Inhibitive Action of Water Extract of *Spondias Mombin* on Corrosion of Low Carbon Steel in 0.5M Sulphuric Acid

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Abstract- Corrosion inhibition of water extract of Spondias mombin on low carbon steel in 0.5 M sulphuric acid was investigated in this paper. Fresh leaves, fruits and bark of this plant, washed properly, ground separately using small amount of distilled water to extract the juice at a ratio of 500 ml (distilled water) to 1 kilogram of plant were used for this experiment. Corrosion inhibitors of 0.4 g/ml, 1 g/ml and 2 g/ml were made from the filterate. Low carbon steel coupons suspended with twine inside 250 ml container of 0.5 M sulphuric acid in the presence of different concentrations of the extracts at room temperature for 35 days. The coupons were retrieved at 7 days interval, and the initial and final weights were recorded. Inhibition efficiency for the leaves extract increased with concentration and got to its peak on the 7th day, that of the fruits extract initially increased with concentration until 1 g/ml after which there was a decline, its highest value was also recorded on the 7th day. The best inhibition efficiencies (in the range of 76.32% to 83.21%) for Spondias mombin water extract were observed in 0.4 g/ml bark extract throughout the days of the experiment, the highest being recorded on the14th day. It can be concluded that Spondias mombin water extract is a good corrosion inhibitor of low carbon steel in 0.5 M sulphuric acid at room temperature, with the best being the bark extract which inhibited for up to 35 days.

Keywords- Inhibition, water extract, Spondias mombin, low carbon steel

1. Introduction

Organic inhibitors have been the most widely used in most industrial processes because of their ability to form a protective layer on the metal surface in media with high hydrocarbons content. Well-known active substances such as essential oils, tannins, pigments, steroids, terpenes, flavones and flavonoids, among others are responsible for corrosion inhibition in organic inhibitors (Martinez-Palou et al., 2004). These compounds present conjugated aromatic structures, long aliphatic chains such as nitrogen, sulphur, and oxygen hetero atoms with free electron pairs that are available to form bonds with the metal surface. In most cases, they act synergistically to exhibit good efficiency regarding the corrosion protection. At present there are a number of organic inhibitors belonging to different chemical families such as fatty amides (Olivares et al., 2006), pyridines (Abd El-Maksoud and Fouda, 2005; Noor, 2009), imidazolines (Martinez-Palou et al., 2004) and other 1, 3-azoles (Popova, Christov and Zwetanova, 2007; Antojevic, Milic and Petrovic, 2009) and polymers (Dennis, 2002) have showed excellent performance as corrosion inhibitors.

The adsorption of amine salts of oleic acid on iron in 0.5M H_2SO_4 was investigated by Szauer and Brandt (1981). It was observed that the adsorption process proceeded through the preferable bonding between oleic acid and the metal surface. The growing interest and attention of the world towards the protection of the environment and the hazardous effects of using chemicals on the ecological balance, coupled with economic interest have gradually changed the traditional approach on corrosion inhibitors.

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From the economic and environmental view, some plant extracts are excellent alternatives as inhibitors because of their availability and biodegradability and can be obtained in a simple way and purification methods are not required (Martinez-Palou et al., 2004). These extracts contain a variety of natural products such as essential oils, tannins, pigments, steroids, terpenes, flavones and flavonoids. This can be demonstrated in the case of Ginkgo bilobain in which the main components, flavonoids and terpenoids have been identified (Martinez-Palou et al., 2004) as excellent corrosion inhibitor with potential applications in the oil industry concerning the corrosion inhibition of Q235A steel.

Obiukwu, Opara and Oyinna (2013) inhibited corrosion of stainless steel in both sulphuric and hydrochloric acids using Vernonia amygdalina (Bitter Leaf) and Azadirachta indica (Dogoyaro) and reported good inhibition performance. Buchweishaija (2009) studied the inhibitive performance of gum exudates from Acacia drepanolobium and Acacia Senegal on the corrosion of mild steel in fresh water using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) studies. The results showed that the gum exudates (Acacia drepanolobium and Acacia senegal) exhibited good inhibition characteristics to mild steel corrosion in fresh water medium with inhibition efficiencies of up to 90.7% and 99.7%.

