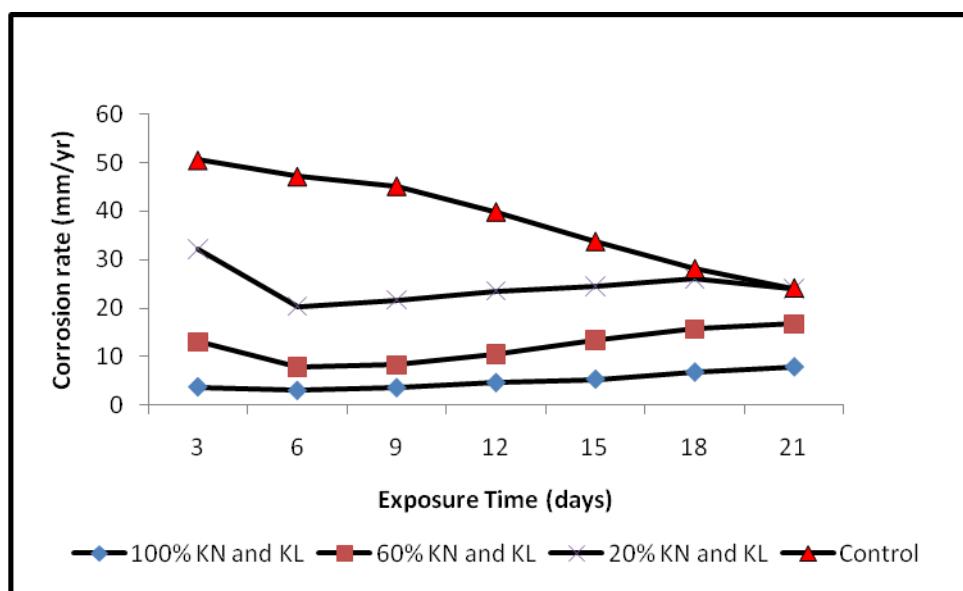


Figure 2: Variation of corrosion rate with exposure time for the mild steel specimen immersed in acid chloride, with varied percent concentrations of added kola nut and kola leaf extracts. (KN, KL = kola nut and kola leaf extracts respectively)

The corresponding corrosion rate vs. the exposure time curves are presented in Fig. 2. The acid test medium with 20% concentration extract addition had the least corrosion inhibition effect of the immersed specimens. The entire specimen was completely consumed by the end of the 21st day achieving a weight loss value of 8.6971g.

