Mild Steel Corrosion Inhibition in Hydrochloric Acid Using Cocoa Pod Husk-*Ficus exasperata*: Extract Preparation Optimization and Characterization

Popoola, Lekan Taofeek*[+]
Unit Operation and Material Science Laboratory, Chemical and Petroleum Engineering Department, Afe Babalola University, Ado-Ekiti, Ekiti State, NIGERIA

Aderibigbe, Tajudeen Adejare
Chemical Science Department, Yaba College of Technology, Yaba, Lagos State, NIGERIA

Lala, Mayowa
Unit Operation and Material Science Laboratory, Chemical and Petroleum Engineering Department, Afe Babalola University, Ado-Ekiti, Ekiti State, NIGERIA

ABSTRACT: *This research aimed at studying the optimization of cocoa pod-Ficus exasperate (CP-FE) extract preparation as mild steel anticorrosive agent in hydrochloric acid solution using a central composite design as an optimization tool. The maximum inhibition efficiency of 95.42% was obtained at ethanol volume, extraction time, CP-FE mixing ratio, and CP-FE mass of 500 mL, 48 h, 5, and 100 g respectively. The coefficient of determination value of 0.9674 between experimental and predicted values suggested that the model developed was exact. The optimum predicted point for CP-FE extract preparation by CCD was 62.02 mL, 9.51 h, 3.42, and 75.68 g for the ethanol volume, extraction time, CP-FE mixing ratio, and CP-FE mass respectively. SEM images revealed an acid attack on the mild steel surface. Adsorption of CP-FE extracts on mild steel surface prevents acid attack. FT-IR revealed the presence of carboxyl (-COOH) and hydroxyl (-OH) functional groups. EDS revealed high iron composition on mild steel surfaces in the presence of CP-FE extracts. Loss of Fe^{2+} into free HCl solution was observed from the AAS result. Conclusively, mixed cocoa pod-Ficus exasperate extracts exhibited effective corrosion inhibitory attributes for mild steel in HCl solution.*

Keywords: *Optimization; Cocoa pod-Ficus exasperate; Hydrochloric acid; Mild steel; Extract.*

INTRODUCTION

The challenges consistently faced by experts in chemical, petrochemical, oil, and gas industries as a result materials (metals or alloys) deterioration resulting from their chemical or electrochemical reaction with the environment

* *To whom correspondence should be addressed.*
+ *E-mail*: *popoolalekantaofeek@yahoo.com*
1021-9986/2022/2/482-492 11/$/6.01

(air, moisture, and soil) to form noble compounds called corrosion is becoming alarming on daily basis [1]. Thus, there is a need to save our lives, economy and time wasted on this destructive phenomenon by defining lasting solutions to its mitigation and control [2]. The ductility [3], weldability [4], abundance [5], cost-effectiveness [6], formability [7] and strength [8] attributes of mild steel have justified its vast application over other materials in these process industries. Major industrial sectors which rely majorly on steel application are categorized as construction (low and high-rise buildings, reinforced concrete, bridge deck plates, harbors, and tunnels), transport (trucks, trains, rails, ships, aircraft undercarriages, and jet engines), energy (wind turbines, transformer cores, transmission towers, electromagnets, pipelines, oil and gas wells), packaging (protection of goods from air, water, and light exposure) and household appliances (fridges, washing machines, microwaves, ovens, cutlery, and sinks) [2]. However, a major hindrance to mild steel industrial application is its low corrosion resistance behavior in acidic media [9]. This cannot be overlooked due to the application of acid solutions (mostly hydrochloric acid) in industrial processes such as oil-wet cleaning, pickling, cleaning, descaling, and so on [10]. This makes consideration of mild steel corrosion control in hydrochloric acid to be highly imperative.

To achieve this, current research works are focusing on using green corrosion inhibitors from plant extracts over previously adopted chromates and nitrates which had proved toxic to our environment and health [11]. These inhibitors lower corrosion rate via adsorption of polar functions of S, O, N, π-electrons, and heterocyclic compounds (present in them) on the metal surface [12] thereby blocking active surface sites by forming thick films [13]. Many extracts from plants used as green corrosion inhibitors for mild steel in HCl solution in previous studies have yielded promising results [14-19]. Recent studies have revealed limitations of using other corrosion inhibition techniques asides application of corrosion inhibitors from greeners [20-22]. However, in recent times, researchers only investigated corrosion process optimization [23-26] but rarely considered optimization of extract (corrosion inhibitor) preparation from greeners that give maximum corrosion inhibition efficiency for mild steel in HCl solution.

