Comparative Effect of Concentration and Exposure Time on Corrosion Inhibition of Alkaloids and Tannins Extracts of Jatropha Curcas and Parkia Biglobosa on Mild Steel in Acidic Media

Agava I. Mohammed[1] Rukaiyat M. Said[2] Abubakar G. Salisu[2*]
1.Department of chemistry, Nigerian Defense Academy
2.Department of Applied Science, Kaduna Polytechnic, Nigeria

Abstract
Comparative corrosion inhibition of mild steel in 0.5 H_2SO_4 by the total alkaloids and tannins extracted from Parkia biglobosa seed bark and Jatropha curcas stem bark was investigated using gravimetric method at 30^0C. Results showed that these phytocompounds inhibit the corrosion process of mild steel in the test solution and the inhibition efficiency depends on the concentration of the alkaloids and tannins as well as the exposure time. Their adsorption was found to obey the Temkin and Langmuir adsorption isotherms and this suggested that the inhibitor molecules have been spontaneously adsorbed onto the surface of mild steel through a physical adsorption mechanism. The inhibition efficiency is markedly higher in addition of alkaloid extracts when compared with that of tannins extracts. The inhibition efficiency increased with an increase of inhibitor concentration but decreased with exposure time.
Keywords: Corrosion, Inhibition, Mild steel, Alkaloids, Tannins

1. Introduction

Mild steel is an alloy of iron with small amounts of carbon (0.1-0.25 per cent) beside carbon there are many elements that form part of the alloy such as chromium, manganese, tungsten and vanadium (Collins, 1998). These elements along with carbon act as hardening agents that prevent corrosion from occurring inside the iron crystal and prevent the lattice layers from sliding past each other. (Malik *et al*., 2011). Mild steel are the most commonly used materials in the fabrication and manufacturing of oil field operating platforms due to their availability, low cost, ease of fabrication, and high strength. Mild steel plates and rod-section have been used as structural member in bridges, buildings, pipelines, heavy vehicles, construction of ships storage vessels and numerous other applications (Osarolube *et al,* 2008).

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment. It occurs in various mechanical, metallurgical, biochemical and medical engineering appliances and more specifically in the design of a much more varied number of mechanical parts which equally vary in size, functionality and useful lifespan (Thompson *et al.,* 2007). Several efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors is one of them (Ashassi-sorkhabi *et al*., 2008), in line with the emerging concept of "Green Chemistry" and the related of principles of 'Less hazardous synthesis. Corrosion inhibitors are chemical compounds that have the ability to decrease the corrosion rate of a metal or an alloy (Taylor and Raja, 2007). There are several classes of inhibitors designated as: Passivators that are usually inorganic oxidizing substances (such as chromates, nitrites, and molybdates) that passivate the metal and shift the corrosion potential several tenths volt in the noble direction. Nonpassivating inhibitors, such as the pickling inhibitors, are usually organic substances that have only slight effect on the corrosion potential, changing it either in the noble or active direction usually by not more than a few milli - or centivolts.). Inhibitors decrease or prevent the reaction of the metal with the media. They reduce the corrosion rate by
(i) Adsorption of ions/molecules onto metal surface.
(ii) Increasing or decreasing the anodic and/or cathodic reaction,
(iii) Decreasing the diffusion rate for reactants to the surface of the metal,
(iv) Decreasing the electrical resistance of the metal surface.

Many factors contribute to the effectiveness and efficiency of a corrosion inhibitor. These factors include quality of water, fluid composition, and flow regime. The mechanism of action of inhibitors involve formation of a thin film passivation layer on the surface of the material that hinders access of the corrosive substances to the metal surface, thereby inhibiting either the oxidation or reduction part of the redox corrosion system or scavenging the dissolved oxygen (Malik *et al* ;2011). However, several factors including cost and amount, easy availability and most importantly safety to environment and its species need to be considered when choosing inhibitors.

Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origin in various corrosive media (Ebenso, 2004). In acid media, nitrogen-base materials and their derivatives, sulphur-containing compounds, aldehydes, thioaldehydes, acetylenic compounds, and various alkaloids, for example, papaverine, strychnine, quinine, and nicotine are used as inhibitors. In neutral media, benzoate, nitrite, chromate, and phosphate act as good inhibitors. (Malik *et al* ;2011 : Ebenso, 2004

Plant is one of the great chemical factories which can supply us with the chemicals required to inhibit the corrosion process, since most naturally occurring substances are safe and can be extracted by simple and cheap procedures (Taylor and Raja, 2007). *Parkia biglobosa* (**seed pod plant)** belong to the plant family Mimosaceae of the order Leguminisae. *Parkia biglobosa is popularly* known as the African locust bean tree in English, Irugba in Yoruba, Dorowa in Hausa and Origili in Igbo. *P.biglobosa* is known to occur in a diversity of agro ecological zones ranging from tropical rain forests to arid zones. It is for this reason that it is found scattered in many countries of West Africa. The fermented seeds of *P. biglobosa* are used in all parts of Nigeria and indeed the West Coast of Africa for seasoning traditional soups. The trees form a crown so are often grown as shade trees (Daziel, 1982). However, the species are used traditionally as foods, medicinal agents and are of high commercial value. The *Parkia biglobosa* plants have been identified as source of tannins, saponins, gums, fuel and wood (Ajaiyeoba, 2002). Seeds of the plant have also been investigated for their protein and amino acid contents (Fetuga *et al*., 2006). Ajaiyeoba, 2002 reported the presence of tannins in the ethylacetate fractions of *Parkia biglobosa* plant, while *Jatropha curcas* or Physic nut is a multipurpose and drought resistant, perennial plant belonging to the family Euphorbiaceae (Okujagu *et al*., 2006). *Jatropha curcas* Linn is commonly called physic nut, purging nut or pig nut. It is known as lapalapa In Yoruba, in Hausa as Binidazugu. It is a tropical plant that can be grown in low to high rainfall areas either in the farm as a commercial crop or on the boundaries as a hedge to protect fields from grazing animals and to prevent erosion (Henry *et al.,* 2009). The leaves are remedy for jaundice, applied by rectal injection (Okujagu *et al*., 2006). Previous studies have reported that the plant contains bioactive compounds that can be used for the treatment of fever, mouth infections, jaundice, guinea worm sores and joint rheumatism (Fagbenro and Beyioku, 1998) Phytochemical screening revealed the presence of Flavonoids, steroids, triterpenoids alkaloids, tannins and saponins in *Jatropha curcas* leaf extract. (Fagbenro and Beyioku, 1998) reported the presence of alkaloids, cardiac glycosides, cyanogenic glycosides, phlobatannins, tannins, flavonoids and saponins in the methanolic leave extract of *J. curcas*. The use of these plants extract is worthwhile as corrosion inhibitors for both socio-economic and environmental benefits. In this paper comparative inhibitive properties of alkaloids and tannins extracts of Jatropha *curcas* and *Parkia biglobosa* on the corrosion of mild steel in H_2SO_4 acidic media is investigated.

2. Materials and Method

*2.1 **Collection and Identification of Sample***

Sample of seed bark of *Parkia biglobosa* and stem bark of *Jatropha curcas* plant were collected from Afaka area of the Nigerian Defence Academy, Kaduna, Nigeria. Identified and authenticated by Mr Yahaya Abdullahi of Botany section, Department of Biological Sciences, Nigerian Defence Academy, Kaduna Nigeria. The voucher specimens were deposited in the Herbarium. Mild steel was purchased from-panteka market, kaduna Nigeria.

2.2 Sample Preparation

The seed bark of *Parkia biglobosa* and stem bark of *Jatropha curcas* plant were carefully removed and oven dried at 40 ^{0}C for 2 hours (Loto, *et al*., 2011). The dried samples were separately pulverized using a wood mill machine. The pulverized samples were weighed and preserved for the extraction.

2.3 Phytochemical Analysis

Phytochemical analysis of the extract of *Parkia biglobosa* and stem bark of *Jatropha curcas* plant was carried out according to the method reported by (Eddy and Ebenso, 2008).

2.4 Total Alkaloids Extraction

Total alkaloids extracts was extracted from the seed bark of *Parkia biglobosa* and the stem bark of *Jatropha curcas* according to method described by Garba and Okeniyi, (2012).