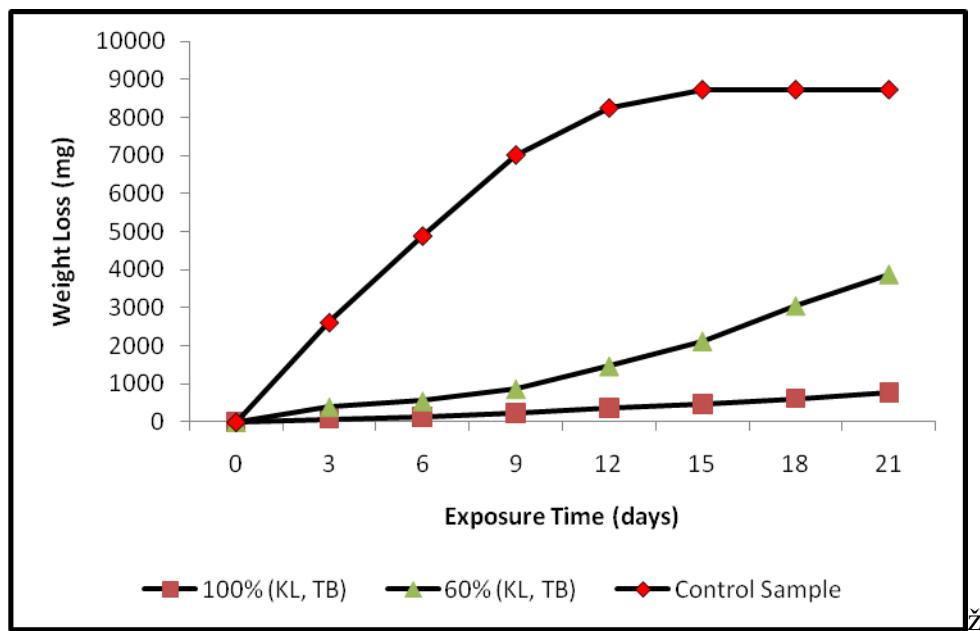


Figure 3: Variation of weight loss with exposure time for the mild steel specimen immersed in acid chloride, with varied % concentrations of added kola leaf tobacco extracts.

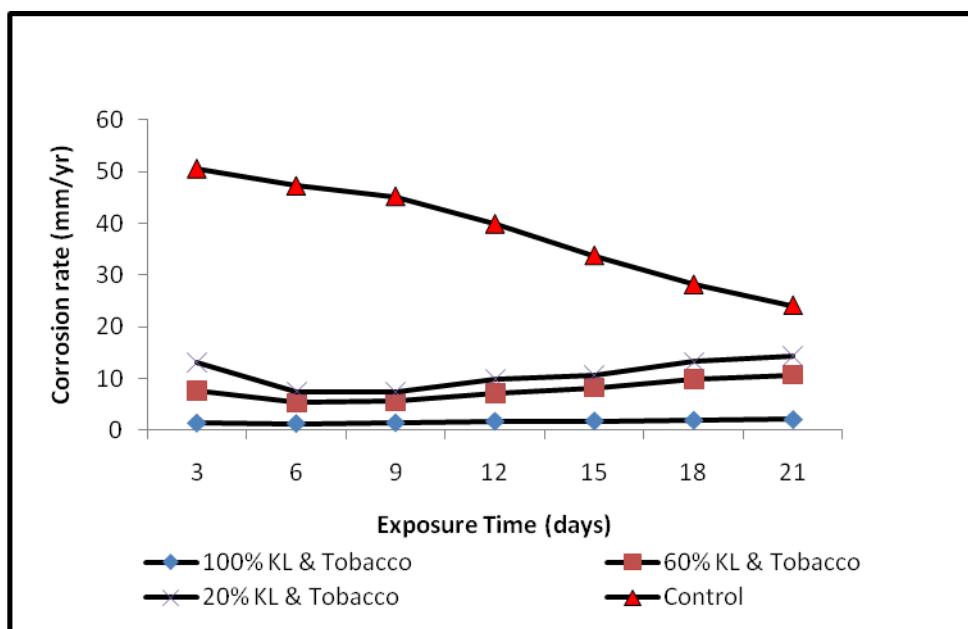


Figure 4: Variation of corrosion rate with exposure time for the mild steel specimen immersed in acid chloride, with varied percent concentrations of added kola leaf and tobacco extracts.

The test medium with added 60% concentration of extract performed better than that of the 20%'s. It recorded a weight loss a value of 6.0598g on the 21st day of the experiment. The acid test medium with 100% concentration of extract addition recorded the lowest weight loss with a value of 2.84g.

The corresponding corrosion rate vs. the exposure time results in Fig. 2 gave a good correlation with the results in Fig. 1. The corrosion rate increased with time. The reason for this behavior is not clear. The test medium with added 100% concentration of solution extract gave the least corrosion rate, which ranged between 2.97 mm/yr on the 2nd day to 7.85 mm/yr on the 21st day. The test medium with 20% concentration of extract addition gave the highest corrosion rate.

3.1.2. Kola leaf and Tobacco solution extract

The results obtained for the variation of weight loss with exposure time for the mild steel test specimen immersed in 0.5M acid chloride with addition of varied concentration of kola leaf and tobacco extracts combined (20%, 60%, 100% concentrations) are presented in Fig. 3. The corresponding corrosion rate vs. the exposure time curves are presented in Fig. 4.

