**Ceratonia siliqua extract** as a green corrosion inhibitor for copper and brass in nitric acid solutions

A.S. Fouda\(^a\), K. Shalabi\(^a\) and A.A. Idress\(^b\)

\(^a\)Department of Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt; \(^b\)Department of Chemistry, Faculty of Science, Omar Almukhtar University, AlBayda, Libya

**ABSTRACT**

The influence of extract of **Ceratonia siliqua** on the corrosion of copper and brass in aqueous 1 M nitric acid was examined by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy and electrochemical frequency modulation techniques. The surface morphology was analyzed using scanning electron microscope and energy dispersive X-ray techniques. Potentiodynamic polarization curves indicated that the plant extract behaves as a cathodic inhibitor. The results indicate that the extract solution of the plant could serve as an effective inhibitor for the corrosion of copper and brass in nitric acid media. As temperature increases, percentage of inhibition decreases. The degree of surface coverage of the adsorbed inhibitor was determined by weight-loss technique, and it was found that the results obeyed the Langmuir adsorption isotherm.

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1. **Introduction**

Copper is easily combined with many metals. It is combined with zinc to form brass, which has a higher corrosion resistance and is easy to manufacture. Moreover, brass is harder and solid. But its exposure in acid media leads to corrosion (1–5). When the brass containing more than 15% of zinc is exposed to a corrosive medium, they are affected by both general corrosion damage and dezincification (preferential dissolution of zinc) process, leaving a spongy mass of copper on the alloy surface (6). Plant extracts are used as corrosion inhibitors for their low cost and are safe for the environment. Inhibitors from plant extracts are renewable resources, readily available, acceptable and environmentally friendly (7–12). The inhibition performance of plant extract is normally related to the presence of heterocyclic constituents such as alkaloids, flavonoids, carbohydrates, proteins. These organic compounds usually contain polar functions with nitrogen, sulfur or oxygen atoms and have triple or conjugated double bonds with aromatic rings in their molecular structures, which are the major adsorption centers (13–15).

The carob tree (**Ceratonia siliqua** L.) is evergreen and widely grown in Mediterranean countries. The carob pod consists mainly of pulp (90% of the pod weight) and less seeds (10% of the pod weight). The pulp is rich in sugars (48–56%, mainly sucrose) and contains 16–20% of condensed tannins (16). Carob has a very low protein content (17). It has been reported that ungrafted cultivars have lower amounts of total soluble sugars than grafted ones (18). This may be due to the higher amount of tannin-lignocelluloses materials in ungrafted cultivars (19, 20). In addition, the carob pod has antioxidant properties related to its polyphenolic composition (21).

The aim of this study is to investigate the corrosion inhibition effect of carob (**C. siliqua**) extract on copper and 60/40 brass in 1 M HNO\(_3\) solutions, using weight loss and some electrochemical measurements.

2. **Experimental**

2.1. **Materials and solutions**

Experiments were conducted using copper (99.98%) and α-brass (60–40 copper–zinc) specimens. They were mounted in Teflon. An epoxy resin was used to fill the space between Teflon and copper and also α-brass electrode. The aggressive solution used in our experiment was prepared by diluting 70% HNO\(_3\) (analytical reagent grade) with bi-distilled water. The stock solution (2000 ppm) of **C. siliqua** was used to prepare the desired concentrations of the same by diluting it with bi-distilled water. The desired
concentration range of C. siliqua used in our experiment was 50–300 ppm.

2.2. Preparation of plant extracts

Fresh carob pods were collected from green mountain, Libya, in spring (June 2013). The carob pods were shade dried at room temperature for 13 days, which were crushed to turn them into a fine powder. The powdered pods (100 g each) were put in 250 ml methanol for 5 days and then repeated extraction (25 × 30 ml) was carried out until exhaustion of plant materials. The extract obtained was then concentrated using a rotary evaporator at a temperature below 55°C. The extract was evaporated to yield a solid form in order to use it for preparation of the stock inhibitor concentration.

Kingdom: Plantae
(unranked): Angiosperms
(unranked): Eudicots
(unranked): Rosids
Order: Fabales
Family: Fabaceae
Genus: Ceratonia
Species: C. siliqua

2.3. Weight-loss measurements

The weight-loss measurements were carried out in a 100 ml capacity glass beaker placed in a thermostat water bath. The solution volume was 100 ml. The copper and brass specimens used had a square form (length = 2 cm, width = 2 cm, thickness = 0.2 cm). The coupons were weighed and suspended in 100 ml of an aerated 1 M HNO₃ solution with and without different concentrations of carob extract for a 3 h exposure time at 25–45°C. At the end of the tests, the coupons were taken out, washed with bi-distilled water, degreased with acetone, washed again with bi-distilled water, dried and then weighed using an analytical balance. The corrosion rate “w” as well as the inhibition efficiency (%IE) over the exposure time was calculated according to the following equations:

\[ CR = \Delta W/at, \]  
(1)

\[ \%IE = \theta \times 100 = \left( 1 - \frac{W_{(inh)}}{W_{(free)}} \right) \times 100, \]  
(2)

where \( W_{(free)} \) and \( W_{(inh)} \) are the weight loss in the absence and presence of inhibitor, respectively. CR is the corrosion rate, \( \Delta W \) is the weight loss in mg cm⁻², \( a \) area in cm² and \( t \) is the time in min.