Vidhya and Rose (2014) employed the leaves extract of *Solanum nigrum* to inhibit Carbon steel corrosion in ground water for one day and maximum efficiency of 86.36% was obtained with 500 ppm of the extract. Iyasara and Ovri (2012) carried out a corrosion inhibition of stainless steel (316l) using Cola Nitida, Cola Acuminata and Cola Garcinia in soil and acidic environments. Their results showed that *Cola Garcinia*

(Bitter Cola) exhibited the best inhibition in the soil and 2M HCl acid environments while *Cola Acuminata* (White Cola) showed the best inhibition in the seawater and 1 M HCl acid environments. Inhibitive performance of acid extract of *Stevia rebaudiana* on mild steel in sulphuric acid was investigated by Cang et al. (2012). The performance was reportedly good.

Inhibition properties of acid extract of *Spondias mombin* leaves on corrosion of aluminium in sulphuric acid was examined by Obi-Egbedi, Obot and Umoren (2012). They investigated the correlation between inhibitive effect and electronic properties of extracts major constituents using density functional theory. They reported that quantum-chemical computations of parameters associated with the electronic structures of specific components confirmed the inhibiting potentials of the extracts. Effective performance of an extract in a certain medium with a given metal may not be guaranteed for the same metal in another medium (Okafor et al., 2005). It is possible too, that a compound may react differently towards different metals even in the same medium. Obi-Egbedi, Obot and Umoren (2012) carried out their work on the leaves extract of *Spondias mombin*, they did not investigate the potential of the fruits and bark extracts.

This study investigated the inhibition efficiency of water extract of the leaves, fruits and bark of *Spondias mombin* on low carbon steel in 0.5M H_2SO_4 acid solution. *Spondias mombin* (Hog plum) belongs to the family of Anacardiacae, and according to Ayoka (2008); it grows in the rain forest and in the coastal areas and can reach a height of 15 – 22 m. The trunk has deep incisions in the bark, which often produces a brown resinous substance. The leaves and the flowers are at the end of the branches. The tree strips itself of most of the leaves before it starts to flower. The fruit is a 0.038m long oval, yellow plum having a leathery skin and a thin layer of fruit pulp with a very exotic taste. It hangs in numerous clusters of more than a dozen on the tree. The fruit is very rich in vitamins B_1 and C_2 and exists as an oval seed. The mode of propagation of the plant is by seeds and cuttings. Other common names, according to Morton (1987) are Bala (Costa Rica), Jobito (Panama), Joboblanco (Colombia), Jobocorronchoso (Venezuela), Hoeboe (Surinam), Acaiba, Caja, Pau da tapera (Brazil), Ubo (Peru), Hobo (Mexico), Iyeye (Yoruba), Uvuru (Igbo).

2. Experimental Methodology

2.1 Preparation of specimen

A 5mm thick low carbon steel sample was cut into rectangular coupons of dimension of 80 mm by 30 mm. A 3 mm diameter hole was drilled in each coupon, through which a twine was passed to aid suspension and total immersion in the corroding medium (Loto and Mohammed, 2003).

2.2 Preparation of *Spondias mombin* extract

Fresh fruits (unripe), bark and leaves of *Spondias mombin* obtained in the community of the Federal University of Agriculture, Abeokuta were cleaned, ground separately using small amount of distilled water to extract the juice (solution) at a ratio of 500 ml (distilled water) to 1 kilogram of plant. Each mixture was filtered to extract the juice. Corrosion inhibitors of 0.4 g/ml, 1 g/ml and 2 g/ml were prepared from each extract (leaves, fruit and bark) and added to 250 ml of 0.5 M sulphuric acid (H_2SO_4) solution serving as the corroding medium (Loto and Mohammed, 2003).

2.3 Gravimetric Studies

Gravimetric analysis was carried out by immersing the specimens into 250 ml of 0.5M sulphuric acid solution in the absence and presence of the extract for the period of 35 days. The experiment was carried out at room temperature (26.6oC) and in triplicates for ease of reproducibility. The specimens were brought out at interval of 7 days. The mass of the specimens before and after immersion was determined using analytical weighing balance. The mass loss (ΔM) was calculated from the difference between initial (Mi) and final (Mf) masses. The average mass loss for three identical experiments was obtained and the Corrosion Rate (CR) is expressed according to Oguzie et al. (2008) using Eq. 1.

$$CR = \frac{\Delta M}{AT} \quad (1)$$

where, CR = the corrosion rate
ΔM = the mass loss in mg
A = the exposed area of the coupons (cm^2)
T = the immersion time in hours

