Electrochemical, Sem, Gc-Ms And Ftir Study Of Inhibitory Property of Cold Extract of Theobroma Cacao Pods For Mild Steel Corrosion In Hydrochloric Acid

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Abstract *- The inhibition capability of cold water extract of Theobroma cacao pods - Cocoa pod (TCP-CP) on mild steel corrosion in 1 M HCl solution was studied using electrochemical polarization, Scanning Electron Microscoy (SEM), Fourier Transform-Infrared Spectrum (FT-IR) analysis and Gas Chromatrography-Mass Spectrometry (GC-MS) analysis. The inhibition efficiency extrapolated from potentiodynamic polarization curves showed that cold water extract of TCP-CP behaved mostly as mixed-type inhibitor in hydrochloric acid. Scanning electron microscopy was used to characterize the surface morphology of uninhibited and inhibited mild steel specimens and the results show a remarkable inhibition of the corrosion process in the presence of the inhibitor. Analysis of the peaks of Fourier Transform-Infrared Spectrum (FT-IR) of the inhibitors indicated presence of functional groups containing Phosphorus, Oxygen, Nitrogen, -OH and -COOH while the peaks of the Gas Chromatrography - Mass Spectrometry (GC-MS) analysis is in agreement with the results of the FT-IR and indicate the presence of corrosion inhibiting compound such as Terpenes, Tannin, Alkaloid, Flavonoid and Phytate in different appreciable concentrations in mg/100g.*
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Keywords — *Electrochemical Polarization, Fourier Transform-Infrared Specrum (FT-IR), Theobroma cacao pods, Mild Steel, Scanning Electron Microscopy (SEM), Gas Chromatrography-Mass Spectrometry (GC-MS)*

I. INTRODUCTION

The report in [1] shows that the cost of all forms of corrosion in United States rose above 1$ trillion in 2012 accounting for about 6.2% of GDP hence, the largest single expense in the economy. The report also acknowledges that in the oil and gas company, corrosion accounts for over 25% of assets failure and is found to be prevalent in every stage of the production cycle. This level of loss is as a result of the exposure of the facilities to environments that supports corrosion. As an example, Oxygen which plays a dominant role in corrosion is normally present in producing formation water while during drilling operation, drilling mud can corrode the well casing, drilling equipment, pipeline, and the environment.

Today, as much as US$2.5 trillion, which is an equivalent to roughly 3.4 percent of the global Gross Domestic Product (GDP) has been spent fighting corrosion worldwide [1]. So, the battle against corrosion is a continuous one with a number of technique to monitor and control it. One monitoring measure that has been effective although simple and cheap is electrochemical polarization, and this is basically so because metal materials have unique polarization characteristics which can be detected by open circuit potential, breakdown potential and passivation potential. Researchers have used electrochemical polarization to determine the inhibitory properties of corrosion inhibitors ([2]; [3]; [4]; [5]; [6], [7]. The use of potentiodynamic polarization is economical and comes handy in the investigation of effectiveness of corrosion inhibitors.

Reference [9] investigated Aloe Vera plant extract as green inhibitor on the corrosion of stainless steel in 1 M H_2SO_4 using electrochemical technique and scanning electron microscopy. [8] reported that Aloe Vera plant extract proved to be an efficient corrosion inhibitor of stainless steel following the result of both linear polarization and electrochemical impedance spectroscopy extract as concentration increased. They also carried out their investigation using electrochemical noise (EN). Reference [9]) took interest in another green extract, Ligularia fischeri as inhibitor in 1 M HCl. In their study using electrochemical and spectroscopic investigation,

techniques Reference [9] identified that Ligularia fischeri an efficient inhibitor with an inhibition efficiency of 92% at a concentration of 500 ppm of the extract. As this field of research continues to expand, another researcher [11] examined the corrosion inhibition efficiency of Adhatoda vasica a plant extract in 0.5 M H_2SO_4 . Reference [11] reported that increase in the concentration of the extract Adhatoda vasica, increased its inhibition efficiency (IE%). He also reported a reduced the IE% as temperature increase. Reference [11] results were determined using potentiodynamics polarisation technique and electrochemical impedance spectroscopy (EIS) amongst others.

