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Inhibition of Mild Steel Corrosion in 0.25 M H_2SO_4 Using *Tetracarpidium conophorum* Shell Extract

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Authors' contributions

This work was carried out in collaboration between both authors. Author KNK carried out the laboratory work and wrote the first draft. Author NCN designed the study, performed the statistical analysis. Both authors read and approved the final manuscript.

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ABSTRACT

The capacity of aqueous *Tetracarpidium conophorum* Shell (TCE) Extract to inhibit pipeline steel corrosion in 0.25 M H_2SO_4 acid was investigated using weight loss and Uv-visible spectroscopy techniques. The phytochemical components of *Tetracarpidium conophorum* were identified using GC-MS analysis. The results obtained shows that aqueous *Tetracarpidium conophorum* shell extract decreased the corrosion rate, while the corrosion inhibition efficiency increased with increase in exatract concentration. The Uv-visible spectra indicated a chemical interaction between the TCE molecules and atoms of Iron on the pipeline steel surface, while GC-MS analysis showed the presence of organic compounds with hetero-atoms for adsorption on the steel surface.

Keywords: Tetracarpidium conophorum shell extract; corrosion; phytochemical; GC-MS; Uv-visible.

1. INTRODUCTION

Corrosion is electrochemical oxidation of materials in reaction with its environment. Refined metals are thermodynamically unstable, as such are prone to react with oxidants in its environment to gain stability [1]. Most public infrastructures are constructed with carbon steel and are exposed to the environment. The more pertinent concern is the more polluted and

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aggressive environment especially in the industrial areas [2]. A good example of polluted and aggressive environment is the Niger delta region of Nigeria [2]. In order to mitigate the consequences of aggressive environment efforts are on at the governmental and nongovernmental levels to reduce emissions. This can only reduce the rate of deterioration of metal and eliminate it because corrosion is thermodynamically inevitable. Hence, the need for measures to further mitigate corrosion.

Application of chemical inhibitors is a veritable option in corrosion mitigation [3]. However, some chemical synthetic inhibitors are toxic to the environment. Hence, the need for eco-friendly inhibitors. Phyto products have severally been successfully applied as corrosion inhibitors because they are cheap, environmentally friendly and renewable [4]. It is noteworthy that most phyto materials are also needed for food security, hence have competing demands. One way of all round beneficial application of phyto materials is to use either the non food plant materials or waste from the phyto materials.

Tetracarpidium conophorum (TC) Shell (Walnut Shell) is waste product after the nut has been prepared and consumed. *Tetracarpidium conophorum* is also known as African walnut, black walnut or Nigerian walnut [5-6]. Morphologically, TC is a small tropical flowering plant, a woody perennial climbing shrub of 6 m to 18 m long on attainment of the reproductive stage [7]. The root of the plant is fasciculate with leaf range between 10 cm long and 5 cm broad while the petiole may be up to 5 cm long. Also, the leaf is simply crenate and ovate with a serrated margin [7-8]. TC tree usually twines around other trees for support, especially the cocoa tree and kola nut tree. The immature TC fruits are usually greenish in colour but turn from dark brown to black as it matures [9-10]. The use of TC shell extract for corrosion inhibition will not only add value to it but help in waste management.

2. MATERIALS AND METHODS

2.1 Preparation of *Tetracarpidium conophorum* Shell Extract (TCE)

The TC was bought from Rumuokwuta market Portharcourt, the nuts were removed. Then the shells were washed with distilled water to eliminate impurities and air-dried for 12 days in order to reduce the moisture level. The dried plant samples were crushed and grounded using electrical blender until a fine powder is formed. The powder was sieved with a mesh size of 150 µm. Fifty grams of the TC shell powder was mixed with 1 litre of distilled water and then heat to 60°C using a thermostatic water bath for 75 mins in a closed system. The extract was preserved for 24 hours, afterwards, it was filtered and the filtrate from the extract was evaporated to dryness at 40°C. The test solution was prepared by using the corrodant solution and TCE to prepare the various serial concentrations of the extract in the acid (0.1 g/L, 0.2 g/L, 0.3 g/L, 0.4 g/L, 0.5 g/l TCE in 0.25 M H_2SO_4 and 0.0 g/L - without TCE).