While the test with 20% concentration extract addition had a weight loss value of 5.1958g on the 21st day of the experiment, that with added 60% concentration of solution extract recorded a weight loss value of 3.880g. The acid test medium with 100% concentration of solution extract addition recorded the lowest weight loss with a value of 0.7613g. Apparently, this can be described as very protective. The corresponding corrosion rate vs. the exposure time results in Fig.4 gave a good correlation with the results in Fig. 3. The corrosion rate increased with time. That the corrosion rate increased with time is an indication of the aggressive corrosive nature of the test medium in which the reacting species of Cl^- and $\text{SO}_4^{=}$ ions had strong penetrating power into the protective film barrier on the test specimens' to cause active corrosion reactions.

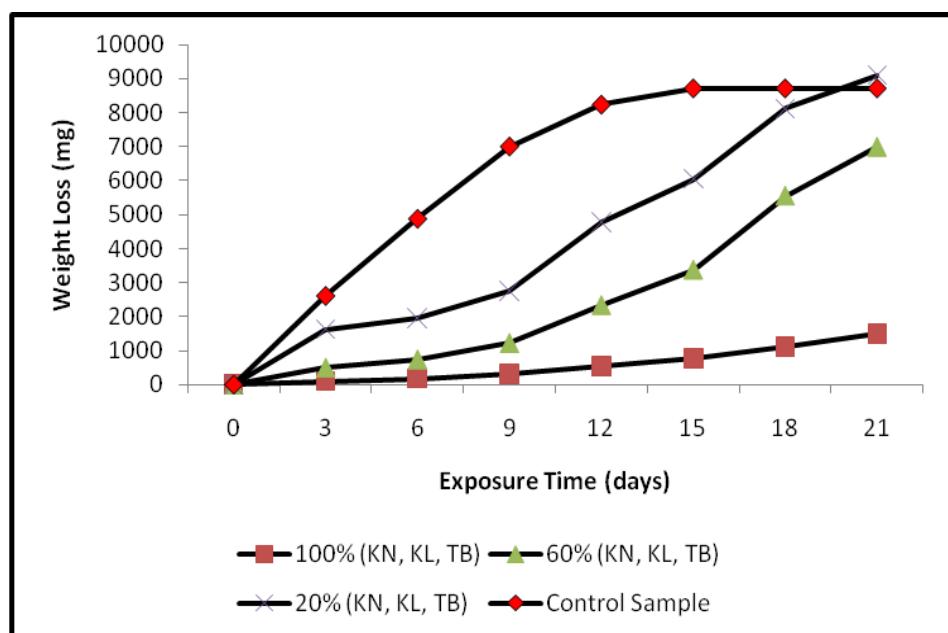


Figure 5: Variation of weight loss with exposure time for the mild steel specimen immersed in acid chloride, with varied percent concentrations of added kola nut, kola leaf and tobacco extracts.