Inhibition Efficiency (IE%) was calculated according to AbdElHaleem et al. (2013) as

$$\%IE = \left(1 - \frac{CR_{in}}{CR_{blank}}\right) \times 100 \quad (2)$$

where,
CR_{in} = Corrosion rate with inhibitor
CR_{blank} = Corrosion rate without inhibitor

3. Results and Discussion

3.1 Chemical composition of steel sample

Analysis of the low carbon steel sample used for this study revealed the chemical composition as: (wt%) Fe (98.4%), C (0.05%), Si (0.072%), Mn (0.4%), Ni (0.17%), Cr (0.0089%), Cu (0.53%), Co (0.183%), Al (0.015%), Mg (0.049%), S (0.062%), P (0.013%) with trace elements making up the balance.

3.2 Mass loss, corrosion rates and inhibition efficiency

Figures 1-7 show the plots of mass loss versus extract concentration for the low carbon steel specimens in 0.5 M sulphuric acid solution with the extracts of the leaves, fruits and bark of *Spondias mombin* in 7, 14, 21, 28 and 35 days of immersion. It can be observed that mass loss generally reduced in the presence of the leaves, fruits and bark extracts of *Spondias mombin* compared with the solution without extracts. In Figure 1, mass loss of low carbon steel specimen increased with the concentration of *Spondias mombin* leaves and decreased with immersion days. The lowest mass loss recorded in the leaves extract occurred in 7 days. Mass loss of the solution with the fruit extract decreased with increase in concentration until 1 g/ml after which it rose again. It can be seen in Figure 2 that mass loss is visible in 7 and 14 days immersion while it is less visible in 21 days and almost non-existent in 28 and 35 days respectively. Mass loss in the presence of *Spondias mombin* bark extract was lowest in 0.4 g/ml and increased with further increase in concentration as depicted by Figure 3. Increase in days of immersion did not particularly affect the reaction of the bark extract.

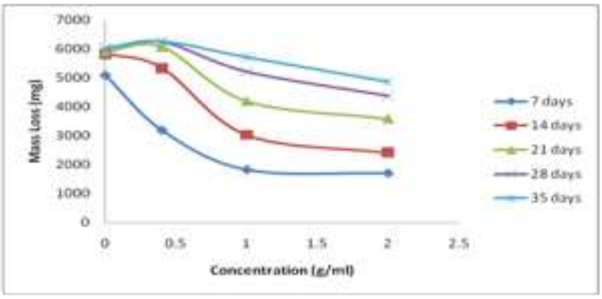

Fig. 1: Variation of mass loss with concentration for leaves extract of *Spondias mombin*

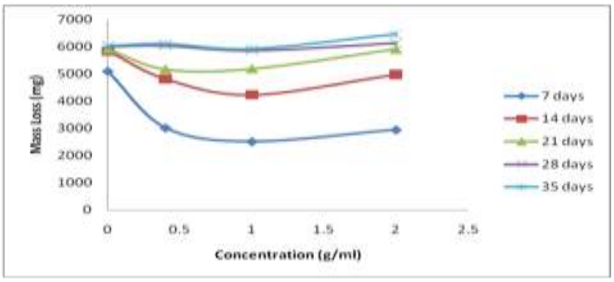

Fig. 2: Variation of mass loss with concentration for fruits extract of *Spondias mombin*

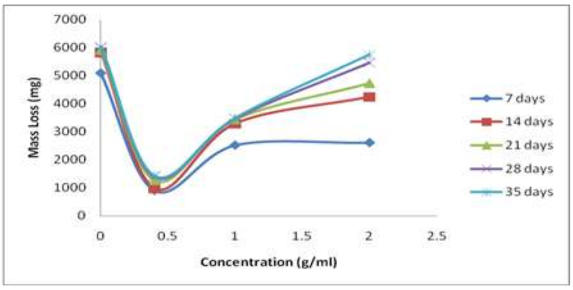

Fig. 3: Variation of mass loss with concentration for bark extract of *Spondias mombin*