2.2 UV-visible Spectroscopic Analysis

The test solution containing 0.5 g/L of TCE in 0.25 M H_2SO_4 was analyzed prior to and after immersion of steel pipeline for a periodof 24 hours using 295 single beam advanced microprocessor UV-Visible spectro-photometer.

2.3 Gravimetric Method

The pipeline steel coupons used for the gravimetric (weight loss) experiments were mechanically pressed or cut into 3 cm x 2.5 cm x 1 cm dimensions. The coupons were subsequently polished repeatedly with various grades (200 to 2000 gritz) of emery paper until a smooth and shiny surface was achieved. The coupons were degreased in ethanol, washed with distilled water and rinsed in acetone and preserved in an active desiccator to prevent interaction with environmental moisture. The pre-weighed pipeline steel coupons were dipped in 100 ml beaker containing 0.25 M H_2SO_4 solution without and with selected concentrations of TCE ranging from (0.1 – 0.5 g/L) at temperature range of 303 K, to 323 K for 24 hours with the aid of a thermostatic water bath. After the exposure time, the coupons were withdrawn from the corrodant solution, brushed, washed with distilled water, rinsed in acetone and air dried before measuring the final weight. The corrosion inhibition efficiency (IE) and inhibitor surface coverage were calculated by using the equations 2 and 3 below [11].

$$\text{Weight Loss} = \Delta W_B - \Delta W_I \tag{1}$$

$$IE = \frac{\Delta W_B - \Delta W_I}{\Delta W_B} \times \frac{100}{1} \tag{2}$$

Where ΔW_B is weight loss of metal coupon without extract and ΔW_I is weight loss of metal with extracts.

$$\text{Surface Coverage} = \frac{\%IE}{100} \quad (3)$$

Material Half Life

$$t_{1/2} = \frac{0.693}{k} \quad (4)$$

Where K is the rate constant

Rate Constant (K)

$$K = \frac{2.303}{Time} log \frac{w_1}{w_2} \quad (5)$$

Where w_1 is the initial weight while w_2 is the final weight.

Corrosion Rates: The corrosion rates of coupons were studied in various test solutions at different temperatures using equation (6)

$$C_R = \frac{87.6\ X\Delta w}{DAT} \quad (6)$$

Where Δw is change in weight loss, D is density of coupon, A is area in centimeters and T is immersion time.

2.4 GC-MS Analysis

GC-MS – Qp2010 PlusShimadzu Japan was used to elucidate the phyto chemicals present in aqueous TCE. The analysis was conducted under preset conditions (standard procedure). At a temperature of 80°C and pressure (108.0 kpa), the injection mode and flow control mode were normal. The linear velocity was 46.3 cm/sec while the column flow is 3.0 ml/min. The oven temperature was set at 200°C for 4 mins and then was held for 5 mins at 250°C at a rate of 10°C/mins and the column dimension was 25 m × 0.25 mm × 0.22 µm.

3. RESULTS AND DISCUSSION

3.1 Effects of Aqueous TCE on Corrosion of Steel Pipeline in 0.25 M H_2SO_4

The effect of aqueous TCE or Wall nut shell extract (WSE) on the corrosion of pipeline steel are presented in Table 1. Table 1 states the effect of concentration of TCE on corrosion rate and corrosion inhibition efficiency at varying temperatures. In the control environment, corrosion rate was increasing as temperature was raising from 303K to 323K. The presence of TCE decreased the corrosion rate of steel pipeline in 0.25 M acid solution. This resulted in increase in corrosion inhibition efficiency which is attributable to adsorption capacity and large surface coverage of aqueous TCE molecules on steel pipeline surface [12]. The optimum inhibition performance of 78.57% and least corrosion rate of 0.00217 (mmpy) was achieved at 0.5 g/L concentration whereas the minimum inhibition efficiency was obtained at 0.1 g/L concentration. Furthermore, Table 1 show that the inhibition performance of WSE decreased from 78.57% at 303 K – 68.57% at 323 K which may implying that physical adsorption occurred [13].