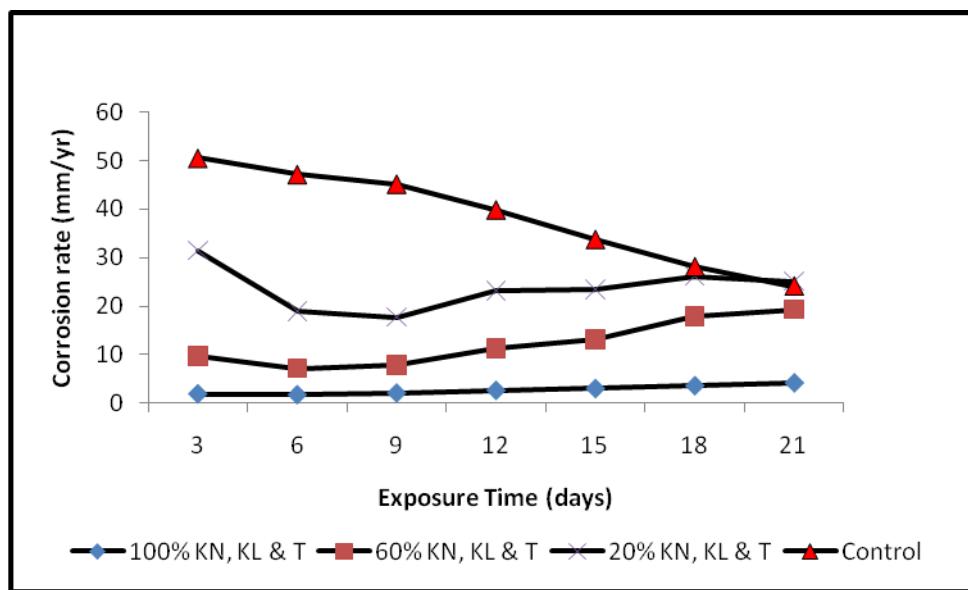


Figure 6: Variation of corrosion rate with exposure time for the mild steel specimen immersed in acid chloride, with varied percent concentrations of added kola nut, kola leaf and tobacco extracts.

The test medium with added 100% concentration of solution extract gave the least corrosion rate, which ranged between 1.32 mm/yr on the 3rd day to 1.96 mm/yr on the 21st day. The test medium with 20% concentration of solution extract addition gave the highest corrosion rate.

3.1.3. Kola nut, Kola leaf and Tobacco Extracts

The results obtained for the variation of weight loss with exposure time for the mild steel test specimen immersed in 0.5M acid chloride with addition of varied concentrations of combined kola nut, kola leaf and tobacco extracts (20%, 60%, 100% concentrations) are presented in Fig. 5. The corresponding corrosion rate vs. the exposure time curves are presented in Fig. 6. The acid test medium with 20% concentration extracts addition provided the least corrosion inhibition of the immersed specimen. By the end of the 21st day, the test sample achieved a weight loss value of 9.1021g out of an initial mass of 9.486g. Apparently, this concentration of the extracts used was not effective at all as indicated by the results. It was an almost total degradation with a tendency towards accelerating the corrosion.

The test with added 60% concentration of extracts recorded a value of 6.9936g by the 21st day; and the test medium with 100% concentration of extract addition recorded the lowest weight loss with a value of 1.5018g at the same test period. These extract combinations, apparently did not show any significant synergistic effect except at the concentration of 100% extracts.

The corresponding corrosion rate vs. the exposure time results in Fig. 6 correlated with the results in Fig. 5. The corrosion rate increased with time. The test medium with added 100% concentration of solution extract gave the least corrosion rate, which ranged between 1.71 mm/yr on

the 3rd day to 3.56 mm/yr on the 21st day. The test medium with 20% concentration of solution extract addition gave the highest corrosion rate.

3.2. Potential measurement

Potential readings for the mild steel specimens were taken over a period of 21 days at an interval of 3 days. The curves obtained for the variation of potential (mV) vs. saturated calomel electrode (SCE) with the exposure time are presented in Figs 7 to 9.

The specimens were immersed separately, in acid chloride ($0.5\text{M H}_2\text{SO}_4 + 5\% \text{NaCl}$ solution) with different extract concentrations of kola nut and kola leaf; kola leaf and tobacco; and the combined kola nut, kola leaf and tobacco extracts respectively. Results for kola nut, kola leaf and tobacco individually, had been previously reported and a partial result is presented in Tables 1 and 2.

The test medium without the solution extract addition increased negatively in potential and attained a value of -512mV at the end of the 21 days. This was a clear indication of active corrosion reactions and can thus be correlated with the results obtained in the weight loss experiments. The curves for variation of potential with exposure time in the test media with additions of combination of kola nut and kola leaf extract; kola leaf and tobacco leaf extract; and kola nut, kola leaf and tobacco extracts show that the extracts in combination also were effective. Though with fluctuations, quite many of the potential values are within the range of passive corrosion reactions with reference to SCE. A comparison of the potential values with the values obtained from the control test also showed good measure of corrosion inhibition performance.