2.5 Total Tannins Extraction

Total Tannins extracts was extracted from the seed bark of *Parkia biglobosa* and the stem bark of *Jatropha curcas* according to Vienna and Screekuma**,** (2002).

2.6 Preparation of Mid Steel Sample

The nominal percent of mild steel used in this study include 0.19 Carbon, 0.25 silicon, 0.64 Mn, 0.05 S, 0.06 P, ,0.09 Ni, 0.08 Cr, 0.02 Mo, and 0.27 Cu, the rest been Fe. The bar was cut into various rectangular pieces of dimensions 4 x 2 x 0.65 cm. The test specimen was washed using a wire brush; ground with silicon carbide abrasive paper of 240, 320 and 400 grits; polished to 1micron and thoroughly cleaned and rinsed in ultrasonic cleaner and dried and kept in desiccators for further tests.

2.7 Preparation of test media with the extracts

The alkaloids and tannins extract of each plant were used in the preparation of the test solutions by dissolving 0.1, 0.2, 0.3, 0.4 and 0.5 g of each alkaloid and tannins extracts in 1 L of 0.5M H_2SO_4 This correspond to the concentration of 0.1, 0.2, 0.3, 0.4 and 0.5 g/L, while the test media without extract is made up of only 1L of 0.5M H_2SO_4.

2.8 Weight Loss Experiment

Previously weighed test specimens of mild steels were totally immersed in each of the test media contained in a 250 cm^3 beaker for 25days. The beaker was inserted into a water bath maintained at a temperature of 303K.

Experiment was performed with acid test media in which some had the solution extract added. Test specimen were taken out of the test media every 5days, washed with distilled water, rinsed with methanol, air dried and re weighed. The difference in the weight before the experiment and after the experiment were used to determine the weight loss. Plot of weight loss versus time of exposure and calculated corrosion rate against time of exposure were used as the percentage inhibitor efficiency, The corrosion rates (CR) for mild steel in different concentrations of H_2SO_4 media was determined. The Temkin and Langmuir adsorption isotherm equation was used to deduced the adsorption chacteristics of the inhibitors.

3. Results and Discussion

3.1 Percentage yield

The percentage yields of the total alkaloids extracted from seed bark of *Pakia biglobosa* and the stem bark of *Jatropha curcas* were found to be 2.2 %,and 1.66% respectively. This shows that the two plants contain higher percentage of alkaloids and this could be one of the reasons why these plants are reported to have antimicrobial properties (Garba and Okeniyi, 2012). The percentage of tannins was found to be 1.73% and 1.53% for *Parkia biglobosa* seed bark and *Jatropha curcas* respectively. These also showed that the two plants contain higher percentage tannins and could also be the contributing factor for the reported antimicrobial activity of the two plants. This result also shows that *Parkia biglobosa* seed bark contains more alkaloids and tannins than *Jatropha curcas*.

3.2 Corrosion Inhibition of the Extracts

The extract contains organic compounds of Tannins and Alkaloids, these active organic inhibitors invariably contain functional groups through which they anchor onto the metal surface. The electron donating substituents increase inhibition by increasing the electron density of the anchoring group. Inhibition of alkaloids and tannis extracted from the two plants, (*Parkia biglobosa* and *Jatropha curcas)* showed that inhibition rates increases with increase in the concentration of the organic inhibitors. These decrease in corrosion rates observed when concentration of alkaloids and tannins were increase could be due to the known fact that organic inhibitors decrease metal dissolution by forming a protective adsorption film that blocks the metals surface, separating it from corrosive medium.

Figure 1a&b shows the variation of weight loss with time of exposure for the corrosion of mild steel in 0.5M H_2SO_4 at various concentrations of alkaloids extract of *J. curcas and P .biglobosa* at 303 K, weight loss of mild steel increases with increase in the period of contact but decreases with increase in concentration of alkaloid extract indicating that the rate of corrosion of mild steel increases as the period of contact increases and that alkaloid extracts inhibited the corrosion of mild steel in H_2SO_4 medium.

