Assessment of the *Bassia muricata* extract as a green corrosion inhibitor for aluminum in acidic solution

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**ABSTRACT**

The inhibiting behavior of aluminum by the *Bassia muricata* extract was examined in 1.0 M H\(_2\)SO\(_4\) solution as a green corrosion inhibitor via weight loss, potentiodynamic polarization (PP), electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. It was found that the addition of the extract reduces the corrosion rate of aluminum alloy. The inhibition efficiency increases with increasing extract concentration and reached 90% at 300 ppm. The inhibitive effect of the tested extract was discussed in view of adsorption of its components on the aluminum surface. The effect of the temperature on the corrosion behavior with the addition of different concentration of *B. muricata* extract was studied in the temperature range of 298 and 318 K. The *B. muricata* extract adsorption isotherm on the aluminum surface was followed the Temkin adsorption model. The activation and adsorption parameters were computed and discussed. Tafel plots showed that the *B. muricata* extract represented as a mixed type inhibitor. The surface morphology was examined via scanning electron microscopy (SEM) and atomic force microscopy (AFM) which confirmed the existence of a protective film of inhibitor molecule on the aluminum surface. The results revealed that the *B. muricata* extract was an effective inhibitor, and the inhibition efficiencies gained from all applied techniques were in good agreement.

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1. Introduction

Aluminum (Al) is one of the most used metals for abundant industrial and engineering applications as a result of its cost value and excellent functional features. Aluminum has a perfect resistance to petroleum products, and Al/2Mg alloy is applied for tank heating coils in crude-oil carriers (1–4). Al is categorized as the 2nd most widely used metal, after iron. It has several applications and is also used in various alloys. It has been established that to resist high corrosion, this metal is mainly dependent on the presence of an in the artificial film of surface oxide. On the other hand, it was also observed that alkaline solutions play a major role in reducing the oxide film. This is due to the fact that the protective oxide is dissolved by the OH\(^-\) ion and the surface of Al develops a negative potential (5,6). Mineral acids are broadly applied in acid pickling, acid cleaning and oil well acidizing. The study of aluminum corrosion

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phomena is becoming very significant, especially in acidic media because of the more industrial applications of acid solutions. As a result, it’s substantial to order inhibitors for the aluminum corrosion in H₂SO₄ solution. The metal protection versus sulfuric acid corrosion has been the subject. A lot of research was specified to study the corrosion of aluminum and its alloys in various aqueous and acidic solutions via organic and inorganic inhibitors (7,8). Otherwise, acids promote the rate of metal dissolution and are responsible for material failure indirectly. Therefore, inserting a corrosion inhibitor is a significant method in order to reduce metal dissolution in that solution. The majority of familiar acid inhibitors are organic compounds involving nitrogen, sulfur and oxygen, but the largest part of the applied organic inhibitors are toxic, hazard to the environment (9–11). Therefore, it is necessary to advance eco-friendly corrosion inhibitors for aluminum in acidic mediums. Hence, we have selected the plant extracts as eco-friendly inhibitors that may be extracted via simple techniques and the cost is very cheap. The photochemical (involves flavonoids and alkaloids) which represent in the plant extract involves hetero atoms such as N, S, O, aromatic ring and π-electrons, through which they will be adsorbed on the metal surface and mitigate corrosion process (12). Newly, the most of the plant extracts have been confirmed to be good inhibitors for aluminum acidic corrosion (13–15). So they are applied in order to resolve the corrosion problem associated with any environmental problems. Hence, the extract from the leaves, heartwood, bark, seeds, fruits and roots of plants have been investigated to mitigate metallic corrosion in acidic environments (16–20). Medicinal plants were previously used as green corrosion inhibitors of aluminum alloys in different media (21–24).

The present work is another assessment to investigate a cheap and Eco-friendly inhibitor for aluminum in 1.0 M H₂SO₄ via the Bassia muricata extract. Weight loss measurements and electrochemical techniques are used to evaluate the inhibition efficiency of the B. muricata extract. The influence of temperature on the corrosion rates in free and treated acid solutions was also estimated.