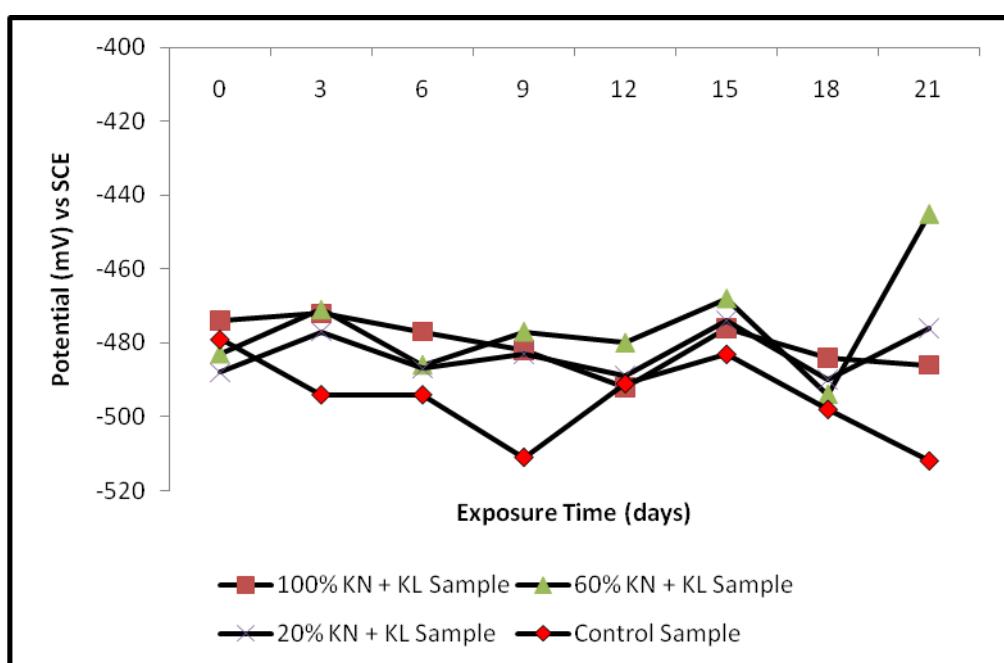


Figure 7: Variation of potential with exposure time for the mild steel specimen immersed in acid chloride, with varied percent concentrations of added kola nut and kola leaf extracts. (KN, KL = Kola nut and leaf extract)

