



Antioxidant activity and corrosion inhibitive behavior of *Garcinia cola* seeds on mild steel in hydrochloric medium

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Abstract

In this work, the extract of *garcinia cola* seeds (EGCS) has been studied as inhibitor mild steel in hydrochloric acid (1.0 M HCl) solution using by weight loss measurement, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The presence of this extract reduces remarkably the corrosion rate of mild steel in acidic solution. Adsorption characteristic of the extract were approximated by the Langmuir isotherm. The results from this corrosion test clearly reveal that the extract behaves as a mixed type corrosion inhibitor with the highest inhibition at 100 ppm. Double layer capacitance, (C_{dl}) decrease indicates that a layer was form indicating the formation of a surface film. This reflects the inhibitor does retard the corrosion rate. Further, antioxidant activity of the extract of *garcinia cola* seeds was determined by free radical 2, 2-diphenyl-1-picrylhydrazyl (DPPH) method.

Keywords: Antioxidant activity, Corrosion inhibition, *Garcinia cola*, Mild steel

1. Introduction

Corrosion is generally regarded as the deterioration of metals due to chemical attack or reaction with a belligerent environment. It is a constant and persistent problem, often difficult to eliminate completely. The corrosion of mild steel and other metals is accentuated in the presence of an aggressive media such as acid. Therefore industrial process such as acid cleaning, acid descaling, acid pickling, and other oil well acidizing, require the use of corrosion inhibitors [1,2]. Many types of inhibitors have been thoroughly synthesized and used to combat corrosion problem. Most effective inhibitors are organic compounds containing N, S and/or O atoms [3-25]. These compounds can be adsorbed on the metal surface, block the active sites and thereby reduce the corrosion rate. Most of the investigated compounds are generally toxic and cause many severe environmental hazards. Hence the use of natural products as eco-friendly and harmless corrosion inhibitors is gaining an increasing popularity [26].

Natural products are nontoxic, biodegradable and readily available. They have been used widely as inhibitors. Many research groups have reported the successful use of naturally plant-derived substances to restrain the metal corrosion. [27-36]. In addition, the natural compounds of plants are derived from the occurrence of biodiversity. Plants produce these compounds to enhance their survival and competitiveness. Due to their biological activities, many plant-derived compounds are used for the treatment of human illnesses or diseases. A World Health Organization (WHO) survey indicated that about 70–80% of the world's population relies on traditional medicine based mainly on plant materials for their primary healthcare [37]. Even though phenolic

compounds are ubiquitous and rich in medicinal herbs and dietary plants, these compounds have gained much attention due to their antioxidant activities and use in medical practice as anti-inflammatory, choleric, anti-tumoral and other agents [38-40].

The seeds of *Garcinia cola* have been reported to possess neuroprotective, anti-inflammatory, antimicrobial, antigenotoxic and hepatoprotective activities in model systems via multiple biochemical mechanisms [41-43]. However, extract of *garcinia cola* seeds have not been exploited as corrosion inhibitors. In the view of the results obtained by antioxidant investigation, it was found worth investigating the corrosion inhibition behavior of this of *garcinia cola* seeds extract. Hence, the present paper reports the results of our investigation on the inhibitive performance of the extract of *garcinia cola* seeds on mild steel at different temperatures in HCl medium using mass loss and electrochemical techniques. The free radical 2, 2-diphenyl-1-picrylhydrazyl (DPPH) method was used for antioxidant assay of *Garcinia Cola* seeds extract.

2. Experimental

2.1. Inhibitor

Garcinia Cola seeds are already dried away from the light and at room temperature, are finely ground and sieved ($\varnothing = 250 \mu\text{m}$). 5 mg of the fine powder thus obtained and then macerated in 5 mL of absolute ethanol for 24 h at room temperature, the extract is filtered and collected in a clean flask for use in antioxidant and anti-corrosive activities.



Photo : *Garcinia Cola* seeds

2.2. Materials

The steel used in this study is a mild steel with a chemical composition 0.09 wt. % P; 0.38 wt. % Si; 0.01 wt. % Al; 0.05 wt. % Mn; 0.21 wt. % C; 0.05 wt. % S and the remainder iron (Fe).