2.4. Electrochemical measurements

Electrochemical measurements were carried out using a glass cell with three-electrode at 25°C, the auxiliary electrode was a platinum foil and the reference electrode was saturated calomel (SCE). The copper electrode was embedded in epoxy resin, leaving a geometrical surface area of 1 cm² exposed to the corrosive solution. Potentiodynamic (Tafel) polarization curves and electrochemical impedance measurements were carried out using a computer-controlled Gamry Instrument PCI-570 Potentiostat/Galvanostat/ZRA. This includes a Gamry Framework system based on the ESA400 – Gamry applications that include DC105 for DC corrosion measurements, EIS300 for electrochemical impedance spectroscopy (EIS) and EFM140 for electrochemical frequency modulation (EFM) measurements – along with a computer for collecting data. Echem Analyst 5.58 software was applied for graphing and fitting data. Accordingly, all tests were carried out after 30 min immersion of metal samples into the electrolyte. Tafel polarization plots were obtained using a sweep rate of 1 mV s⁻¹ in the potential range from -1000 to 1200 mV with respect to the open circuit potential. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities. Then \( i_{corr} \) was performed for the calculation of inhibition efficiency and surface coverage (θ) as shown below (22):

\[ \%I_E = \theta \times 100 = \left( 1 - \frac{i_{corr(\text{inh})}}{i_{corr(\text{free})}} \right) \times 100, \]  
(3)

where \( i_{corr(\text{free})} \) and \( i_{corr(\text{inh})} \) are the corrosion current densities in the absence and presence of inhibitor, respectively.

Electrochemical impedance spectra were obtained in the frequency range of 100 mHz to 1 MHz with perturbation amplitude of 5 mV at the corrosion potential. The efficiency of the inhibition and the surface coverage (θ) obtained from the impedance measurements are defined by the following relations:

\[ \%IE = \theta \times 100 = \left( 1 - \frac{R_{ct(\text{inh})}}{R_{ct(\text{free})}} \right) \times 100, \]  
(4)
where $R^*_0$ and $R_{ct}$ represent the charge-transfer resistance in the absence and presence of inhibitor, respectively. EFM was carried out using two frequencies: 2 and 5 Hz. The larger peaks were used to estimate the corrosion current density ($i_{corr}$), the Tafel slopes ($\beta_c$ and $\beta_a$) and the causality factors CF-2 & CF-3.

2.5. Surface examination

Hitachi S-550 scanning electron microscope (SEM) was used to examine copper and brass surface after 24 h of their exposure to the 1 M HNO$_3$ solution, without and with carob (C. siliqua) extract. Rough elemental analyses for the exposed surface were conducted by energy dispersive X-ray (EDX) technique.

3. Results and discussion

3.1. Weight-loss measurements

Figure 1 shows the mass loss-time curves for copper (brass curve not shown) in 1 M nitric acid in the presence and absence of different concentrations of C. siliqua at 25°C. These curves are characterized by a sharp rise in weight loss from the beginning. Curves for additives-containing system fall below that of the free acid. These curves indicated that, the weight loss of both copper and brass depends on the concentration of this additive. Increase in concentration and therefore increase in surface coverage by the additive increases the inhibition efficiency toward copper and brass dissolution. The results of the Table 1 observed that the inhibition efficiency of C. siliqua raises with the increase in the concentration in the corrosive medium. It is thus clear that increase in bulk concentration and thus increase in surface area coverage by the additive retards the dissolution of both copper and brass.

Table 1. Corrosion rate (CR) and inhibition efficiency data obtained from weight-loss measurements for copper and α-brass in 1 M HNO$_3$ solutions without and with various concentrations of C. siliqua at 25°C.

| Conc. (ppm) | Weight loss (mg cm$^{-2}$) | CR (mg cm$^{-2}$ min$^{-1}$) | $\theta$ | %IE |
|------------|-----------------------------|-----------------------------|---------|-----|
| Copper 1 M HNO$_3$ | 4.004 | 0.0333 | –– | –– |
| 50 | 0.0123 | 0.0123 | 0.638 | 63.8 |
| 100 | 0.0114 | 0.0114 | 0.657 | 65.7 |
| 150 | 0.0098 | 0.0098 | 0.706 | 70.6 |
| 200 | 0.0087 | 0.0087 | 0.740 | 74.0 |
| 250 | 0.0074 | 0.0074 | 0.770 | 77.0 |
| 300 | 0.0057 | 0.0057 | 0.828 | 82.8 |
| α-Brass 1 M HNO$_3$ | 14.636 | 0.1214 | –– | –– |
| 50 | 3.1834 | 0.0265 | 0.781 | 78.1 |
| 100 | 2.5952 | 0.0216 | 0.822 | 82.2 |
| 150 | 1.6184 | 0.0135 | 0.889 | 88.9 |
| 200 | 1.3272 | 0.0111 | 0.909 | 90.9 |
| 250 | 0.8370 | 0.0070 | 0.943 | 94.3 |
| 300 | 0.4331 | 0.0036 | 0.970 | 97.0 |

