

Full Length Research Paper

Corrosion and plants extracts inhibition of mild steel in HCl

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Corrosion and plants extracts inhibitive protection of mild steel specimens immersed in 0.5 M hydrochloric 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 metallographic observations from metallurgical microscopy. Addition of different concentrations of the plants extracts gave considerable reduction in the weight loss and in the corrosion rate of the test samples. This apparent corrosion inhibition was associated with the protective film provided on the steel's surface by the complex chemical constituents of the plants extracts. Effective protection of the mild steel was achieved more from the tobacco extract and also from the extract of kola leaf.

Key words: Inhibition, corrosion, mild steel, kola tree, tobacco, hydrochloric acid, protection.

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 resources that could be used to control/prevent incessant corrosion problems apart from the synthesized inorganic and other organic chemicals, some of 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, 2003; Okafor, 2007; Davis et al., 2003, 2001; Fraunhofer, 1995, 2000). Very encouraging results have been obtained in this regard. An attempt at making a contribution to this growing research area has necessitated the present investigation.

Plant parts 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 (nuts, leaves) and tobacco. Extracts of tobacco (genus – *Nicotiana*: family- Solanaceae), as an environmental benign corrosion inhibitor had been shown (Davis et al., 2003; Fraunhofer, 2000; Loto, 2003; WHO, 1985) 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 (Fraunhofer, 1995; Davis et al., 2001; Fraunhofer, 2000). Tobacco plants produce ~ 4,000 chemical compounds – including terpenes, alcohols, polyphenols, carboxylic acids, nitrogen – containing compounds (nicotine), and alkaloids (WHO, 1985). These constituents may be effective in exhibiting corrosion inhibition performance as in the present investigation. Likewise, kola nut tree's chemical composition consists of caffeine (2.0 to 3.5%), theobromine (1.0 to 2.5%), theophylline, phenolics – such as phobaphens, epicachins, D- catechin, tannic acid

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(tannin), sugar – cellulose, and water (www.wikipedia.org. 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 to exhibit electrochemical activity such as corrosion inhibition for mild steel in HCl.

In this work, a positive result is anticipated that could be beneficial technologically and economically.

EXPERIMENTAL PROCEDURE

Preparation of specimen

The mild steel test specimen used had a nominal percentage composition of: 0.15 C, 0.20 Si, 0.04 S, 0.85 Mn, 0.10 Ni, 0.20 Cr, 0.02 Mo, 0.001 V, 0.35 Cu, the rest being Fe. The steel bar was cut into various pieces of different lengths and the specimens were descaled by wire brushing. They were then ground with silicon carbide abrasive paper of 240, 320, 400, 600, and up to 800 grits. They were thoroughly cleaned, rinsed in ultrasonic cleaner, dried, and kept in a desiccator for further weight loss tests.

Test media

The experiments were performed in 0.05 M HCl 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. Details of the juice extraction are presented subsequently.

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 uniformly to 0.70 kg 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 extraction 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

100 ml of 0.5 M HCl 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 10 ml 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 HCl; this served as the control experiment.

Weight loss experiment

Weighed test specimens were fully immersed in each of the test

media contained in a 250 ml beaker for 24 days. Experiments were performed with hydrochloric acid test medium in which some had the solution extracts added. The 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 (Figures 1 to 6) were made. All the experiments were performed at ambient temperature(s). The percentage inhibitor efficiency, P, was calculated from the 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 percent inhibitor efficiency was calculated for all the inhibitors for every 3 days of the experiment, and the results are presented in Table 1.

Micrographs

Some optical micrographs of the test specimen before and after immersion in hydrochloric acid were made in the experiments. The representative ones are presented in Figure 7a to 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 mild steel test specimens immersed in 0.5 M hydrochloric acid with varied concentrations of added kola tree (leaves and nuts) and tobacco extracts are presented in Figures 1 to 6.

Kola tree leaf 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 a low weight loss value of 1.250 g –the lowest weight loss value of the three concentrations used. With 60% concentration of the added kola leaves extract, the weight loss value at the same period of the experiment was 1.740 g; while for 30% concentration, the recorded value was 2.8 g.