2.3. Preparation of solutions

The aggressive solutions of 1.0 M HCl were prepared by dilution of analytical grade 37% HCl with distilled water. Inhibitor were dissolved in acid solution at the required concentrations (in ppm), and the solution in the absence of inhibitor was taken as blank for comparison purposes. The test solutions were freshly prepared before each experiment by adding extract of *garcinia cola* seeds directly to the corrosive solution. Concentrations of extract of *garcinia cola* seeds (EGCS) 10, 25, 50 and 100 ppm.

2.4. Antioxidant activity

The antioxidant activity in vitro was evaluated by measuring the trapping power of radical DPPH (1,1-Diphenyl-2-picrylhydrazyl) as described by Burits and Bucar [44], where 50 μL of each ethanolic solutions of the extract tested at different concentrations (200, 400, 600, 800 and 1000 $\mu\text{g/mL}$) are mixed with 1.95 mL a ethanoic solution of DPPH (0.004%). The mixture was strongly shaken and left to stand at room temperature for 30 min in the dark. The absorbance was measured at 517 nm against a blank. The inhibition of DPPH free radical by vitamin C was also analyzed at the same concentration for comparison. We determine the kinetics of the reaction and the calculation parameters of antioxidant activity for the vitamin C and the extract (Percent Inhibition, IC50 index. The values expressed are the average of three measurements performed in parallel.

The radical-scavenging activity was expressed as percentage of inhibition (Inhibition%) according to the following formula [45]:

$$I(\%) = \left(\frac{A_{Blank} - A_{Sample}}{A_{Blank}} \right) \times 100 \quad (1)$$

A_{Blank} : Absorbance of the blank (containing all reagents except for the test compound),

A_{Sample} : Absorbance of the test compound.

2.5. Corrosion tests

2.5.1. Gravimetric study

Gravimetric experiments were performed according to the standard methods [46], the mild steel sheets of $1 \times 1 \times 0.1$ cm were abraded with a series of emery papers SiC (120, 600 and 1200) and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed in a 100 mL beaker containing 250 mL of 1.0 M HCl solution with and without addition of different concentrations inhibitor. All the aggressive acid solutions were open to air. After 6 h of acid immersion, the specimens were taken out, washed, dried, and weighed accurately. In order to get good reproducibility, all measurements were performed few times and average values were reported to obtain good reproducibility. The inhibition efficiency ($\eta_{WL}\%$) and surface coverage (θ) were calculated as follows:

$$C_R = \frac{W_b - W_a}{At} \quad (2)$$

$$\eta_{WL}(\%) = \left(1 - \frac{w_i}{w_0} \right) \times 100 \quad (3)$$

$$\theta = \left(1 - \frac{w_i}{w_0} \right) \quad (4)$$

where W_b and W_a are the specimen weight before and after immersion in the tested solution, w_0 and w_i are the values of corrosion weight losses of mild steel in uninhibited and inhibited solutions, respectively, A the total area of the mild steel specimen (cm^2) and t is the exposure time (h).

2.5.2. Electrochemical measurements

The electrochemical measurements were carried out using Volta lab (Tacussel- Radiometer PGZ 100) potentiostat and controlled by Tacussel corrosion analysis software model (Voltmaster 4) at under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode of surface area of 1 cm^2 . The working electrode was mild steel of the surface 0.32 cm^2 . All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 30 min to establish steady state open circuit potential (E_{ocp}). After measuring the E_{ocp} , the electrochemical measurements were performed. All electrochemical tests have been performed in aerated solutions at 308 K. The EIS experiments were conducted in the frequency range with high limit of 100 kHz and different low limit 0.1 Hz at open circuit potential, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the x-axis.

The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following equation:

$$\eta_z \% = \frac{R_{ct}^i - R_{ct}^\circ}{R_{ct}^i} \times 100 \quad (5)$$

Where, R_{ct}° and R_{ct}^i are the charge transfer resistance in absence and in presence of inhibitor, respectively.