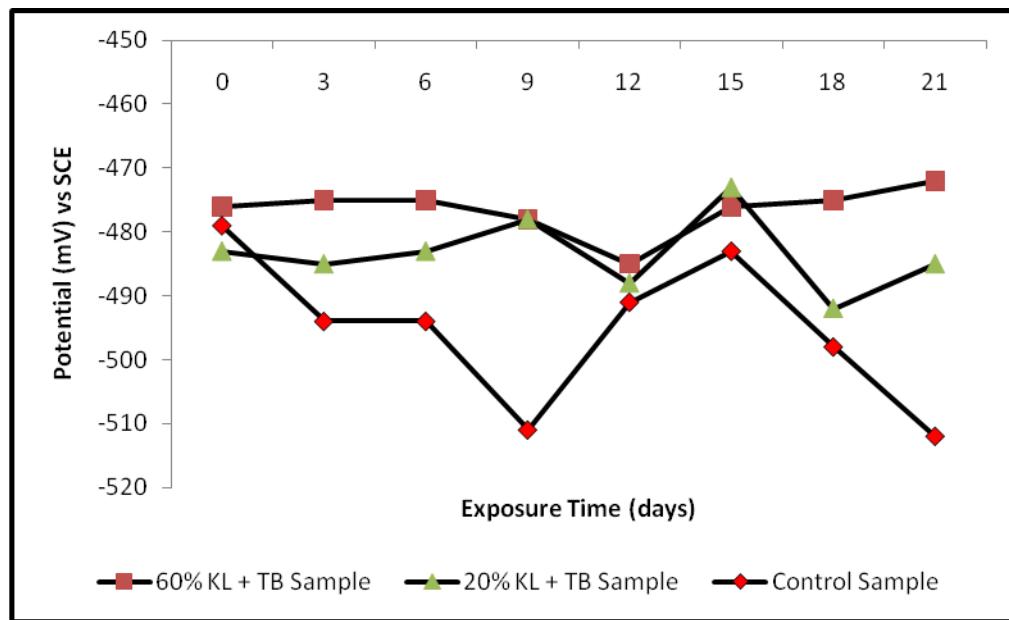


Figure 8: Variation of potential with exposure time for the mild steel specimen immersed in acid chloride, with varied percent concentrations of added kola leaf and tobacco extracts. (KL, TB = Kola leaf and tobacco extracts)

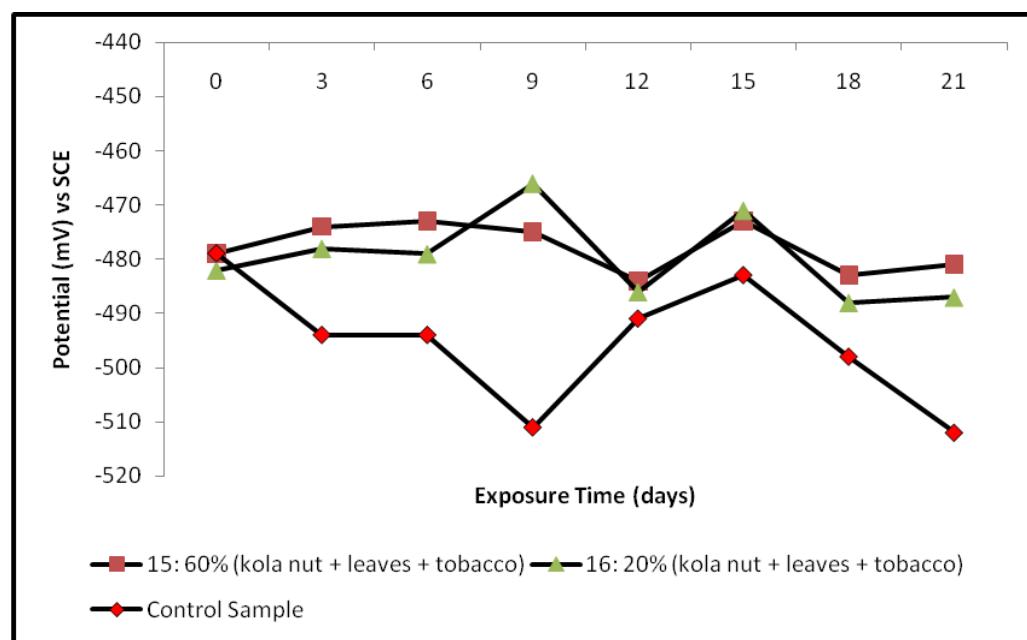


Figure 9: Variation of potential with exposure time for the mild steel specimen immersed in acid chloride, with varied percent concentrations of added kola nut, kola leaf and tobacco extracts. (KN, KL, TB = Kola nut, Kola leaf and tobacco extracts)

3.3. Photomicrographs

Some of the micrographs made during the experiments are presented in Figs. 10 to 12. All the micrographs are at the magnification of x100.