Figure 2a&b below show the variation of weight loss with time exposure for the corrosion of mild steel in 0.5 M H_2SO_4 at various concentrations of tannins extracts of *J. curcas and P .biglobosa* at 303 K . In this medium, similar trends were also observed except that values of weight loss were relatively larger than those obtained using alkaloids extracts.

a b

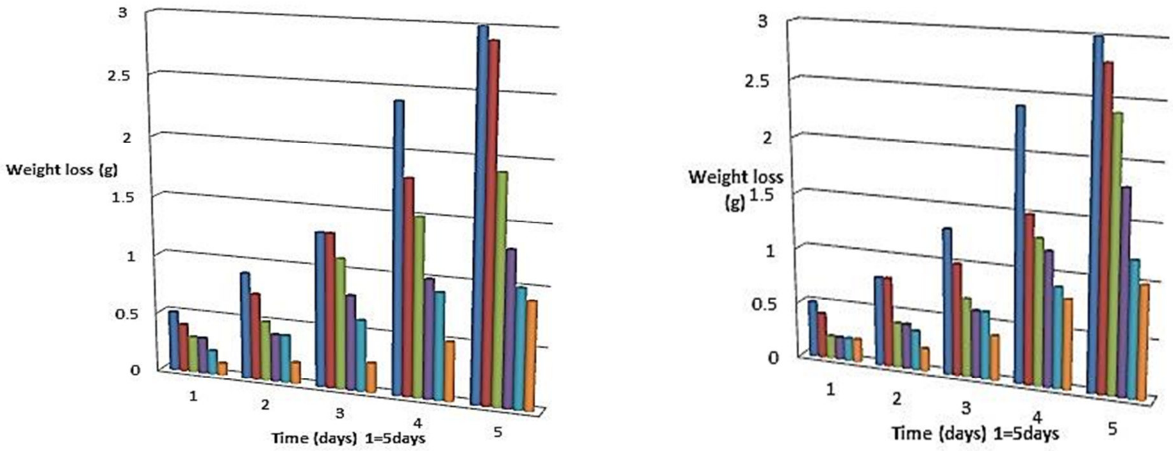

Figure 1a&b: Results of weight loss experiment of Alkaloid extracts of *Jatropha curcas and Parkia biglobosa* respectively in H_2SO_4 medium at 30 ^{0}C.

a b

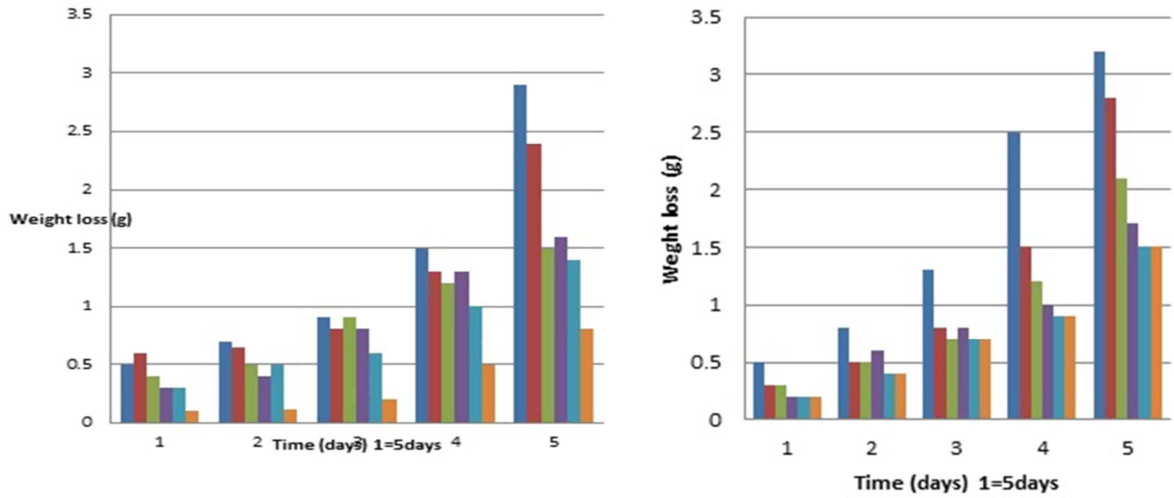

Figure 2a &b: Results of weight loss experiment of Tannins extracts of *Jatropha curcas and Parkia biglobosa* respectively in H_2SO_4 medium at 30 ^{0}C**.**

This revealed that the rate corrosion inhibition increases with increase in the period of contact but decreases with increase in the concentration of tannins extracts of all the concentrations indicating that the rate of corrosion of mild steel in H_2SO_4 increases with increase in the period of contact but decreases with increase in the concentration of Tannins extracts.