As a contribution to knowledge, this study investigated the corrosion inhibition efficiency of cold water extract of TCP-CP as corrosion inhibitor using potentiodynamic polarization. The study also characterized the inhibitor using Gas Chromatography- Mass Spectrometry, Fourier Transform-Infrared Spectrum (FT-IR) and Scanning Electron Microscopy (SEM).

II. Materials and Method

An aggressive solution of I M HCl used as the corrodent was prepared by diluting analytical grade HCl (33%) with distilled water. Ethanol and acetone were used in their pure state to degrease and dry the coupons before they were used. The TCP-CP pods were air dried in a shade to conserve their active ingredients although experimental drying of the pods at 30, 40 and 50oC has investigated (Izionworu, Unpublished result). The stock solution of the TCP-CP was prepared following the procedure reported in [12].

The mild steel coupons that were used for this investigation were mechanically cut to a dimension of 1 cm x 1 cm. The metals were encapsulated in epoxy resin in such a way that only one surface was left uncovered. The exposed area (1cm^2) was wet polished with different grades of emery papers, degreased in acetone, washed with ethanol, rinsed with distilled water and dried in warm air prior to use ([13], [14]).
Electrochemical polarization test was carried out as reported in [5] in a conventional three-electrode configuration with graphite rod as counter electrode and saturated calomel electrode (SCE) as the reference electrode using an electrochemical work station PARC-2273 Advanced Electrochemical System controlled by a computer with Powersuit software. The potentiodynamic polarization (PDP) studies were carried out in a potential range ±250 mV versus corrosion potential, at a scan rate of 0.333mV/s. Each test was run in triplicate to verify the reproducibility of the system.

The values of the corrosion current density in the absence ($i_{corr,bl}$) and presence of inhibitor ($i_{corr,inh}$) were used to estimate the inhibition efficiency (IE%) from polarization data using the expression of equation 1:

$$IE\% = \left(\frac{I_{corr(bl)} - I_{corr(inh)}}{I_{corr(bl)}}\right) x\ 100$$

where $I_{corr(bl)}$ and $I_{corr(inh)}$ respectively represents the corrosion current density in the absence and presence of the inhibitor. Inhibitor E_{corr} value greater than 85 mV, classified as anodic or cathodic, whereas values lesser than 85 mV may be seen as a mixed type [6].

Morphological investigations of the mild steel electrode surface were undertaken by SEM examinations of the electrode surfaces exposed to different test solutions using XL-30FEG Scanning Electron Microscope. Mild steel specimens of dimensions 15 x 15 x 2 mm were cleaned as previously described [15] and immersed for 9 h in the blank solutions (1 M HCl) in the absence and presence of TCP-CP at 30 ±1 ºC, and then washed with distilled water, dried in warm air, and subjected to SEM surface examination [16].

Infrared spectroscopy was used to determine the functional groups in TCP-CP molecule. 20 g of TCP-CP grounded to fine powder was divided into two and used for the study. Fourier transform infrared (FTIR) spectra (KBr) were recorded using an FTIR MODEL IS-630 Cary Series by Agilent Technologies spectrophotometer at a frequency of 4000 to 400 cm^{-1}. ([17], [18]).
Also, phytochemical composition of the sample was determined using Gas Chromatography–Mass Spectrometry (GC-MS) - Agilent 6820 gas chromatograph with a 5973 MS detector equipped with 60 m×0.25 mm, i.d. 0.25 µm/MS DB-WAX capillary column (Agilent). The characterization and identification of the plant chemicals from the sample was completed in the SCAN mode with the m/z range varied from 35 to 450.

