SOLVENTS EFFECT ON THERMAL STABILITY AND ELECTROCHEMICAL BEHAVIOUR OF *GRIFFONIA SIMPLICIFOLIA* EXTRACTS AS STEEL CORROSION INHIBITOR IN ACIDIC ENVIRONMENT

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Different solvents were used to extract *Griffonia simplicifolia* and tested corrosion inhibitors for as X80 steel in 1 M HCl solution. The corrosion tests were conducted by thermo-gravimetric analyses (TGA), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) while the surface morphologies were checked by scanning electron microscopy (SEM). The essence was to investigate the effects of the solvents on the yield, phytochemical profile, corrosion inhibition properties and thermal stability of the extracts. The highest yields of 63.24 g kg⁻¹ and 51.63 g kg⁻¹ were obtained with seeds (SEGS) and leaves (LEGS) extracts respectively in ethanol-water (1:1) system. Acetone extract showed presence of all the tested phytochemicals namely alkaloids, tannins, saponins, glycosides, steroids and terpenoids. The highest inhibition efficiencies of 95.86 % (SEGS) and 82.14 % (LEGS) were obtained with acetone extracts. Acetone extract was also most thermally stable being 66.4 % (SEGS) and 50.05 % (LEGS) efficient at 90 °C, followed by ethanol extract while methanol extract was least stable and least efficient. Inhibitors act as mixed type and their addition increased charge transfer resistance and decreased corrosion current density with respect to the free acid solution. Micrographs of the steel surface in some systems show evidence of slight surface protection by the inhibitors. It has been inferred from this study that both acetone and ethanol are better solvents for extraction of *Griffonia simplicifolia* based corrosion inhibitors.

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Introduction

Corrosion of metals and alloys in various aggressive media has been an active area of research. In the oil and gas industry where corrosion is associated with various operations such as pickling, well acidizing and fracture, corrosion inhibitors are usually deployed to reduce the rate of corrosion. Several chemicals and organic compounds have been reported to be capable of inhibiting corrosion in various oilfield environments.[1] Many of these compounds are toxic and very expensive. Environmental and economic concerns have triggered preference for green corrosion inhibitors derived from sustainable and cheap sources. A vast number of plant extracts have been investigated and some of them have shown excellent inhibitive effects especially at low temperatures.[2-4]

If plants that are meant for food are used to produce corrosion inhibitors, food scarcity may set in. Therefore, inedible plants and agricultural wastes are better options. Previously, we have reported the efficiency of extracts of seeds (SEGS) and leaves (LEGS) of *Griffonia simlicifolia* as corrosion inhibitor for different oilfield grades of steel in various simulated acidizing and fracture fluids.[5,6] Detailed information on *Griffonia simplicifolia* were also given in the articles cited while others are available in literature,[7] the picture is shown in figure 1. In these reports, both LEGS and

SEGS were extracted in acetone. The acetone extracts were efficient at low temperatures but performed poorly at high temperatures perhaps due to thermal degradation. This made it difficult to commercialize the product of that research. It was also difficult to predict if the potency of the extracts could change if they were extracted in other solvents. This study was therefore designed to investigate the effects of solvents on the inhibitive efficiency of SEGS and LEGS in acidizing environment.

Figure 1. Leaves and seeds of *Grifonia simplicifolia*.

In this study, the plant parts were extracted in different solvents and the phytochemical profile of each solvent fraction was screened. The extracts were subjected to corrosion tests using X80 steel with 1 M HCl being the corroding medium. Standard techniques such as TGA, EIS and PDP were used for the corrosion tests. SEM was also used to probe the surface of the steel in the absence and presence of the inhibitors. The effects of the different solvents on the corrosion inhibitive potential of the extracts were evaluated. The choice of X80 steel was motivated by its widespread application in construction of casings, tubing, pipe works and transport lines in the oil and gas industry.[8-14] On the other hand, the choice of *Griffonia simplicifolia* is due to the broad alkaloid composition which has been reported about the plant, especially the presence of 5-hydroxytryptophan.[15]

Experimental

Steel samples and surface preparation

X80 steel samples were purchased from Qingdao Tengxiang Instrument and Equipment Co. Ltd., China and were cut into coupons of dimension 2 cm x 2 cm for thermogravimetric experiments and 1 cm x 1 cm for electrochemical studies. The surface of each coupon was treated as provided by NACE Recommended Practice RP-0775 and ASTM G-1 & G-4 for surface finishing and cleaning of weight-loss coupons. The coupons for electrochemical studies were abraded using different grades of silicon carbide paper and finished to mirror surface with CC-22F P1000. The prepared specimens were put in sealed water-proof containers and stored in moisture free desiccator prior to use. The chemical composition of the X80 steel was C (0.065), Si (0.24), Mn (1.58), P (0.011), S (0.003), Cu (0.01), Cr (0.022), Nb (0.057), V (0.005), Ti (0.024), B (0.0006), and Fe (balance).