2. Experimental procedure

2.1. Sample material composition

The Aluminum sheets were supplied by the Aluminum Company of Nag Hammadi, Egypt, and its chemical composition was (% weight):

| Element | Value |
|---------|-------|
| Al      | 99.555|
| Ti      | 0.007 |
| Zr      | 0.001 |
| V       | 0.007 |
| Na      | 0.001 |
| Ga      | 0.012 |
| Zn      | 0.002 |
| Ni      | 0.008 |
| Cr      | 0.007 |
| Mg      | 0.047 |
| Mn      | 0.250 |
| Fe      | 0.100 |
| Si      |       |

The Aluminum samples were cut from Aluminum sheets and mounted in Teflon. An epoxy resin was utilized to block the space between the electrode and the Teflon. The auxiliary electrode was a platinum wire (1.0 cm²), while a saturated calomel electrode (SCE) joined to a conventional electrolytic cell of capacity 100 ml via a bridge with a Lugging capillary, in order to make the surface of the working electrode very close to reduce the IR drop (ohmic potential drop).

2.2. Solutions

Our applicable acid solution utilized was created via dilution of analytical reagent grade, 90% H₂SO₄ with bidistilled water. The B. muricata extract stock solution (1000 ppm) was produced to provide the required concentrations via dilution with bidistilled water. The B. muricata extract concentrations range was from 50-300 ppm.

2.3. Plant extract preparation

Fresh parts of the B. muricata extract were gathered to produce a fine powder. The collected materials (100 g) were saturated in 500 ml of ethanol for 4 days and then undergo two further extractions until the consumption of plant materials. The produced extract was then concentrated under reduced pressure using a rotary evaporator at a temperature below 50°C. The ethanol evaporated in order to provide a fine solid extract that was produced in support of the application as a green corrosion inhibitor (25).

2.4. Weight loss measurements

Seven equivalent cubic specimens of aluminum with dimensions 2.0 × 2.0 × 0.2 cm³ were used for weight loss measurements. The cleaned and dried specimens were weighed before immersion into the respective test solutions of the B. muricata extract using an analytical balance (GM1502-Sartorius). Tests were conducted with different concentrations of inhibitor. After the immersion period, the specimens were carefully washed with double-distilled water and degreased with AR grade acetone, and then reweighed. Triplicate experiments were performed in each case and the mean values reported (26). The average weight loss of seven equivalent aluminum sheets could be achieved. The surface coverage (θ) and the inhibition efficiency (IE%) of the B. muricata extract for the corrosion of aluminum were computed as follows (27–29):

\[
IE_C^{\%} = \theta \times 100 = [1 - \frac{W}{W^*}] \times 100 \quad (1)
\]
where $W$ and $W'$ are the average weight loss values in the absence and presence of the *B. muricata* extract, respectively.

### 2.5. Electrochemical measurements

Electrochemical measurements were achieved via a perfect three-closet glass cell. It consists of a saturated calomel electrode (SCE) as a reference electrode, a platinum blade (1 cm$^2$) as a counter electrode and aluminum specimen as the working electrode (1 cm$^2$). The reference electrode was joined to a luggin capillary and the tip of the luggin capillary was made very close to the surface of the working electrode to minimize IR drop. All the measurements were applied in open solutions exposed to atmosphere under unstirred conditions. All potential values were recorded versus SCE. Before each experiment, the electrode was scraped with successive various grades of emery paper, cleaned with bidistilled water and degreased with acetone, and finally dried. Tafel plots curves were gained via a variation of the electrode potential automatically from $(-1.0–1.0$ V vs. SCE) at open circuit potential with a scan rate of $1.0$ mV s$^{-1}$. The corrosion current determination is gained by extrapolation of anodic and cathodic Tafel lines to a point which gives ($\log i_{corr}$) and the corresponding corrosion potential ($E_{corr}$) for inhibitor free acid and for each concentration of inhibitor (30–33). Then ($i_{corr}$) was utilized for computing the surface coverage ($\theta$) and the inhibition efficiency ($IE\%$) as in the following equation:

$$IE\% = \theta \times 100 = \left[1 - \frac{i_{corr(inh)}}{i_{corr(free)}}\right] \times 100$$  \hspace{1cm} (2)

where $i_{corr(free)}$ and $i_{corr(inh)}$ are the corrosion current densities in the absence and presence of the *B. muricata* extract, respectively.