Clearly, the order of increasing percent corrosion inhibition performance was: 100 >60 >30. They all performed well when compared with the test medium which contained no extract addition; this recorded a significant weight loss value of 4.400 g as at the 21st day of the exposure time.

The results obtained for the corrosion rate versus the exposure time, Figure 2, followed the same trend of corrosion inhibition performance. The test medium with 100% concentration of added leaves extract, recorded the corrosion rate values that ranged between 3.12 at the beginning to 2.54 mm/year at the end of the experiment. For 60% concentration of the same extract at the end of the experiment, the corrosion rate value achieved was 4.00 mm/year; and for 30% concentration of the same

Table 1. Inhibitor efficiency for mild steel sample in hydrochloric acid.

Environment	Concentration (M)	Inhibitor	Inhibitor concentration	Inhibitor efficiency (%)								
				Exposure time (days)	3	6	9	12	15	18	21	24
Hydrochloric acid	0.5	None			Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Hydrochloric acid	0.5	Kolanut	30%	-2.26608	56.016	70.31676	73.48179	71.21823	69.34466	59.30748	34.36193	
		Leaves	60%	18.12865	56.85711	64.10053	76.19532	77.4337	77.90476	71.05558	59.48936	
		Extract	As obtained	35.5629	64.76562	77.89089	81.27247	79.54696	80.39839	77.44878	73.81883	
Hydrochloric acid	0.5	Kolanut	30%	62.5396	77.89089	83.38167	84.95043	84.37086	82.72583	80.08598	77.24748	
		Fruit	60%	48.68421	82.35716	85.78793	87.23397	83.19337	81.62686	81.07005	78.60294	
		Extract	As obtained	47.62427	76.60273	84.14217	79.15063	79.6989	58.85131	53.06127	44.42616	
Hydrochloric acid	0.5	Tobacco extract	30%	53.98392	73.87424	84.01824	85.89152	84.87845	85.36854	83.21667	79.9744	
			60%	44.99269	78.40804	87.27011	90.36742	90.24586	89.95448	88.81189	87.79401	
			80%	60.59942	84.99333	90.88385	92.91554	92.5221	92.58271	91.87783	91.25694	
			As obtained	94.1155	95.63032	96.46557	97.28328	97.06354	96.8334	96.53507	96.09362	

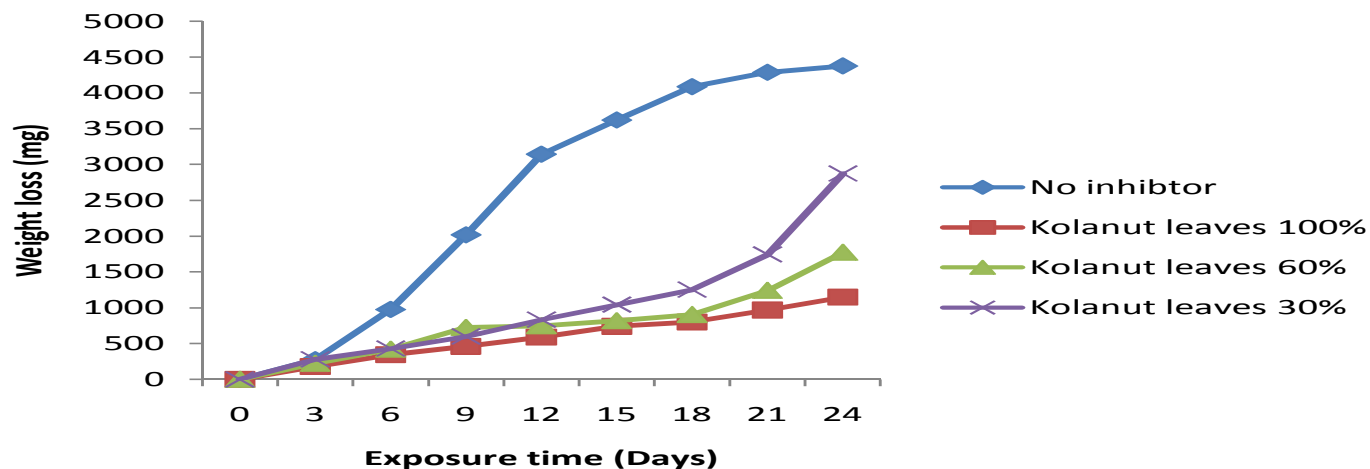


Figure 1. Variation of weight loss with exposure time for the steel specimen immersed in 0.5 M HCl with varied concentrations of added kola tree leaves extract.