Preparation of plant extracts

Mature seeds and leaves of *Griffonia simplicifolia* were harvested from a local bush in Ikot Ambon Ibesikpo, Uyo, Nigeria. The seed pericarps were removed and the seeds were washed and air-dried in the laboratory for one week, ground to powder and soaked in the different solvents for 48 h, then retrieved and filtered. The filtrate was concentrated using rotary evaporator at room temperature. The washed leaves were air-dried in the absence of light for one week, ground and extracted as described above.

Phytochemical screening

The extract was screened for the presence of alkaloids, tannins, terpenoids, glycosides, flavonoids, saponins, and steroids using standard procedures reported in literature.[15]

Preparation of extract for corrosion study

The dry extracts were accurately weighed and prepared in 1 M HCl (analytical grade) to concentration of 1000 ppm

with distilled water and labelled SEGS (seed extract) and LEGS (leave extract).

Control experimental sample

A commercially corrosion inhibitor for acidizing was purchased and also tested under the same conditions. It was a reddish brown liquid with pH around 3-5. About 5ml of the liquid was dissolved in 995 ml 1 M HCl and well shaken before use in the corrosion experiment. This sample was labeled CTR-INH.

Thermogravimetric analysis (TGA)

Pre-weighed steel coupons were immersed in the test solutions in the absence and presence of the studied inhibitors for 5 h at 30 °C in a water bath. They were retrieved, cleaned using standard procedures[16] and weighed to determine the weight loss. Experiments were carried out in triplicates and the mean values of the weight losses were used for computation. By denoting the initial and final weights of the coupons as w_1 and w_2 respectively, corrosion rate of iron, percentage inhibitor effectiveness (inhibition efficiency ε_{WL}, and degree of surface coverage (θ), were calculated as follows:

$$CR = \frac{87.6(w_1 - w_2)}{\rho At} \quad (1)$$

$$\varepsilon_{WL} = 100\left(\frac{CR_b - CR_i}{CR_b}\right) \quad (2)$$

$$\theta = 0.01\varepsilon_{inh} \quad (3)$$

where

CR_b and CR_i are the corrosion rates (mmpy) in the absence and presence of the inhibitor, ρ is the density of iron, A is the average surface area (cm^2) of the metal specimens and t is the immersion time. This procedure was repeated at 60 °C and 90 °C. Also, the procedure was followed using CTR-INH at the different temperatures.

Electrochemical measurements

The corrosion process was monitored using Gamry ZRA REF 600-18042 electrochemical workstation. The conventional three electrode set up was used consisting of saturated calomel electrode (SCE) as reference electrode, platinum as counter electrode and the different steel coupons as working electrode. EIS measurements were conducted at frequency of 10^5 to 10^{-2} Hz for immersion time of 30 min at 30 °C. The voltage was changed to -0.15 V to +0.15 V vs. E_{OC} at scan rate of 1 mV/s for PDP measurements. E-Chem software package was used for data fitting and analyses. Electrochemical studies were conducted for only SEGS.

Charge transfer resistance from EIS measurements were used to compute the inhibition efficiency according to Eqn.

(4) while the inhibition efficiencies from PDP was calculated from the corrosion current densities using Eqn. (5).

$$\varepsilon_{EIS} = 100 \left(\frac{R_{ctI} - R_{ctB}}{R_{ctI}} \right) \qquad (4)$$

where

R_{CtB} and R_{ctI} are charge transfer resistances in the absence and presence of inhibitor respectively.

$$\varepsilon_{PD} = 100(1 - \frac{I_{corr}^i}{I_{corr}^b}) \qquad (5)$$

where

I_{corr}^b and I_{corr}^i are the corrosion current densities in the absence and presence of the inhibitor respectively. The magnitude of the double layer capacitance (C_{dl}) of the adsorbed film was calculated from constant phase element (CPE) constant (Y_0) and charge transfer resistance (R_{ct})) using eqn (6).

$$C_{dl} = \left(Y_0 R_{ct}^{n1} \right)^{1/n} \qquad (6)$$

where n is a constant showing degree of roughness of the metal surface obtained from the phase angle given that (j^2=-1)α and $n=2\alpha/\pi$ and is the CPE exponent. EIS and PDP measurements were also conducted using CTR-INH at 30 °C.