Corrosion rates also reduced generally in the presence of the leaves, fruits and bark of *Spondias mombin*. Whereas corrosion rate decreased with concentration of the leaves extract in 7 and 14 days, almost no effect can be seen in 21, 28 and 35 days of immersion as given by Figure 4. Figure 5 shows a similar trend with Figure 4 where reduction in corrosion rate is well pronounced in 7 days immersion and almost non-existent in 21, 28 and 35 days immersion for fruits extract. Lowest corrosion rate occurred at 1 g/ml concentration. Corrosion rates in the presence of *Spondias mombin* bark extract are presented in Figure 6. Good reduction in corrosion rate was observed in 7 days of immersion followed by 14 days with 28 and 35 days immersion having no noticeable effect. Reduction in performance observed with days in the solutions of leaves and fruits extracts may be due to reduction in the potency of their active ingredients responsible for inhibition or equilibrium in corrosion reaction. The potency of the active ingredients in the bark extract did not decrease drastically unlike those of the leaves and the fruits. The inhibition efficiency and surface coverage for the leaves, fruits and bark extracts are shown in Tables 1 - 3. Figures 7, 8 and 9 showcase the inhibition efficiencies of leaves, fruits and bark extract of Spondias mombin.

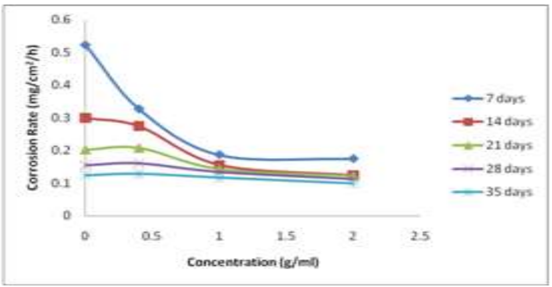

Fig. 4: Variation of corrosion rate with concentration for leaves extract of *Spondias mombin*

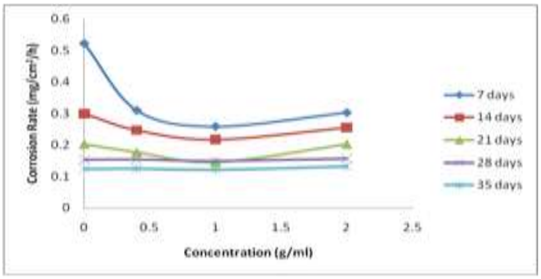

Fig. 5: Variation of corrosion rate with concentration for fruits extract of *Spondias mombin*

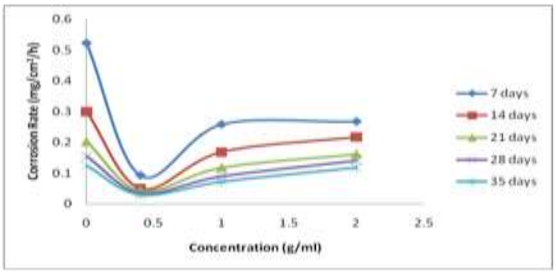

Fig. 6: Variation of corrosion rate with concentration for bark extract of *Spondias mombin*

Inhibition efficiency for the leaves extract increased with concentration having highest value (66.67%) at 2 g/ml concentration as can be seen in Figure 7. This agrees with the results obtained on the performance of plant extracts of *Spondias mombin* (Obi-Egbedi, Obot and Umoren (2012)); Opuntia (El-Etre, 2003); Gum Arabic (Umoren, 2008); *Phoenix dactylifera* (Shalabi et al., 2014) and Date Palm (Al-Haj-Ali, 2014). Increase in the number of extract components adsorbed on the surface of the low carbon steel, blocking the active sites where corrosion could take place as a result of increase in concentration was responsible for increase in inhibition efficiency (Obi-Egbedi, Obot and Umoren, 2012). This prevented direct attack of the acid solution on the metal surface thereby preventing corrosion. Highest inhibition efficiency recorded for the fruits extract was 50.59% and it occurred at 1 g/ml concentration as shown by Figure 8.

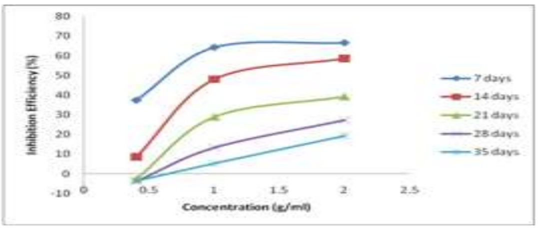

Fig. 7: Variation of inhibition efficiency with concentration for leaves extract of *Spondias mombin*

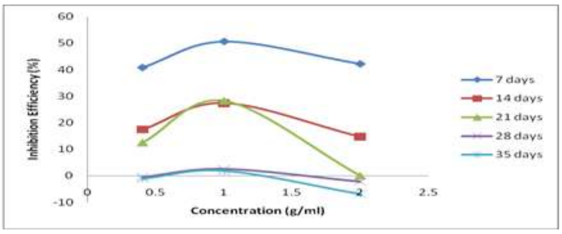

Fig. 8: Variation of inhibition efficiency with concentration for fruits extract of *Spondias mombin*

