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Corrosion Inhibition Study Of Cocoa Pod Husk Extract On Api5l In Sulphuric Acid

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***Abstract*—Corrosion of infrastructures in the petrochemical industry has been a major concern. Organic inhibitors are used because they are eco-friendly and bio-degradable. This research studied the inhibitory effect of crude cocoa pod extract and ashed cocoa pod extract on API5L steel in 0.5M H_2SO_4 and 1.0M H_2SO_4 using potentiodynamic polarization method. The elemental compositions of the extracts were characterized using atomic absorption spectroscopy (AAS) and the result confirms the eco-friendliness of crude and ashed cocoa pod extract. The phenolic and aromatic functional groups in the extracts were revealed with Fourier transform infrared Spectroscopy (FTIR). The potentiodynamic results showed that crude and ashed cocoa pod extract possessed good inhibitory properties in both 0.5M H_2SO_4 and 1.0M H_2SO_4. Optimum inhibition efficiencies of 90.8% and 95.5% were attained at 0.5M H_2SO_4 and 1.0M H_2SO_4 respectively with 2v/v% crude cocoa extract concentration. Ashed cocoa pod extract exhibited maximum inhibition efficiencies of 97% and 99% in 0.5M H_2SO_4 and 1.0M H_2SO_4 respectively with 3.5v/v% ashed cocoa extract concentration. The adsorption model obey Langmuir adsorption isotherm. There was an improved surface condition due to the adsorption and then formation of monolayer film protection on the surface of the API5L steel. The good inhibitory properties of ashed and crude cocoa pod extracts were attributed to the presence of aromatic and phenolic functional groups present in the extracts**

Keywords—Corrosion, API5L, Cocoa pod husk, Inhibitor, Sulphuric Acid.

1. INTRODUCTION

Corrosion can be defined as the deterioration of materials by chemical interaction with their environment [1]. This has caused a major setback to most chemical and heavy metal industries as it reduces productivity in the industry and results in economic loss [2]. Combating corrosion in the heavy chemical industries especially oil and gas is important since the economic loss in these industries due to corrosion is extremely high [3]. Corrosion is present at each stage, from the crude exploration, transportation and distribution to safe storage [4]. There are side effects to corrosion in oil field such as rupturing of pipelines and storage facilities, shut down of plant for maintenance, loss of integrity of structures and flow problems [5] and [6]. A large number of the corrosion difficulties that occur in the industry are due to water, hydrogen sulphide, carbon dioxide, sulphuric acid and sodium chloride. If corrosion of the pipe networks is not properly controlled, leakage can occur this causes loss of the product and also allows penetration of water thereby leading to corrosion damage [3]. Steel is one of the major construction materials, which is extensively used in chemical and allied industries for handling of acid, alkali and salt solutions [7]. API5L steels are used for gas, water and sour crude transportation [8]. This is due to its low cost and resistance to crack propagation. The effective delivery of crude oil to refineries and depots are often disrupted due to corrosion processes. Corrosion causes degradation of material which with time results in damage to storage tanks or transmission systems and finally leads to leakage. Structures and equipment corrode at the stage of exploration, production (corrosion of drilling equipment) and petroleum processing (corrosion of refinery plants). It is gathered that the standard life span of a pipe line is less than 40 years coupled with research findings that 18% percent of pipe line is eroded by corrosion [9].The inhibition of the corrosion of carbon steel by using inhibitors is of great importance because of its large scale usage [10].

There are several methods of controlling corrosion of which the use of inhibitors has been the best. Inhibitors usually protect metals by adsorbing themselves to the substrate and thus providing protection through the formation of a thin passive layer [11].Corrosion inhibitors are chemicals substances that reduces the rate of metal corrosion when added to the environment [12] and [13].Corrosion inhibitors are either organic and inorganic inhibitors [14]. Because of toxicity and high cost of inorganic inhibitors, there has been a shift to the use of organic inhibitors which are more eco-friendly, cheaper and effective such as plant parts and wastes [15]; [16]; [17]; [18]; [19] and [20]. Good eco-friendly organic inhibitors should have compounds which are antioxidant and can give electrons, an example is the plant extracts. Plant extracts consist of organic compounds which have polar atoms through which they are adsorbed on the surface of metallic materials to form protective films [21].

Cocoa pod is an agricultural waste and is known to be cheap in south west Nigeria [22]. Cocoa pods when left to decay on the farms causes pollution and breed a causative agent of black pod disease [23]; [24]; [25] and [26]. Cocoa production is about 39 million tons annually [27]. With the increasing demand for cocoa, it is projected that the production of cocoa pod will continue to increase in the years ahead hence there is need for disposal alternatives in order to avoid environmental pollution. A lot of agro wastes are produced yearly and globally, they create pollution that has adverse effect on human health and environment [28]. In lieu of extending the beneficial use of plants and also converting agro waste to wealth, cocoa pods have found use in several areas like pharmaceutical and food sciences.

Alyafirnadya *et al*., [29] investigated the inhibitive effect of *Malus domestica* vinegar on API5L steel in 0.1M HCl using potentiodynamic polarization and electrochemical Impedance Spectroscopy (EIS). Maximum inhibition efficiency reached was 79.93% at a concentration of 7ml. *Theobroma cacao* (cocoa) pod husk extract was used as inhibitor for carbon steel in 1M HCl by [30]. Extract concentrations of 1-10%v/v were used and at 10%v/v a maximum inhibition efficiency of 70% was achieved. In Yetri *et al*., [31] work on the inhibitive effect of cocoa peel extract weight loss, polarization and electrochemical impedance was determined. Cocoa peel extract was studied in 1.5M HCl and NaCl and reported to have maximum inhibition efficiency of 96.3% and 91.93% respectively at 2.5%v/v extract concentration.