Impedance measurements were achieved via the frequency range ($1 \times 10^4$ Hz to $5 \times 10^2$ Hz) with a capacity of 10 mV peak-to-peak by Ac signals at open circuit potential. The experimental impedance was investigated with acetone, and paper, cleaned with bidistilled water and degreased with acetone, and finally dried. Tafel plots curves were gained via a variation of the electrode potential automatically from $(-1.0–1.0$ V vs. SCE) at open circuit potential with a scan rate of $1.0$ mV s$^{-1}$. The corrosion current determination is gained by extrapolation of anodic and cathodic Tafel lines to a point which gives ($\log i_{corr}$) and the corresponding corrosion potential ($E_{corr}$) for inhibitor free acid and for each concentration of inhibitor (30–33). Then ($i_{corr}$) was utilized for computing the surface coverage ($\theta$) and the inhibition efficiency ($IE\%$) as in the following equation:

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Electrochemical frequency modulation (EFM) measurements were achieved via two frequencies 2 and 5 Hz. The base frequency was 0.1 Hz, so the waveform repeats after 1 s. The high peaks were utilized in order to compute the corrosion current density ($i_{corr}$), the Tafel slopes ($\beta_a$ and $\beta_c$) and the causality factors CF-2&CF-3 (34,35). The electrode potential was allocated to stabilize 30 min before starting all measurements. All the tested experiments were proceeding at 25°C.

All electrochemical measurements were achieved via Gamry Instrument (PCI4/750) Potentiostat/Galvanostat/ZRA. This involves a Gamry framework system based on the ESA 400. Gamry applications include DC105 software for potentiodynamic polarization, EIS 300 software for electrochemical impedance spectroscopy, and EFM 140 software for electrochemical frequency modulation measurements via computer for collecting data. Echem Analyst 6.03 software was utilized for plotting, graphing, and fitting data. To examine the reliability and reproducibility of the measurements, duplicate experiments, which achieved in each case at the same conditions.

### 2.6. Surface morphology

#### 2.6.1. Scanning electron microscopy

Investigation of aluminum specimen surface in the absence and presence of the maximum dose of the *B. muricata* extract (300 ppm) which were inundated for 24 h at room temperature were studied via (JEOL JSM-5500, Japan) model.

#### 2.6.2. Atomic force microscopy

AFM had been a positive tool to contact the fine points of corrosion process on the aluminum surface. The area of aluminum specimens was 1 cm $\times$ 1 cm which scraped with emery papers from 220 to 1500 and gave ultrasmooth surfaces. After inundation in 1.0 M $\text{H}_2\text{SO}_4$ immersed in 300 ppm of the *B. muricata* extract at 25°C for 24 h, the specimens were washed with distilled water, dried with a jet of air blaster, and then used for analysis. The a Pico SPM2100 AFM apparatus was utilized for AFM tests.

### 3. Results and discussion

#### 3.1. Weight loss measurements

From the weight loss measurements of aluminum in 1.0 M $\text{H}_2\text{SO}_4$ in the absence and presence of different concentrations of the *B. muricata* extract which are illustrated in Figure 1. The gained inhibition efficiency (IE\%) data are represented in Table 1. From this table, it is noted that the IE\% raises gradually with rising the dose of the *B. muricata* extract and reduce with temperatures
rising from 25 to 45°C. The surface coverage ($\theta$) and the inhibition efficiency (IE%) are computed by Equation (1) and presented in Table 1.

The observed inhibitory effect of the B. muricata extract might be referred to the adsorption of its components on aluminum surfaces. The created layer, of the adsorbed molecules, separates the metal surface from the applicable aggressive medium which limits the dissolution of the aluminum surface by preventing their corrosion sites and so reducing the corrosion rate, with improving efficiency as their doses improved (36).

### 3.2. Adsorption isotherm

The mode and interaction degree between an inhibitor and a metallic surface are commonly applied via the adsorption isotherms. The adsorption of an organic compound happens due to the interaction energy between the inhibitor and a metallic surface is larger than that between the water molecules and a metallic surface (37,38). In order to gain the adsorption isotherms, the surface coverage degree ($\theta$) gained from the weight loss test was located as an inhibitor concentration function. The data of $\theta$ are then graphed to fit the more appropriate adsorption model (39). Efforts are made to fit the gained experimental data to different isotherms such as Frumkin, Langmuir, Temkin and Freundlich isotherms. The best fitted results are obeyed Temkin adsorption isotherm model as presented in Figure 2(a) (40).

$$a/2.303\theta = \log K_{ads} + \log C$$  \hspace{1cm} (4)

The equilibrium constant of adsorption $K_{ads}$ obtained from the intercepts of Temkin adsorption isotherm is related to the free energy of adsorption $\Delta G_{ads}^o$ as follows:

$$K_{ads} = 1/55.5 \exp \left( - \Delta G_{ads}^o / RT \right)$$ \hspace{1cm} (5)

Where 55.5 is the molar concentration of water in the solution in M$^{-1}$. The values obtained are given in Table 2.

