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INHIBITIVE AND MECHANICAL PROPERTIES OF COCK'S COMB AND AFRICAN STAR APPLE LEAVES EXTRACT ON THE CORROSION OF MEDIUM CARBON LOW ALLOY STEEL IN 1M H_2SO_4 SOLUTION

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ABSTRACT: In the present research efforts focused on the effects of African star apple (AS) and Cock's comb (CC) leaves extract on the corrosion and mechanical behavior of medium carbon low alloy (MCLA) steel in 1M H_2SO_4 solution. Inhibitive properties of AS and CC extracts on MCLA steel were studied using electrochemical measurements and the effect of concentrations ranging from 100ppm to 500ppm of formulated inhibitors in 1M H_2SO_4 solution were investigated and discussed. FTIR analysis was used to identify the active compounds present in the extracts and nature of films formed on the surface of the MCLA coupons. Mechanical tests such as hardness, impact and tensile strength of the specimens were evaluated before and after corrosion inhibition of MCLA steel in 1M H_2SO_4 solution. This work has demonstrated that mechanical properties reduced drastically in uninhibited (in as absence of inhibitor) but improve with inhibitive ones (in present of inhibitors) as compared to the as-received specimens. Unhibited specimens gave the lowest values of impact strength, tensile strength and hardness as 48.70J, 342.72Nmm^{-2} and 142.84HB respectively. The improved properties were observed in AS inhibited specimens with a value of 56.75J for impact strength, 440.12Nmm^{-2} for tensile strength and 223.73HB for hardness values. This further implies that the formulated inhibitor namely African Star apple effectively lower the corrosion rate of MCLA steel in the acidic medium.
Keywords: steel, electrochemical measurements, mechanical properties, FTIR analysis

1. INTRODUCTION

Carbon steels (CSs) have been widely used in the petrochemical and metallurgical industries owing due to its cost effectiveness in procurement and fabrication [1]. However, due to lower overall corrosion resistance, CS assets require more frequent inspection, monitoring, and chemical injection to ensure functional integrity. Corrosion is known as the destruction or deterioration of material due to reaction with its environment [2]. Its significant role and problem cannot be overemphasized as the scope is very wide and covers practically all classes of materials used in engineering application [3]. Among various methods of combating corrosion, the use of an inhibitor is a common practice and widely used for steels in the oil and gas industry [4].

Several studies have proven the use of plant extracts as new type of green corrosion inhibitors in different media via gravimetric based mass loss, electrochemical, kinetic and thermodynamic techniques. In spite, researchers have continued to identify inhibitors for specific application [5 - 6]. The present research efforts focused on the use of African star apple and Cock's comb bio-extracts as corrosion inhibitors for medium carbon low alloy steel in acidic medium. Sulfuric acids are widely used for oxide removal prior to metallurgical processes such as galvanizing, electroplating and electropolishing of stainless steel in the industry [7].

The use of agro-based organic inhibitors to protect structures in services had been reported to have little or no adverse effects on the environment, as well as reduce the rate of corrosion in industrial practice such as acid cleaning, oil well acidizing, transmitting pipelines and offshore drilling operations. Although, several research efforts on the suitability of plants as corrosion inhibitors has been widely reported in the literature. Irrespective of type and part used; the exact mechanisms of inhibition is the formation of protective layers on the metal surface, which is a major controlling factor in acidic medium. Thus, various plants have different modes of inhibiting action [8 -12]. This is the thrust of this work and focuses on African star apple (AS) and Cock's comb (CC) leaves, with a view to studying its performance on the corrosion of medium carbon steel low alloy (MCLA) steel in acidic medium.

2. EXPERIMENTAL

2.1. Preparation of test solution

1M H_2SO_4 solution was prepared from Fishers certified analytical grade solution with appropriate distilled water and various inhibitors concentrations were prepared by successive dilution from AS and CC extracts obtained by conventional method using the Soxhlet apparatus.