After ac impedance test, the potentiodynamic polarization measurements of mild steel substrate in inhibited and uninhibited solution were scanned from cathodic to the anodic direction, with a scan rate of 1 mV s^{-1} . The potentiodynamic data were analysed using the polarization VoltMaster 4 software. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities

(I_{corr}). From the polarization curves obtained, the corrosion current (I_{corr}) was calculated by curve fitting using the equation:

$$I = I_{corr} \left[\exp\left(\frac{2.3\Delta E}{\beta_a}\right) - \exp\left(\frac{2.3\Delta E}{\beta_c}\right) \right] \quad (6)$$

The inhibition efficiency was evaluated from the measured I_{corr} values using the following relationship:

$$\eta_{Tafel}(\%) = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100 \quad (7)$$

where I_{corr} and $I_{corr(i)}$ are the corrosion current densities for steel electrode in the uninhibited and inhibited solutions, respectively.

3. Results and discussion

3.1. Antioxidant activity

3.1.1. Reaction kinetics

The reduction kinetics of the free radical DPPH obtained at each concentration of vitamin C and of the extract are shown in Figure 1.

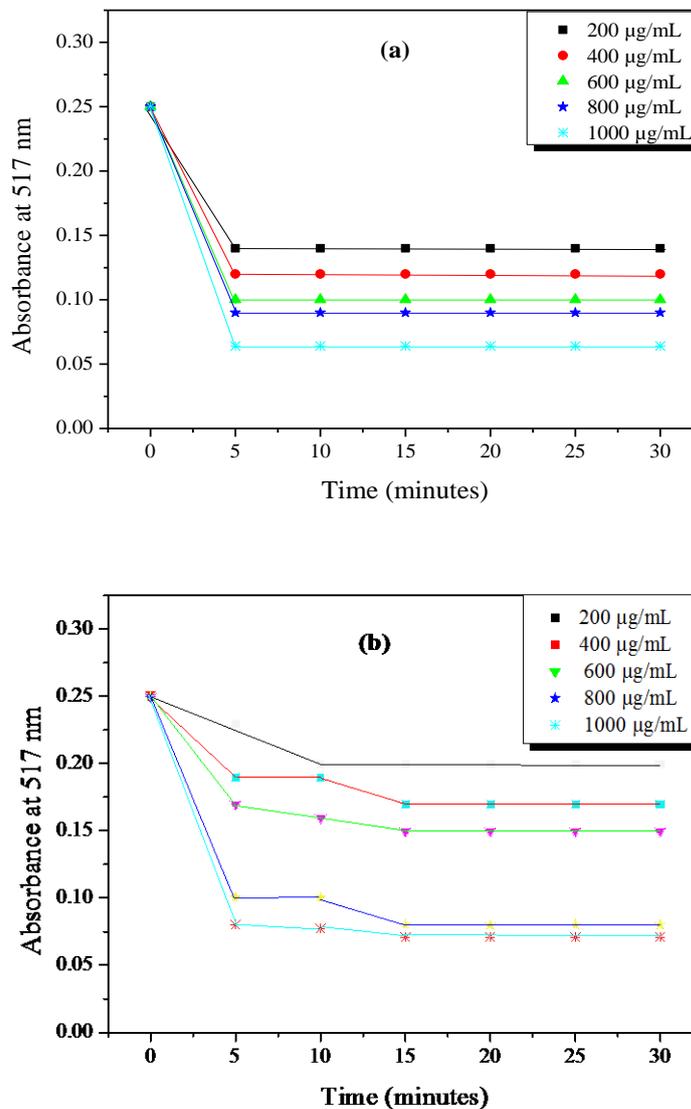


Figure 1: Kinetics of the reduction reaction of DPPH by: (a) Vitamin C and (b) Extract.