### Table 1. Weight loss measurement data for aluminum in 1.0 M H$_2$SO$_4$ solution in the absence and presence of different concentrations of the B. muricata extract at 25°C.

| Conc. (ppm) | C.R. (mg cm$^{-2}$ min$^{-1}$) | % IE | $\theta$ |
|-------------|-------------------------------|------|---------|
| Blank       | 0.7440                        | -    | -       |
| 50          | 0.3330                        | 55.2 | 0.552   |
| 100         | 0.2897                        | 61.1 | 0.611   |
| 150         | 0.2474                        | 66.7 | 0.667   |
| 200         | 0.2117                        | 71.5 | 0.715   |
| 250         | 0.1527                        | 79.5 | 0.795   |
| 300         | 0.1048                        | 85.9 | 0.859   |

Figure 1. Weight loss-time curves for the corrosion of aluminum in 1.0 M H$_2$SO$_4$ in the absence and presence of different concentrations of the B. muricata extract at 25°C.
aluminum surfaces as shown in Figure 2(b). From the intercept of the lines, the enthalpy ($\Delta H_{\text{ads}}^o$) can be determined such as:

$$D_{\text{G}}^{\circ \text{ads}} = D_{\text{H}}^{\circ \text{ads}} - T D_{\text{S}}^{\circ \text{ads}}$$

(6)

The high negative values of $\Delta G_{\text{ads}}^o$ for the inhibitory molecules over the temperature range tested, indicating that the investigated $B. \text{muricata}$ extract spontaneously adsorb on the aluminum surface by strong intermolecular attraction force (41). Furthermore, it is well-established in the literature that the value of $\Delta G_{\text{ads}}^o$ is commonly used to investigate the nature of adsorption. In general, adsorption of an inhibitor with large negative value of $\Delta G_{\text{ads}}^o$ ($\sim -40 \text{ kJ mol}^{-1}$ or more negative) is associated with charge transfer between inhibitor and metal (chemisorption), while one with lower negative value of $\Delta G_{\text{ads}}^o$ ($\sim -20 \text{ kJ mol}^{-1}$ or less negative) might involve electrostatic interaction (physisorption) between charged inhibitor molecules and metallic surface (42,43). In the present study, the values of $\Delta G_{\text{ads}}^o$ vary from $-62.4$ to $-70.2 \text{ kJ mol}^{-1}$, which indicates that the chemisorption mode is possibly to be in the majority (44).

### 3.3. Kinetic-thermodynamic corrosion parameters

Weight loss test is achieved at different temperatures (25–45°C) with different concentrations of the $B. \text{muricata}$ extract. It is found the corrosion rate of Aluminum without the $B. \text{muricata}$ extract raised gently from 25 to 45°C. Whereas; with the $B. \text{muricata}$ extract the corrosion rate reduced slowly. The inhibition efficiency was found to reduce with temperature and presented in Table 1. The corrosion parameter in the absence and presence of the extract in the temperature range of 25–45°C has been illustrated in Table 2. The apparent activation energy ($E_a^*$) for dissolution of Aluminum in 1.0 M H$_2$SO$_4$ was calculated by using the Arrhenius equation:

$$\log k = \frac{-E_a^*}{2.303RT} + \log A$$

(7)

Where $k$ is the corrosion rate, $E_a^*$ is the apparent activation energy is the universal gas constant, $T$ is absolute temperature and $A$ is the Arrhenius pre-exponential factor.

By graphing $\log k$ against $1/T$, the data of the activation energy ($E_a^*$) has been calculated ($E_a^* = (\text{slope}) \times 2.303 \times R$) which is presented in Figure 3. The activation parameters for aluminum dissolution in the absence and presence of different concentrations of the $B. \text{muricata}$ extract in 1.0 M H$_2$SO$_4$ is illustrated in Table 3.