Table 1: Result of corrosion inhibition efficiency of alkaloids and tannins extracts from *pakia biglobosa* and *jatropha curcas* in H_2SO_4 medium at the 25th day

Plant	Extracts	Concentration (g/L)	Corrosion Rate ($gh^{-1}cm^{-2}$) (10^{-4})	Extracts Inhibition Efficiency (%)	Surface coverage Θ
Pakia Biglobosa	Akaloids	0.1	5.21	7	0.07
		0.2	4.79	20	0.20
		0.3	3.13	60	0.60
		0.4	2.50	60	0.60
		0.5	2.08	70	0.70
	Tannins	0.1	6.04	7	0.07
		0.2	5.63	20	0.20
		0.3	3.96	40	0.40
		0.4	3.33	60	0.60
		0.5	2.50	67	0.67
Jatropha Curcas	Alkaloids	0.1	5.01	13	0.13
		0.2	3.32	27	0.27
		0.3	3.13	40	0.40
		0.4	2.91	50	0.50
		0.5	1.66	70	0.70
	Tannins	0.1	5.83	7	0.03
		0.2	5.01	20	0.10
		0.3	2.50	40	0.36
		0.4	2.31	60	0.47
		0.5	1.88	67	0.60

From the results above,(Table 1) the corrosion rates of mild steel was found to decrease as the concentration of both alkaloid and tannins extracts of these plants increases, while its inhibition efficiency increases with increase in the concentration of alkaloids and tannins extract of *J. curcas and P. biglobosa*. The results also shows that the alkaloids and tannins extracts of this plants in H_2SO_4 acid corrosion inhibition performance was best at 0.5g/L of extracts concentrations at 30^0C.

3.3 Temkin and Langmuir Adsorption Isotherms

Fig 3-6, showed Temkin and Langmuir adsorption isotherms of both alkaloids and tannins exracts of *P. biglobosa and J. curcas* plant in H_2SO_4 acidic medium. The straight line plot indicates that the adsorption of both alkaloids and tannins on the mild steel was found to obey both Langmuir and Temkin Adsorption Isotherms and this suggested that the inhibitor molecules have been spontaneously adsorbed onto the surface of mild steel through a physical adsorption mechanism. The obtained plot for Langmuir and Temkin adsorption isotherm is linear with a correlation coefficient; R^2 about 0.98.

The result indicates that Temkin and Langmuir Adsorption isotherms are valid for various concentrations of *P. biglobosa and J. curcas* plant. Temkin adsorption isotherm considers lateral interactions between adsorbed inhibitor molecules as well as those among inhibitor and water molecules, indicating that the inhibitor is displacing water molecules from the metal surface. With increasing corrosion of inhibitor, concentration inhibitor molecules probably start to desorbs due to interaction between the inhibiting molecules already adsorbed at the surface and those present in the solution. With increasing concentration of the inhibitor, the interactions become stronger, leading to secondary desorption.