2.2. Corrosion testing

Medium carbon low alloy (MCLA) steel rod of chemical composition as Fe- 97.860, C- 0.500, Mn- 0.7760, Si- 0.0214, Cu- 0.2010, Cr- 0.1700, Ni- 0.0848, Si- 0.0214, P- 0.0120 and others -.> 0.0131 (wt %) were obtained by spectrochemical analysis and used in the present work. This grade of MCLA Steels are intended primarily for use in structural members, where savings in weight and added durability are critical such as cars, trucks, cranes, bridges, roller coasters and other structures that are designed to handle large amounts of stress or need a good strength-to-weight ratio. Corrosion test was investigated by electrochemical measurements using samples embedded in epoxy resins with an exposed area of 0.87 cm^2 served as working electrodes were abraded in sequence under running tap water using emery paper of successive grit size 220, 320, 400, 600 and 800, washed with running tap water followed by distilled water, dried with clean clothes, immersed in benzene and acetone, dried again prior to immersion in electrochemical cell. Linear Polarization Resistance (LPR) test was carried out according to ASTM G59-97 using AC Potentiostat device where a saturated calomel reference, platinum auxiliary (model: PP-50) and samples embedded in epoxy resins with an exposed area of 0.87 cm^2 served as working electrodes placed in electrolyte cell filled with 200ml of 1M HCL acid solution, equilibrate to generate electrochemical measurements at constant time of 20 minutes and polarizing the specimen from +25 to -25 mV with respect to Ecorr, at a determined scanning rate of 1mV/s^{-1}. The first sets of electrochemical investigation were carried out with inhibitor to serve as control, subsequently in test solution of prepared inhibitors of 100ppm; 200ppm; 300ppm; 400ppm; and 500ppm concentrations. The polarization resistance (Rp) values were determined according to Stern Geary equation using Tafel extrapolation method while Inhibition efficiency (IE %) were calculated using corrosion density (Icorr) measurements according to equations 1 and 2.

$$I_{corr} = \frac{\beta_a \beta_c}{2.303\,(\beta_a + \beta_c)}\, {}^{1}/_{R_p} \tag{1}$$

$$IE\,(\%) = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} * 100 \tag{2}$$

where: I_{corr} is the corrosion current density and measured in solutions without inhibitor, $I_{corr\ (inh)}$ determined in solutions containing inhibitor

2.3. Determination of mechanical properties

Mechanical properties such as hardness, impact and tensile strength of the MCLA steel specimen before and after corrosion tests were determined using Rockwell Hardness Testing Machine, Izod Impact testing machine, and Hounsfield Tensometer as follows: hardness values were obtained in accordance with the ASTM E140 standard using the Brooks universal hardness tester (model: CRBD) where specimens cut to required dimensions of 19mm (diameter) and 15mm (thickness) were placed on the anvils of the machine with a diamond ball indenter of 2.5mm diameter, under minor and major loads of 10kg and 187.5kg respectively. Impact strengths were obtained according to ASTM A370 standard using the Izod impact machine where prepared specimens of 12mm (diameter) and 60mm (thickness) given a notched of 1mm depth at the center were first positioned in the vice of the impact testing machine. Tensile tests were conducted in accordance with the ASTM E8-04 standard using the Hounsfield tensometer of capacity 20kN where specimens cut to required dimensions of 7.5mm (outside diameter) and 5mm (inside diameter) by 37mm (outside height) and 31mm (inside height) were mounted and gripped in between the chucks of hydraulic controlled load system of the extensometer.

2.4. Chemical analysis

Identification of the active compounds present in the plant extracts and nature of the films formed on the surface of the metal specimens was conducted using Fourier Transform Infrared Red (FTIR) spectroscopy as follows: samples were mixed with KBr salt using a mortar and pestle, furthered compressed into a thin pellet and recorded on Shimadu FT-IR Spectrometer.

3. RESULTS AND DISCUSSION

3.1. Linear Polarization Resistance (LPR) Studies

Table 1 shows of values of MCLA steels electrochemical parameters such as corrosion potential (E_{corr}), current density (I_{corr}), tafel slopes (β_c and β_a), resistance polarization (R_p) and inhibition efficiency (η%) obtained for electrochemical measurements in 1M H_2SO_4.

Table 1: LPR parameters for corrosion of steel sample in 1.0M H_2SO_4 solution

Inhibitor	Conc. (ppm)	$-E_{corr}$ (mV)	I_{corr} (mA cm^2)	$-\beta_c$ (mV dec^{-1})	β_a (mV dec^{-1})	R_p (ohm cm^2)	η%
Blank	0	910	2.611	123	96	8.967	0
AS	100	978	1.678	168	623	15.663	35.7
	200	962	0.573	89	114	9.972	78.1
	300	959	0.336	73	681	22.426	87.1
	400	940	0.116	65	47	26.913	95.6
	500	944	0.106	38	106	30.043	95.9
CC	100	1046	0.307	82	268	23.348	88.2
	200	968	0.268	50	114	14.852	89.7
	300	1005	0.157	48	95	23.255	94.0
	400	997	0.150	42	132	24.175	94.3
	500	986	0.129	49	108	30.005	95.1