### Table 2. Temkin adsorption isotherm parameters for the $B. \text{muricata}$ extract in 1.0 M H$_2$SO$_4$ at different temperature on aluminum surfaces.

| Temp. (K) | $\log K_{\text{ads}}$ (M$^{-1}$) | $-\Delta G_{\text{ads}}^o$ (kJ mol$^{-1}$) | $\Delta H_{\text{ads}}^o$ (kJ mol$^{-1}$) | $\Delta S_{\text{ads}}^o$ (J mol$^{-1}$ K$^{-1}$) |
|-----------|-------------------------------|---------------------------------|-----------------|-----------------|
| 298       | 78                            | 70.2                            | 29.8            | 33.6            |
| 303       | 68                            | 67.6                            | 32.2            | 33.6            |
| 308       | 65                            | 65.1                            | 30.8            | 32.2            |
| 313       | 60                            | 63.8                            | 29.9            | 30.8            |
| 318       | 52                            | 62.4                            | 29.0            | 29.9            |

### Table 3. Activation parameters for aluminum dissolution in the absence and presence of different concentrations of the $B. \text{muricata}$ extract in 1.0 M H$_2$SO$_4$.

| Conc. (ppm) | $E_a^*$ (kJ mol$^{-1}$) | $\Delta H^*$ (kJ mol$^{-1}$) | $-\Delta S^*$ (J mol$^{-1}$ K$^{-1}$) |
|-------------|------------------------|-----------------------------|-----------------------------------|
| Blank       | 60.8                   | 57.9                        | 83.5                              |
| 50          | 69.8                   | 71.0                        | 80.7                              |
| 100         | 70.9                   | 72.2                        | 59.9                              |
| 150         | 72.2                   | 71.9                        | 61.1                              |
| 200         | 74.5                   | 69.9                        | 58.8                              |
| 250         | 74.8                   | 72.8                        | 57.9                              |
| 300         | 77.1                   | 74.1                        | 58.2                              |
energy for the reaction of aluminum in 1.0 M H₂SO₄ rises in the presence of extract recorded in Table 3. This rising in activation energy \( E^* \) is a sign of the creation of chemical bonds were strengthened via raising the temperature. On the other hand, the magnitude of the growth rate in the inhibited solution is larger than that in the free acid solution. As a result, the inhibition efficiency (IE\%) of the \( B. \ muricata \) extract reduces clearance with rising temperature. This data assists the idea that the extract component adsorption on the Aluminum surfaces may be a chemical adsorption process. Therefore, as the temperature raises the number of adsorbed molecules raised, which leads to an increase in the inhibition efficiency (IE\%). The gained results suggest that the \( B. \ muricata \) extract reduces the corrosion reaction by rising its activation energy via the adsorption on the Aluminum surfaces, making a block of mass and charge transfer. But, such types of inhibitors achieve a good inhibition at high temperature with a major increase in inhibition efficiency at higher temperatures (45). Furthermore, the comparatively higher values of activation energy in the presence of the \( B. \ muricata \) extract propose a chemical adsorption process.

The change of entropy (\( \Delta S^* \)) and change of enthalpy (\( \Delta H^* \)) data can be computed via the following equation:

\[
k = \left( \frac{RT}{Nh} \right) \exp \left( \frac{\Delta S^*}{R} \right) \exp \left( \frac{\Delta H^*}{RT} \right)
\]

Where \( k \) is the corrosion rate, \( h \) is Planck’s constant, \( N \) is Avogadro number, \( \Delta S^* \) is the entropy of activation, and \( \Delta H^* \) is the enthalpy of activation. A graph of \( \log (k/T) \) vs. \( 1/T \) which is presented in Figure 4 should give a straight line, with a slope of \( (\Delta H^*/2.303R) \) and an intercept of \( (\log (R/Nh) + \Delta S^*/2.303) \), from which the \( \Delta S^* \) and \( \Delta H^* \) data can be calculated and presented in Table 3. The negative value of \( \Delta S^* \) of the inhibitor point to an activated complex in the rate determining step performs an association rather than a dissociation step, meaning that a reduction in disorder occurs through the transition from reactant to the activated complex (46). The negative sign of \( \Delta H^* \) point to the adsorption of inhibitor molecules is an exothermic process. In general, an exothermic process is referring to either physisorption, chemisorption or both.