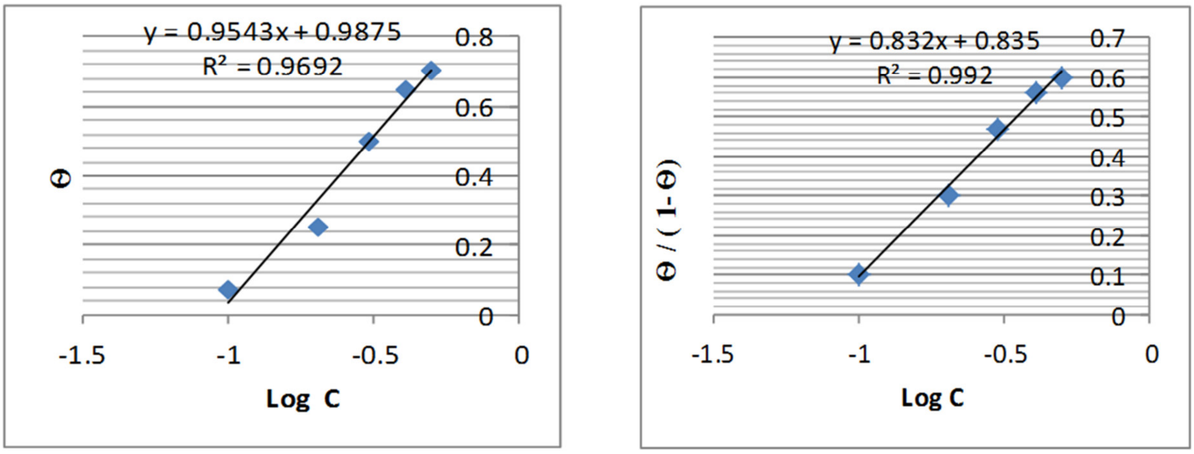

Figure 3a&b; Temkin and Langumuir isotherms respectively for Alkaloids extracted from *Pakia biglobosa* on mild steel in H_2SO_4 medium at 30^o

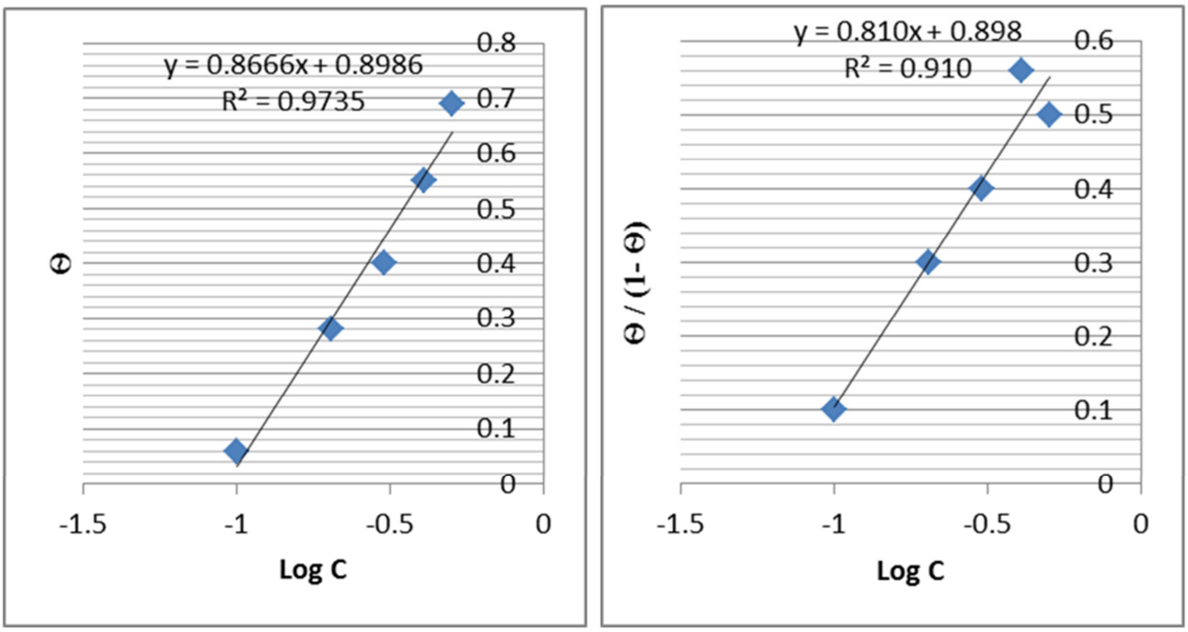

Figure 4a&b; Temkin and Langmuir isotherms respectively for tannins extracted from *Pakia Biglobosa* on mild steel in H_2SO_4 medium at 30^o C.