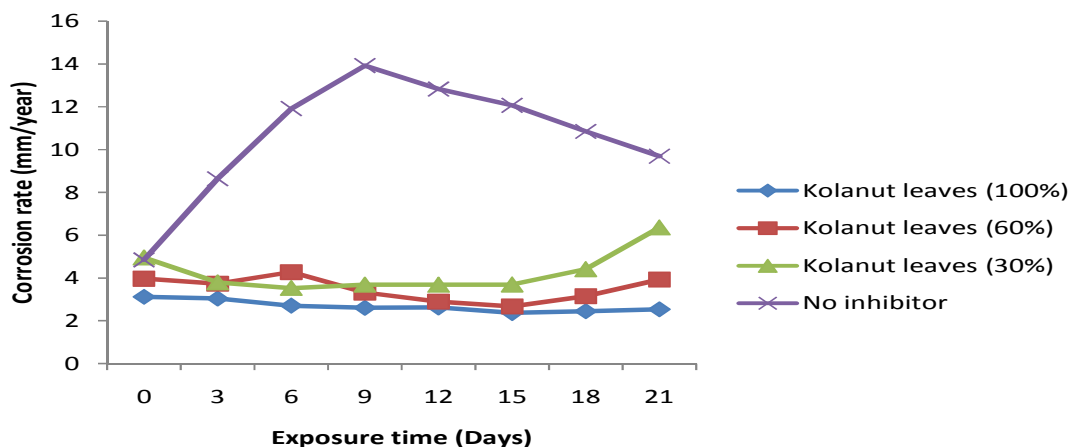


Figure 2. Variation of corrosion rate with exposure time for the steel specimen immersed in 0.5 M HCl with varied concentrations of added kola tree leaves extract.

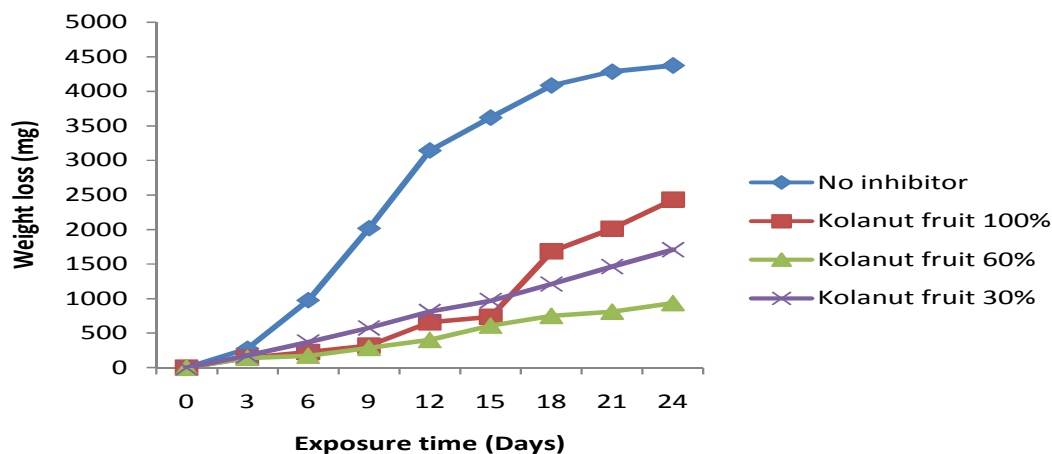


Figure 3. Variation of weight loss with exposure time for the steel specimen immersed in 0.5 M HCl with varied concentrations of added kola nut (fruit) extract.

extract, the recorded values ranged between 4.85 at the beginning to 6.4 mm/year at the end of the experiment. The test without the addition of the extract recorded a corrosion rate value of 9.69 mm/year at the end of the exposure time.