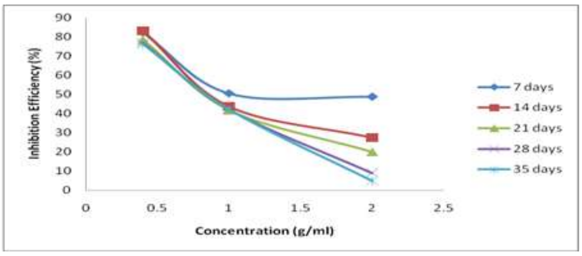

Fig. 9: Variation of inhibition efficiency with concentration for bark extract of *Spondias mombin*

Further concentration of extract led to decline in inhibition efficiency, whereas this disagrees with the reports of the authors quoted earlier, it agrees with Oloruntoba, Abbas and Olusegun (2012) on *Eichhornia crassipes* where further increase in concentration of extract beyond a particular concentration did not give a significant change. This could be because unripe fruits were used for this work, as there were no ripe fruits when the experiment was conducted. Unripe fruits are more acidic than ripe fruits which may reduce their inhibitive action. Effect of the bark extract of *Spondias mombin* on corrosion inhibition is represented by Figure 9 where the highest inhibition of 83.21% occurred at 0.4 g/ml concentration. Further increase in concentration led to decrease in inhibition efficiency, this also agrees with Oloruntoba, Abbas and Olusegun (2012).

3.3 Effect of Exposure Time

Inhibition performance of the extract of leaves, fruits and bark of *Spondias mombin* generally was sensitive to exposure time. Inhibition efficiencies for the leaves, fruits and bark extract of *Spondias mombin* initially increased with exposure time, reaching the highest of 66.67% and 50.59% on the 7th day for both the leaves and fruits extracts respectively, and 83.21% on the 14th day for the bark extract as can be seen in Figures 7, 8 and 9. Increase in exposure time beyond these days mentioned led to decline in the inhibition efficiency for all the extract concentrations considered.

This agrees with the report of Leelavathi et al. (2013) that, increase in exposure time may lead to desorption of the extract from the low carbon steel surface. According to Shriver et al. (1994), decrease in inhibition for prolonged immersion can be as a result of depletion of available inhibitor molecules in the solution due to chelate formation between iron and the inhibitor ligands. It is worthy of note that the highest inhibition efficiency for this work was 83.21% and it occurred with the bark extract at 0.4 g/ml and on the 14th day. The bark extract gave the highest inhibition efficiencies of 82.35%, 83.21%, 78.51%, 76.87% and 76.32% for the 7th, 14th, 21st, 28th and 35th day among all the extracts considered. Tables 1 - 3. Figures 7, 8 and 9 showcase the inhibition efficiencies of leaves, fruits and bark extract of *Spondias mombin*.

Table 1. Inhibition efficiency and surface coverage for the corrosion of low carbon steel in 0.5 M sulphuric acid solution in the presence of leaves extract of *Spondias mombin*

Concentration (g/ml)	Inhibition Efficiency (%)					Surface Coverage, θ (IE/100)				
	7th day	14th day	21st day	28th day	35th day					
Blank	-	-	-	-	-	-				
0.4	37.45	8.56	-2.71	-3.83	-3.64	0.38	0.09	-0.03	-0.04	-0.04
1	64.31	48.12	28.93	13.31	5.3	0.64	0.48	0.29	0.13	0.05
2	66.67	58.73	39.26	27.29	19.37	0.67	0.59	0.39	0.27	0.19

Table 2. Inhibition efficiency and surface coverage for the corrosion of low carbon steel in 0.5 M sulphuric acid solution in the presence of fruits extract of *Spondias mombin*

Concentration (g/ml)	Inhibition Efficiency (%)					Surface Coverage, θ (IE/100)				
	7th day	14th day	21st day	28th day	35th day					
Blank	-	-	-	-	-	-				
0.4	40.78	17.47	12.52	0.5	-0.01	0.41	0.17	0.13	0.005	-0.0001
1	50.59	27.4	12.18	2.50	1.82	0.51	0.27	0.12	0.03	0.02
2	42.16	14.72	0	2.16	-6.95	0.42	0.15	0	0.02	-0.07