The behaviour of the inhibitor molecule and the interaction with the surface of the metal is described as adsorption isotherms [32]. The adsorption of organic compounds to the metal surface can be by physical adsorption or chemisorptions interaction. The adsorption is influenced by the nature of the change of the metal, the chemical structure of inhibitor, pH, the type of electrolyte and temperature [33]. The nature of the reaction between the adsorbed film and the adjoining metal surface can be determined by adsorption isotherms. There are several types of adsorption isotherms that can be used as a reference in studying the adsorption mechanism of corrosion inhibitors, including the Langmuir, Freundlich and Temkin adsorption isotherm. Langmuir adsorption isotherm is the simplest model of adsorption, provided that there is no interaction between molecules adsorbat [34]. A monolayer coating formed, homogeneous adsorbate surface so that each has a surface area equal to the bond energy, and the adsorbed molecules localized or not moving on surface [35].

This research is to determine the inhibitory effect of crude cocoa pod and ashed cocoa pod extracts on API5L steel in 0.5M sulphuric acid and 1.0M H_2S0_4 solutions using potentiodynamic polarization method.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The metal sample used for this study is low carbon steel. The steel was mechanically cut into 10 x 10 mm, and then polished using different grades of emery paper from 320 down to 2,000 grits. The surfaces of the steels were washed with distilled water and degreased with ethanol. Analytical grade H_2SO_4 and distilled water was used for the preparation of the acid solution. Ripe Cocoa pods (*Theobroma cacao*) pods were sourced from a farm located in Akure, Ondo state. Nigeria. The pulp and seeds were removed and the whole pod was thoroughly washed with distilled water. The pods were chopped into smaller sizes and sun dried for 14days. The dried pods were pulverized. 250g of the cocoa pod powder was measured. The measured cocoa pod powder was ashed at 415°C for 4hours in a muffle furnace at the heat treatment laboratory of Department of Metallurgical and Materials Engineering, Federal University of Technology, Akure (FUTA). The ashed cocoa pod was labeled as “ashed cocoa pod husk extract (ACPH)”. Another 250g of the cocoa pod powder was measured and labeled as “crude cocoa pod husk extract (CCPH)”. Ethanol was used as a medium of extraction by mixing differently, the crude and ashed cocoa pods powder with 750ml ethanol at ratio 1:1. The mixture was left for 72 hours in a tightly covered container, and then sieved. The filtrate was heated to 80°C until all ethanol was evaporated and the remaining filtrate was used for the research. Cocoa pod extract concentrations of 0.25–5v/v% were used for this work.

2.2 Characterization of extracts

Elemental composition of the extract was determined using Atomic Absorption Spectroscopy (AAS). This was carried out at Afe Babalola University, Ado-Ekiti, Ekiti State. Determination of the functional group present in the extract was carried out at Federal University of Technology, Oye-Ekiti, Ekiti State.

2.3 Potentiodynamic polarization measurements

A computer controlled AUTOLAB potentiostat PGSTAT204 equipped with Nova software was used for this study. The experiments were conducted using a three-electrode set up comprising of graphite rod or platinum rod as counter electrode (CE), silver/silver chloride as reference electrode (RE) and the API5L steel as working electrode (WE). The working electrodes were prepared by attaching an insulated copper wire to one face of the sample using an aluminum conducting tape, and cold mounting it with epoxy resin. The test set-up and testing procedure was in accordance with ASTM G59-97 [36]. The working electrodes were immersed in the environment which is 1M and 0.5M H_2SO_4 with and without the inhibitors at a scan rate of 1 mV/S. Potentiodynamic polarization was used to observe the corrosion behavior of the working electrode immersed in the environment. The percentage inhibition efficiency (I.E%) from the polarization measurement was calculated using the following equation;

$$(\%)I.E = \frac{CR_0 - CR_1}{CR_0} X\ 100 \quad (1)$$

Where I.E =inhibition efficiency, CR_0 = corrosion rate without inhibitor and

$CR_{1=}$ corrosion rates with inhibitor addition

Adsorption Study

The surface coverage values obtained from potentiodynamic polarization test were used to evaluate the best isotherm that fits the data obtained.

$$\text{Surface coverage } \theta = \frac{CR_{uninhibited} - CR_{inhibited}}{CR_{uninhibited}} \quad (2)$$

Langmuir adsorption isotherm is described by equation 2;

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

Where CR is the corrosion rate, C is the inhibitor concentration, θ is the surface coverage and K_{ads} is the adsorption equilibrium constant.

3. RESULTS AND DISCUSSION

3.1 Spectrometric Analysis of Low carbon steel

The composition of low carbon steel is presented in Table 1.

Table 1: Chemical composition of low carbon steel

Element	C	Si	Mn	P	Cr	Cu	Ni	Mo	Fe
%Composition	0.16	0.28	1.28	0.02	0.02	0.02	0.02	0.003	Balance

3.2 Characterization of Crude and Ashed Cocoa Pod Extract

Elemental compositions of crude and ashed cocoa pods are presented in Table 2.

Table 2: Elemental Composition of Crude and Ashed Cocoa Pod Extract

Element (ppm)	Ca	Fe	Mg	Cu	Mn	Pb	Ni	Cr	Cd	Zn
Ashed	28.500	0.202	3.916	0.418	0.211	0.056	0.126	0.094	ND	0.380
Crude	18.700	0.315	5.026	0.191	0.274	0.012	0.041	0.006	ND	0.214

From the table, heavy metals are observed to be below detection limits there by establishing its eco-friendliness