Undoubtedly, 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 that was already known to be an effective inhibitor of corrosion of mild steel in some other media such as H_2SO_4 and NaCl solution. However, the performance here could also be due to the synergistic effect of combination of other constituents that were mentioned previously in the introduction.

Kola nut extract

The curves for the variation of weight loss and corrosion rate with exposure time respectively, for the steel specimen immersed in 0.5 M HCl with varied concentrations of added kola nut (fruit) extract are presented in Figures 3 and 4. In Figure 3, the trend of weight loss values obtained with respect to percent concentrations of added extract was different from the one obtained in Figure 1 for the leaf extract values. After 15 days of maintaining almost the same weight loss values with the added 60% extract concentration to the test medium, the curve for added 100% extract concentration moved up significantly to achieve a value of 2.43 g on the last day of the experiment. The weight loss achieved by the sample with 60% concentration of extract was 0.75 g at that same period of the experiment. The reason for this sudden out

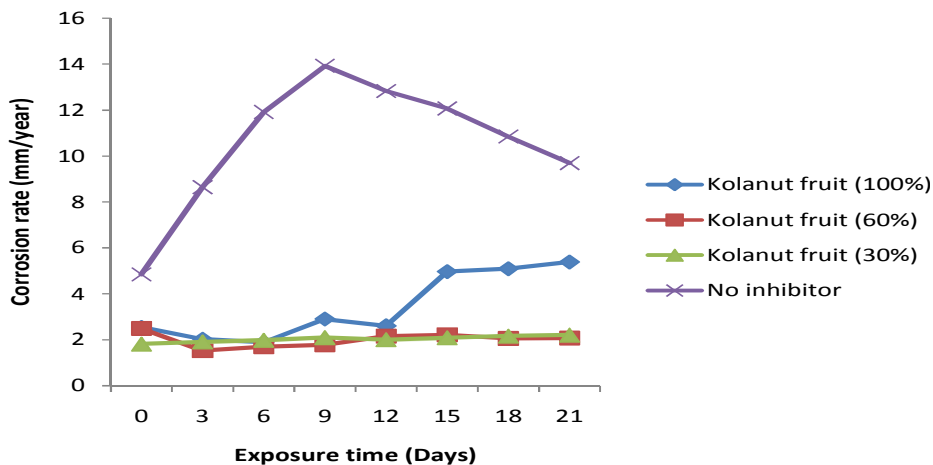


Figure 4. Variation of corrosion rate with exposure time for the steel specimen immersed in 0.5 M HCl with varied concentrations of added kola nut (fruit) extract.

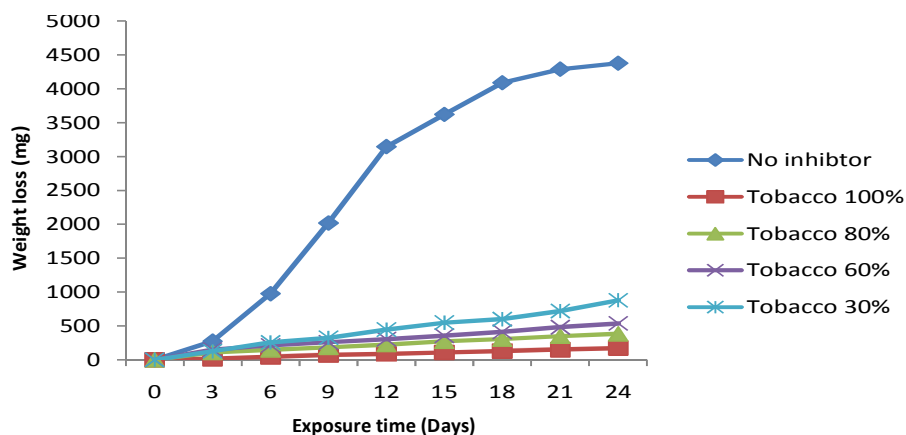


Figure 5. Variation of weight loss with exposure time for the steel specimen immersed in 0.5 M HCl with varied concentrations of added tobacco extract.

of trend curve and weight loss value is difficult to explain. Perhaps, some experimental error was involved here. For the 30% kola nut extract concentration, the weight loss value at the end of the experiment was 1.706 g. The blank test was the same as in Figure 1. Apparently, except for the obvious anomaly with the added 100% - concentration kola nut extract weight loss values recorded, this extract gave a good corrosion inhibition performance that seemed to rate better than the leaf extract for each of the other concentrations of 60 and 30%, respectively. The same reason adduced for the appreciable corrosion inhibition performance of the leaf extract was also obtained here.