III. Result and Discusion

A. Potentiodynamic Polarization Measurement Result of the Inhibitor TCP-CP

To establish the effect of cold extracts of TCP-CP on the anodic and cathodic reactions of mild steel in 1 M HCL solution, polarization measurements were performed using TCP-CP as inhibitor. Figures1, shows the typical potentiodynamic polarization (PDP) curves of mild steel in 1 M HCl in the absence and presence of different concentrations of TCP-CP at 303 K, while Table 15 presents the polarization parameters for Mild Steel in 1 M HCl in the absence

and presence of TCP-CP at 303 K extrapolated from the graph of Figure 1.

Careful observation of the plots reveal that the presence of the inhibitor affected both the cathodic and anodic polarization curves. The presence of TCP-CP shifted the polarization curves to areas of lower corrosion current values, this phenomenon was more pronounced at higher concentration (67% volume concentration) of TCP-CP inhibitor. Again, careful scrutiny of the corrosion potential (E_{corr}) shows that the presence of TCP-CP shifted the corrosion potential towards the anodic direction by 19 mV when 16% volume concentration of the inhibitor was used to make up the 200 ml corrodent solution, (that is in upward direction from the blank solution E_{corr}, commonly referred to as the noble direction with an E_{corr} value of -537.4 mV). At 67% inhibitor content the E_{corr} value of 29.9 mV was recorded. It is generally accepted that if the change in E_{corr} is more than 85 mV the inhibitor is classified as either cathodic or anodic inhibitor, otherwise it is a mixed type inhibitor ([4], [19], [20]). The result presented here indicates that the change in E_{corr} is not up to 85 mV, hence TCP-CP is classified as mixed type inhibitor.

Again, the extrapolated electrochemical parameters of the PDP for TCP-CP presented in Table 1 shows that the corrosion current density (I_{corr}) reduced from 183 µA/cm^2 for blank solution to 32.4 µA/cm^2 in the presence of TCP-CP at 16% volume concentration and 19.7 µA/cm^2 for 67% volume of inhibitor in corrodent. This observation again supports the fact that the inhibitor TCP-CP actually inhibited corrosion of mild steel in 1 M HCl by blocking available active sites on the mild steel coupon. The I_{corr} values indicate that increase in concentration of the inhibitor resulted in decrease in I_{corr} and this is essentially so because with the increase in the inhibitor content more active sites for corrosion are blocked by the extract particles. The corrosion inhibition efficiency (IE_{corr}%) of 82.5 and 89.2 % for corrodent with 16 and 67 % volume concentrations of TCP-CP also supports the fact that the inhibitors TCP-CP is an effective inhibitor.

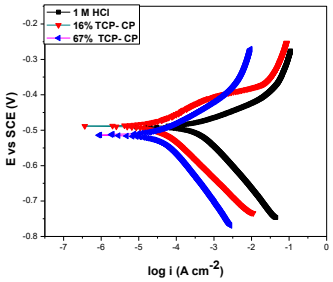

Fig 1: Potentiodynamic polarization curves of mild steel in 1 M HCl solution in the absence and presence of TCP-CP at 30ºC.

Table 1: Polarization Parameters for Mild Steel in 1 M HCl in the Absence and Presence of TCP-CP, CVB-WC and BP-LP at 303 K

	I_{corr} (µA/cm^2)	E_{corr} (E vs SCE)	IE%
1 M HCl	183	-518.3	
16 V% TCP-CP	32.4	-537.4	82.5
67 V% TCP-CP	19.7	-548.2	89.2

B. Results of the Characterization of the Inhibitors Using Fourier Transform Infrared (FTIR)

The Infrared spectrum of the plant extracts TCP-CP in 1 M HCl base stock corrodent are presented along with the interpretation of the spectrums following the practical guidelines articulated in [21].

The interpretation of the infrared spectrum of TCP-CP in 1 M HCL corrodent seen in Figure 3 is detailed in Table 2. It shows that TCP-CP in 1 M HCl have O - H stretch that suggests the presence of Tannin (a compound in plants), weak (w) but broad (r) COOH dimmers and medium C = C aromatic stretch indicating the presence of Phenol, and variable N - H bend present in amines suggesting presence of heteroatoms like nitrogen. Again, it can be deduced that these contribute to the inhibiting property exhibited by TCP-CP. This is in agreement with [22] whose report was corroborated by [23] that heteroatoms in functional groups play a prominent role in the inhibition process of crude extracts.