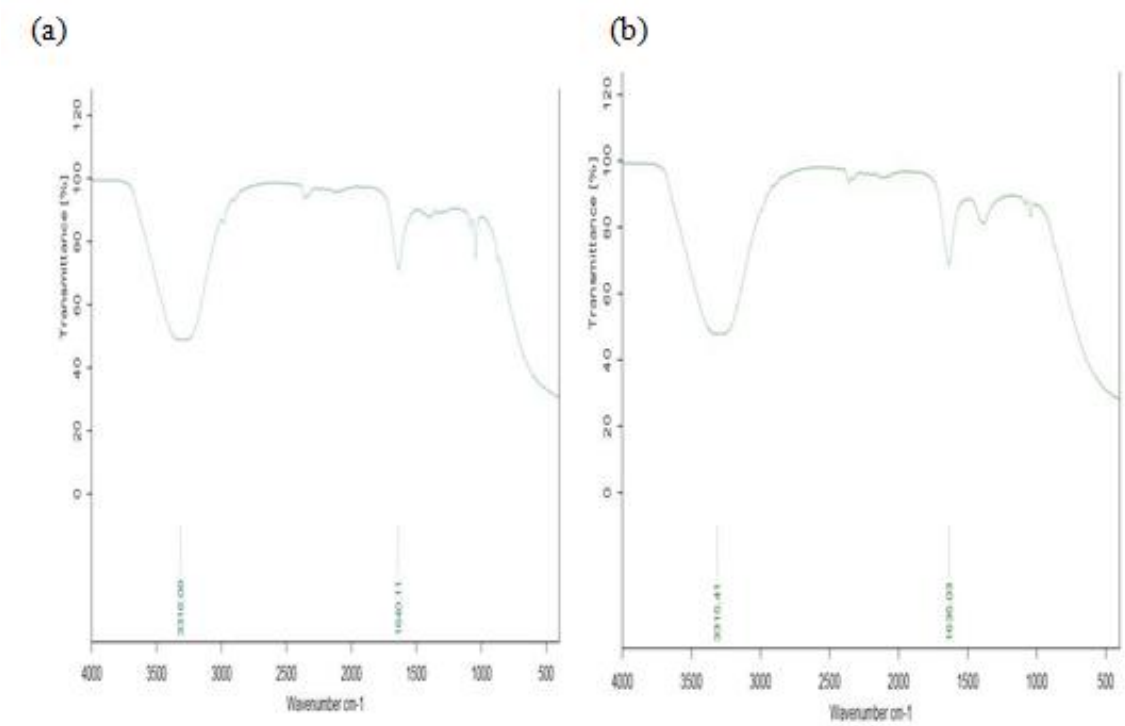

Figure1: FTIR spectra of crude cocoa pod extract (a) and a shed cocoa pod extract (b) measured by Perkin-Elmer spectrophotometer using the KBr pellets.

FTIR of crude and ashed cocoa pod extracts are presented in Figure 1(a) and (b) respectively. The two peaks at 3316 and 3315 cm^{-1} are assigned to OH stretching, while the peaks 1636cm^{-1}and1635$cm^{-1}$are due to C=C asymmetric stretching. A similar observation was reported by [37] in *bidenpilosa* extract which pod exhibited effective corrosion inhibition of mild steel in HCl. Organic molecules that exhibit same functional groups as crude and ashed cocoa pod extracts are proven to interact well with metals there by leading to their inhibition in aggressive environment [38].

3.3 Corrosion Behaviour of the Material

The corrosion behavior of API5L (LCS) with different concentration of cocoa pod extract in 0.5M and 1M H_2SO_4 is shown in Figure 3 - 5

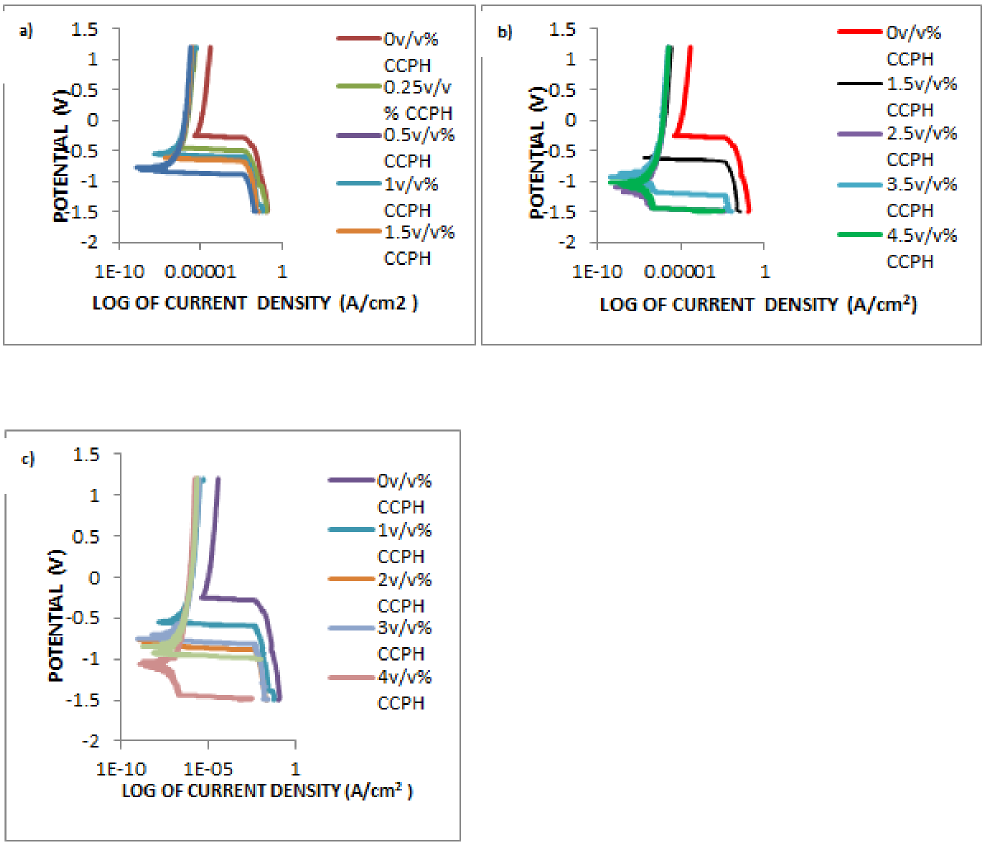

Figure2: Potentiodynamic polarization result of API5Lsteel with 0– 2v/v% crude cocoa pod extract in 0.5M H_2SO_4(a), with 0– 4.5v/v% Crude cocoa pod extract in 0.5M H_2SO_4 (b) and with 0– 5v/v% Crude cocoa pod extract in 0.5M H_2SO_4 (c) measured by computer controlled AUTOLAB potentiostat PGSTAT204 equipped with Nova software