Table 2. Results of mass loss measurements for copper in 1 M HNO$_3$ solution with and without of different concentrations of C. siliqua at 25–45°C.

| Conc. (ppm) | Temp. (°C) | CR (mg cm$^{-2}$ min$^{-1}$) | $\theta$ | IE% |
|------------|------------|-----------------------------|---------|-----|
| 50 | 25 | 0.0123 | 0.631 | 63.1 |
| 30 | 0.0254 | 0.422 | 42.2 |
| 35 | 0.0334 | 0.319 | 31.9 |
| 40 | 0.0909 | 0.238 | 23.8 |
| 45 | 0.0627 | 0.177 | 17.7 |
| 100 | 25 | 0.0114 | 0.657 | 65.7 |
| 30 | 0.0218 | 0.504 | 50.4 |
| 35 | 0.0364 | 0.365 | 36.5 |
| 40 | 0.0569 | 0.309 | 30.9 |
| 45 | 0.0748 | 0.257 | 25.7 |
| 150 | 25 | 0.0098 | 0.706 | 70.6 |
| 30 | 0.0186 | 0.576 | 57.6 |
| 35 | 0.0339 | 0.428 | 42.8 |
| 40 | 0.0485 | 0.411 | 41.1 |
| 45 | 0.0676 | 0.390 | 39.0 |
| 200 | 25 | 0.0087 | 0.741 | 74.1 |
| 30 | 0.0174 | 0.604 | 60.4 |
| 35 | 0.0306 | 0.493 | 49.3 |
| 40 | 0.0451 | 0.452 | 45.2 |
| 45 | 0.0518 | 0.487 | 48.7 |
| 250 | 25 | 0.0074 | 0.779 | 77.9 |
| 30 | 0.0153 | 0.653 | 65.3 |
| 35 | 0.0271 | 0.573 | 57.3 |
| 40 | 0.0385 | 0.533 | 53.3 |
| 45 | 0.0518 | 0.487 | 48.7 |
| 300 | 25 | 0.0057 | 0.828 | 82.8 |
| 30 | 0.0129 | 0.707 | 70.7 |
| 35 | 0.0228 | 0.637 | 63.7 |
| 40 | 0.0370 | 0.551 | 55.1 |
| 45 | 0.0467 | 0.526 | 52.6 |
The inhibitory action of this extract against copper corrosion can be related to the adsorption of *C. siliqua* on the copper surface, which reduces the dissolution of the latter by blocking its corrosion sites and hence decreasing the corrosion rate, with increasing efficiency as their concentrations increase. This extract can be adsorbed by the interaction between the lone pairs of electrons of the nitrogen, sulfur and oxygen atoms with the copper and brass surfaces. These processes are facilitated by the presence of low-energy d vacant orbitals in the copper ions, as observed in transition group metals. Recently it was found that the formation of donor–acceptor surface complexes between free electrons of an inhibitor and a vacant d orbital of a metal is responsible for the inhibition of the corrosion process (23).

### 3.1.1. Effect of temperature and activation parameters of corrosion process

Both copper and brass dissolution in 1 M HNO₃ acid increases with an increase in temperature; the dissolution of copper and brass in 1 M HNO₃ with *C. siliqua* at 50–300 ppm was studied using the mass loss method over a temperature range of 25–45°C. The corrosion rate of copper and brass dissolution increases as the temperature increases, but at a lower rate than in uninhibited solutions, as shown in Tables 2 and 3. The inhibition efficiency of the extract decreases with raising the temperature, which proves that the adsorption of this extract on the surface of copper and brass occurs through physical adsorption of the components of the extract on the metal surface. Desorption is aided by increasing the reaction temperature. The apparent activation energy (*Eₗ*), the enthalpy of activation (ΔH*) and the entropy of activation (ΔS*) for the corrosion of copper and brass in 1 M HNO₃ solution in the absence and presence of different concentrations of *C. siliqua* were calculated from the Arrhenius-type equation:

\[
\frac{-E}{k_B T} \quad \text{and the transition-state equation:}
\]

\[
\log k = \log A + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}.
\]