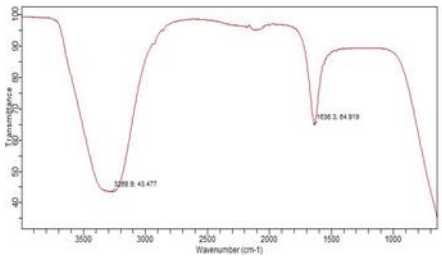

Fig 3: FT-IR spectrum of TCP-CP alone and in 1 M HCL

Table 2: FT-IR Result of TCP–CP in 1M HCL Solution

Peaks from FT-IR Spectra (Vcm^{-1})	Possible functional groups
1636.3	C = C aromatic stretch (m) N - H bend (v)
3268.9	N - H stretch, amines (v)
	O - H stretch, COOH dimmers (w, br)
	C - H stretch, C = C - H (sh)

C. Results of the Characterization of TCP-CP Using Gas Chromatography – Mass Spectrometry

The Gas Chromatography – Mass Spectrometry (GC-MS) "full spectrum" analysis presenting all the peaks within the spectrum for TCP-CP alone is shown in

Fig. 10 and the full spectrum for corrodent with TCP-CP in in 1 M HCl base stock solution is shown in Fig. 11. Tables 4 and 5 gives the quantitative values of the phytochemical composition of the inhibitor - TCP-CP alone and in 1 M HCl solution respectively, while a summary of the quantitative phytochemical analysis is presented in Tables 3.

From Table 3, it can be seen that TCP-CP in its raw state has 9.79 mg/100g of Tannin, 21.27 mg/100g of Alkaloid, 5.26 mg/100g of Flavonoid and 16.43 mg/10g of Phenol. These phytochemical concentration values increased, when TCP-CP was introduced into the corrodent solution, to 18.08, 24.67 and 5.81 mg/100g for Tannin, Alkaloid and Flavonoid respectively. Again, the structures of these compounds seen in Figs. 4,5 and 6 reveals the presence of the hetero atoms, (Nitrogen, Oxygen, Phosphorus), that have replaced carbon atom in the backbone of the molecular structures. The presence of these compounds some among which researchers have used to classify wood type [24] is in agreement with the FT-IR spectrum that had peak of 1636.3 Vcm^{-1} for C = C aromatic stretch (m), –OH and –COOH groups ([20], [25], [7]).

The nature of Alkaloid present originate from amino acids and are classified based on the similarity of their carbon skeleton either as indole-, isoquinoline-, and pyridine (Fig. 5). However, it is observed that the introduction of the inhibitor into the corrodent solution resulted in the reduction of phenol and phytate. The presence of Flavonoid, Fig. 4 explains why there is yellow colouration, which indicative of a pigment that is very important in inhibitors.

Fig 4: Structure of (a) Tannin (b) Flavonoid ([26], [27])

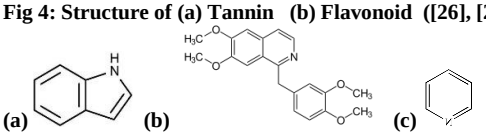

Fig 5: Structure of (a) Indole [10] (b) isoquinoline (c) pyridine ([28])

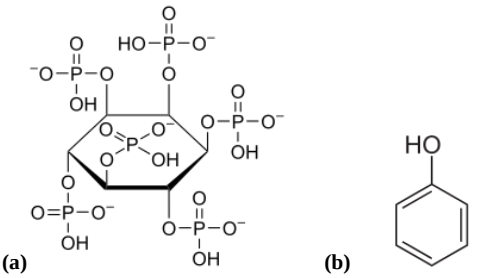

Fig 5: Structure of (a) Phytic acid [29] (b) Phenol [30]