Figure 2a, 2b and 2c showsthe polarizationcurvesofAPI5Lwithoutandwith crude cocoa pod husk extract in 0.5M H_2SO_4. The API5L steel without crude cocoa pod husk extract was observed to have the highest current density of 332µA/cm^2 and also the highest corrosion rate of 3.86mm/yr. A distinct shift in the curve from high to lower current density region was observed with addition of 0.25v/v% crude cocoa pod husk extract. The polarization curves shift to a lower current density region with corrosion potential decreasing with addition of crude cocoa pod husk extract. The curves showed that both the anodic and cathodic curves are being affected by the addition of crude cocoa pod husk extract. Table 3 shows the corrosion parameters obtained from the polarization tests and it was noticed that current density decreased with addition of crude cocoa pod husk extract. Inhibition efficiency was also observed to increase from 55.3% to 87% with an increase in extract concentration from 0.25 v/v% to 1v/v%, similar behaviour was reported to occur in the use of *Nauclea latifolia* and *Chenopodimam brosioides* extract [39] and [40]. At 1.5v/v% as light increase was observed in the current density from 43µA/cm^2 to 72µA/cm^2 and an increase in the corrosion rate from 0.50mm/yr to 0.84mm/yr this can be attributed to dissolution of the protective film on the metal surface. On further addition of the extract, current density was observed to reduce drastically to 30µA/cm^2 at 2v/v% crude cocoa pod husk extract addition. At 2.5v/v/% and 3v/v% crude cocoa pod husk addition, a similar increase in current density like in 1.5v/v% occurred. Further addition of the extract from 3.5v/v% to 5.0v/v% was observed to cause a decrease in current density and corrosion rate Maximum inhibition efficiency of 90.8% and lowest corrosion rate of 0.354mm/yr was achieved at 2v/v% crude cocoa pod husk extract addition in 0.5M H_2SO_4

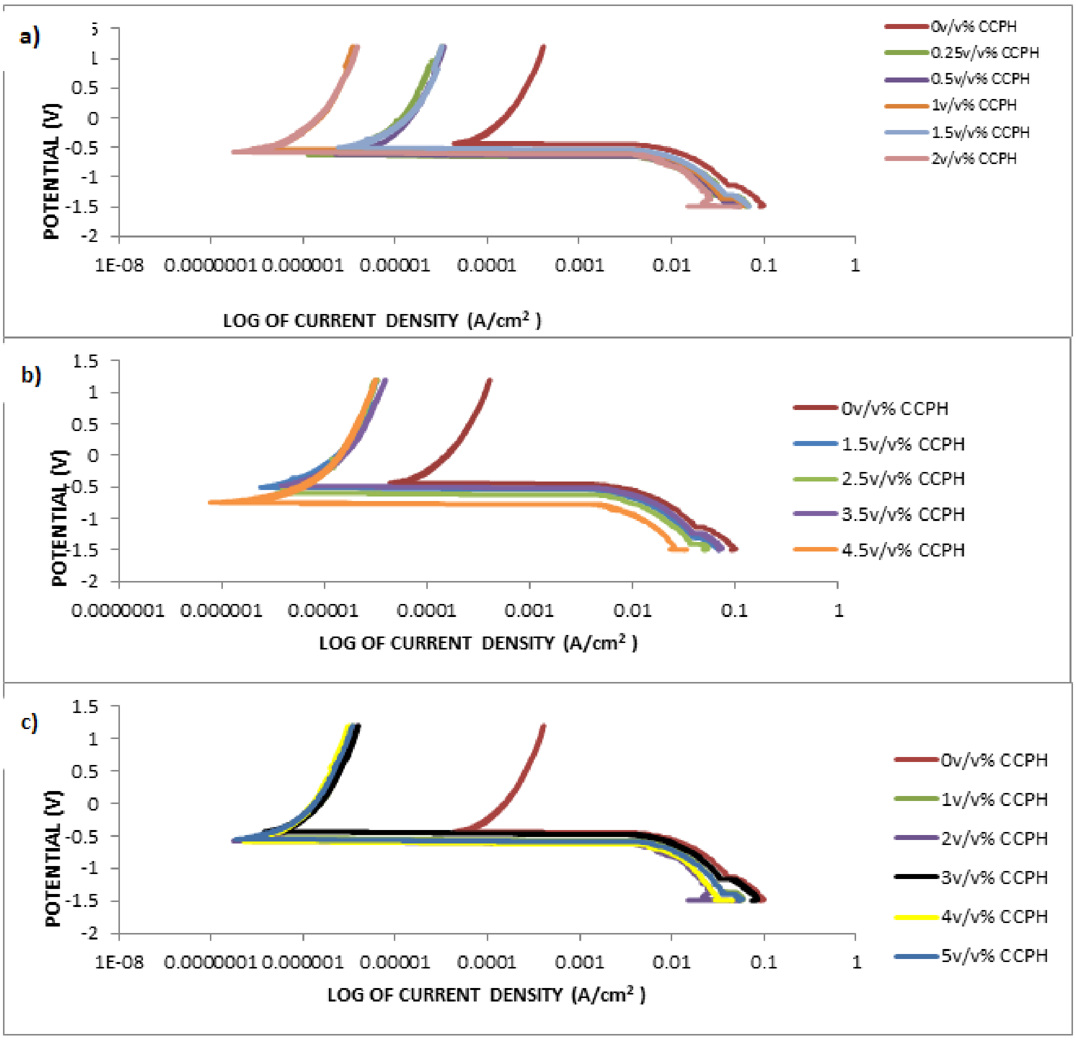

Figure3: Potentiodynamic polarization result of API5Lsteel with 0– 2v/v% crude cocoa pod extract in 1M H_2SO_4(a), with 0– 4.5v/v% Crude cocoa pod extract in 1M H_2SO_4 (b) and with 0– 5v/v% Crude cocoa pod extract in 1M H_2SO_4 (c) measured by computer controlled AUTOLAB potentiostat PGSTAT204 equipped with Nova software