This study tested the inhibitory effect of the mixed cocoa pod and *Ficus exasperate* by investigating optimum extract preparation that gives higher corrosion inhibition efficiency using Central Composite Design (CCD) of Design Expert 7.0.0 software as an optimization tool. Examined mild steel and extracts were characterized at optimum conditions using SEM, EDS, FT-IR, and AAS.

EXPERIMENTAL SECTION

Materials

The mild steel (Fe = 98.81%, C = 0.68%, Mn = 0.27%, P = 0.061%, Si = 0.083% and Cr = 0.095%) was obtained from central mechanical engineering workshop of Afe Babalola University. Ethanol, hydrochloric acid, and acetone, all analytical grades, were supplied by Top-Jay Scientific, Ado-Ekiti. Grades of silicon carbide paper were purchased from a local market in Ibadan, Oyo State, Nigeria. Distilled water was prepared from a water distiller available in the biochemistry laboratory of the University. The waste Cocoa Pod (CP) and *Ficus Exasperata* (FE) leaves were obtained from a local farm.

Mild Steel Coupon Preparation

Different grades of silicon carbide paper were severely used to polish the mild steel before being cut into coupons with the same dimension of 5×4×0.2 cm and exposed surface area of 20 cm^2. The equality of coupons dimension was measured using a digital vernier caliper. Measured coupons were subjected to degreasing and thoroughly rinsed using acetone and distilled water respectively. Samples were dried and kept in a desiccator in preparation for weight loss experiments.

Extract Preparation Optimization and Mathematical Model Development

Clean water was used to thoroughly wash waste cocoa pods before being cut into bits and then dried at 80ºC for 24 h in an oven. A mechanical grinder was used to obtain a powdery form of the dried bits to obtain particles of less than 63 µm after sieving. Similar procedures were repeated for *Ficus Exasperata* leaves. Particles were separately kept in clean polythene bags and buckets to prevent moisture contamination. Extracts were prepared by mixing separate particles based on Central Composite Design (CCD) of Design Expert 7.0.0 software coded levels result for ethanol volume, extraction time, mixing ratio, and mass of

Table 1: Process variables coded levels for corrosion inhibitor preparation optimization.

Process variables	Unit	Factor	Values of Coded levels				
			-α	-1	0	+1	+α
Ethanol volume	mL	X_1	35	50	275	500	725
Extraction time	hr	X_2	1	3	25.5	48	70.5
CP-FE Mixing ratio	-	X_3	0.5	1	3	5	7
Mass of CP and FE	g	X_4	5	10	55	100	145

cocoa pod-*Ficus Exasperata* particles as presented in Table 1. The mixed particles were soaked in ethanol and filtered such that the obtained filtrate (extract) was further subjected to evaporation for ethanol removal. Each extract prepared was stocked for further experimental purposes.

Mathematical model development

The optimization objective is to minimize extract preparation conditions that give optimum corrosion inhibition efficiency (IE%) of mild steel in HCl acid medium. To achieve this, 30 experiments were conducted such that the response function can be presented as Eq. (1) while the quadratic model relating the response (IE%) and process variables (X_1, X_2, X_3, and X_4) can be expressed as Eq. (2) thus:

$$IE\% = f(X_1, X_2, X_3, X_4) \tag{1}$$

$$IE\% = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \ldots\ldots + \beta_k X_k + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \ldots\ldots + \beta_{kk} X_k^2 + \beta_{12} X_1 X_2 + \ldots\ldots + \beta_{k-1,k} X_{k-1} X_k + \varepsilon \tag{2}$$

Where X_1 = ethanol volume, X_2 = extraction time, X_3 = cocoa pod- *Ficus exasperata* mixing ratio, X_4 = mass of cocoa pod and *Ficus Exasperata*, $\beta_o, \beta_1, \beta_2 \ldots \beta_k$ = coefficients associated with the variables, k = number of factors considered, and ε = error associated with the model. Analysis of variance (ANOVA-Type III) of the central composite design of Response Surface Methodology (RSM) was used to evaluate the fitness of the developed model.