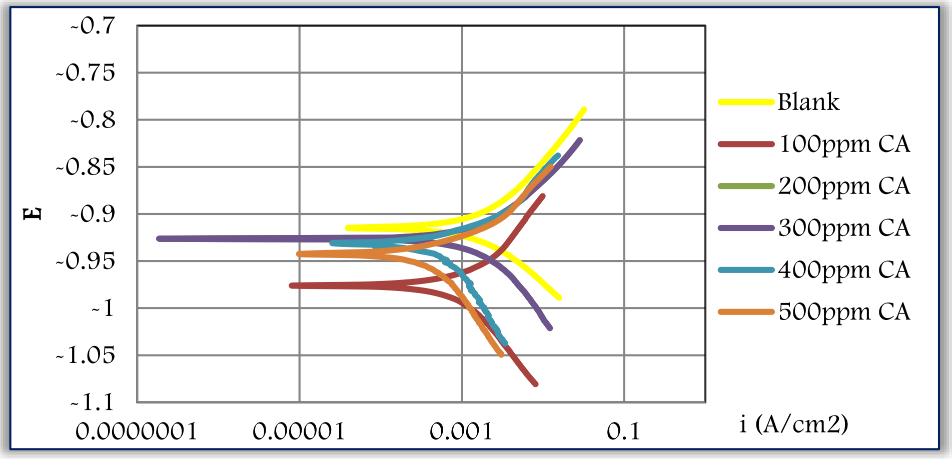


Figure 1: Polarization curve of the corrosion of steel sample in 1.0M H_2SO_4 solution in the presence of formulated inhibitor of African star apple (AS).

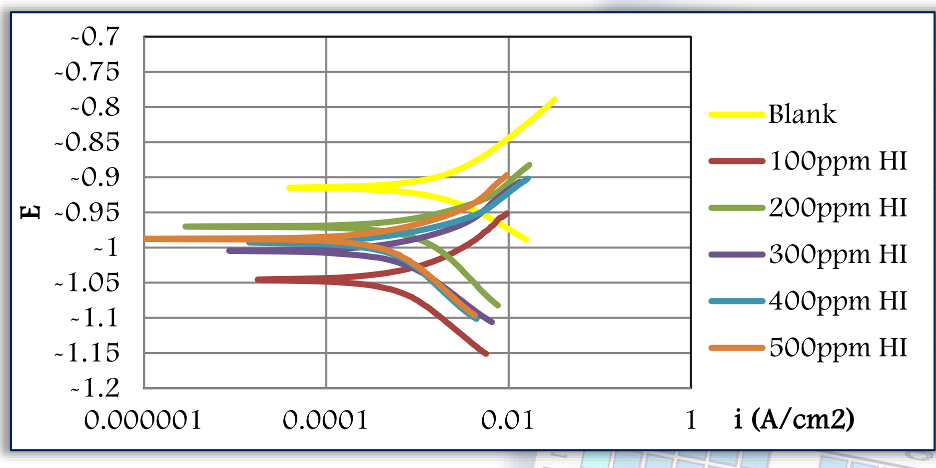


Figure 2: Polarization curve of the corrosion of steel sample in 1.0M H_2SO_4 solution in the presence of formulated inhibitor of Cock's comb (CC)

From the record Ecorr values obtained which show a mixed mode of inhibition of formulated inhibitors as they do not increase or decrease in a regular manner from the blank value. The mixed mode of inhibition is again proved by the values of βc and β_a, which also do not increase or decrease in a regular manner [11]. This is an evident shown by the increased in Rp values with increase in concentration of inhibitors and curves of polarization behaviour (figures 1 - 2). The inhibitive nature both in the absence and presence of inhibitors in 1M H_2SO_4 system is associated with increase in resistance polarization ((R_p)) values from 8.967 ohm cm^2 in the absence of inhibitor (free blank acid) to 30.04 ohm cm^2 and 30.01 ohm cm^2 in the presence of AS and CC at 500ppm concentration respectively, this suggests that a protective film was formed on the metal surface as the corrosion current decreases from 2.611 (blank) to 0.106 and 0.129 mA cm^2 in the presence of AS and CC at optimum concentration [12 – 14].

3.2.Mechanical behavior

Figure 3 presents the mechanical behavior (i.e. impact, tensile and hardness) of test specimens before and after the corrosion test for 21days in 1M H_2SO_4 acid solution.