SEM studies

X80 steel coupons of dimensions 1 cm × 2 cm were abraded to mirror finish as earlier described. The morphologies of the surfaces immersed in 1 M HCl and those of acetone and ethanol SEGS for 12 h were scanned by SEM.

RESULTS AND DISCUSSION

Yield of extract

The yield of the crude extract obtained by direct extraction of 1.0 kg of the ground leaves and seeds of *Griffonia simplicifolia* at room temperature is given in Table 1. The highest yield of 63.24 g/1000 g and 51.63 g/1000 g was obtained with 1:1 (v/v) water-ethanol solvent mixer for SEGS and LEGS respectively. As can be observed in table 1, the seeds yield higher than the leaves, and the yield follows the trend ethanol-water > acetone > water > ethanol > methanol.

Table 1. Yield of LEGS and SEGS in different solvents at room temperature.

Solvent	Yield (g kg⁻¹ dry weight)	
	LEGS	SEGS
Acetone	43.23	58.16
Methanol	16.72	20.45
Ethanol	48.18	52.86
Water	44.73	57.45
Ethanol-Water (50-50)	51.63	63.24

Phytochemical profile of extract

Phytochemical screening of the extracts from the different solvents reveals that acetone extracts of LEGS and SEGS contained all the groups of compounds tested namely alkaloids, tannins, saponins, glycosides and terpenoids. These substances are rich in functionalities containing lone pair of electrons and π-electrons which are potential adsorption sites of established corrosion inhibitors.[1] Table 2 shows the phytochemical profile of LEGS and SEGS in the different solvents studied. Alkaloids are detected in extracts of all the solvents studied while flavonoids were not detected in any. These result are in partial agreement with those reported for seeds of *Griffonia simplicifolia* in Ghana.[17]

TGA studies

In other to determine which solvent would provide the highest inhibition efficiency, LEGS and SEGS were extracted using methanol (MeOH), ethanol (EtOH), acetone, water and ethanol-water (1:1) (EtOH-H₂O) as solvents. Results (Table 3) show that acetone extract gave the highest inhibition efficiency which also sustained appreciably at high temperature. It was earlier observed that acetone extract contained all the phytochemicals tested, which may be responsible for the high inhibition efficiency obtained.

EIS studies

EIS measurements for corrosion of X80 in 1 M HCl were carried out in the absence and presence the SEGS as well as CTR-INH. Nyquist plots shown in Fig. 2 were constructed using the experimental data obtained. The plots yielded imperfect semicircles with diameters influenced in the presence of SEGS from that of HCl solution. The differences in sizes of the diameters of the curves obtained can be due to the influence of the different solvents on the efficiency of SEGS. It can be observed that all the curves are larger in diameter in the inhibited solutions than the free acid solution which may be due to corrosion inhibition.

The diameters increase according to the trend CTR-INH > ETOH > ETOH-H₂O > Acetone > H₂O > MeOH > HCl which is similar to the trend of inhibition efficiency obtained from TGA. This indicates that TGA and EIS are in agreement. A close look at table 2 also reveals that the inhibition efficiencies obtained from both measurements are comparable.

Table 2. Phytochemical profile of SEGS and LEGS in different solvents.

Solvent	Alkaloids		Tannins		Saponins		Glycosides		Steroids		Terpenoids	
	LEGS	SEGS	LEGS	SEGS	LEGS	SEGS	LEGS	SEGS	LEGS	SEGS	LEGS	SEGS
Acetone	+	+	+	+	+	+	+	+	+	+	+	+
Methanol	+	+	-	+	-	-	+	-	+	+	+	-
Ethanol	+	+	-	+	+	-	+	+	+	+	+	-
Water	+	+	+	+	+	+	+	+	-	-	+	+
EtOH-H$_2$O	+	+	+	+	+	+	+	+	-	+	+	-

Table 3. Effect of solvent on the inhibition efficiency of LEGS and SEGS using weight loss measurement.

T, °C	EtOH-H$_2$O		MeOH		EtOH		H$_2$O		Acetone		CNTR-INH
	SEGS	LEGS	SEGS	LEGS	SEGS	LEGS	SEGS	LEGS	SEGS	LEGS	
30	91.73	79.68	84.63	56.08	91.02	78.43	90.31	76.17	95.86	82.14	100.0
60	78.41	65.18	62.54	42.17	78.91	67.02	73.02	61.13	82.64	69.42	99.8
90	56.25	41.45	42.49	36.34	57.14	42.85	50.42	39.12	66.04	50.15	94.2