3.2 Effects of Aqueous TCE on Material Half-life of Pipeline Steel in 0.25 M H_2SO_4

The effects of aqueous TCE on Material Half-life of pipeline steel in 0.25 M H_2SO_4 was calculated and presented in Table 2. Table 2 shows that for the solution without addictive, as temperature increased from 303 K to 323 K there was an increase in corrosion rate constant followed by a decrease in half-life of pipeline steel in acidic medium. However, the addition of aqueous WSE shielded the steel against corrosive acid

Table 1. Corrosion rate and inhibition efficiency and inhibitor surface coverage values obtained from weight loss measurement for aqueous TCE on pipeline steel in H_2SO_4

Conc.(s) g/L	Corrosion rate			Inhibition efficiency (%IE)			Degree of surface coverage(θ)		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
Blank	4.94	5.47	5.79						
0.1	3.05	3.52	4.01	38.23	35.65	30.74	0.38	0.36	0.31
0.2	1.36	1.61	2.06	55.41	54.26	48.63	0.55	0.54	0.49
0.3	0.45	0.57	0.89	66.92	64.60	56.80	0.67	0.65	0.57
0.4	0.14	0.19	0.35	68.89	66.67	60.67	0.69	0.67	0.61
0.5	0.03	0.05	0.11	78.57	73.68	68.57	0.79	0.74	0.69

Table 2. The kinetic values for pipeline steel in 0.25 M H_2SO_4 solution containing TCE from weight loss method

Concentration (g/L)	Rate constant, k (day^{-1})			Half-Life, $t_{1/2}$ (days) x 10^2		
	x 10^{-3}	x 10^{-3}	x10^{-3}			
	303k	313k	323k	303K	313K	323K
Blank	1.92	14.8	24.84	360.4167	46.75676	27.85829
0.1	0.92	9.20	15.85	752.1739	75.21739	43.65931
0.2	0.72	6.81	13.98	961.1111	101.6153	49.49928
0.3	0.57	5.32	11.26	1214.035	130.0752	61.45648
0.4	0.51	5.33	10.49	1356.863	129.8311	65.96759
0.5	0.42	4.32	9.97	1647.619	160.1852	69.40822

solution thereby reducing the corrosion rate constant and improving the half-life of pipeline steel. This observation corresponds to observation previously made by researchers [11,13].

3.3 UV-spectra for the Interaction of TCE on Pipeline Steel during Its Corrosion in H_2SO_4

The UV-Visible investigations for 0.25 M H_2SO_4 solution in the presence of 0.5 g/L of TCE before and after the steel pipeline immersion were carried out and the results presented in Fig. 1. The spectra revealed a new compound was formed. The wave band of aqueous TCE before immersion occurred at 249 nm. This could be due to to π- π and n- π transitions. After immersion of steel pipeline, there was an increase in absorbance and wavelength.

Thus, there was a bathochromic and hyper chromic effect. Although, the shape of the spectra remain unchanged which indicates that there was an interaction between Fe^{2+} and aqueous WSE.

3.4 GC-MS Analysis of Aqueous TCE

The GC-MS analysis of aqueous TCE was carried out and the result presented in Table 3 and Fig. 2. The phyto chemicals presents shows presence of functional groups that can bond with Iron in order to be adsorbed on the metallic surface.

3.5 Inhibition Mechanism

The corrosion inhibition characteristics of pipeline steel in acidic environment with and without aqueous TCE showed that TCE significantly reduced the dissolution of the metal due to interaction with its environment. The data acquired from Uv-Visible and GC-MS strongly suggests the molecules of aqueous TCE interacted with Iron and was adsorbed on the surface. The GC-MS result also confirms the presence of OH, C=O, COOH and alkyne groups. These functional groups contain polar atoms that have pi and lone pairs of electrons, which can function as adsorption site on the surface of electrode. It is noteworthy that these phytochemicals containing oxygen atoms were protonated in the acid solution. The protonated molecules reduce the rate of hydrogen evolution at the cathodic area of the electrode. Also chemically, adsorption at the anodic area of the electrode due to the interaction between metal and lone pairs of electron from O atom and Pi electrons from alkyne group, thereby reducing the dissolution of metal can take place [14].