Table 3: Summary of Phytochemical Quantification Report of TCP-CP and TCP-CP in 1 M HCl,

Compound	Concentration (mg/100g)	
	TCP-CP	TCP-CP in HCl
Terpenes	4.27	4.38
Phytosterol	0.82	2.13
Oxalate	0.41	0.17
Steriod	0.08	1.51
Tannin	9.76	18.08
Phenol	16.43	5.42
Saponin	2.51	3.34
Alkaloid	21.27	24.67
Coumarin	0.68	0.83
Anthocyanins	1.49	2.58
Flavonoid	5.26	5.81
Phytate	18.06	9.39
Cardiac Glycoside	0.19	ND
Cyanogenic Glycoside	2.73	0.01

ND : Not Detected

D. Results of the Characterization of the Inhibitors Using Surface Morphology

Scanning Electron Microscopy (SEM) examination of the mild steel surface before and after immersion for 9 hours at 303 K in a base stock solution of 1 M HCl, in the absence and presence of the inhibitors TCP-CP, presented in Fig. 7 shows a mild steel with a surface morphology that is badly damaged in the absence of TCP-CP inhibitor. This damage is attributed to mild steel metal dissolution in the aggressive acidic – 1 M HCl, environment. It can however be seen that the mild steel coupon surface in the acidic environment with TCP-CP inhibitor were not damaged like those immersed in the acidic environment without the inhibitor. The reason for the later observation is due to the formation of protective layers on the surface of the mild steel coupons. Reference [31], [32] reported a similar observation in separate research works.

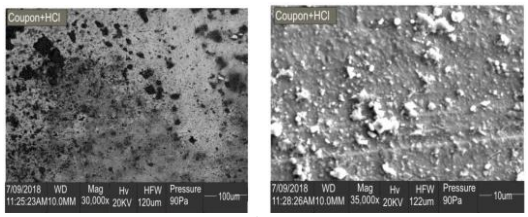

Fig 7: SEM image of mild steel in 1 M HCL solution after 9 h of immersion at 303 K

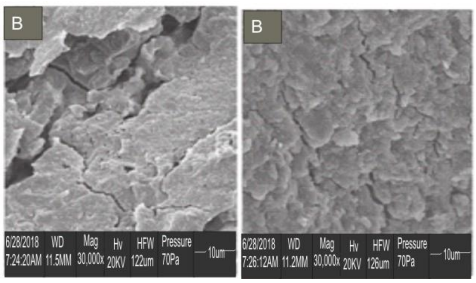

Fig 8: SEM image of mild steel in 1 M HCL corrodent after 9 h of immersion at 303 K in the presence of TCP-CP