Weight Loss Measurement

The optimization of corrosion inhibitor preparation condition via checking optimum inhibition efficiency of the cocoa pod- *Ficus exasperata* extract on mild steel in hydrochloric acid solution was achieved using weight loss measurement [27]. Mild steel coupons were tested for corrosion effect in an acidic medium (1.5M, 15% HCl) *via* weight loss measurement by checking the mild steel coupon's weight before and after immersion in the medium with and without the corrosion inhibitor for 24 h. All experiments were conducted based on the experimental design values presented in Table 2. After each immersion time is over, mild steel coupons were carefully removed from the test solution using tong and washed using distilled water and acetone simultaneously. Subsequently, hot air was used to dry the specimens and then left for some minutes to cool down. Equations 3 and 4 were used to calculate corrosion rates and inhibition efficiency respectively using weight loss (taken as the mean of three runs) recorded after each experiment with the aid of a digital weighing balance.

$$CR\ (mm/y) = \frac{87{,}500W}{A\rho t} \tag{3}$$

$$I.E.\% = \left(1 - \frac{CR_{inh}}{CR_{blank}}\right) \times 100 \tag{4}$$

Where CR = corrosion rate (mm/y), W = weight loss (g), A = mild steel coupon area (cm^2), ρ = density (g/cm^3), t = immersion time (hr), $I.E.\%$ = inhibition efficiency, CR_{inh} = corrosion rate in the presence of inhibitor and CR_{blank} = corrosion rate in the absence of inhibitor.

Extract and Metal Coupon Characterization

Nicolet iS10 Fourier transforms infra-red spectrophotometer was used to execute FT-IR of cocoa pod-*Ficus exasperate* extract and corrosion products of mild steel in 1.5 M HCl at optimum extract preparation. SEM/EDX-JEOL-JSM 7600F was used to examine scanning electron microscope coupled with energy dispersive spectroscopy (EDS) analysis of mild steel

Table 2: Central Composite Design for Optimization of Corrosion Inhibitor Preparation.

Inhibitor Code	Ethanol Volume (mL) (X_1)	Extraction Time (hr) (X_2)	CP-FE Mixing Ratio (X_3)	Mass of CP-FE(g) (X_4)	Inhibition Efficiency (%)		
					Experimental	Predicted	
						CCD	Absolute Error (%)
CP-FE1	275.0	25.5	3	145	69.56	72.27	2.71
CP-FE2	275.0	25.5	3	55	50.00	51.88	1.88
CP-FE3	275.0	25.5	3	55	43.72	45.88	2.16
CP-FE4	50.0	48	5	10	59.77	57.99	1.78
CP-FE5	35.0	25.5	3	55	42.22	43.53	1.31
CP-FE6	275.0	25.5	7	55	61.46	65.39	3.93
CP-FE7	500.0	48	1	10	81.05	78.69	2.36
CP-FE8	500.0	3	5	100	73.61	70.33	3.28
CP-FE9	500.0	48	5	100	95.42	93.83	1.59
CP-FE10	500.0	48	1	100	88.73	86.48	2.25
CP-FE11	275.0	70.5	3	55	77.07	76.39	0.68
CP-FE12	500.0	3	1	10	53.06	50.29	2.77
CP-FE13	50.0	3	5	10	51.55	47.19	4.36
CP-FE14	275.0	25.5	3	55	52.56	51.88	0.68
CP-FE15	50.0	48	1	100	75.89	72.55	3.34
CP-FE16	500.0	3	1	100	64.33	61.83	2.5
CP-FE17	500.0	3	5	10	57.61	58.67	1.06
CP-FE18	50.0	3	5	100	64.81	62.88	1.93
CP-FE19	50.0	3	1	100	56.93	51.35	5.58
CP-FE20	275.0	25.5	3	55	58.13	60.88	2.75
CP-FE21	275.0	25.5	3	55	61.09	58.88	2.21
CP-FE22	275.0	25.5	3	55	45.78	48.88	3.1
CP-FE23	275.0	1	3	55	31.37	36.95	5.58
CP-FE24	50.0	48	5	100	83.77	79.93	3.84
CP-FE25	50.0	3	1	10	37.49	34.79	2.7
CP-FE26	50.0	48	1	10	66.07	61.74	4.33
CP-FE27	500.0	48	5	10	83.95	79.92	4.03
CP-FE28	275.0	25.5	3	5	28.61	34.8	6.19
CP-FE29	725.0	25.5	3	55	70.70	73.61	2.91
CP-FE30	275.0	25.5	0.5	55	46.67	50.64	3.97
Average Absolute Error							2.925

Note: Immersion time of 24 hrs was considered for mild steel in 1.5 M HCl in the absence and presence of corrosion inhibitor for each of the experimental runs to calculate corrosion rate.

surface morphology in the presence and absence of corrosion inhibitors. The concentration of Fe^{2+} after mild steel immersion in 1.5 M HCl solution in the absence and the presence of CP-FE extract at 323 K was measured using AAS Buck Scientific 210 VGP atomic absorption spectrometer.