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**Table 3. Results of mass loss measurements for brass in 1 M HNO₃ solution with and without various concentrations of *C. siliqua* at 25–45°C.**

| Conc.(ppm) | Temp (°C) | CR (mg cm⁻² min⁻¹) | θ%IE |
|------------|-----------|---------------------|------|
| 50         | 25        | 0.0265              | 78.1 |
|            | 30        | 0.1083              | 58.4 |
|            | 35        | 0.4183              | 59.0 |
|            | 40        | 0.3572              | 6.7  |
|            | 45        | 0.6873              | 5.7  |
| 100        | 25        | 0.0216              | 82.2 |
|            | 30        | 0.0789              | 69.7 |
|            | 35        | 0.1406              | 66.4 |
|            | 40        | 0.5121              | 14.3 |
|            | 45        | 0.6369              | 12.6 |
| 150        | 25        | 0.0135              | 88.9 |
|            | 30        | 0.0529              | 79.7 |
|            | 35        | 0.1045              | 75.0 |
|            | 40        | 0.3974              | 33.5 |
|            | 45        | 0.5459              | 25.1 |
| 200        | 25        | 0.0111              | 90.9 |
|            | 30        | 0.0358              | 86.2 |
|            | 35        | 0.0837              | 80.0 |
|            | 40        | 0.2020              | 51.2 |
|            | 45        | 0.4227              | 42.1 |
| 250        | 25        | 0.0070              | 94.3 |
|            | 30        | 0.0251              | 90.4 |
|            | 35        | 0.0447              | 89.3 |
|            | 40        | 0.1525              | 74.5 |
|            | 45        | 0.2366              | 67.6 |
| 300        | 25        | 0.0036              | 97.0 |
|            | 30        | 0.0239              | 90.8 |
|            | 35        | 0.0358              | 91.1 |
|            | 40        | 0.0890              | 85.1 |
|            | 45        | 0.1116              | 84.7 |

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**Figure 2.** Log corrosion rate – 1/T curves for copper dissolution in 1 M HNO₃ in the absence and presence of different concentrations of *C. siliqua*.

**Figure 3.** Log (corrosion rate/T) – (1/T) curves for copper dissolution in 1 M HNO₃ in the absence and presence of different concentrations of *C. siliqua*. **Table 3. Results of mass loss measurements for brass in 1 M HNO₃ solution with and without various concentrations of *C. siliqua* at 25–45°C.**
where $A$ is the frequency factor, $h$ is the Planck’s constant, $N$ is Avogadro’s number and $R$ is the universal gas constant.

Figure 2 indicated kinetic parameters obtained from plots of log corrosion rate vs. $(1/T)$ and Figure 3 observed log (corrosion rate$/T$) vs. $(1/T)$ graphs for the studied C. siliqua. The information for both metals are given in Table 4. Table 4 shows that higher values were obtained for ($E^*_a$) and ($\Delta H^*$) in the presence of inhibitor, indicating the higher protection efficiency observed for this inhibitor. There is also a parallelism between increases in inhibition efficiency and increases in ($E^*_a$) and ($\Delta H^*$) values. These results indicate that this tested extract acted as inhibitor through increasing activation energy of copper and brass dissolution by making a barrier to mass and charge transfer by their adsorption on copper surface. The increase in the activation enthalpy ($\Delta H^*$) in the presence of the extract implies that the addition of the extract to the acid solution increases the height of the energy barrier of the corrosion reaction to an extent depending on the type and concentration of the present extract. Also, the entropy $\Delta S^*$ widely decreases with the content of the extract. This means that an ordered stable layer of extract formed on copper and brass surface.

3.1.2. Adsorption isotherms

The surface fraction covered by adsorbed molecules of the inhibitor ($\theta$) was estimated by $E/h/100$ ratio. Data released graphically were examined by fitting to various isotherms. The plot of $\theta/1-\theta$ against extract concentration (C) yields a straight line with correlation coefficient being equal to unity (Figure 4). The good correlation represents that C. siliqua extract (CSE) was adsorbed on the copper and brass surface electrodes related to the Langmuir isotherm. i.e. there is no interaction between the adsorbed species on the electrode surface (25). The equilibrium constant of the adsorption process, $K$, which is related to the standard free energy of adsorption ($\Delta G_{ads}$), can be determined by (26)

$$\frac{\theta}{1-\theta} = KC,$$

$$\text{(7)}$$

Table 4. Effect of concentration of C. siliqua on the activation energy of copper and $\alpha$-brass dissolution in 1 M HNO$_3$

| Conc. (ppm) | $E^*_a$ (kJ mol$^{-1}$) | $\Delta H^*$ (kJ mol$^{-1}$) | $-\Delta S^*$ (J mol$^{-1}$ K$^{-1}$) |
|-------------|--------------------------|-----------------------------|----------------------------------|
| Copper 1 M HNO$_3$ | 41.5 | 16.9 | 142.6 |
| 50          | 67.2 | 29.2 | 54.7  |
| 100         | 67.9 | 30.0 | 49.0  |
| 150         | 69.5 | 30.5 | 47.1  |
| 200         | 65.6 | 30.2 | 49.1  |
| 250         | 65.4 | 29.8 | 53.7  |
| 300         | 71.3 | 33.8 | 25.8  |
| $\alpha$-Brass 1 M HNO$_3$ | 81.1 | 33.3 | 154.6 |
| 50          | 129.9 | 54.8 | 40.5  |
| 100         | 140.5 | 58.1 | 50.8  |
| 150         | 151.1 | 63.5 | 51.9  |
| 200         | 149.5 | 63.2 | 40.8  |
| 250         | 138.1 | 59.5 | 39.1  |
| 300         | 130.6 | 55.2 | 23.1  |