Imperfections in the shapes of the semicircles can be attributed to roughness or heterogeneity of the steel surface.[18] The shapes of the plots were similar in both inhibited and free acid solution indicating that the mechanism of steel corrosion is not influenced by SEGS. However, slight differences can be observed in ethanol-water mixture and acetone. This implies that in addition to charge transfer mechanism, SEGS adsorption in these two solvents may also be associated with diffusion mechanism For uniformity, the same equivalent circuit in Figure 3 corresponding to $R_s(R_{ct}\emptyset_{CPE})$ model was used to analyze the obtained data. Goodness of the fits obtained was in the order of 10^{-4} indicating good correlation with the model. The surface roughness or heterogeneity of the steel was compensated by introduction of a non-integer element dependent on frequency called constant phase element, CPE, estimated in terms of Y_0 and n, related to impedance by Eqn. (7).

$$Z_{CPE} = (Y_0)^{-1}(j\omega)^{-n} \qquad (7)$$

where

Z_{CPE} is the impedance of the CPE,

Y_0 is the CPE constant,

ω is the angular frequency,

j is an imaginary complex number, $(j^2=-1)\alpha$ is the phase angle of CPE and $n=2\alpha/\pi$,

Table 4. Some EIS parameters determined for the inhibition of X80 steel corrosion in 1 M HCl without and with SEGS extracted from different solvents.

Test solution	R_{CT} Ω cm^2	R_S Ω cm^2	n	C_{dl} μF cm^{-2}	ε_{EIS}, %
1 M HCl	68.9	0.982	0.736	15.4	-
MeOH	429.8	1.225	0.724	11.4	83.9
H$_2$O	630.1	1.122	0.805	8.6	89.0
Acetone	825.1	1.410	0.786	5.8	91.6
EtOH-H$_2$O	767.0	1.136	0.811	9.2	91.0
EtOH	837.6	1.213	0.816	4.7	91.7
CTR-INH	1089.1	1.679	0.776	2.6	93.6

Some of the EIS parameters calculated are presented in Table 4. The value of n can be used to predict the degree of roughness or inhomogeneity of the steel surface. This value decreases on addition of SEGS suggesting that the surface roughness of the steel is increased by adsorption of inhibitor molecules.[20] It also shows that there is relative and/or integrated influence on the CPE and not just a single resistance, capacitance or inductive element. Decrease in n on addition inhibitors also signifies insulation of the metal/solution interface by formation of a surface film, which results in increase in charge transfer resistance in the presence than in the absence of inhibitor. The charge transfer resistance increases according to the trend of inhibition efficiency showing that the 'insulating' property of the film improved as solvent elicits better cooperative or synergistic effect with the extract.

The C_{dl} values obtained decreases in the presence of inhibitors similar to results reported in literature.[18] This has been attributed to decrease in the local dielectric or increase in the thickness of the double layer or both, caused by the adsorbed protective film of the inhibitors.[18]
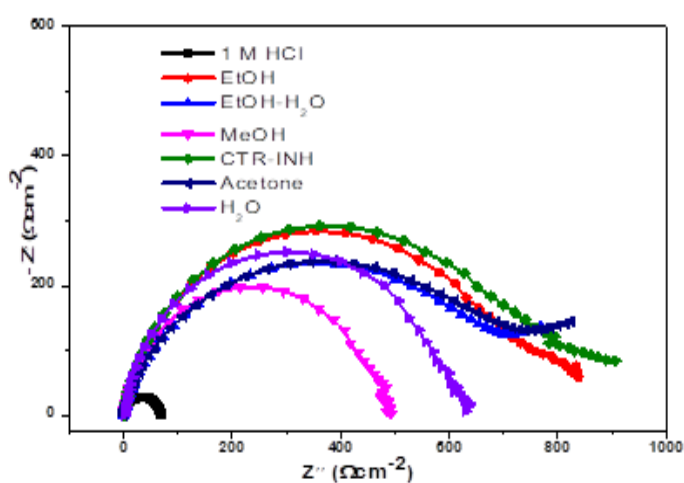
Figure 2. Nyquist plot for the inhibition of X80 steel corrosion in 1 M HCl using SEGS in different solvents.