From Figure 1a we notice that there's a rapid decrease in absorbance within the first five minutes, followed by a relative balance, then there are two zones at different concentrations of vitamin C: a high kinetic scavenging zone of radical DPPH, a second area tend toward equilibrium observed after 5 minutes, in the presence of the extract we see the same thing but equilibrium is reached from 15 minutes.

3.1.2. Results of the Antioxidant Activities

The antioxidant activity of the extract of *garcinia cola* seeds, has been evaluated for its DPPH radical scavenging activity (table 1). The extract reduced the stable, purple-colored DPPH radical to a yellow colored DPPH-H with an IC₅₀ value of 401 µg/mL. Reduction of the DPPH absorbance was concentration dependent. Vitamin C, which was used as a standard, showed an IC₅₀ value of 202 µg/mL.

Table 1: Antioxidant activity of the extract of *garcinia cola* seeds and antioxidant reference.

	IC ₅₀ (µg/mL)
Vitamin C	202±0.81
Extract	401±2.44

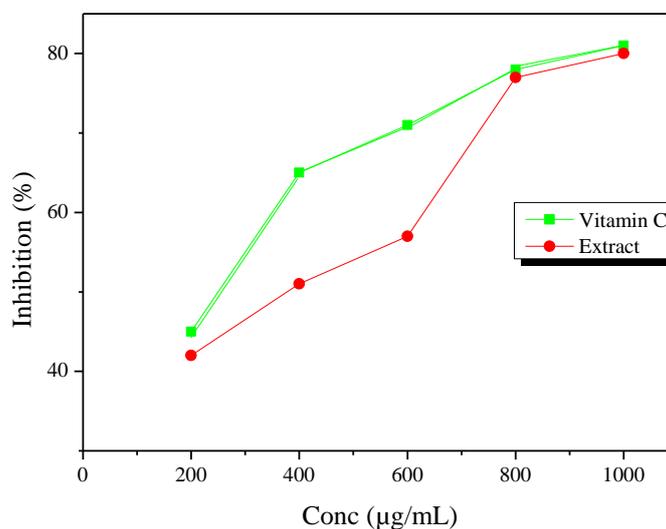


Figure 2: Variation of the inhibition percentage of vitamin C and extract in relation to its concentration (DPPH test).

It is well-known that the antioxidant activity of extract is due to their capacity to be donors of hydrogen atoms or electrons and to capture the free radicals. DPPH analysis is one of the tests, used to prove the ability of the components of the the extract of *garcinia cola* seeds to act as donors of hydrogen atoms. The obtained results are shown in Figure 2. The extract showed a significant effect in inhibiting free radicals produced by DPPH, reaching up to 80% at 1000 µg/ml and IC₅₀ value was found as 401 µg/mL. This capability was decreased with the decrease of extract concentration 800 (77), 600 (57), 400 (51) and 200 µg/mL (42%). These findings suggested that extract was able to reduce the stable free radical 2, 2-diphenyl-1- picrylhydrazyl to the transparent diphenyl- picryl-hydrazine.

The inhibitive effect of extract on the corrosion mild steel is confirmed by weight loss and electrochemical techniques. Therefore, it is pertinent to say that the adsorption of these compounds onto mild steel surface is responsible for corrosion inhibition effect. One of the main criticisms of the use of extract as corrosion inhibitors is the inability to pinpoint the major active component that is responsible for the inhibiting action owing to the complex chemical composition of the crude extract. However, the synergistic effect of various constituents of the extracts efficiently inhibits the corrosion of metals. The adsorption of these compounds on the metal surface reduces the surface area available for corrosion [47].

3.2. Corrosion tests

3.2.1. Weight loss measurements

3.2.1.1. Effect of concentration

The weight loss method has found broad practical application [48]. A major advantage of this method is its relative simplicity and availability. In addition, the method uses a direct parameter for the quantitative evaluation of corrosion, i.e., the loss in mass of the metal. The data obtained for the corrosion behavior of mild steel in 1.0 M HCl solution with and without the addition of different concentrations of *garcinia cola* seeds extract (EGCS), after 6 h of immersion period at room temperature, are presented in Fig 3, as well as table 2. The analysis of these results (Table 2) shows clearly that the weight loss decreases while the inhibition efficiency increases with increasing inhibitor concentration reaching a maximum value of 93% at a concentration of 100 ppm. This behavior can be attributed to the increase of the surface covered θ ($\% \eta_{WL} \times 100$), and that due to the adsorption of natural compounds on the surface of the metal [49], as the inhibitor concentration increases. We can conclude that EGCS is a good corrosion inhibitor for steel in 1.0 M HCl solution.