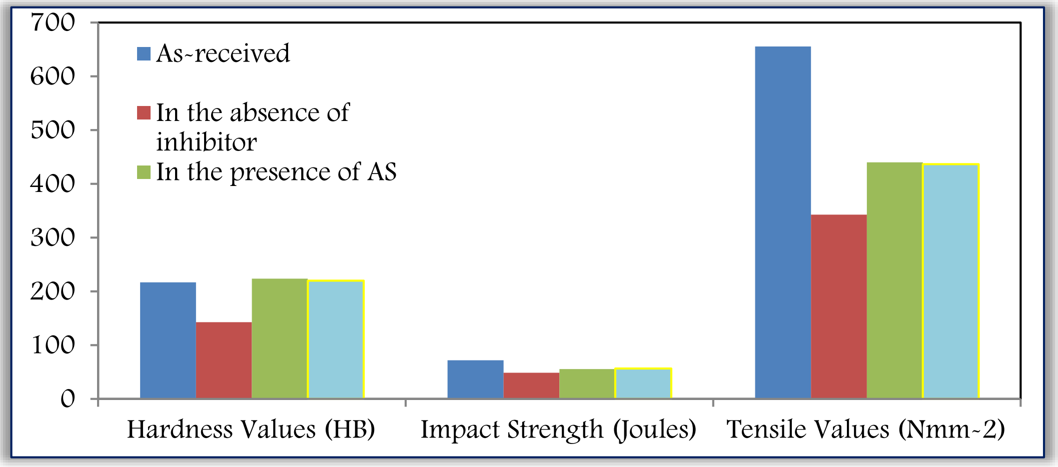
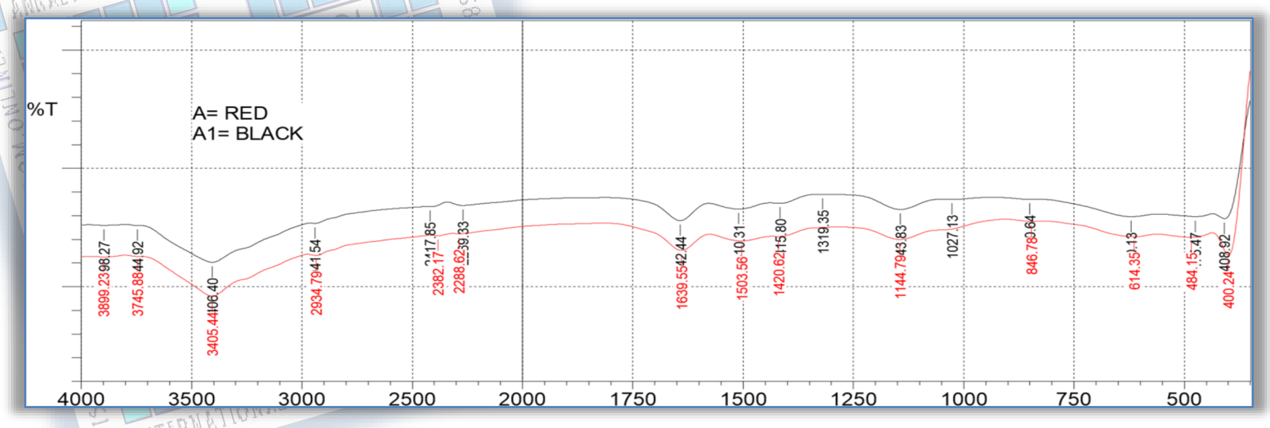


Figure 3: Mechanical behaviors of MCLA steel after 21 days of immersion period

The average hardness, impact and tensile values of the inhibited are greater than the uninhibited samples. This shows that the effect of corrosion on the MCLA specimen is higher on the inhibited compared to inhibited samples which could be due to protective layers formed on the metal surface while the decrease in impact and tensile strength of the uninhibited is attributed to the reduction in area of the steel sample as a result of gradual weight loss. It revealed that the mechanical properties of the steel reduced drastically in uninhibited media but improve with inhibitive ones in comparison before corrosion tests. This implies that AS and CC formulated inhibitors effectively lower the corrosion rate of MCLA steel in the test media.

3.3.FTIR analysis

FTIR spectrum of AS indicated the presence of four functional groups, notably, the C=O stretch at 2288.62 cm^{-1}, C=C bends at 2382 cm^{-1}, the C≡C stretch at 2934.79 cm^{-1}, and the OH stretches at 3405.44 cm^{-1}, 37545.88 cm^{-1} and 3889.23 cm^{-1}, while the FTIR spectrum of CC indicated the presence of some functional groups, notably, the C=O stretches at 2180.60 cm^{-1}, C-H aliphatic stretch at 2930.93 cm^{-1}, and the OH stretches at 3368.79 cm^{-1}, 3739.13 cm^{-1} and 3864.51 cm^{-1}, respectively. A comparison of the spectrum of AS and CC extracted compounds indicated that they contained different function groups and chemical structures [12].