Figure 3a, 3b and 3c shows the polarization curves of API5L without and with crude cocoa pod husk extract in 1MH_2SO_4.From figure3a, there was a significant shift in the polarization curves on addition of crude cocoa pod husk extract. API5L without crude cocoa pod husk extract had the highest current density and corrosion rate of 602µA/cm^2 and 6.99mm/yr respectively. Addition of crude cocoa pod husk extract of 0.25-1 v/v% concentration decreases the current density from 602µA/cm^2 to 94µA/cm^2 and corrosion rates from 6.99mm/yr to 0.95mm/yr as shown in Table 3. Corrosion potential decreases from 442mV to 535mV within 0.25v/v% and 1v/v% extract concentration. At 1.5v/v% crude cocoa pod husk extract concentration there was a slight increase in current density and corrosion rate to 132µA/cm^2 and 1.539mm/yr. At 2v/v% a decrease in corrosion rate and current density was observed. Though the corrosion potential of the API5L without crude cocoa pod husk extract is more positive than those with crude cocoa pod husk extract yet they recorded the lowest corrosion rate and current density than the uninhibited steel. Similar behavior was reported by [41], in alcoholic extract of medicagosative where inhibitor concentration of 1.6x10^{-2}w/v has the lowest corrosion potential but has a lower current density and corrosion rates when compared to that of 1.0x10^{-2} and 1.4x10^{-2} inhibitor concentration that has higher corrosion potential. Inhibition efficiency was equally increases from77.6% to 95.5% with an increase in crude cocoa pod husk extract concentration from 0.25v/v% to 2v/v%. Increase in inhibition efficiency was attributed to the effectiveness of crude cocoa pod husk extract to block the anodic and cathodic reaction sites as reported by [39] for *Nauclea latifolia* extract. Maximum inhibition efficiency of crude cocoa pod husk extract in 1M $H_2SO_4$was 95.5% and this was obtained at 2v/v%.

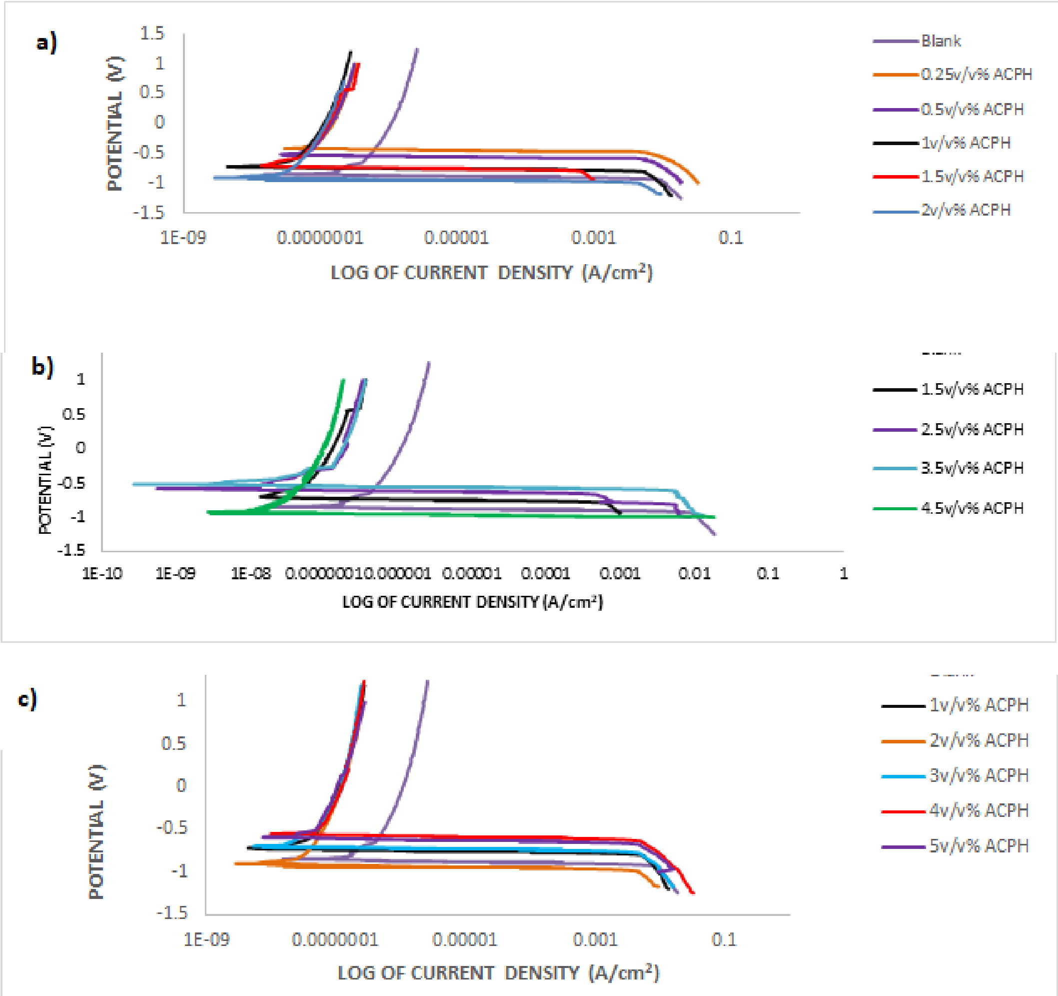

Figure 4: Potentiodynamic polarization result of API5Lsteel with 0– 2v/v% Ashed cocoa pod extract in 0.5M H_2SO_4(a), with 0– 4.5v/v% Ashed cocoa pod extract in 0.5M H_2SO_4 (b) and with 0– 5v/v% Ashed cocoa pod extract in 0.5M H_2SO_4 (c) measured by computer controlled AUTOLAB potentiostat PGSTAT204 equipped with Nova software