Table 5. Thermodynamic parameters for copper and brass in 1 M HNO$_3$ for C. siliqua at 25–45°C

| Temp. (K) | $K_{ads}$ (g$^{-1}$ l) | $-\Delta G_{ads}$ (kJ mol$^{-1}$) | $-\Delta H_{ads}$ (kJ mol$^{-1}$) | $-\Delta S_{ads}$ (J mol$^{-1}$ K$^{-1}$) |
|-----------|------------------------|---------------------------------|---------------------------------|---------------------------------|
| Copper 298 | 11.91 | 16.1 | 45.4 | 98.3 |
| 303 | 6.37 | 14.8 | 101.0 |
| 308 | 5.12 | 14.5 | 100.4 |
| 313 | 3.87 | 13.9 | 100.4 |
| 318 | 3.65 | 14.0 | 98.6 |
| $\alpha$-Brass 298 | 104.00 | 21.5 | 68.1 | 156.5 |
| 303 | 61.00 | 20.5 | 157.2 |
| 308 | 36.60 | 19.5 | 157.8 |
| 313 | 21.10 | 18.4 | 158.8 |
| 318 | 18.71 | 18.4 | 156.4 |

Figure 4. Adsorption isotherm curves for the adsorption of C. siliqua on copper in 1 M HNO$_3$ at different temperatures.

Figure 5. Log $K$ vs. $(1/T)$ curves for copper and brass dissolution in 1 M HNO$_3$ in the presence of C. siliqua.
\[ K = \frac{1}{55.5} e^{-\frac{\Delta G_{\text{ads}}}{RT}}. \]  

where 55.5 is the concentration of water molecule in (mol L\(^{-1}\)) at metal/solution interface.

**Table 6.** Effect of concentration of C. siliqua on the electrochemical parameters calculated by the potentiodynamic polarization technique for the corrosion of copper and brass in 1 M HNO\(_3\) at 25°C

| Conc. (ppm) | \(i_{\text{corr}}\) (µA cm\(^{-2}\)) | \(-E_{\text{corr}}\) (mV vs SCE) | \(\beta_a\) (mV dec\(^{-1}\)) | \(\beta_c\) (mV dec\(^{-1}\)) | CR (mpy) | \(\theta\) | %IE |
|-------------|---------------------------------|---------------------------------|----------------------------|----------------------------|----------|--------|-----|
| Copper      | 1 M HNO\(_3\)                  |                                 |                            |                            |          |        |     |
| 50          | 125.0                          | 3.79                            | 95.7                       | 212.8                      | 57.25    | 0.670  | 67.0 |
| 100         | 104.0                          | 16.70                           | 94.6                       | 197.7                      | 47.57    | 0.726  | 72.6 |
| 150         | 79.3                           | 8.01                            | 83.6                       | 209.7                      | 36.24    | 0.791  | 79.1 |
| 200         | 68.5                           | 6.96                            | 77.6                       | 207.1                      | 31.28    | 0.819  | 81.9 |
| 250         | 59.9                           | 10.10                           | 78.3                       | 207.0                      | 27.34    | 0.842  | 84.2 |
| 300         | 56.50                          | 21.90                           | 83.0                       | 192.5                      | 25.79    | 0.85   | 85.09|
| α-Brass     | 1 M HNO\(_3\)                  |                                 |                            |                            |          |        |     |
| 50          | 179.0                          | 29.30                           | 86.0                       | 224.1                      | 88.66    | 0.904  | 90.38|
| 100         | 139.0                          | 6.100                           | 71.0                       | 233.1                      | 68.81    | 0.925  | 92.53|
| 150         | 108                            | 11.10                           | 76.7                       | 211.6                      | 53.73    | 0.942  | 94.19|
| 200         | 98.3                           | 55.20                           | 95.7                       | 202.4                      | 48.74    | 0.947  | 94.72|
| 250         | 75.9                           | 37.20                           | 90.7                       | 223.9                      | 37.64    | 0.959  | 95.92|
| 300         | 32.80                          | 24.10                           | 75.1                       | 238.5                      | 16.28    | 0.982  | 98.24|

**Figure 6.** Polarization diagram for the corrosion of copper in 1 M HNO\(_3\) solution without and with various concentrations of C. siliqua at 25°C.

**Figure 7.** Nyquist plots recorded for copper in 1 M HNO\(_3\) without and with various concentrations of C. siliqua at 25°C.