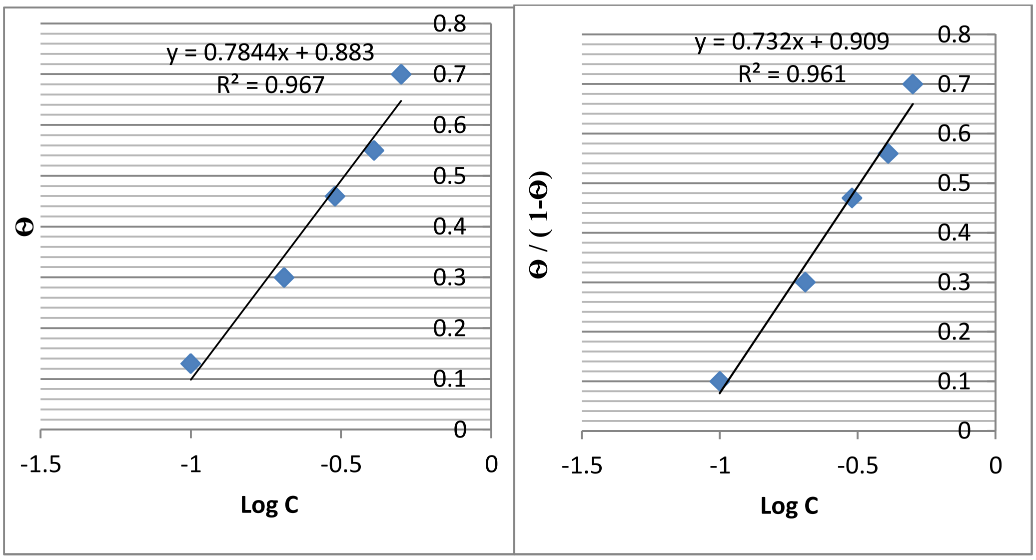

Figure 5a&b; Temkin and Langmuir isotherms respectively for Alkaloids extracted from *Jatropha curcas* on mild steel in H_2SO_4 medium at 30^o C

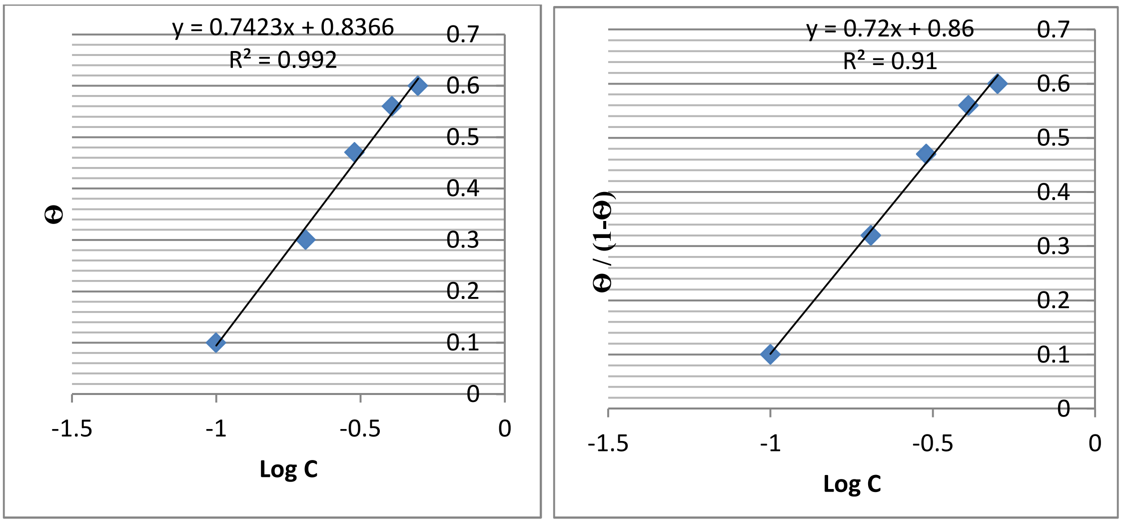

Figure 6a&b; Temkin and Langmuir isotherms respectively for tannins extracted from *Jatropha curcas* on mild steel in H_2SO_4 medium at 30^{o}C.

4. Conclusion

The gravimetric method was found to have proved the inhibitive nature of the alkaloids and tannins extracts. The *Parkia biglobosa* seed bark contains more alkaloids and tannins than *Jatropha curcas*.