Figure 4a, 4b and 4c shows the polarization curves of API5L without and with 0.25–5v/v% ashed cocoa pod husk extract in 0.5M H_2SO_4. API5L steel without ashed cocoa pod husk extract have the highest current density of 302µA/cm^2 and corrosion rate of 3.505mm/yr with a potential of -904mV, but on addition of 0.25v/v% ashed cocoa pod extract there was a displacement of the polarization curve to a higher potential and lower current density of -455mV and 187µA/cm^2 (Figure 4a, 4b, and 4c).By displacing the potential in the positive direction, the extract acted as an anodic inhibitor by forming a passive film on the metallic surface there by retarding metallic deterioration [42] and [43]. Increase of ashed cocoa pod extract content to 0.5v/v% reduces the potential from -455mV to-564mV, also current density and corrosion rate decreases to 15 µA/cm^{2}and 1.7mm/yr. A reduction in the potential makes the extract a cathodic inhibitor [42]. Subsequent addition of ashed cocoa pod extract was observed to cause a decrease from the polarization curves obtained, ashed cocoa pod extract was confirmed to retard the metallic deterioration of the API5L steel in and also reduce the hydrogen evolution reaction, making it a mixed inhibitor. Optimum inhibition efficiency of 97.7% was attained at 3.5v/v% ashed cocoa pod extract and this value is higher than 90.8% achieved with 2v/v% crude cocoa pod in 0.5M H_2SO_4.

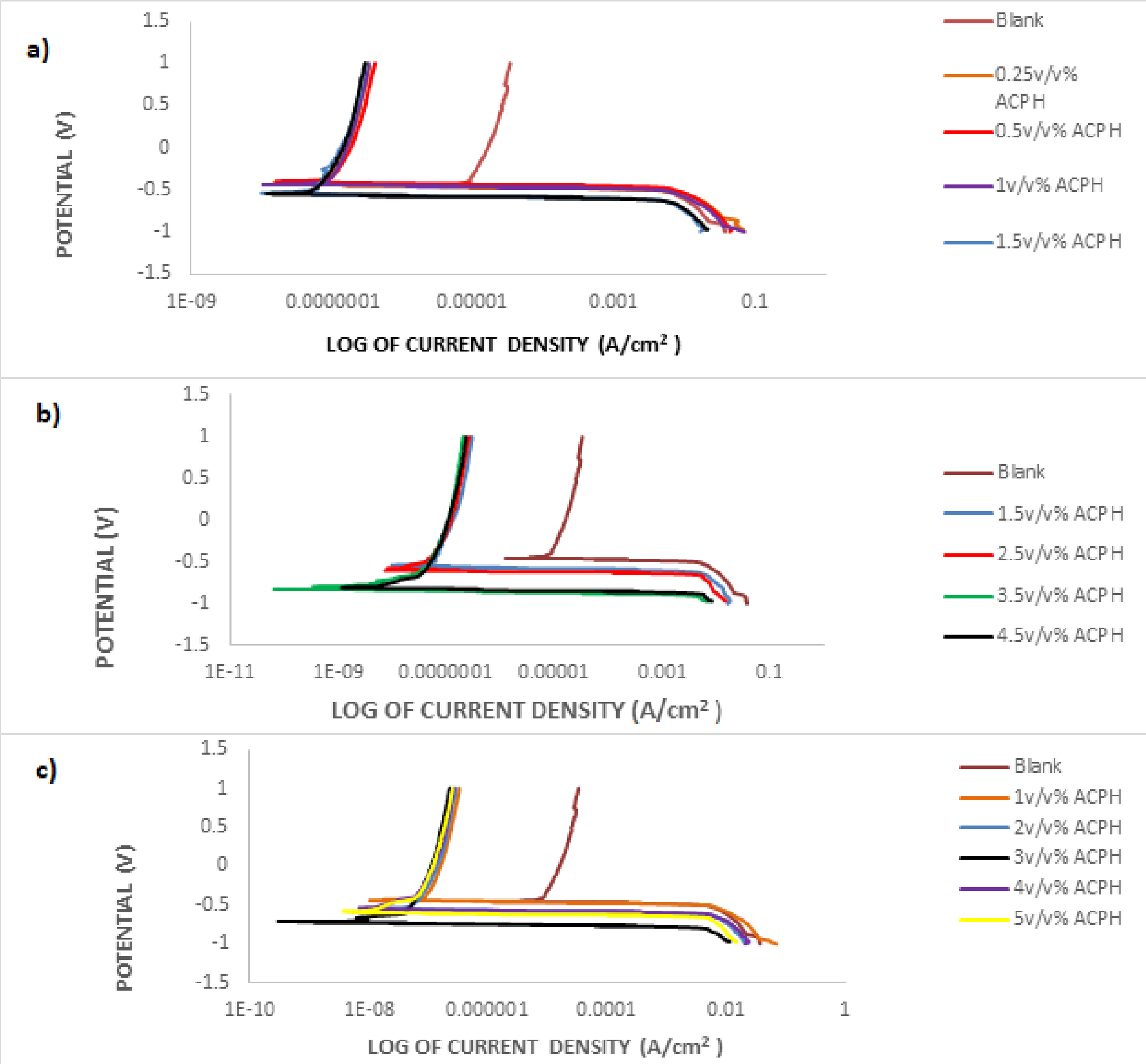

Figure 5: Potentiodynamic polarization result of API5Lsteel with 0– 2v/v% Ashed cocoa pod extract in 1M H_2SO_4(a), with 0– 4.5v/v% Ashed cocoa pod extract in 1M H_2SO_4 (b) and with 0– 5v/v% Ashed cocoa pod extract in 1M H_2SO_4 (c) measured by computer controlled AUTOLAB potentiostat PGSTAT204 equipped with Nova software**.**