RESULTS AND DISCUSSION

Extract preparation optimization, model development, and optimum point Prediction

Table 2 presents the results obtained from the 30 experimental runs as predicted by Central Composite Design (CCD) of design expert 7.0.0 software in order

Table 3: ANOVA (Type III) result of the CCD for Corrosion Inhibitor Preparation Optimization.

Source	Sum of Squares	Df	Mean Square	F-Value	Prob>F
Model	6655.0296	14	475.35926	4.5888719	0.0029
X_1	1045.9681	1	1045.9681	10.097233	0.0062
X_2	2962.8148	1	2962.8148	28.601478	< 0.0001
X_3	243.97127	1	243.97127	2.3551721	0.1457
X_4	1581.7761	1	1581.7761	15.269646	0.0014
X_1X_2	41.667025	1	41.667025	0.4022319	0.5355
X_1X_3	0.000625	1	0.000625	6.033×10^{-06}	0.9981
X_1X_4	25.250625	1	25.250625	0.2437564	0.6287
X_2X_3	37.8225	1	37.8225	0.3651188	0.5547
X_2X_4	3.0625	1	3.0625	0.0295638	0.8658
X_3X_4	17.0569	1	17.0569	0.1646585	0.6906
X_1^2	361.7555	1	361.7555	3.4922001	0.0813
X_2^2	258.7923	1	258.7923	2.4982467	0.1348
X_3^2	252.304	1	252.304	2.4356121	0.1395
X_4^2	87.679433	1	87.679433	0.8464118	0.3721
Residual	1553.8435	15	103.58957	-	-
Lack of Fit	1322.1645	10	132.21645	2.85	0.1293
Pure Error	231.679	5	46.3358	-	-
Cor Total	8208.8732	29	-	-	-
R^2 = 0.9674; Adj-R^2 = 0.9663; Std. Dev. = 3.091; Conf. Level = 95%					

to determine extract preparation condition that gives optimum corrosion inhibition of mild steel in hydrochloric acid solution. The laboratory result revealed that CP-FE9 extract prepared at ethanol volume, extraction time, CP-FE mixing ratio, and CP-FE mass of 500 mL, 48 hr, 5, and 100 g respectively gave the optimum corrosion inhibition efficiency of 95.42% for mild steel in hydrochloric acid media. The contributory effect of these main factors in enhancing corrosion inhibition is evident in their respective F-values of 10.10, 28.60, 2.36, and 15.27 as obtained from Type III ANOVA analysis results presented in Table 3. Nonetheless, the authenticity of the developed quadratic model equation relating response and process variables (presented as Equation 5) suggested by CCD was also validated by Type III ANOVA. The model revealed an F-value and probability value (Prob> F) of 4.59 and 0.0029 respectively showing the model equation's high significance level. Model equation and operating parameters having F-value greater than 2.0 and a p-value less 0.05 imply a high significance level [28 ,29].

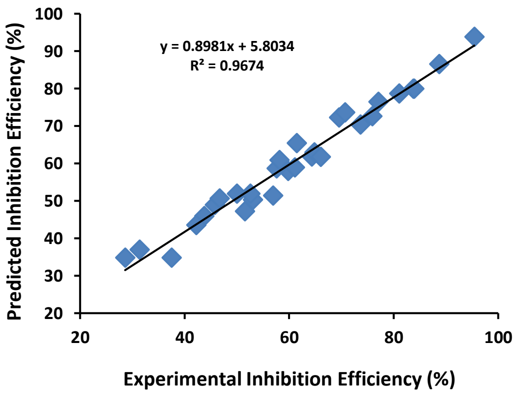


***Fig. 1:** Experimental versus predicted values of inhibition efficiency for extract preparation optimization.*

The plot of experimental versus predicted values of inhibition efficiency presented in Fig. 1 revealed values of R^2, lower standard deviation, and confidence level to be 0.9647, 3.09, and 95% supporting developed model exactness as well. Fig. 2 represents 3D surface plots