**Figure 8.** Bode plots recorded for copper in 1 M HNO\(_3\) without and with various concentrations of C. siliqua.

**Figure 9.** Electrical equivalent circuit used to fit the impedance data.

All thermodynamic parameters data are listed in Table 5. The negative value of \(\Delta G_{\text{ads}}\) in Table 5 suggested that the adsorption of extract molecules onto copper and brass surface is a spontaneous process. Generally, values of \(\Delta G_{\text{ads}}\) up to \(-20\) kJ mol\(^{-1}\) are consistent with electrostatic interaction between the charged molecules and the charged metal (physical adsorption) while those more negative than \(-40\) kJ mol\(^{-1}\) involve charge sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption). \((27, 28)\)

The heat of adsorption was calculated using the Van’t Hoff equation \((29)\):

\[
\ln K = -\frac{\Delta H_{\text{ads}}}{RT} + \text{const.}
\]  

\((9)\)
Figure 5 shows a plot of log $K$ vs. $1/T$ for copper and brass dissolution in 1 M HNO$_3$ in the presence of $C.$ siliqua. The $\Delta H^o_{ads}$ values (Table 5) are negative, which show that the adsorption is an exothermic process. Finally, the standard adsorption entropy $\Delta S^o_{ads}$ can be calculated by the following equation:

$$\Delta S^o_{ads} = \frac{\Delta H^o_{ads} - \Delta G^o_{ads}}{T}.$$  

(10)

The values of $\Delta S^o_{ads}$ (Table 5) are negative; this means that the adsorption is an exothermic process and this exothermic process always accompanied by a decrease in entropy. The reason could be due to “the adsorption of organic inhibitor molecules from the aqueous solution” (31, 32). Table 5 lists all the above-calculated thermodynamic parameters.

### 3.2. Polarization Curves

Figure 6 shows the polarization diagrams for copper dissolution in 1 M HNO$_3$ with and without different concentrations of $C.$ siliqua at 25°C. Similar curves were obtained for brass (not shown).

The numerical values of the corrosion current density ($i_{corr}$) variation, the potential of corrosion ($E_{corr}$), Tafel slopes ($\beta_a$ and $\beta_c$), the surface coverage degree ($\theta$) and the inhibition efficiency (%IE) with various concentrations of extract for both copper and brass are reported in Table 6. The potentiodynamic curves show that there is an obvious reduction in both anodic and cathodic currents in the presence of extract compared with those of blank solution. It is found that hydrogen evolution and the metal dissolution were inhibited. The cathodic Tafel slope ($\beta_c$) values are found to increase with the added extract. The Tafel slope variation supposes that the investigated extract influences the kinetics of the hydrogen evolution reaction (33). This indicates an increase in the energy barrier, leading to less gas evolution (34). The approximately constant values of $\beta_a$ for extract indicate that components of this extract were first adsorbed onto the copper and brass surface and impeded by merely blocking the reaction sites of the electrode surface without affecting the anodic reaction mechanism (35). The tiny changes in corrosion potential, $E_{corr}$, which indicate that this extract

### Table 7. Electrochemical kinetic parameters obtained from the EIS technique for copper and brass in 1 M HNO$_3$ solution containing various concentrations of $C.$ siliqua at 25°C

| Conc. (ppm) | $R_a$ (Ω cm$^2$) | $C_a$ (µF cm$^{-2}$) | $\theta$ | %IE |
|------------|-----------------|----------------------|-------|-----|
| Copper 1 M HNO$_3$ | 53.51 | 270 | – | – |
| 50 | 307.70 | 196 | 0.826 | 82.6 |
| 100 | 391.60 | 176 | 0.863 | 86.3 |
| 150 | 443.70 | 153 | 0.879 | 87.9 |
| 200 | 474.60 | 137 | 0.887 | 88.7 |
| 250 | 586.20 | 119 | 0.909 | 90.9 |
| 300 | 591.00 | 106 | 0.910 | 91.0 |
| α-Brass 1 M HNO$_3$ | 102.10 | 281 | – | – |
| 50 | 129.00 | 255 | 0.207 | 20.9 |
| 100 | 232.50 | 193 | 0.560 | 56.1 |
| 150 | 359.20 | 158 | 0.715 | 71.6 |
| 200 | 431.10 | 133 | 0.763 | 76.3 |
| 250 | 576.60 | 126 | 0.823 | 82.3 |
| 300 | 1053.00 | 114 | 0.903 | 90.3 |

### Table 8. Electrochemical kinetic parameters obtained by the EFM technique for copper and brass in 1 M HNO$_3$ solution containing different concentrations of $C.$ siliqua at 25°C