The polarization curves of API5L without and with 0.25–5v/v% ashed cocoa pod husk extract in 1M H_2SO_4 is shown in Figure 5a, 5b and 5c. API5L steel without crude cocoa pod husk extract have the highest current density of 471μA/cm^2 and also the highest corrosion rate of 5.475 mm/yr with a potential of -481mV while on addition of 0.25v/v% ashed cocoa pod extract there was a displacement of the polarization curve to a lower potential and lower current density of -484mV and 163μA/cm^2 (figure 5a, b and c). The decrease in current density can be attributed to the inhibition or formation of a passive film on the metallic surface there by retarding metallic deterioration [43]. Subsequent addition of ashed cocoa pod extract causes a decrease in the potential of the curve to -861mV. Current density and corrosion rates were equally observed to decrease to 4μA/cm^2 and 0.052mm/yr respectively. From the polarization curves, ashed cocoa pod extract was confirmed to retard the metallic deterioration of the API5L steel in and also reduce the hydrogen evolution reaction, making it a mixed inhibitor. Optimum inhibition efficiency of 99.1% was attained at 3.5v/v% ashed cocoa pod extract and this value is higher than 91% achieved by *sesbania sesban* extract and 89% exhibited by green tea extract [44] and [43].

Table 3: Corrosion Parameters of API5L in 0.5M H_2SO_4 and API5L in 1M H_2SO_4 with and without Crude Cocoa Extract

	API5L in 0.5M H_2SO_4				API5L in 1M H_2SO_4			
Inhibitor Concentration (v/v %)	-Ecorr (mV)	Icorr (μA/cm^2)	Corrosion Rate (mm/yr)	Inhibition Efficiency (IE %)	-Ecorr (mV)	Icorr (μA/cm^2)	Corrosion Rate (mm/yr)	Inhibition Efficiency (IE %)
0	267	332	3.864	-	442	601	6.990	-
0.25	475	149	1.727	55.3	640	135	1.564	77.6
0.5	606	88	1.02	73.6	630	127	1.474	78.9
1	571	43	0.501	87	536	95	0.945	86.5
1.5	648	72	0.839	78.3	520	132	1.539	78
2	865	30	0.354	90.8	587	22	0.315	95.5
2.5	455	42	0.493	87.2	601	129	1.497	78.6
3	675	64	0.74	80.8	455	109	1.272	81.8
3.5	1197	49	0.57	85.2	492	198	2.306	67
4	1447	38	0.402	89.6	602	34	0.395	94.3
4.5	1449	34	0.396	89.8	754	118	1.374	80.3
5	979	38	0.422	89.1	567	52	0.605	91.3

Table 4: Corrosion Parameters of API5L in 0.5M H_2SO_4 and API5L in 1M H_2SO_4 with and without Ashed Cocoa Extract

	API5L in 0.5M H_2SO_4				API5L in 1M H_2SO_4			
Inhibitor Concentration (v/v %)	-Ecorr (mV)	Icorr (μA/cm^2)	Corrosion Rate (mm/yr)	Inhibition Efficiency (IE %)	-Ecorr (mV)	Icorr (μA/cm^2)	Corrosion Rate (mm/yr)	Inhibition Efficiency (IE %)
0	904	302	3.505		482	471	5.475	
0.25	455	187	2.17	38.1	484	163	1.895	65.4
0.5	564	147	1.713	57.1	447	87	1.018	81.4
1	772	27	0.228	93.5	479	79	0.920	83.2
1.5	761	24	0.219	93.8	595	39	0.457	91.7
2	873	22	0.199	94.3	594	34	0.394	92.8
2.5	637	14	0.167	95.2	623	31	0.364	93.4
3	728	11	0.130	96.3	760	13	0.146	97.3
3.5	577	9	0.106	97	865	4	0.052	99.1
4	602	23	0.212	94	627	19	0.216	96.1
4.5	853	20	0.200	94.3	849	16	0.181	96.7
5	631	23	0.209	94	582	18	0.201	96.2

Adsorption behavior of inhibitor

Table 5 shows how the surface coverage and the parameter C/θ vary with the concentration of cocoa pod husk extract. While figures 6 (a, b, c and d) are plots of C/θ against C, which are linear for all the systems investigated. These suggested that the adsorption of inhibitor compounds/molecules onto the API5L (LCS) steel surfaces followed the Langmuir adsorption isotherm, in which case the adsorption of the inhibitor molecules belonged to a monolayer adsorption.

Table 5: Variation of Surface Coverage with Crude Cocoa pod Husk Extract Concentration and Ashed Cocoa pod Husk Extract Concentration in 0.5M H_2SO_4 and 1M H_2SO_4

Concentration (C) (v/v%)	Surface Coverage (θ)	C/θ (v/v%)	Surface Coverage (θ)	C/θ (v/v%)	Surface Coverage (θ)	C/θ (v/v%)	Surface Coverage (θ)	C/θ (v/v%)
	Crude Cocoa Pod Extract in 0.5M H_2SO_4		Crude Cocoa Pod Extract in 1M H_2SO_4		Ashed Cocoa Pod Extract in 0.5M H_2SO_4		Ashed Cocoa Pod Extract in 1M H_2SO	
0	0	0	0	0	0	0	0	0
0.25	0.553	0.452	0.776	0.322	0.380	0.656	0.654	0.382
0.5	0.736	0.679	0.789	0.634	0.510	0.978	0.814	0.614
1.0	0.870	1.149	0.865	1.156	0.934	1.070	0.832	1.202
1.5	0.783	1.916	0.780	1.923	0.938	1.599	0.917	1.636
2.0	0.908	2.202	0.955	2.094	0.943	2.121	0.928	2.155
2.5	0.872	2.867	0.786	3.180	0.952	2.626	0.934	2.677
3.0	0.808	3.713	0.818	3.667	0.963	3.115	0.973	3.083
3.5	0.852	4.108	0.670	5.224	0.970	3.608	0.991	3.532
4.0	0.896	4.464	0.943	4.242	0.940	4.255	0.961	4.162
4.5	0.898	5.011	0.803	5.604	0.943	4.772	0.967	4.654
5.0	0.891	5.612	0.913	5.476	0.940	5.319	0.962	5.198

The plot of C/θ versus C yielded a slope near to 1 and a regression coefficient (R^2) of 0.99 as shown in Figure 6. This suggests that the adsorption of the Crude Cocoa Pod Husk Extract and Ashed Cocoa Pod Husk Extract inhibitor on API5L (LCS) steel surface in 0.5M H_2SO_4 and 1M H_2SO_4 solution obeys the Langmuir adsorption isotherm.