Table 2: Gravimetric results of steel corrosion in 1.0 M HCl (6 h immersion) without and with various concentrations of EGCS at room temperature.

Medium	Inhibitor (ppm)	C_R ($\text{mg cm}^{-2} \text{h}^{-1}$)	η_{WL} (%)	θ
Blank	—	0.430	—	—
EGCS	10	0.162	62	0.62
	25	0.115	73	0.73
	50	0.048	88	0.88
	100	0.030	93	0.93

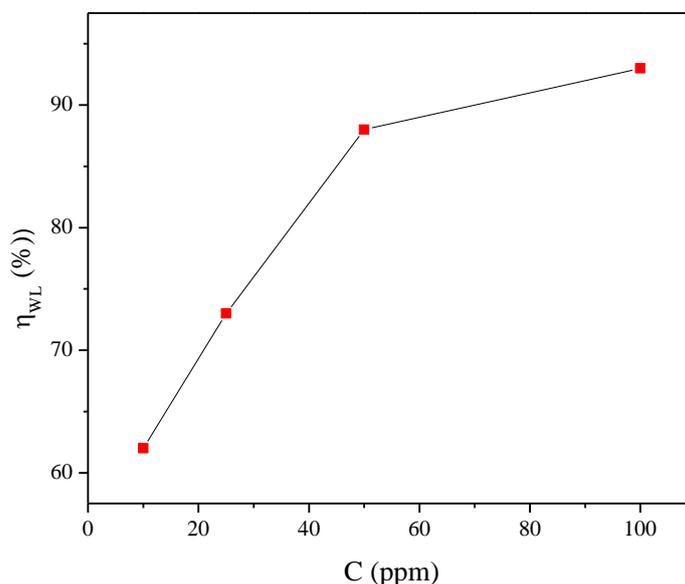


Figure 3: Inhibition efficiency ($\% \eta_{WL}$) vs. concentration (ppm) of EGCS at room temperature.

3.2.1.2. Adsorption isotherm

The values of surface coverage to different concentrations of inhibitors, obtained from weight loss measurements at 308 K, have been used to explain the best isotherm to determine the adsorption process. Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions [50]. The most frequently used isotherms are Langmiur, Temkin, Frumkin, Parsons, Hill de Boer, Flory-Huggins and Dahar-Flory-Huggins and Bockris-Swinkel [51-57]. All these isotherms are of the general form:

$$\int(\theta, x) \exp(2a\theta) = KC_{inh} \quad (8)$$

where $\int(\theta, x)$ is the configurational factor which depends upon the physical model and the assumptions underlying the derivation of the isotherm. “ θ ” is the surface coverage degree, “ C ” is the inhibitor concentration in the bulk of solution “ a ” is the lateral interaction term describing the molecular interactions in the adsorption layer and the heterogeneity of the surface. “ K ” is the adsorption-desorption equilibrium constant. The surface coverage θ for different concentrations of EGCS in 1.0 M HCl at 308 K for 6 h of immersion time has been evaluated from weight loss. The data were tested graphically, see Fig. 4, by fitting to Langmuir isotherm which given by equation 9.

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (9)$$

where C_{inh} is the equilibrium inhibitor concentration, K_{ads} adsorptive equilibrium constant, θ representing the degree of adsorption ($\eta_{WL}\%/100$).