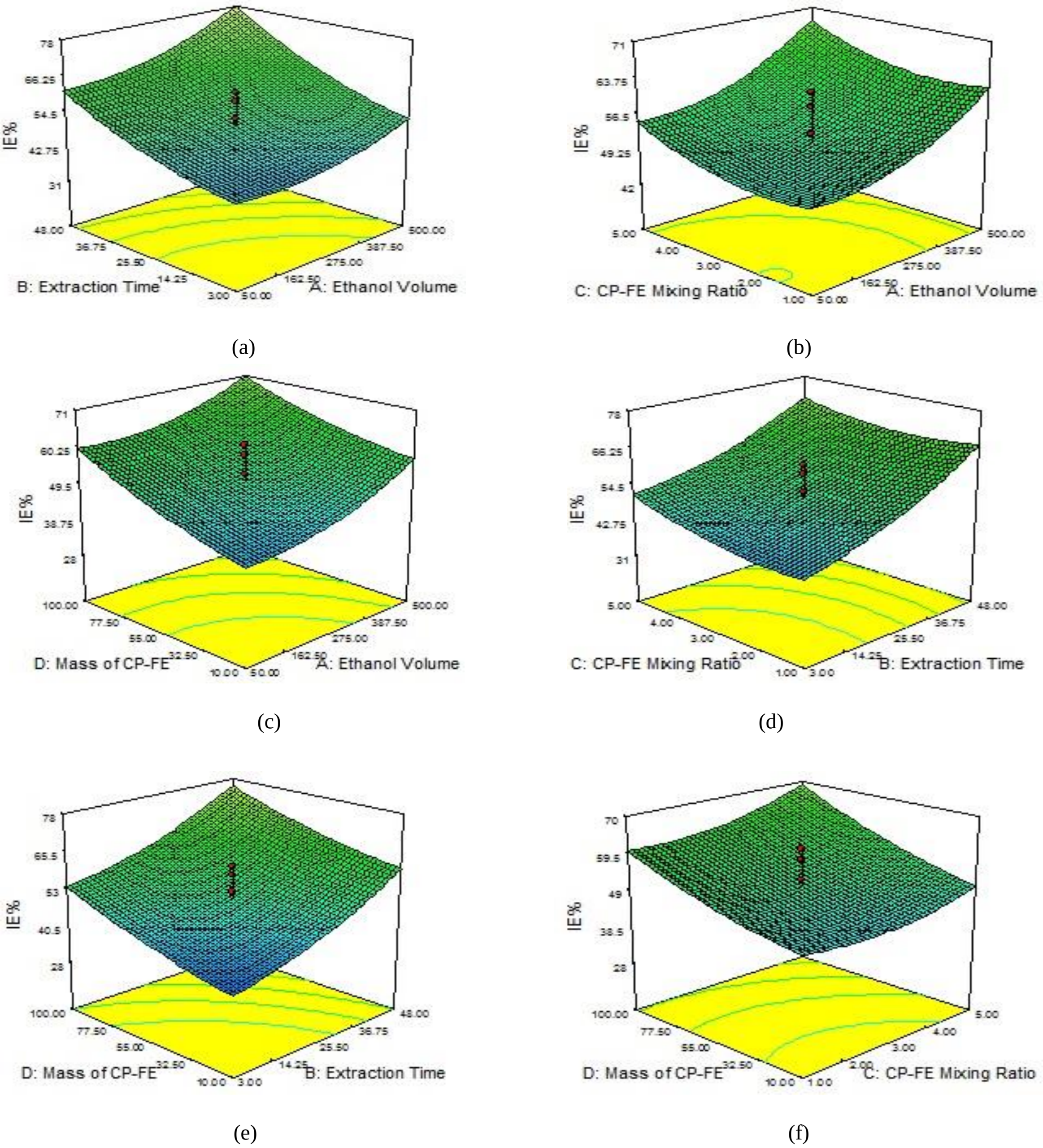
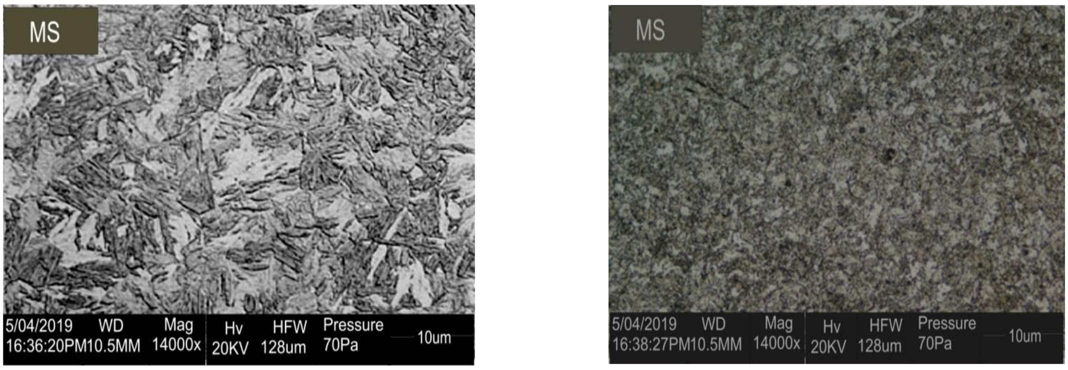