Table 3. Inhibition efficiency and surface coverage for the corrosion of low carbon steel in 0.5 M sulphuric acid solution in the presence of bark extract of *Spondias mombin*

Concentration (g/ml)	**Inhibition Efficiency (%)**					**Surface Coverage, θ (IE/100)**				
	7th day	**14th day**	**21st day**	**28th day**	**35th day**					
Blank	-	-	-	-	-	-				
0.4	82.35	83.21	78.51	76.87	76.32	0.82	0.83	0.79	0.77	0.76
1	50.59	43.66	41.79	42.26	42.22	0.51	0.44	0.42	0.42	0.42
2	48.82	27.4	19.97	8.99	4.80	0.49	0.27	0.20	0.90	0.05

3.4 Adsorption considerations

Inhibition is by the adsorption of active ingredients of the extract on metal surface either by physical or chemical means (Al-Haj-Ali, 2014). The mechanism of inhibition can be further understood by studying the adsorption isotherms which provide further information on the variation of adsorption with the concentration of extracts at constant temperature (Alaneme and Olusegun, 2012). The more the surface coverage, the more the inhibitor's efficiency (Khadom et al., 2009).

The experimental data was fitted into Langmuir isotherm model given according to Abd El Haleem et al. (2013) by Eq. 3.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (3)$$

where, θ = surface coverage (fraction, dimensionless),
C = extract concentration and
K_{ads} = adsorptive equilibrium constant

The correlation coefficients (R2) of the system obtained from the linear plots of C/ θ against C plot are as given in Table 4. The mechanism of corrosion inhibition is generally believed to be due to the formation and maintenance of a protective film on the metal surface (El-Etre, Abdallah and El-Tantawy, 2005). The correlation coefficients (R2) for the leaves extract as given by Table 4 were 0.981, 0.128, 0.688, 0.608 and 0.339 for the 7th, 14th, 21st, 28th and 35th day respectively. The protective film that was formed could not be sustained after the 7th day and so it desorbed, resulting in the very low correlation coefficients after the 7th day. This shows that the water extract of Spondias mombin leaves was not an excellent corrosion inhibitor for low carbon steel in 0.5 M sulphuric acid environment.

The correlation coefficients (R2) for the fruits extract were 0.985, 0.929, 0.867, 0.050 and 0.007 for 7th, 14th, 21st, 28th and 35th day respectively (Table 4). This showed that the protective film that was formed could not last beyond the 7th day resulting in the decline of the correlation coefficients. The bark extract correlation coefficients (R2) were 0.998, 0.985, 0.963, 0.910 and 0.888 for the 7th, 14th, 21st, 28th and 35th day respectively (Table 4). The correlation values, as can be seen are close to unity indicating strong adherence to Langmuir adsorption isotherm (Manimegalai and Manjula, 2015). The bark extract of *Spondias mombin* gave the best corrosion inhibition in this study.

Table 4. Adsorption parameters for corrosion of mild steel in 0.5 M sulphuric in the presence of *Spondias mombin* leaves, fruits and bark extracts

Days	**Correlation Coefficients (R2)**		
	Leaves	**Fruits**	**Bark**
7	0.981	0.985	0.998
14	0.128	0.929	0.985
21	0.688	0.867	0.963
28	0.608	0.050	0.910
35	0.339	0.007	0.888

5. CONCLUSION

The corrosion inhibition of *Spondias mombin* water extract on low carbon steel in 0.5 M H2SO4 was investigated in this paper. The results obtained showed that mass loss generally decreased in the presence of all the extracts with the lowest occurring with the bark extract on the 14th day. Corrosion rates followed the same trend with the lowest also associated with the bark extract at 0.4 g/ml on the 14th day. The highest inhibition efficiency for the leaves extract was 66.67% while that of the fruits extract was 50.59% and that of the bark extract was 83.21%. Inhibition efficiency for the leaves extract increased with concentration and got to its peak on the 7th day, that of the fruits extract initially increased with concentration until 1 g/ml after which there was a decline, its highest value was also recorded on the 7th day. The best inhibition efficiencies (in the range of 76.32% to 83.21%) for *Spondias mombin* water extract were observed in 0.4 g/ml bark extract throughout the days of the experiment, the highest being observed on the14th day. It can be concluded that the bark extract of *Spondias mombin* exhibited the best corrosion inhibition properties in this study followed by the leaves and then the fruits.

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