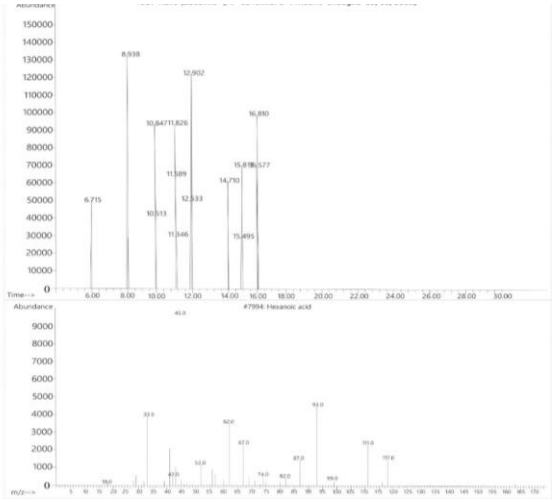

Fig 9: GC-MS Spectrum for TCP-CP

Table 4: Tabulated Result from the GC-MS Spectrum for TCP-CP

	compound	R.T (min)	Qion Response	Conc. (mg/100g)	Dev. (min)
1)	Terpenes	6.715	4826	4.27	25
2)	Phytosterol	8.938	8135	0.82	18
3)	Oxalate	10.513	5942	0.41	12
4)	Steriod	10.847	3189	0.08	15
5)	Tannin	11.346	6247	9.76	22
6)	Phenol	11.589	5135	16.43	13
7)	Saponin	11.826	3801	2.51	29
8)	Alkaloid	12.533	9244	21.27	45
9)	Coumarin	12.902	8230	0.68	11
10)	Anthocyanins	14.710	6093	1.49	14
11)	Flavonoid	15.495	7192	5.26	68
12)	Phytate	15.813	2648	18.06	21
13)	cardiac Glycoside	16.577	3122	0.19	34
14)	Cyanogenic Glycoside	16.810	6184	2.73	42

(#) = qualifier out of range (m) = manual integration (+) = signals summed

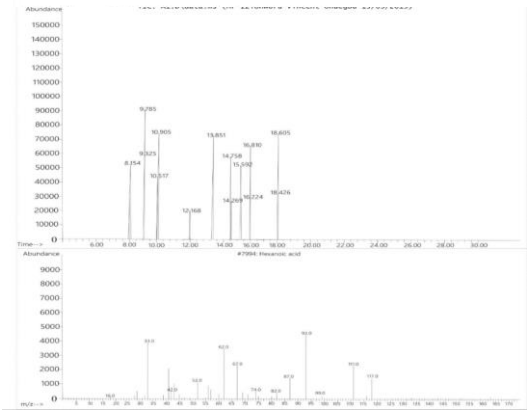

Fig 10: GC-MS Spectrum for TCP-CP in 1 M HCl Solution

Table 5: Tabulated Result from GC-MS Spectrum forTCP-CP in 1 M HCl Solution

	compound	R.T (min)	Qion Response	Conc. (mg/100g)	Dev. (min)
1)	Terpenes	8.154	3189	4.38	16
2)	Phytosterol	9.325	5924	2.13	12
3)	Oxalate	9.785	9048	0.71	19
4)	Steriod	10.517	8369	1.51	10
5)	Tannin	10.905	7158	18.08	26
6)	Phenol	12.168	5246	5.42	23
7)	Saponin	13.851	5159	3.34	13
8)	Alkaloid	14.269	8186	24.67	38
9)	Coumarin	14.758	3924	0.83	18
10)	Anthocyanins	15.592	4167	2.58	13
11)	Flavonoid	16.224	3931	5.81	28
12)	Phytate	16.810	6821	9.39	27
13)	cardiac Glycoside	18.426	7921	ND	17
14)	Cyanogenic Glycoside	18.605	3284	0.01	35

(#) = qualifier out of range (m) = manual integration (+) = signals summed

E. Conclusion

This Potentiodynamic polarization investigation shows that the cold distilled water extract of TCP-CP behaves mostly as mixed-type inhibitor in hydrochloric acid. This result is in agreement with the results of an investigation conducted by [12]**.** Also the surface morphology result of the uninhibited and inhibited mild steel specimens from Scanning Electron Microscopy show a remarkable inhibition of the corrosion process in the presence of the inhibitor. The Scanning Electron Microscopy (SEM) analysis further showed that cold distilled water extract of TCP-CP is an effective inhibitor of corrosion of mild steel in HCl environment. This finding is supported by the peaks of Fourier Transform-Infrared Specrum (FT-IR) of the inhibitor which indicate the presence of functional groups containing P, O N, -OH and -COOH, while the peaks of the Gas Chromatrography - Mass Spectrometry (GC-MS) analysis corroborates the results of FTIR as it identified the presence of Tannin, Alkaloid, Flavonoid, Phenol and Phytate - compounds that contain P, O N, -OH and -COOH

Reference

[1] National Association of Corrosion Engineers, NACE International, International Measures of Prevention, Application and Economics of Corrosion Technology (IMPACT) http://impact.nace.org/documents/Nace-International-Report.pdf, 2016.