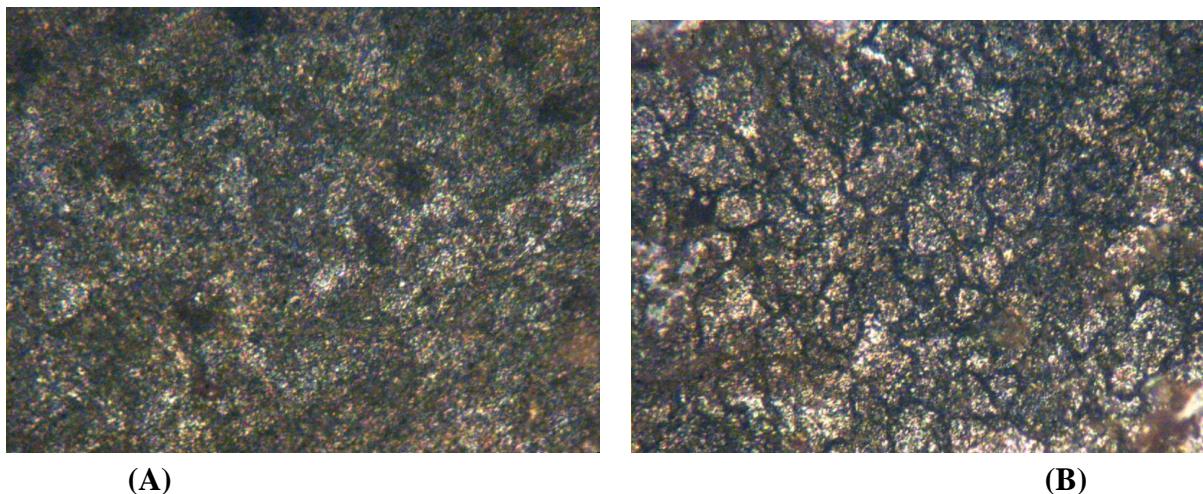


Figure 10: Mild steel test specimen: (a) and (b) after 21- day immersion in 60% kola leaf; and in 100% kola nut and tobacco leaf extracts concentrations respectively.

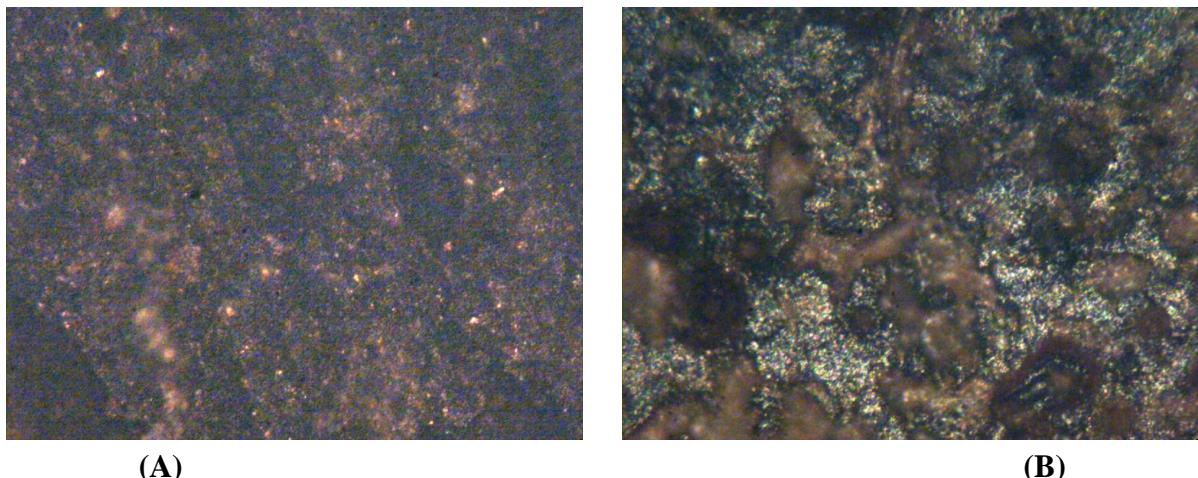


Figure 11: Mild steel test specimens: (a) after 21 day immersion in 60% concentrations of added kola leaf and tobacco; and (b) 21 days in 60% concentrations of added kola nut, kola leaf and tobacco extracts respectively.