PDP study

Polarization (Tafel) curves for X80 steel corrosion in 1 M HCl in the absence and presence of SEGS from different solvents obtained at 30 °C is shown in figure 3. The corrosion potential (E_{corr}) and the corresponding corrosion current density (I_{corr}), Tafel anodic slope constant (β_a), Tafel cathodic slope constants (β_c) and inhibition efficiency (ε_{PD}) deduced from the plots are listed in Table 5. The E_{corr} values obtained in the presence of SEGS are more positive than that of the free acid solution indicating that SEG has influenced the corrosion rate of the steel. E_{corr} values shift to more positive regions on addition of SEGS from all the solvents signifying that the SEGS has more effects on anodic half reaction by suppressing the oxidation or corrosion of iron.[21] In the literature, when the shift in E_{corr} values is up to -85 mV, the inhibitor is classified as anodic or cathodic type inhibitor.[22] The shifts in E_{corr} values obtained is not up to -85 mV indicating that SEGS acts as a mixed type inhibitor with anodic predominance.[22]

SEM analyses

The surfaces of the coupons in 1 M HCl and those in acetone and ethanol SEGS were scanned by SEM. Results (Figure 4) show that roughness of the micrographs of the steel surface were more highly attacked in the uninhibited acid solution compared to the inhibited solutions. This demonstrates that the extracts inhibit X80 steel corrosion. Though the adsorbed film is not very visible, it can be seen inferred that corrosion inhibition is due to adsorption of the extracts on the steel surface.
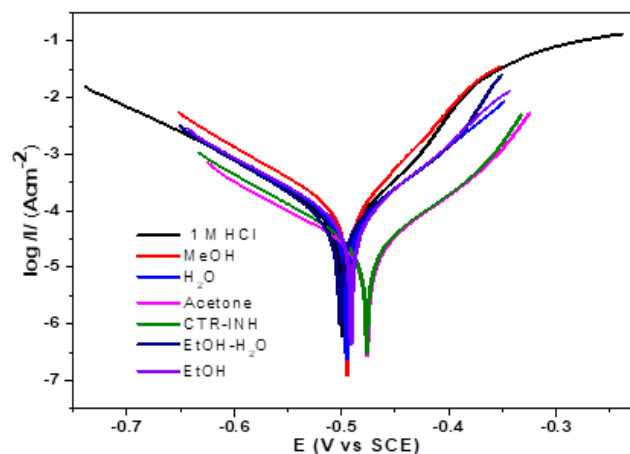

Figure 3. Tafel plots for the inhibition of X80 steel corrosion in 1 M HCl using SEGS in different solvents.

Table 5. Some PDP parameters determined for the inhibition of X80 steel corrosion in 1 M HCl without and with SEGS extracted from different solvents.

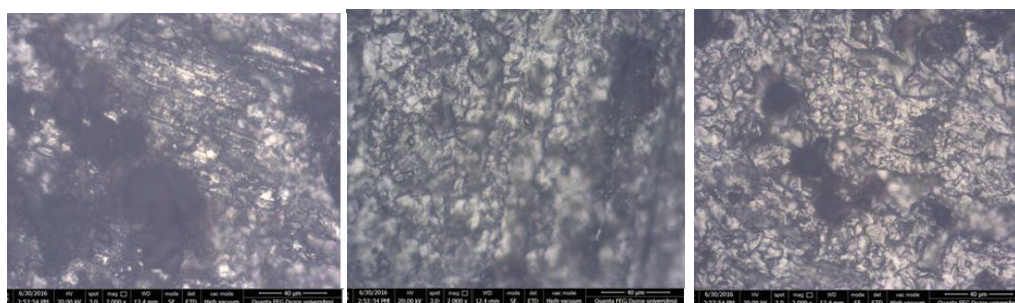| Test Solution	E_{corr}, mV vs SCE	I_{corr}, µA cm^{-2}	β_a, mV dec^{-1}	β_c, mV dec^{-1}	ε_{PD}, %
1 M HCl	-499	693.1	82.5	98.4	−
MeOH	-492	119.2	103.7	110.6	82.8
H$_2$O	-481	74.8	99.4	108.5	89.2
Acetone	-464	56.8	101.7	131.2	91.8
EtOH-H$_2$O	-494	63.1	98.5	102.4	90.9
EtOH	-483	53.4	112.1	109.7	92.3
CTR-INH	-463	41.6	107.9	99.8	84.0

Figure 4. SEM micrographs of X80 steel immersed in 1 M HCl (left), Acetone SEGS (middle) and EtOH SEGS (right).

Conclusion

Effects of solvents on the yield, phytochemical profile, corrosion inhibition properties and thermal stability of the *Griffonia simplicifolia* extracts have been investigated. Based on the results, the following conclusions are drawn: Acetone produces the highest yield while methanol produces the lowest yield of the extracts per 1000 g of solvent. Acetone extract contains alkaloids, tannins, saponins, glycosides, steroids and terpenoids. Acetone extract is most efficient in the inhibition of X80 steel corrosion in 1 M HCl while methanol extracts is the least efficient. Acetone and ethanol extracts are more thermally stable at 90 °C while methanol is least thermally stable at that temperature. Extracts of in the solvents act as mixed type inhibitors.

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