[2] F. Santiago, R. G. Federico, B. Violeta, C. G. Juan, and F. Sebastian. A Critical Review of the Application of Electrochemical Techniques for Studying Corrosion of Mg and Mg Alloys: Opportunities and Challenges. ttp://dx.doi.org/10.5772/intechopen.79497

[3] R. Loto. Potentiodynamic polarization studies of the pitting corrosion resistance and passivation behavior of P4 low carbon mold steel in chloride and acid chloride solution. Materials Research Express, No. 11, 2018. Volume 5,

[4] M. Yadav, L. Gope and T.K. Sarkar. Synthesized amino acid compoundas eco-friendly corrosion inhibitor for mild steel in hydrochloric acid solution: electrochemical and quantum studies. Research on Chemical Intermediates 42 (3), Pp. 2641-2660, 2015.

[5] I.O. Arukalam, N.T. Ijoma, S.C. Nwanonenyi, H.C. Obasi, B.C. Aharanwa and P.I. Anyanwu. "Studies on acid corrosion of aluminium by a naturally occurring polymer (xanthan gum)," International Journal of Scientific & Engineering Research, Volume 5, Issue 3, pp. 663-673, 2014.

[6] X. Wang, H. Yang and F. Wang. An investigation of benzimidazol derivative as corrosion inhibitor for mild steel in different concentration HCl solutions. Corrosion Science, Elsevier 53, Pp. 113-121, 2011.

[7] Karthikaiselvi, R. and Subhashinis, K. Study of adsorption properties and inhibition of mild steel corrosion in hydrochloric acid media by water soluble composite poly (vinyl albholar o-methoryaniline). Journal of the Association of Arab Universities for Basic and Applied Sciences 16, 74-82, 2014.

[8] B. Ramezanzadeh, and S.Y. Arman, Electrochemical noise investigation of Aloe plant extract as green inhibitor on the corrosion of stainless steel in 1 M H_2SO_4 Journal of Industrial and Engineering Chemistry. Volume 21, Pp. 318-327, 2015.

[9] P. Mayakrishnan, S. HyunKim, K. Kalaiselvi, V. Hemapriya, Ill-Min. Highly efficient Ligularia fischeri green extract for the protection against corrosion of mild steel in acidic medium: Electrochemical and spectroscopic investigations. Journal of the Taiwan Institute of Chemical Engineers Volume 59, Pp. 553-562, 2016.