The same tannins extract of both extract with the highest percentage efficiency of 67% while the alkaloids extracts gave percentage inhibition of 70% and are therefore better inhibitors. The plant extracts were found to obey Temkin and Langmuir adsorption isotherm from the fit of experimental data and comparative results of Temkin and Langmuir adsorption isotherm indicates that the extracted secondary metabolites forms strong protective film on the surface of mild steel to conform with physical adsorption mechanisms.

The plants part used for corrosion inhibition would be economically viable as the plants are found widely available and would be of great impact. Some direction for further research on this area may include other Phytocompounds such as phenols, as they are reported to have great inhibitive properties. Studies on the plants should be expanded to cover additional media and metals not covered by this research.

References

Ajaiyeoba, E. O., (2002).”Phytochemical and antibacterial properties of *Parkia biglobosa* and *Parkia bicolor* Leaf extracts”. *Afr. J. Biomed. Res.* Vol.5 (3).pp 677-684.

Ashassi-sorkhabi H, Shaabani B, Aligholipour B, & Seifzadeh D (2008). “The effect of Schiff bases on the corrosion of aluminium in HCl solution". Appl. Surf. Sci. 252: 4039-4047

Collins, English Dictionary – Complete and Unabridged © HarperCollins Publishers 1991, 1994, 1998, 2000, 2003.

Daziel,G.. (1982) "Microbial exopolymers: ecological and econimic considerations," *American Society Microbiology News*, vol. 48, pp. 9–11

Eddy .O & Ebenso, (2008). "Adsorption and inhibitive properties of ethanol extracts of *Musa sapientum* peels as a green corrosion inhibitor for mild steel in H_2SO_4", African J. Pure Appl. Chem., 2(6):046-054.

Ebenso, N., &. Eddy, O. (2008) "Corrosion inhibition and adsorption properties of methacarbanol on mild steel in acidic medium", Portugaliae Electrochemica Acta, vol.27, no.1, pp.13-22, 2009

Fagbenro,S.A., & Bayioku E. A (1998). "Inhibition of mild steel corrosion in acidic medium using synthetic and naturally occurring polymers and synergistic halide additives," *Corrosion Science*, vol. 50, (7), pp. 198–200.

Fetuga, M, Sherif, E. S, & Park, M. (2006) "Effects of 1,4-naphthoquinone on aluminum corrosion in 0.50 M sodium chloride solutions," *Electrochimica Acta*, vol. 51, no. 7, pp. 1313–1321.

Garba, S. & Okeniyi S. O. (2012). "Antimicrobial activities of total alkaloids extracted from some Nigerian medicinal plants" Journal of Microbiology and Antimicrobials Vol. 4(3), pp. 60-63,

Henry, W. Trabelsi, M. Zheludevich, & M. G. S. Ferreira, (2009) "Modification of bis-silane solutions with rare-earth cations for improved corrosion protection of galvanized steel substrates,*Progress in Organic Coatings*, vol. 57, (1)pp. 67–77,.

Malik L. Z, R. Serra, M. F. ,Montemor, & M. G. S. Ferreira, (2011) "Oxide nanoparticle reservoirs for storage and prolonged release of the corrosion inhibitors," *Electrochemistry Communications*, vol. 7, no. 8, pp. 836–840.

Okujagu, M.A., Arora, P., Kumar, S., Mathur, S.P., & Ratani, R. (2006). Inhibitive effect of prosopispineraria on mild steel in acidic medium. Corros. Eng. Sci. Tech. 43:213-218.

Osarolube Torres, R. S. Amado, C. Faia de (2008) "Inhibitory action of aqueous coffee ground extracts on the corrosion of carbon steel in HCl solution," *Corrosion Science*, vol. 53, no. 7, pp. 2385–2392,.

Taylor & Raja, P. B. (2007)"Corrosion inhibition of mild steel by Datura metel in acidic medium," *Pigment and Resin Technology*, vol. 34, no. 6, pp. 327–331,

Thompson, P., Tandel ,B & Oza, B. N. (2007) "Performance of some dyestuffs as inhibitors during corrosion of mild-steel in binary acid mixtures ($HCl + HNO^3$)," *Journal of the Electrochemical Society of Ind ia*, vol. 49, pp. 49–128,

Vienna, D.M. & SreeKuma,S.G (2002)." Biochemistry for medical students" 5th edition.