| Conc. (ppm) | $i_{corr}$ (µA cm$^{-2}$) | $\beta_a$ (mV dec$^{-1}$) | $\beta_c$ (mV dec$^{-1}$) | CR (mm y$^{-1}$) | CF-2 | CF-3 | $\theta$ | %IE |
|------------|-----------------|-----------------|-----------------|-------------|-----|-----|-------|-----|
| Copper 1 M HNO$_3$ | 291.10 | 57 | 95 | 143.70 | 1.96 | 3.44 | – | – |
| 50 | 89.05 | 82 | 180 | 43.94 | 1.95 | 2.69 | 0.694 | 69.4 |
| 100 | 73.12 | 88 | 160 | 36.08 | 1.77 | 2.80 | 0.749 | 74.9 |
| 150 | 54.98 | 73 | 120 | 27.13 | 1.84 | 2.97 | 0.811 | 81.1 |
| 200 | 52.24 | 88 | 150 | 43.94 | 1.79 | 2.25 | 0.821 | 82.1 |
| 250 | 49.95 | 66 | 126 | 22.13 | 1.95 | 3.08 | 0.846 | 84.6 |
| 300 | 44.85 | 66 | 215 | 98.33 | 1.88 | 2.94 | – | – |
| α-Brass 1 M HNO$_3$ | 199.30 | 63 | 120 | 22.13 | 1.95 | 3.08 | 0.846 | 84.6 |
| 50 | 127.70 | 60 | 104 | 63.02 | 1.90 | 3.09 | 0.359 | 35.9 |
| 100 | 72.33 | 65 | 99 | 35.69 | 1.95 | 2.78 | 0.637 | 63.7 |
| 150 | 57.24 | 74 | 155 | 28.25 | 1.90 | 2.85 | 0.713 | 71.3 |
| 200 | 54.85 | 68 | 127 | 27.07 | 1.90 | 3.12 | 0.725 | 72.5 |
| 250 | 33.75 | 72 | 131 | 16.66 | 2.02 | 3.07 | 0.831 | 83.1 |
| 300 | 10.03 | 42 | 53.4 | 4.95 | 1.86 | 3.30 | 0.950 | 95.0 |
acts as mixed-type but mainly as cathodic inhibitors for copper and brass corrosion in 1 M HNO₃ solution. The orders of inhibition efficiency of this extract at different concentrations as given by polarization measurements are in good agreement with those obtained from weight-loss measurements.

3.3. EIS measurements

The corrosion parameters of copper and brass in nitric acid solution in the absence and presence of different concentrations of *C. siliqua* were also examined by EIS at 25°C after 30 min of immersion (Figures 7 and 8).
EIS spectra of the these compounds were analyzed using the equivalent circuit in Figure 9, where $R_s$ represents the solution resistance, $R_{ct}$ denotes the charge-transfer resistance and a CPE instead of a pure capacitor represents the interfacial capacitance (36).

After analyzing Nyquist plots, it is concluded that the curves approximated by a single capacitive semicircles, showing that the corrosion process was mainly charge-transfer-controlled (37, 38). The general shape of the curves is very similar for all samples (in the presence or in the absence of inhibitors at different immersion times), indicating that no change in the corrosion mechanism (39).

The charge-transfer resistance ($R_t$) values are calculated from the difference in impedance at lower and higher frequencies. The double layer capacitance ($C_{dl}$) and the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) are determined. The impedance parameters derived from these investigations are summarized in Table 7. The results obtained from Table 7 reveal that the presence of the C. siliqua led to decreasing $C_{dl}$ values due to the decrease in the local dielectric constant and/or from the increase in thickness of the electrical double layer. It was suggested that the inhibitor molecules were functioned by adsorption at the metal/solution interface. Thus, the decrease in $C_{dl}$ values and the increase in $R_{ct}$ values and consequently the inhibition efficiency may be reported as the gradual replacement of water molecules by the adsorption of the inhibitor molecules from the metal surface, and by decreasing the extent of dissolution reaction.
3.4. EFM measurements

The result of EFM experiments is a spectrum of current response as a function of frequency. The spectrum is called the “intermodulation spectrum”. Figure 10 shows the corresponding current response in the intermodulation spectrum for copper in 1 M HNO₃ at 25°C, respectively. Electrochemical kinetic parameters calculated from EFM for copper and brass in 1 M HNO₃ are listed in Table 8.

Table 8 shows the corrosion kinetic parameters such as inhibition efficiency (IEEFM%), corrosion current density (µA cm⁻²), Tafel constants (βᵃ, βᶜ) and causality factors (CF-2, CF-3) at different concentration of C. siliqua in 1 M HNO₃ at 25°C. It is obvious from Table 8 that the corrosion current densities decrease by increasing the concentrations of C. siliqua. The inhibition efficiencies increase by increasing CSE concentrations. The causality factors in Table 8 are very close to the theoretical values, which, according to the EFM theory (40, 41), should guarantee
the validity of Tafel slopes and corrosion current densities. Inhibition efficiency ($I_{EFM} \%$) is depicted in Table 8.

It is clear from Table 8 that the corrosion current densities decrease with increase in $C. siliqua$ concentrations. Values of the causality factors in Table 8 indicate that the measured data are of good quality. The standard values for CF-2 and CF-3 are 2.0 and 3.0, respectively. The causality factors are calculated from the frequency spectrum of the current response. If the causality factors differ significantly from the theoretical values of 2.0 and 3.0, then

Figure 14. EDX spectra of brass surface (a) before immersion in 1 M HNO$_3$, (b) after 24 h of immersion in 1 M HNO$_3$ and (c) after 24 h immersion in 1 M HNO$_3$ + 300 ppm $C. siliqua$ at 25°C.
it can be deduced that the measurements are influenced by noise. If the causality factors are approximately equal to the predicted values of 2.0 and 3.0, i.e. there is a causal relationship between the perturbation signal and the response signal. Then the data are assumed to be reliable (42). The great strength of the EFM is the causality factors which serve as an internal check on the validity of the EFM.