Table 3. GC-MS analysis for aqueous TCE

Retention time	Peak area	Compounds	MW	Mol. formular
15.288	3.37	1- Octadecyne	250	C18H34
17.907	12.13	n- Hexadecanoic acid	256	C16H32O2
19.981	2.88	11- Octadecenoic acid, methyl ester	296	C19H36O2
20.221	1.46	Phytol	296	C20H36O
20.811	50.75	Oleic acid	282	C18H34O2
21.051	12.94	Octadecanoic acid	270	C18H36O2
22.448	2.11	Decane, 1- fluoro	160	C10H21F
23.285	4.82	Eicosanoic acid	312	$C_{20}H_{40}O_2$
24.269	6.01	2- Methyl-z-z-3,13-octadecadienol	280	$C_{19}H_{36}O$

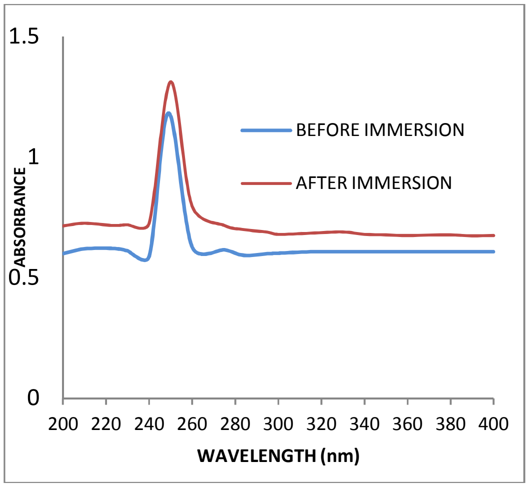

Fig. 1. Uv-Visible investigations for 0.5 M HCl solution in the presence of 0.5 g/L of TCE before and after the steel pipeline immersion

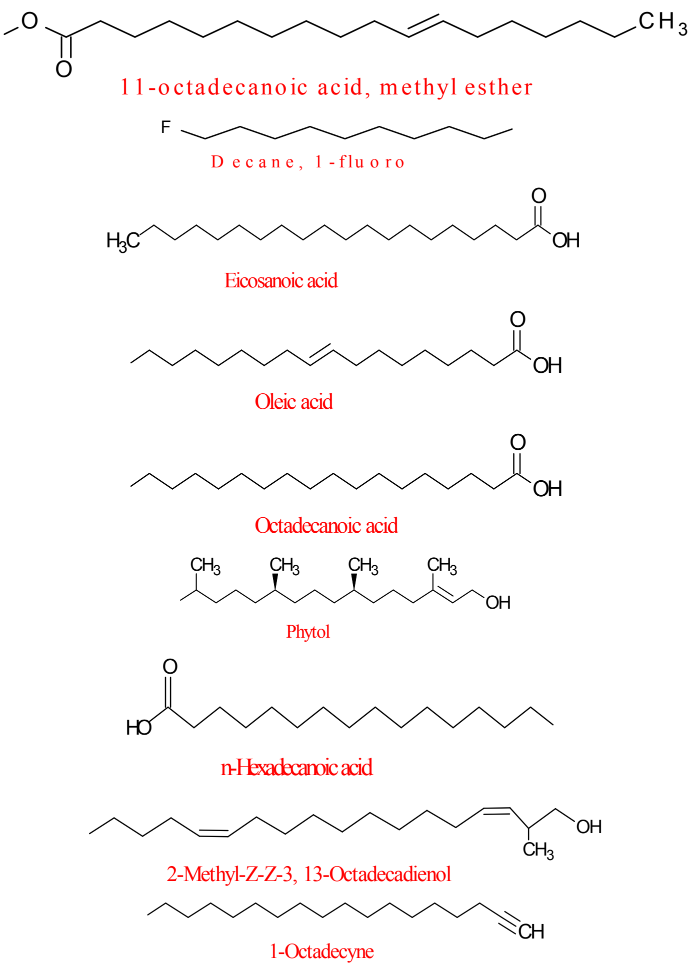

Fig. 2. Structures of chemical components present in aqueous TCE

4. CONCLUSION

The corrosion inhibition performance and phyto-chemical constitution of aqueous TCE was studied. The results obtained showed that TCE inhibited the corrosiveness of H_2SO_4 on pipeline steel up to 78.57% at 313 K. Also the GC-MS result confirmed the presence of 9 compounds that includes plant organic acids, alcohol and alkyne. The UV-visible analysis disclosed that there was an interaction between aqueous molecules of TCE and Fe^{2+}.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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