Fig. 2: 3D response surface plot showing the effect of (a) extraction time and ethanol volume (b) CP-FE mixing ratio and ethanol volume (c) mass of CP-FE and ethanol volume (d) CP-FE mixing ratio and extraction time (e) mass of CP-FE and extraction time (f) mass of CP-FE and CP-FE mixing ratio on inhibition efficiency of prepared extracts.

showing the effect of operation parameters on inhibition efficiency of prepared extracts on mild steel in hydrochloric solution during acidization of oil well while actual factors were kept at 275 mL, 25.50 hr, 3.0, and 55.0 g for ethanol volume, extraction time, CP-FE mixing ratio and mass of CP-FE respectively. The 3-D surface plots exhibited the existence of a corresponding relationship among the factors examined for the optimization of extract preparation for the corrosion process. However, of all the surface plots, Fig. 2(a) reveals that an increase in values of extraction time and ethanol volume has a severe effect on the corrosion inhibition efficiency which substantiates the orderliness of F-values earlier presented. It was believed that the higher the number of the period the mixed cocoa

Table 4: Optimum point prediction by CCD and experimental result of mild steel corrosion inhibition in HCl solution using cocoa pod-Ficus exasperate extract

Parameter	Predicted Optimum Value	Inhibition Efficiency (%)	
		Predicted	Experimental
Ethanol volume (X_1)	62.02 mL	82.67%	84.84%
Extraction time (X_2)	9.51 hr	-	-
CP-FE Mixing ratio (X_3)	3.42	-	-
Mass of CP and FE (X_4)	75.68 g	-	-



(a) (b)

Fig. 3: SEM images of mild steel surfaces after immersion in (a) free 1.5 M HCl solution (b) 1.5 M HCl solution in the presence of extract prepared at optimum condition predicted by CCD (ethanol volume = 62.02 mL, extraction time = 9.51 hr, CP-FE mixing ratio = 3.42 and mass of CP-FE = 75.68) for 24 hrs.

pod-*Ficus exasperata* stays in more volume of ethanol, the higher the concentration of the extract obtained and thus, the more its inhibition efficiency on the mild steel in 1.5 M HCl medium.

$$IE\% = +51.88 + 6.60X_1 + 11.11X_2 + 3.19X_3 + 8.12X_4 + 1.61X_1X_2 - 6.25\times10^{-3}X_1X_3 - 1.26X_1X_4 - 1.54X_2X_3 - 0.44X_2X_4 + 1.03X_3X_4 + 3.63X_1^2 + 3.07X_2^2 + 3.03X_3^2 + 1.79X_4^2 \quad (5)$$

The result of the experimental run for mild steel corrosion inhibition in HCl acid medium using cocoa pod-*Ficus exasperate* extract at the predicted optimum point by CCD is presented in Table 4. The optimization objective is to minimize corrosion inhibitor preparation conditions which give optimum corrosion Inhibition Efficiency (IE%) of mild steel in HCl acid medium during acidization of the oil well. At the predicted point (ethanol volume = 62.02 mL, extraction time = 9.51 hr, CP-FE mixing ratio = 3.42 and mass of CP-FE = 75.68), experimental result revealed 84.84% for corrosion inhibition efficiency with relative error of 2.17% as compared to 82.67% predicted by the developed model (Equation 5). This is an indication of good agreement between experimental and predicted results at optimum points which also confirms the exactness of the developed model. A similar study has also revealed similar results [30].