The corresponding corrosion rate values obtained (by calculation) are presented in Figure 4. For all the kola nut extract percent concentrations, the corrosion rate values were very close indeed for the first 15 days before it increased for the 100% concentration extract, but about

the same with the 30 and 60% extract concentrations throughout the rest days of the experiment, achieving a value of 2.00 mm/year. The corrosion rate values had good correlation with the weight loss values in Figure 3.

Tobacco leaf extract

The results for the variation of weight loss with exposure time for the steel specimen immersed in 0.5 M HCl 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%). Just like the previous extracts of kola tree parts, the 100% here represents the original extract without dilution. As can be seen in Figure 5, very good corrosion inhibition performance was exhibited in all the

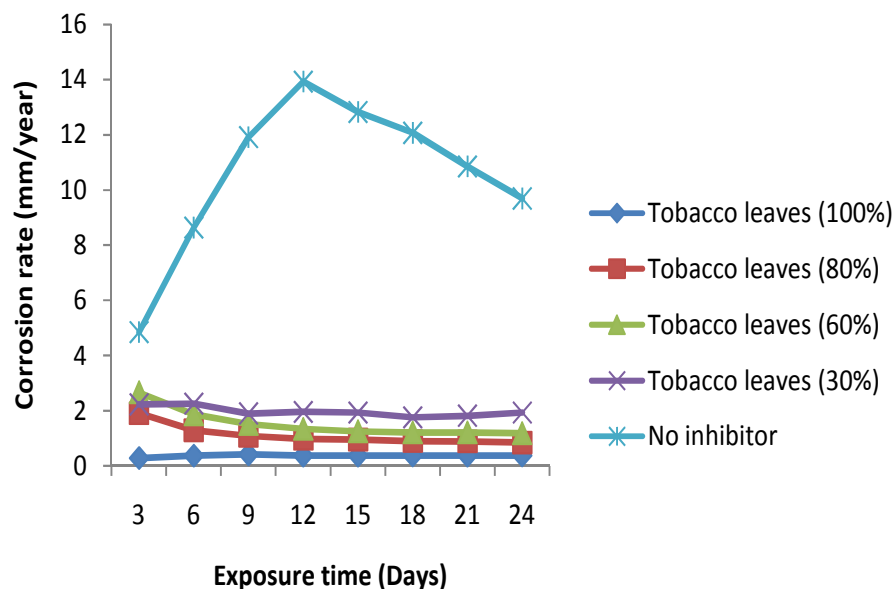


Figure 6. Variation of corrosion rate with exposure time for the steel specimen immersed in 0.5 M HCl with varied concentrations of added tobacco extract.

concentrations of tobacco extract used. The 30% extract concentration recorded a weight loss value of 0.76 g as at the last day of the experiment while the 60% extract concentration addition gave a weight loss value of 0.40 g at the same end period of the experiment, and 0.25 g for the 80% extract concentration. The 100% extract concentration addition to the test medium, recorded a weight loss value of 0.19 g. When compared with the weight loss value of 4.40 g recorded for the test in HCl alone, the inhibition electrochemical activity, the tobacco extract exhibited at all concentrations used was indeed significant for the mild steel in hydrochloric acid.

The corresponding corrosion rate values obtained, Figure 6, followed the same trend of results as obtained in Figure 5. The corrosion rate values were very low. The 30% extract concentration addition to the test medium, recorded both at the beginning and end of the experiment, a value of 2 mm/year. For the 60, 80 and 100% extract concentrations used, the corrosion rate values obtained at the end of the experiments were 1.5, 1.0, and 0.5 mm/year respectively.