By far the best fit was obtained with the Langmuir isotherm (the strong correlation ($R^2 = 0.99829$)). The plots of C_{inh}/θ vs. C_{inh} yield a straight line (Fig. 4). This confirms that this inhibitor (EGCS) obeys Langmuir adsorption isotherm at 1.0 M HCl medium. It indicates that the adsorbing EGCS species occupies typical adsorption site at the metal/solution interface. It is very important to note that discussion of the adsorption isotherm behaviour using natural product extracts as inhibitors in terms of thermodynamic parameters (such as the standard free energy of adsorption value (ΔG_{ads})) is not possible because the molecular mass of the extract components is not known. For example, there are a several phenolic compounds in the aqueous extract. Valek and Martinez [58], in their study on acid corrosion with Azadirachta indica leaf extract, noted the same limitation.

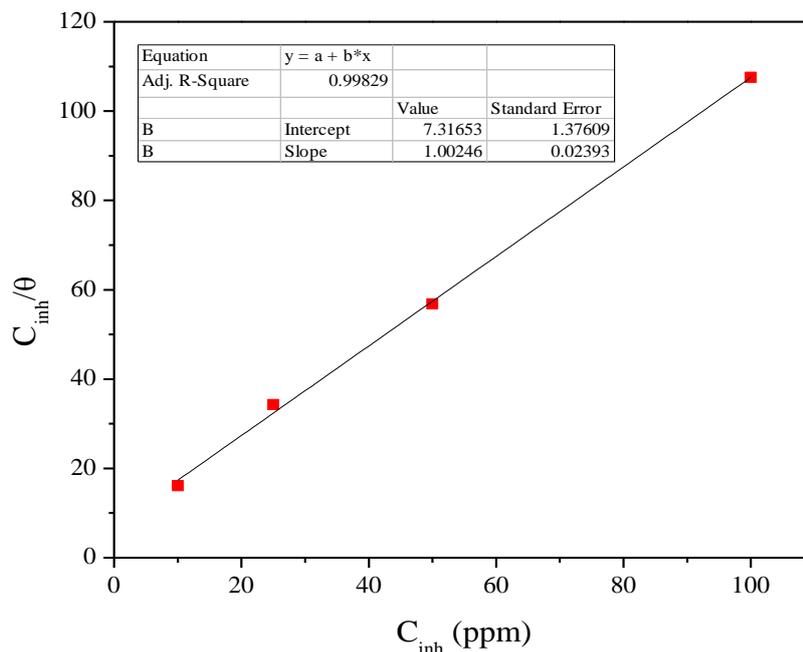


Figure 4: Langmuir isotherm adsorption of EGCS on the mild steel electrode in 1.0 M HCl.

3.2.2. Potentiodynamic polarization measurement

From the anodic and cathodic polarization curves (Fig. 5) for *garcinia cola* seeds extract (EGCS) in 1.0 M HCl media at different concentrations, various electrochemical parameters were computed and listed (Table 3). From the I_{corr} values, the inhibition efficiency was calculated as in Eq. (7). It was illustrated from the data that the addition of *garcinia cola* seeds extract (EGCS) decreased the corrosion current density (I_{corr}). The decrease may be due to the adsorption of the inhibitor on metal/acid interface [59]. The maximum inhibition was obtained at the concentration of 100 ppm (81 % η_{Tafel}).