1 /cm

Figure 4: The IR spectrum of AS extract (red) and protective film (black)

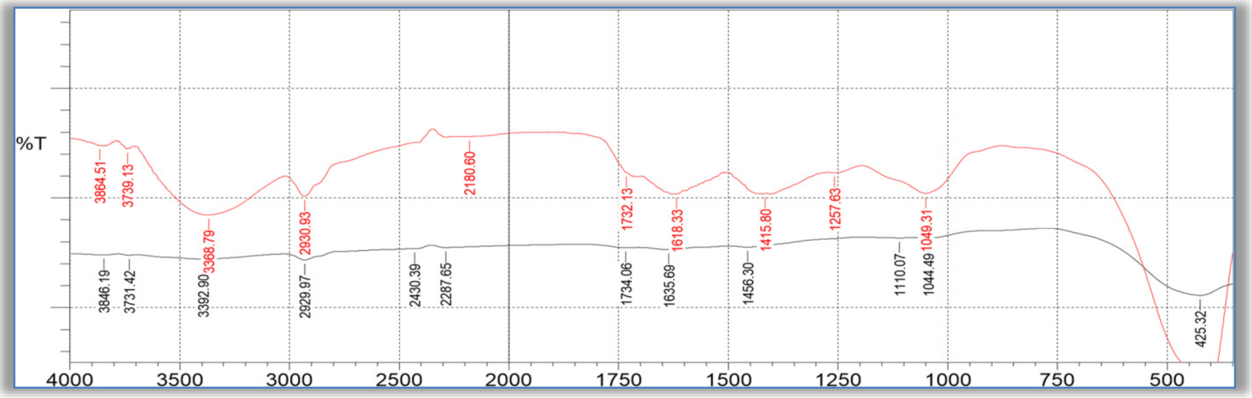


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Figure 5: The IR spectrum of CC extract (red) and protective film (black)

Also, Figures 4 - 5 reveals the FTIR spectrum of the protective film (superimposed with black) formed on the surface of the metal after corrosion inhibition in solution containing 500ppm of AS and CC for 21 days. A comparison of the notable spectrum of AS extracts and that of the corrosion product after the extracts has been used as inhibitor indicated that the C=O stretch at 2288.62 cm^{-1} is shifted to 2239.33 cm^{-1}, C=C bends at 2382 cm^{-1} is shifted to 2417.85 cm^{-1}, the C≡C stretch at 2934.79 cm^{-1} is shifted to 2941.54 cm^{-1}, and the OH stretches at 3405.44 cm^{-1}, 3745.88 cm^{-1} and 3889.23 cm^{-1} are shifted to 3406.40 cm^{-1}, 3744.92 cm^{-1} and 3898.27 cm^{-1} while CC indicated that the C=O stretches at 2180.60 cm^{-1} is shifted to 2287.65 cm^{-1}, C-H aliphatic stretch at 2930.93 cm^{-1} is shifted to 2929.97 cm^{-1}, and the OH stretches at 3368.79 cm^{-1}, 3739.13 cm^{-1} and 3864.51 cm^{-1} are shifted to 3392.90 cm^{-1}, 3731.42 cm^{-1} and 3846.19 cm^{-1} , among others respectively. Also, new functional groups were found in the spectrum of formulated AS and CC inhibitors protective films. These included, the C-O stretch at 1319.35 cm^{-1} and C-N stretch at 1027.13 cm^{-1} for CA and C=C stretches at 2430.39 cm^{-1} for HI. These shifts in frequencies and formation of new bonds suggest the existence of an interaction between the inhibitors and steel surface [15].

4. CONCLUSIONS

Based on the result obtained the following conclusions were drawn:

(1) The formulated Inhibitors of Cock's comb and African star apple were found to be effective inhibitor for medium carbon low alloy steel in 1M H_2SO_4 solutions medium.

(2) Corrosion inhibition efficiency increases with increase in inhibitor concentration up to the values of 98.0% (AS) AND 96.0% (CC) and affected both anodic and cathodic thus act as mixed-type inhibitors on corrosion of the medium carbon low alloy steel.

(3) Mechanical properties of medium carbon steel deteriorated after corrosion test but there was improvement in the hardness value, impact and tensile strengths of the as- corroded inhibited medium carbon low alloy steel compared to uninhibited specimens.

(4) FTIR analysis suggests the existence of an interaction between the plant extracts and metal surface due to the absorption of inhibitor molecules onto the metal surface.

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