Metal Coupon and Extract Characterization

Scanning Electron Microscopy (SEM)

The SEM image of mild steel surface after immersion in free 1.5 M HCl solution for 24 hours is shown in Fig. 3(a) revealed a serious attack of HCl solution on the mild steel surface leading to pitting formation. However, active molecules present in cocoa pod-*Ficus exasperate* extract (prepared at the optimum condition) were strongly adsorbed on a mild steel surface forming a thick layer of protective film which prevents it from acid attack (Fig. 3b).

Table 5: Energy dispersive spectroscopy (EDS) of mild steel surfaces after immersion in 1.5 M HCl solution in the presence and absence of cocoa pod-Ficus exasperate extract prepared at optimum condition predicted by CCD (ethanol volume = 62.02 mL, extraction time = 9.51 hr, CP-FE mixing ratio = 3.42 and mass of CP-FE = 75.68) for 24 hrs.

Mild steel element	Wt (%) in free 1.5 M HCl	Wt (%) in 1.5 M HCl + Optimized extract
Fe	42.82	96.09
C	6.74	0.18
Ni	1.92	0.027
Ti	1.41	0.081
Au	0.356	0.059
Cr	12.08	0.073
Cl	0.024	1.33
O	34.65	2.16

Energy Dispersive Spectroscopy (EDS)

Table 5 presents the energy dispersive spectroscopy result of mild steel surfaces after being immersed in 1.5 M HCl solution in the presence and absence of cocoa pod-*Ficus exasperate* extract prepared at optimum condition predicted by CCD for 24 hrs. The result revealed a low percentage of iron (Fe = 42.82%) on mild steel substrate immersed in free 1.5 M HCl solution after 24 hours as compared to a high iron percentage (96.09%) when immersed in 1.5 M HCl solution in the presence of optimized extract. This affirms great loss of iron in solution due to acid attack in free 1.5 M HCl solution. The latter affirms cocoa pod-*Ficus exasperate* extract efficacy as a corrosion inhibitor for mild steel in HCl solution. Also, the presence of chlorine (1.33%) on mild steel substrate immersed in 1.5 M HCl solution in the presence of optimized extract substantiates little or non-occurrence of interaction between HCl and mild steel surface [31].

Atomic Adsorption Spectroscopy (AAS)

Fig. 4 presents a variation of Fe^{2+} concentration in solution after mild steel immersion in 1.5 M HCl solution in the absence and presence of CP-FE extract at 323 K within an exposure period of 24 hours as revealed by the atomic absorption spectroscopy analysis. The drastic increase in Fe^{2+} concentration in solution from 0.17 to 0.83 ppm for mild steel exposed to free 1.5 M HCl solution within 6 to 24 hours was noticed. However, the concentration of Fe^{2+} in the solution was reduced when the optimized extract was added. This suggests protection of mild steel surface from acidic attack via formation of adsorbed thick film layer on

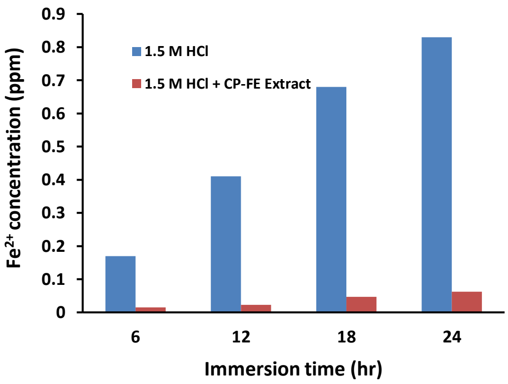


***Fig. 4:** Variation of Fe^{2+} concentration in solution with exposure period after mild steel immersion in 1.5 M HCl solution in the absence and presence of CP-FE extract at 323 K.*

its surface by active ingredients of CP-FE extract. Recent studies have also shown great loss of metals into free acidic media in the absence of different corrosion inhibitors [19, 25, 31].