The results obtained for the use of tobacco extracts as inhibitor in this investigation were indeed very unique. It means this extract has the characteristic inhibitor specificity for mild steel inhibition in HCl medium. It is still not clear which of the many constituents of tobacco that is/are responsible for this inhibition activity of relative passive film stability on the steel surface in interaction with the corrosive environment. However, it could be said, plausibly, that the synergistic combination of many constituents out of over 4,000 were responsible for the relative passivity and hence very good inhibition under the test conditions.

Photomicrographs

Some of the micrographs made before and after immersion of the test specimens in hydrochloric acid, with and without the use of the plants' extracts are presented in Figures 7a to d.

There was massive general corrosion of the mild steel in the test medium without added tobacco, kola leaf and kola nut extracts as observed in Figure 7a. Figure 7b shows a surface feature with very moderate or minimal corrosive action for the test with the addition of kola nut extract. A far better surface feature was obtained as presented in Figure 7c for the test with added 100% concentration of tobacco extract. These observations from the micrographs bear very close correlation with the results obtained from the gravimetric experiments (weight loss) and the corresponding corrosion rates.

Inhibitor efficiency

The results of the inhibitor efficiency obtained by calculations are presented in Table 1. The best result obtained for mild steel was provided by tobacco extract at 100% concentration with an efficiency of 96.09% on the 24th day of the experiment; and 97.28% on the 12th day. The overall average inhibitor efficiency for this extract is 96.25%. Kola leaf extract at 100% concentration addition also gave a very good corrosion inhibition performance with an inhibitor efficiency of 73.82%. For the kola nut extract, the best inhibitor efficiency was obtained with the 60% concentration extract which recorded 78.60%.