### 3.5. Surface Examinations

The SEM image of the surface of copper and brass before immersion in 1 M HNO₃ surface shows the clear polishing lines is almost free from corrosion (Figures 11(a) and 12(a)). Once metals were immersed in 1 M HNO₃, the surface is damaged by acid (Figures 11(b) and 12(b)). But in the case of immersion in 1 M HNO₃ with 300 ppm of *C. siliqua*, the surface is protected and we observed a much lower density of pits at the materials surface compared with the sample in 1 M HNO₃ (Figures 11(c) and 12(c)). EDX spectrum of copper and brass before immersion in 1 M HNO₃ shows a high peak of copper and zinc as shown in Figures 13(a) and 14(a), while in the presence of 1 M HNO₃, the rate of corrosion is increased, and the reduced intensity of copper peak of EDX spectrum (Figures 13(b) and 14(b)) is due to the increase of corrosion products (copper oxides). For the solution containing *C. siliqua* (300 ppm), the EDX spectrum showed an increase again in copper and zinc peak compared with the sample in 1 M HNO₃ (Figures 13(c) and 14(c)) and a carbon peak, which indicate that the inhibitor molecules have adsorbed on the metal surface Table 9, and so the protection of metal surface is confirmed.

### 3.6. Mechanism of corrosion inhibition

Most organic inhibitors contain at least one polar group with an atom of nitrogen or sulfur or in some cases selenium and phosphorus. The inhibiting properties of many compounds are determined by the electron density at the reaction center (43). With an increase in electron density in the center, the chemisorption between the inhibitor and the metal are strengthened (44, 45). The plant extract *C. siliqua* is composed of numerous naturally occurring organic compounds such as protein, carbohydrates, fats and tannins. Accordingly, the inhibitive action of *C. siliqua* could be attributed to the adsorption of its components on the copper and brass surfaces. *C. siliqua* contains phytochemical constituents rich in sugars, condensed tannins and a very low protein content; it has antioxidant properties related to its polyphenolic composition. Most of these phytochemicals are organic compounds having a π-electron center and hetero atoms such as oxygen and nitrogen; hence, the adsorption of these components on the surface of copper and brass is enhanced by their presence. The inhibition efficiency of methanolic extract of *C. siliqua* is due to the formation of multi-molecular layer of adsorption between copper and some of these phytochemicals. Results of the present study have shown that *C. siliqua* inhibits the acid-induced corrosion of copper and brass by virtue of adsorption of its components onto the metal surface. The inhibition process is a function of the metal, inhibitor concentration and temperature as well as inhibitor adsorption abilities, which is so much dependent on the number of adsorption sites. The mode of adsorption (physisorption) observed could be attributed to the fact that *C. siliqua* contains many different chemical compounds, of which some can be adsorbed physically. This observation may derive the fact that adsorbed organic molecules can influence the behavior of electrochemical reactions involved in corrosion processes in several ways. The action of organic inhibitors depends on the type of interactions between the substance and the metallic surface. The interactions can bring about a change either in electrochemical mechanism or in the surface available for the processes (46).

### 4. Conclusions

From the overall experimental results, the following conclusions can be deduced:

1. *C. siliqua* shows a good inhibitive action against the corrosion of copper and brass in 1 M HNO₃.

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### Table 9. Surface composition (weight %) of copper and brass before and after immersion in 1 M HNO₃, without and with 300 ppm of *C. siliqua* at 25°C.

| (Mass %) | Cu | Zn | Si | S  | Fe | Al | Sn | C   |
|----------|----|----|----|----|----|----|----|-----|
| Copper   |    |    |    |    |    |    |    |     |
| Copper alone | 99.6 | –  | 0.4 | –  | –  | –  | –  | –   |
| blank    | 98.9 | –  | 0.5 | 0.3| –  |–   | 0.3| –   |
| blank + 300 ppm CSE | 99.1 | –  | 0.4 | 0.3| –  |–   | 0.3| 0.2 |
| α-Brass  |    |    |    |    |    |    |    |     |
| α-brass alone | 63.4| 34.4| 0.3 | –  | 1.1| –  | 0.8| –   |
| blank    | 62.8| 34.1| –  | 0.5| 0.9| 0.4| 1.3| –   |
| blank + 300 ppm CSE | 63.2| 34.2| –  | –  | 1.2| 0.4| 0.7| 0.3 |
2. The value of inhibition efficiency increases with increasing the inhibitor concentration and decreases with rising the temperature.

3. The adsorption of *C. siliqua* on copper and brass is physical and obeys the Langmuir adsorption isotherm.

4. The negative values of the free energy of adsorption and adsorption heat indicate that the process was spontaneous and exothermic.

5. *C. siliqua* is a good inhibitor and act as mixed-type but mainly as cathodic inhibitors for copper and brass corrosion in 1 M HNO₃ solution.

6. There is good agreement between the data obtained from chemical method and that from electrochemical methods.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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