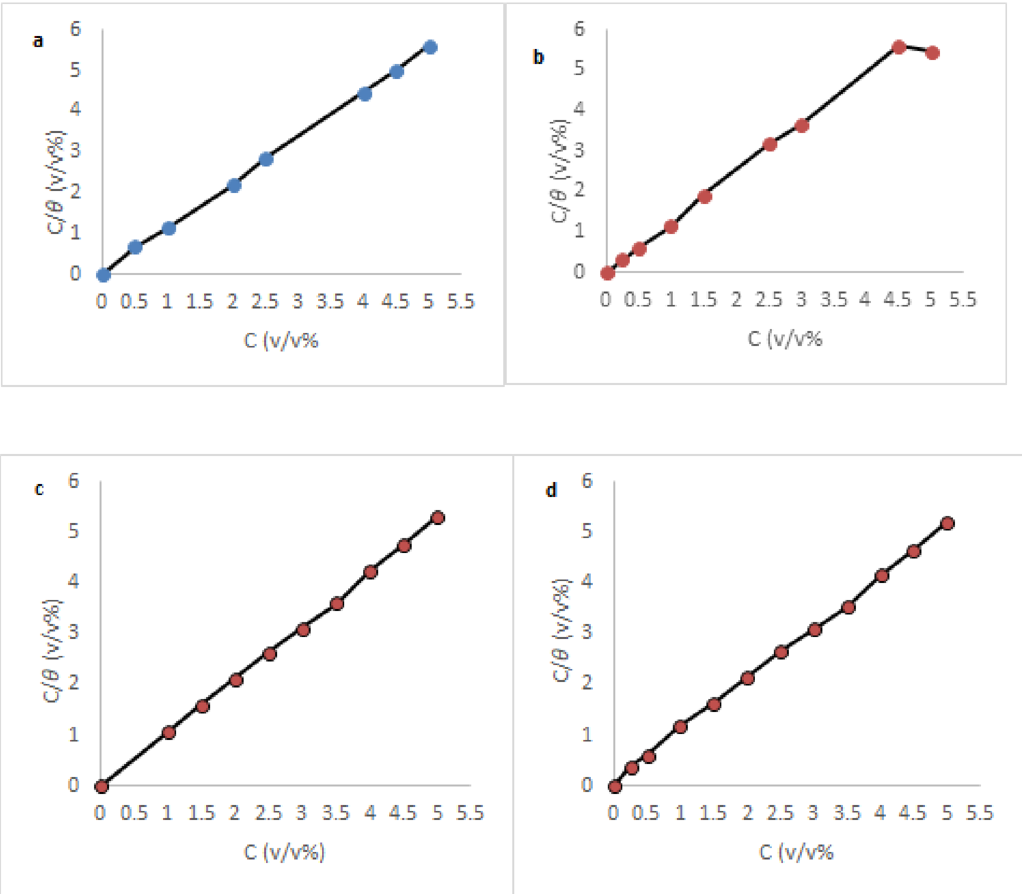

Figure 6: Langmuir Adsorption Isotherm Plot for the adsorption of Crude Cocoa Pod Husk Extract on API5L (LCS) in 0.5 MH_2SO_4 (a), Crude Cocoa Pod Husk Extract on API5L (LCS) in 0.5 MH_2SO_4 (b), Ashed Cocoa Pod Husk Extract on API5L (LCS) in 0.5 MH_2SO_4 (c) and Ashed Cocoa Pod Husk Extract on API5L (LCS) in 0.5 MH_2SO_4 (d).

According to Langmuir model, the cocoa pod husk extract molecules occupy specific adsorption sites at the metal/solution interface resulting in the slight deviation of the slope from unity. The R^2 values of 0.998 and 0.999 indicate strong adherence to Langmuir adsorption isotherm [45]. Though the linearity of the Langmuir plot may be interpreted to suggest that the experimental data for the systems obeyed the Langmuir adsorption isotherm, the considerable deviation of the slope from unity shows that the isotherm cannot be strictly applied.

Conclusion

The inhibitory properties of ashed and crude cocoa pod extracts as an ecofriendly corrosion inhibitor of API5L steel in 0.5M and 1M H_2SO_4were investigated. The results obtained in the present study can be summarized as follows:

- Ashed and crude cocoa pod extracts acts as an inhibitor for API5L steel in 0.5M and 1M H_2SO_4 solution.
- The inhibition efficiency increased with increase in the concentration of Ashed and crude cocoa pod extracts.
- The inhibition is due to the presence of some phytochemical constituents in the Ashed and crude cocoa pod extracts which is adsorbed on the surface of the API5L steel.
- The present study provides new information on the inhibition characteristics of Ashed and crude cocoa pod extracts under the specified conditions.
- Inhibition efficiency of both ashed and crude cocoa pod husk extract was higher in 1M H_2SO_4 compared to 0.5M H_2SO_4.
- The electrochemical results of polarization showed that the extract of plant acts as mixed type inhibitor; they retarded both anodic and cathodic corrosion reactions.
- The Adsorption of inhibitor obeys Langmuir adsorption isotherm.

Conflict of interest

None.

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