[10] https://en.wikipedia.org/wiki/Indole
[11] M. R. Singh, A green Approach:A corrosion inhibition of mild steel by adhatoda vasica plant extract in 0.5 M H_2SO_4 . Journal of Material and Environmental Science 4 (1) 119-126, 2012.
[12] V. O. Izionworu, and C.P. Ukpaka, Inhibition of Mild Steel Corrosion In Acidic Medium Using Theobroma Cacao Pod. International Journal of Scientific & Engineering Research, 2020.
[13] E. E. Oguzie, Corrosion inhibition of aluminum in acidic and alkaline media by Sansevieria trifasciata extracts.Corrosion Science, 49, 1527-1539, 2007.
[14] E. E. Oguzie, C. K. Enenebeaku, C. O. Akalezi, S. C., Okoro, A. A. Ayuk and E. N. Ejike, Adsorption and Corrosion inhibiting effect of Dacryodis edulis extract on low carbon steel corrosion in acidic media. Journal of Colloid Interface Science, 349, 283, 2010.
[15] E. E. Oguzie, Y. Li, and F. H. Wang, Corrosion inhibition and adsorption behaviour of methionine on mild steel in sulphuric acid and synergistic effect of iodide ion. Journal of Colloid Interface Science. 310, 90, 2007a.
[16] X. H. Li, G. N. Mu, Tween-40 as corrosion inhibitor for cold rolled steel in sulphuric acid: weight loss study, electrochemical characterization, and AFM, Applied Surface Science. 252, 1254–1265, 2005.
[17] S. P. Ramesh, K. P. Vinod Kumar and M. G. Sethuraman, Extract of andrographis paniculata as corrosion inhibitor of mild steel in acid medium, Bulletin of Electrochemistry, 17, 141–144, 2001.
[18] B. S. Shylesha, T. V. Venkatesha and B. M. Praveen, Corrosion inhibition studies of mild steel by new inhibitor in different corrosive medium. Research Journal of Chemical Sciences, 1(7), 46-50, 2011.
[19] M.S. Al-Otaibi, A.M. Al-Mayouf, A. Khan, A.A. Mousa, S.A. Al-Mazroa, and H.Z. Alkhathlan, Corrosion Inhibitory Action of Some Plant Extracts on the Corrosion of Mild Steel in Acidic Media. Arabian Journal of Chemistry, 7, 340-346. http://dx.doi.org/10.1016/j.arabjc.2012.01.015, 2014.
[20] H. Ashassi-Sorkhabi, and N. Ghalebsaz-Jeddi, Inhibitioneffect of polyethylene on the corrosion of carbon steel in sulphuric acid. Material Chemistry and Physics. V. 92, Issues 2–3, p 480-486. https://doi.org/10.1016/j.matchemphys.2005.01.059.
[21] J. Coates, Interpretation of Infrared Spectra: A Practical Approach. In: Meyers, R.A., Ed., Encyclopedia of Analytical Chemistry, John Wiley & Sons Ltd., Chichester, 10881-10882, 2000.
[22] K. Khairou, and A, Elsayed, Inhibition effect of some polymers on the corrosion of Cd in a hydrochloric acid solutions. Journal of Applied Polymer Science 88 (4). Pp. 866 – 871, 2003.
[23] K. F. Khaled, A. El-mghraby, O. B. Ibrahim, O. A. Elhabib and M. A. M. Ibrahim, Inhibitive effect of thiosemicarbazone derivative on corrosion of mild steel in hydrochloric acid solution. Journal of Material and Environmental Science. 1 (3) p139-150, 2010.
[24] V. O. Izionworu, and I.O. Alabi, Characterisation of Sawdust from Entandrophragma Cylindricum (Sapele), Diospyruscrassiflora (Ebony), Triplochitonscleroxylon (Obeche) and Chlorophora Excelsa (Iroko) Woods. International Journal of Scientific & Engineering Research Volume 9, Issue 2, Pp. 1569 – 1576, 2018.
[25] N. Ayssar, I.A. Ideisan and A. Ibrahim, Inhibition of Mild Steel Corrosion by 3-Benzoylmethyl Benzimidazolium Hexafluoroantimonate in Acidic Solution.International Journal of Corrosion, V.2012, ID 246013, 2012.
[26] Flavonoid, Wikipedia, the free encyclopedia Retrieved, https://en.wikipedia.org/wiki/Flavonoid April 2nd, 2019
[27] https://en.wikipedia.org/wiki/Tannin
[28] https://en.wikipedia.org/wiki/Alkaloid
[29] https://en.wikipedia.org/wiki/Phytic_acid
[30] https://en.wikipedia.org/wiki/Phenol
[31] V. O. Izionworu, Modeling of Experimental Drying Kinetics of Cocoa Pod. Department of Chemical/Petrochemical Engineering, Rivers State University, Nkpolu-Oroworukwo, Port Harcourt, Nigeria, 2020.
[32] M. Yadav, R.R. Sinha, T.K. Sarkar, I. Bahadur, and E. E. Ebenso, Application of new isonicotinamides as a corrosion inhibitor on mild steel in acidic medium: Electrochenical, SEM, EDX, AFM and DFT investigations. Journal of Molecular Liquids 212. Pp 686-698, 2015.
[33] S. K. Saha, A. Dutta, P. Ghosh, D. Sukul ,and P. Banerjee, Adsorption and corrosion inhibition effect of Schiff base molecules on the mild steel surface in 1 M HCl medium: A combined experimental and theoretical approach. Phys. Chem. Chem. Phys. Pp 2-11. DOI10.1039/C4CP05614K, 2015.