The micrographs made from the experiments of added extracts in combinations (Figs. 10 and 11), did not present any surface feature of complete total degradation and devastation of mild steel that are known for sulphuric acid and (even worse) in sulphuric acid chloride environment that was used in this investigation. Evidence of corrosive action could be seen in these micrographs, but they were minimal; most particularly as seen in Figs 10(a) and 11 (a) respectively. These observations are in agreement with the results obtained with the weight loss, corrosion rate and potential values for each of the three different combinations of extracts. The micrograph for the test specimen before immersion is presented in Fig. 12.

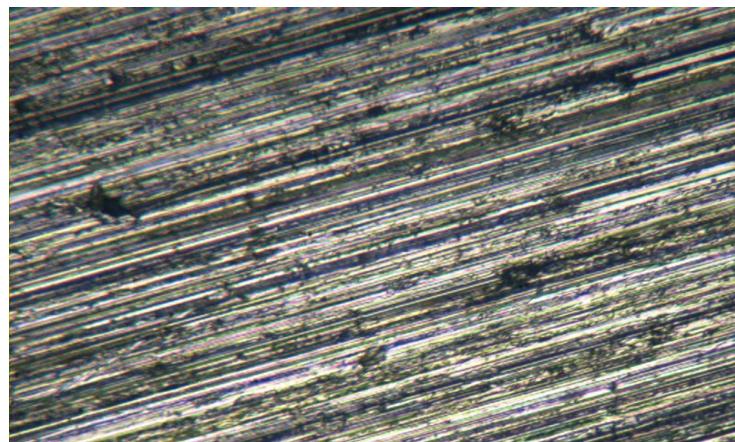


Figure 12: Mild steel specimen before immersion

3.4. Summary

The overall corrosion and inhibition profile showed that a good corrosion inhibition was achieved with the use of these extracts. This protective inhibition performance is also evident in the micrographs. The potential values obtained as presented in the curves bear correlation with the results obtained gravimetrically. The potential values obtained for the combined extracts of kola tree and tobacco fell within the accepted range for fairly good protection for mild steel with reference to saturated calomel electrode. In general, 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^{2-} 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.

3.5. Inhibitor Efficiency

The results of the inhibitor efficiency obtained by calculations are presented in Table 3.

Table 3. Inhibitor Efficiency for mild steel in the various media

Plant Extracts	Concentration of extracts	Corrosion rate (mm/yr)	Inhibitor Efficiency (%)
Kola leaf + Tobacco extracts	20%	14.3620	40.42
	60%	10.7260	55.50
	100%	2.1043	91.27
Kola nut + Kola leaf+ Tobacco extracts	20%	25.1595	-4.38
	60%	19.3313	19.80
	100%	4.1512	82.78

A very good result was obtained for the mild steel specimen by the combined tobacco and kola leaf extracts at 100% concentration with an inhibitor efficiency of 91.27%. A combination of the extracts of the kola nut, kola leaf, and tobacco gave good inhibition also at a concentration of 100%, with a percent inhibition efficiency of 82.78%. This confirms the clear synergy exhibited by the combined solution extracts as an effective corrosion inhibitor. The inhibitor efficiency for the individual extract (from another report) is given in Table 2 at different concentrations. While the tobacco and kola leaf extracts each gave good inhibition performance individually, the kola nut extract did not as much comparatively. The reason which is difficult to explain; but may not be unconnected with the different chemical composition that was less effective. However, their combinations including the kola nut, as reported here, performed well by synergism.

4. CONCLUSION

At the ambient working temperature, the best corrosion inhibition performance for mild steel was obtained using the solution extracts of kola leaf and tobacco combined solution extracts at 100% concentration with an inhibitor efficiency of 91.27%. The combination of kola leaf, nut and tobacco at 100% concentration was effective at an inhibitor efficiency of 82.78%. In spite of the very strong corrosive sulphuric acid chloride test environment used, the extracts in combinations at 100% concentration, gave good results that confirmed synergism in their corrosion inhibition reactions and protective performance of the tested mild steel.

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