In general, the effective corrosion inhibition performance

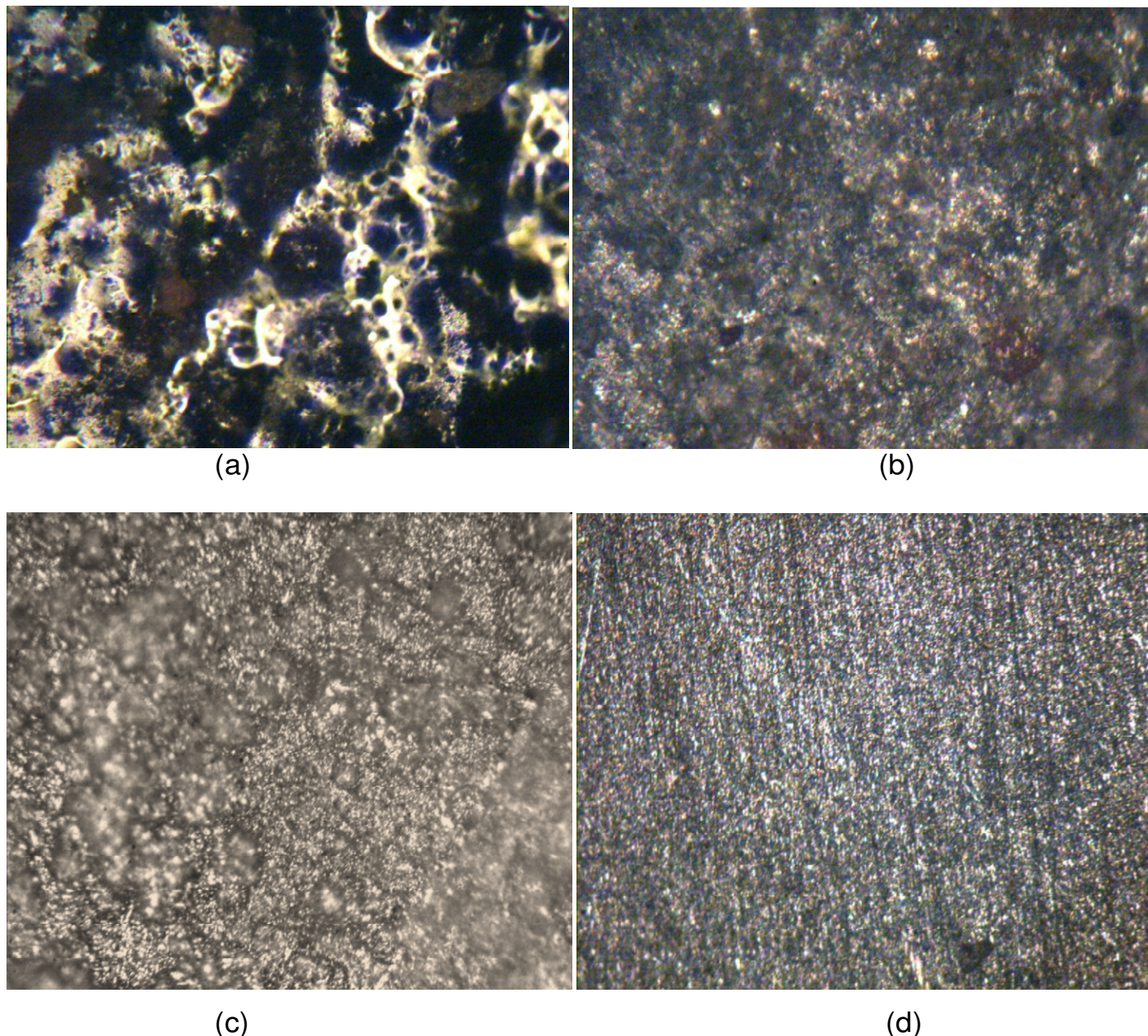


Figure 7. Micrographs of mild steel sample, (a) immersed for 24 days without added extract; (b) and (c) after immersion for 24 days in HCl with added kola nut and tobacco leaves extracts, respectively; (d) before immersion in HCl.

of kola tree and tobacco extracts could be associated with their complex chemical compounds which include tannin as earlier mentioned. 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 of anodic oxidation/ dissolution and cathodic reduction processes. 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^- 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.

Conclusion

At the ambient working temperature, the best corrosion inhibition performance for mild steel was obtained using the solution extracts of tobacco at 100% concentration in 0.5 M HCl. The use of tobacco for the inhibition of corrosion of mild steel in this acid proved very effective with an average inhibitor efficiency of 96.25%. Kola leaf had a very fairly good performance at 73.82% inhibitor efficiency; and Kola nut had 78.60% as mentioned earlier. The extracts of tobacco, kola leaf and kola nut at the concentrations used, and under other working environmental conditions could be said to be very effective as environment friendly extracted inhibitors for mild steel in hydrochloric acid.

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REFERENCES

- Davis GD, Fraunhofer JA (2003). Tobacco Plant Extracts as Environmentally Benign Corrosion Inhibitors. *Mat. Perform.*, 2: 56-60.
- Davis GD, Fraunhofer JA, Krebs LA, Dacres CM (2001). The use of Tobacco Extracts as Corrosion Inhibitors, *CORROSION/2001*, Paper no. 58 (Houston, TX: NACE).
- Fraunhofer JA (1995). Tobacco Extract Composition and Methods, U.S. Patent, 43: 941.
- Fraunhofer JA (2000). Inhibiting Corrosion with Tobacco, *Adv. Mat. Proces.*, 158: 33.
- Loto CA (2003). The effect of bitter leaf extract on the inhibition of mild steel in HCl and H₂SO₄. *Corrosion Prev. Control*, 50(1): 43-49.
- Loto CA (2005). Inhibition of cashew juice on the corrosion of mild steel in sulphuric acid. *Corrosion Prev. Control*, 52: 13 – 21.
- Okafor PC (2007). 'Eco-friendly corrosion inhibitors: inhibitive action of ethanol extracts of *Garcinia kola* for the corrosion of mild steel in H₂SO₄ solutions', *Pigment Resin Technol.*, 36: 5.
- WHO, IARC (1985). *Monographs on the Evaluation of the carcinogenic Risk of Chemicals to Humans*, 37: 9.
- www.Wikipedia.org (2011) – Answers.com: Kolanut Internet, 10th March.