Fourier Transforms InfraRed (FT-IR)

Table 6 presents the sharp peaks obtained at different band numbers of FTIR analysis obtained for pure cocoa pod-*Ficus exasperate* extract and corrosion products of mild steel i n 1.5 M HCl solution in the presence of optimized extract. Assignments for each of the band numbers were presented based on FT-IR results of previous studies [25, 31, 32]. Results revealed the presence of carboxyl (-COOH) and hydroxyl (-OH) which acted as active functional groups in cocoa pod-*Ficus exasperate* extract inhibiting mild steel

Table 6: FTIR analysis of pure cocoa pod-Ficus exasperate extract and corrosion products of mild steel in 1.5 M HCl.

FT-IR Wavelength (cm^{-1})		Assignments
Pure CP-FE extract	Corrosion products of mild steel in 1.5 M HCl solution in the presence of optimized extract	
-	3775.00	-OH stretch of phenols and alcohols
3461.00	3462.91	N-H stretching of aliphatic primary amine
-	2922.20	Alkanes and cycloalkanes asymmetric C-H stretching
-	2344.79	O=C=O stretching of CO_2
1797.20	1799.38	-C=O stretching of carboxylate groups
1635.42	1637.70	Symmetric and asymmetric COO^- vibrations
1442.58	1443.00	C-O-C stretching
1346.00	-	Stretching nitro of NO_2
1255.00	-	C-O stretching of alkyl aryl ether
-	1041.41	CO-O-CO stretching of anhydride

corrosion in HCl solution [33]. Nevertheless, recorded changes in band numbers of N-H stretching of aliphatic primary amine, -C=O stretching of carboxylate groups, COO^- asymmetric vibrations, and C-O-C stretching suggested adsorption of cocoa pod-*Ficus exasperate* extract molecules on mild steel substrate which serve as a barrier for HCl attack.

Corrosion Inhibition Mechanism

In free acid solution, dissolution of HCl and Fe occurs in solution as presented in Equations 6-8. In the absence of a corrosion inhibitor, the chloride ion from the acid forms iron chloride complexes on the mild steel surface which enhances corrosion of its surface as presented in Eq. (9).

HCl dissolution:

$$HCl_{(aq)} \rightleftarrows H^+ + Cl \quad (6)$$

Fe dissolution:

$$Fe(OH)_{2\,(ads)} + H_2O + 2H^+ \rightleftarrows Fe^{2+} + 3H_2O + 2e^- \quad (7)$$

$$Fe(OH)_{2\,(ads)} + H_2O + 2H^+ \rightleftarrows Fe^{2+} + 3H_2O + 2e^- \quad (8)$$

Complexes formation (in the absence of inhibitor):

$$Fe^{2+} + Cl^- \rightleftarrows [FeCl]^+ \quad (9)$$

However, FT-IR analysis suggested (1) the presence of carboxyl (-COOH) and hydroxyl (-OH) in cocoa pod-*Ficus exasperate* extract and (2) corrosion inhibition *via* their adsorption on a mild steel substrate. Protonation of CP-FE active ingredients occurs in HCl medium such that Fe^{2+} complexes are formed on a mild steel surface resulting from electrostatic forces of attraction. As immersion time progresses, protective films are formed serving as a barrier between HCl and mild steel surface which prevents it from pitting.

CONCLUSIONS

The results obtained have revealed extract from cocoa pod-*Ficus exasperate* to have corrosion inhibitory potential for mild steel in HCl environment. The maximum inhibition efficiency of 95.42% was obtained at ethanol volume, extraction time, CP-FE mixing ratio, and CP-FE mass of 500mL, 48h, 5, and 100g respectively as presented by the CCD experimental design. The coefficient of determination value between experimental and predicted values being 0.9674 suggested the exactness of the developed model. The optimum predicted point for CP-FE extract preparation by CCD was 62.02 mL, 9.51 hr, 3.42, and 75.68 g for the ethanol volume, extraction time, CP-FE mixing ratio, and CP-FE mass respectively. SEM images revealed HCl attack on mild steel substrate causing pitting corrosion and adsorption of CP-FE extracts on mild steel surface as acid attack prevention means. The presence of carboxyl (-COOH) and hydroxyl (-OH) functional groups were revealed by FT-IR as mild steel corrosion inhibitory ingredients in HCl medium. High iron composition on mild steel surface in the presence of CP-FE extracts was shown by EDS. AAS revealed loss of Fe^{2+} into a free HCl solution. Conclusively, extracts from mixed cocoa pod-*Ficus exasperate* were shown as an effective corrosion inhibitor for mild steel in HCl solution.

Received : Apr. 20, 2021 ; Accepted : Jul. 5, 2021

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