### 3.4. Open circuit potential tests

The deviation of the open potential circuit (OCP) of aluminum with time in absence and presence of various doses from extract was followed until achievement of steady states (Figure 5). The figure displays a common trend in OCP. The OCP values first increased into the positive direction of potential, followed by semi-stabilization characterized by a small change in potential. This trend indicates that the corrosion reaction quickly starts off as the sample is immersed in the electrolyte and slows down with time, and then reaches a quasi-steady state within the time interval investigated; the shift to less negative values implies increased corrosion. The plateau OCP increased to more positive values with an increase in extract dose in the electrolyte.
This is indicative of adsorption of the *B. muricata* extract on the aluminum surface which in turn influenced anodic corrosion reaction. As reported before (47), it is practical to categorize corrosion inhibitors as cathodic or anodic if OCP in the existence of the inhibitor changes at least +85 or −85 mV, correspondingly, relative to OCP in the absence of the inhibitor. Nevertheless, the positive and the negative move to OCP in the maximum calculated

![Figure 4](image_url)

**Figure 4.** Aluminum corrosion rates ($k_{corr}/T$) obtained from Transition-state in 1.0 M H$_2$SO$_4$ in the absence and presence of different concentrations of the *B. muricata* extract.

![Figure 5](image_url)

**Figure 5.** Time-potential diagrams for aluminum in 1.0 M H$_2$SO$_4$ in the absence and presence of various doses of the *B. muricata* extract at 25°C.
dose (300 ppm) of the extract in 1.0 M H₂SO₄ is about 24 mV relative to its blank solution. This value is lesser than 85 mV which led to that the extract function as a mixed-kind corrosion inhibitor, that is, both dissolutions of aluminum at the anode and the hydrogen evolution (HE) at the cathode were occurred by the extract.

3.5. Polarization curves

Figure 6 illustrates the potentiodynamic polarization plot recorded for aluminum in 1.0 M H₂SO₄ solution in the absence and presence of various concentrations of the *B. muricata* extract at 25°C. The presence of the *B. muricata* extract alternates both anodic and cathodic areas to the lower values of corrosion current densities and as a result causes a significant reduction in the corrosion rate. The parameters gained from the polarization plots in Figure 6 are shown in Table 4. The Tafel slopes ($\beta_a$ and $\beta_c$) at 25°C do not change extremely upon increment of the *B. muricata* extract, which points to the presence of the *B. muricata* extract does not change the mechanism of hydrogen evolution and the metal dissolution process. In general, an inhibitor shall be classified as a cathodic type, if the shift of corrosion potential in the presence of the inhibitor is higher than 85 mV with respect to that in the absence of the inhibitor (48,49). In the presence of the *B. muricata* extract, $E_{corr}$ shifts to less negative, but this shift is very small (about 20–30 mV), which point to the *B. muricata* extract can be approved as a cathodic inhibitor.

3.6. Electrochemical impedance spectroscopy

The corrosion of aluminum in 1.0 M H₂SO₄ solution in the absence and presence of different concentrations of the *B. muricata* extract was investigated by EIS method at 25°C.

Table 4. Potentiodynamic polarization parameters of aluminum in 1.0 M H₂SO₄ in the absence and presence of different concentrations of the *B. muricata* extract at 25°C.

| Conc. (ppm) | $-E_{corr}$ (mv vs. SCE) | $i_{corr}$ (µA cm⁻²) | $\beta_a$ (mV dec⁻¹) | $\beta_c$ (mV dec⁻¹) | C.R Mpy | % IE | Θ |
|-------------|--------------------------|-----------------------|----------------------|----------------------|---------|-----|---|
| Blank       | 8                        | 897                   | 62                   | 202                  | 407.7   | –   | – |
| 50          | 14                       | 598                   | 55                   | 232                  | 271.8   | 33.3| 0.333 |
| 100         | 17                       | 224                   | 51                   | 219                  | 101.8   | 75.0| 0.750 |
| 150         | 24                       | 158                   | 48                   | 179                  | 71.8    | 82.4| 0.824 |
| 200         | 31                       | 96.0                  | 36                   | 175                  | 43.6    | 89.3| 0.893 |
| 250         | 37                       | 81.5                  | 30                   | 188                  | 37.3    | 90.9| 0.909 |
| 300         | 45                       | 74.3                  | 32                   | 191                  | 33.6    | 91.7| 0.917 |
C. Impedance parameters, such as, charge transfer resistance $R_{ct}$, which is equivalent to $R_p$, and the double layer capacitance $C_{dl}$ are derived from the Nyquist plot (Figure 7) and are given in Table 5 for aluminum in 1.0 M H$_2$SO$_4$ acid solution in the presence and absence of the extract. It is observed that the values of $R_{ct}$ increase with increasing the concentration of the extract and this in turn leads to a decrease in corrosion rate of aluminum in 1.0 M H$_2$SO$_4$ acid solution. Impedance diagram has a semicircular appearance; the diagram indicates that the corrosion of aluminum is mainly controlled by a charge transfer process (50,51). The values of double layer capacitance, $C_{dl}$, decrease with increasing the concentration of the B. muricata extract. A low capacitance may result if water molecules at the electrode interface are replaced by inhibitor molecules of lower dielectric constant through adsorption. When such low capacitance values in connection with high $R_{ct}$ values, it is apparent that a relationship exists between adsorption and inhibition (52,53).