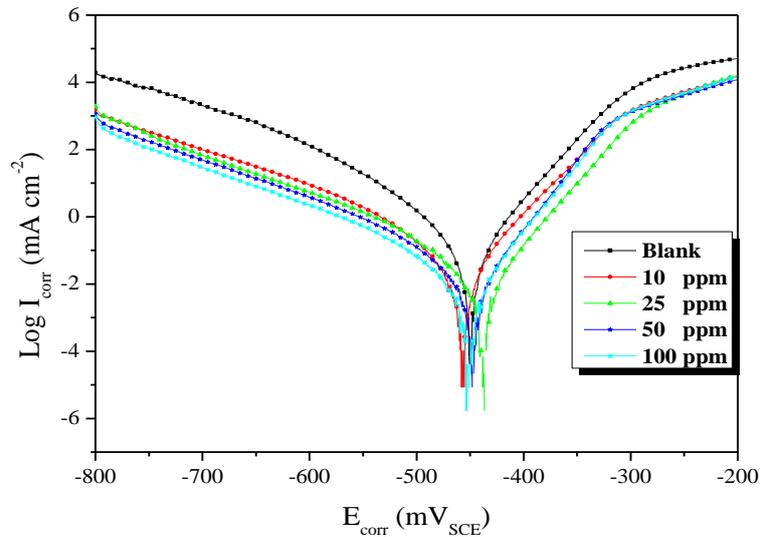


Figure 5: Potentiodynamic polarization curves for mild steel in 1.0 M HCl containing different concentrations of EGCS.

Table 3: Potentiodynamic polarizations parameters of mild steel in 1.0 M HCl for various concentrations of EGCS.

Medium	Conc (ppm)	$-E_{\text{corr}}$ (mV _{SCE})	β_a (mV/dec)	$-\beta_c$ (mV/dec)	I_{corr} ($\mu\text{A cm}^{-2}$)	η_{Tafel} (%)
1.0 M HCl	—	450	71.9	105.2	420	—
EGCS	10	457	84.0	172.6	99	76
	25	430	83.0	172.0	95	77
	50	448	105.1	91.5	90	78
	100	451	105.0	61.0	76	81

From Fig. 5, it is also cleared that both cathodic reduction and anodic metal dissolution reactions were inhibited when the *garcinia cola* seeds extract (EGCS) were added to the acid solution. The inhibition is increased with increase in extract concentration. The cathodic Tafel slope (β_c) show slight changes with the addition of EGCS, which suggests that the inhibiting action occurred by simple blocking of the available cathodic sites on the metal surface, which lead to a decrease in the exposed area necessary for hydrogen evolution. The parallel cathodic Tafel plots obtained in Fig. 5 indicate that the hydrogen evolution is activation-controlled and the reduction mechanism is not affected by the presence of inhibitor [60]. Therefore, it could be concluded that EGCS acts as a mixed inhibitor [61]. Furthermore, the displacement of E_{corr} was <85 mV, hence the inhibitor can be seen as a mixed type inhibitor [62]. This also indicates that the inhibitor merely blocks the reaction sites of the mild steel surface and changes the mechanism of metal dissolution (anodic) and/or hydrogen evolution (cathodic) reaction.

3.2.3. Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance diagrams for mild steel in 1.0 M HCl solution in the absence and presence of increasing extract concentrations of EGCS are shown in Figure 6. Table 4 summarizes the impedance data. Double layer capacitance values (C_{dl}) and charge-transfer resistance values (R_{ct}) were obtained from impedance measurements.

The double layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximal ($-Z_{\text{max}}$) are found as represented in equation 10:

$$C_{dl} = \left(\frac{1}{\omega R_{ct}} \right) \quad \text{Where} \quad \omega = 2\pi f_{max} \quad (10)$$

The Nyquist plots for all EGCS concentrations are characterized by one semicircular capacitive loop. The presence of inhibitor introduces the diffusion step in corrosion process and the reaction becomes diffusion-controlled. Hence, the corrosion process can have two steps as in any electrochemical process at the electrochemical interface, first, the oxidation of the metal (charge transfer process) and second, the diffusion of the metallic ions from the metal surface to the solution (mass transport process). Inhibitor gets adsorbed on the electrode surface and thereby produces a barrier for the metal to diffuse out to the bulk and this barrier increases with increasing the inhibitor concentration [63]. The diameter of the semicircular capacitive loop (Fig. 6), the impedance of the double layer increased with increasing concentration of the EGCS. The general overview of the electrochemical impedance results meets the expectations from the theory of the technique, but it must be noted that the capacitive loops are depressed ones with centers under the real axis even though they have a semicircle appearance. Deviations of this kind are mostly referred to as frequency dispersion and they are attributed to irregularities and heterogeneities of the solid surfaces [64,65]. In addition in the real corrosion systems, the double layer on the interface of metal/solution does not behave as a real capacitor. On the metal side of the double layer, the charge distribution is controlled by electron, whereas on the solution side it is controlled by ions [66].

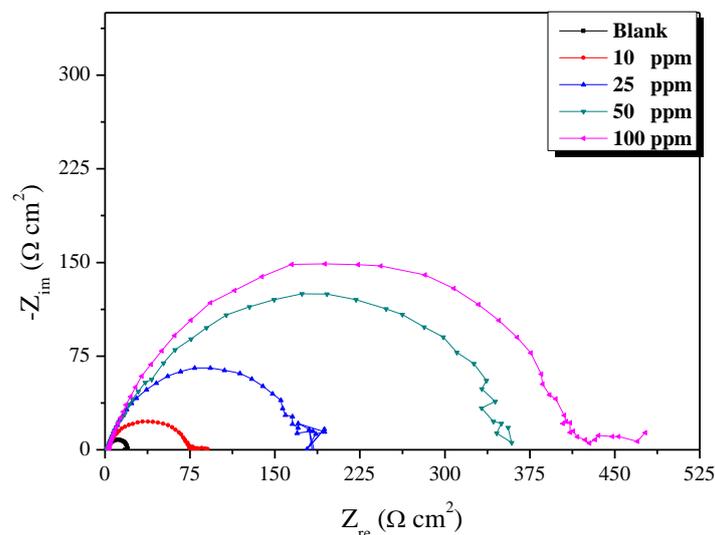


Figure 6: Nyquist diagrams for mild steel in 1.0 M HCl containing different concentrations of EGCS at 308 K.

It is found (Table 4) that, as the EGCS concentration increases, the R_{ct} values increase, but the C_{dl} values tend to decrease. The decrease in C_{dl} values is interpreted by the adsorption of EGCS on the metal surface [67]. It is apparent from Nyquist diagrams that the charge-transfer resistance value of mild steel in uninhibited 1.0 M HCl solution changes significantly after the addition of the inhibitor. Furthermore, C_{dl} decreases with increase of the concentration of inhibitor. This phenomenon is generally related to the adsorption of organic molecules on the metal surface and then leads to a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer [68].

$$C_{dl} = \frac{\epsilon_o \epsilon S}{\delta} \quad (11)$$

Where δ is the thickness of the protective layer, S is the electrode area, ϵ_o the vacuum permittivity of vide and ϵ is dielectric constant of the medium.

A low capacitance may result if water molecules at the electrode interface are largely replaced by organic inhibitor molecules through adsorption [69]. The larger inhibitor molecules also reduce the capacitance through the increase in the double layer thickness [70]. The inhibiting effectiveness increases with the concentration of the inhibitor to reach a maximum value from 96% to 100 ppm.

Table 4: Electrochemical impedance spectroscopy parameters of mild steel in 1.0 M HCl for various concentrations of EGCS.

Conc	R_{ct} ($\Omega \text{ cm}^2$)	f_{max} (Hz)	C_{dl} ($\mu\text{F cm}^{-2}$)	η_z (%)
1.0 M HCl	17.0	111.6	84.0	—
10	74.4	25.0	85.6	77
25	174	12.5	73.2	90
50	357	6.3	70.8	95
100	415	6.3	60.9	96

Conclusions

The following results can be drawn from this study:

- ✓ Extract of *garcinia cola* seeds (EGCS) exhibit corrosion inhibition properties for mild steel in 1.0 M HCl. The inhibition efficiency for all electrochemical tests and weight loss measurements were in good agreement at the concentration of 100 ppm.
- ✓ Potentiodynamic polarization measurements demonstrate that inhibitor acts as a mixed-type inhibition.
- ✓ The adsorption of EGCS on the mild steel surface follows the Langmuir adsorption isotherm.
- ✓ EIS measurements show that charge transfer resistance (R_{ct}) increases and double layer capacitance (C_{dl}) decreases in the presence of EGCS indicating the adsorption of natural compounds at the surface mild steel.
- ✓ The Extract of *garcinia cola* seeds (EGCS) under investigation plays an important role as a potential source of natural antioxidant.

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