The impedance data of aluminum in 1.0 M H$_2$SO$_4$ are analyzed in terms of an equivalent circuit model shown in Figure 8, which includes the double layer capacitance $C_{dl}$ which is placed in parallel to the charge transfer resistance $R_{ct}$, due to the charge transfer reaction (54). $C_{dl}$ can be calculated from the angular frequency ($\omega = 2\pi f$) at the maximum imaginary component and the charge transfer resistance according to the following equation:

$$C_{dl} = \left[ \frac{1}{\omega_{max} f_p} \right] = \left[ \frac{1}{2\pi f_{max} R_p} \right]$$  \hspace{1cm} (9)$$

where $f$ is maximum frequency, $\omega$ is the angular velocity.

The Bode plot for the aluminum is shown in Figure 9 where the high-frequency limit corresponds to electrolyte resistance $R_Ω$, while the low-frequency limit represents the sum of $(R_Ω + R_p)$, where $R_p$ is the first approximation determined by both the electrolytic conductance of the oxide film and polarization resistance of the dissolution and passivation process (55). The data obtained showed that the values of $R_{ct}$ increase and the values of $C_{dl}$ decrease with increasing the concentration of the investigated organic compounds which accompanied with increasing % IE, due to the adsorption of these molecules on the electrode surface leading to a
film formation on the metal surface. The obtained Nyquist impedance diagram in most cases does not show perfect semicircle. This may be attributed to the frequency dispersion because of the heterogeneity of the electrode surface. In 1.0 M H₂SO₄ and in the presence of different concentrations of the investigated B. muricata extract; the impedance diagram showed the same trend. However, the diameters of the capacitive loop increase with increasing concentrations of investigated B. muricata extract.

The major parameters produced from the Nyquist diagram analysis are:

The charge transfer resistance $R_{ct}$ (diameter of the high-frequency loop)

The double layer capacitance $C_{dl}$ which is realized as:

$$C_{dl} = \frac{1}{2\pi R_{ct} f_{max}}$$

(10)

Where $f_{max}$ is the upper frequency at which the $Z_{imag}$ of the impedance became larger. Since the electrochemical theory supposed that $(1/R_{ct})$ is directly proportional to the double layer capacitance $C_{dl}$, the inhibition efficiency (%IE) of the inhibitor for Aluminum in 1.0 M H₂SO₄ solution was calculated from $R_{ct}$ values gained from impedance data at different concentration of extract via the following equation:

$$%IE = \left(1 - \frac{R_{ct}}{R_{ct}^0}\right) \times 100$$

(11)

Where $R_{ct}^0$ and $R_{ct}$ are the charge transfer resistance in the absence and presence of the examined extract, respectively.

From the impedance data shown in Table 5, we can deduce that the $R_{ct}$ values rise with the rising in the concentration of the examined extract and this refers to the creation of a protective film on the aluminum surface via the adsorption and an improvement in the corrosion inhibition efficiency in applicable solution. Although the $C_{dl}$ values reduce with rising the concentrations of extract in comparison with that of blank solution.

Figure 8. A parallel circuit for modeling impedance data for aluminum in 1.0 M H₂SO₄.

Figure 9. Bode plot for aluminum in 1.0 M H₂SO₄ in the absence and presence of the different B. muricata extract concentrations at 25°C.
(uninhibited). Therefore, the replacement of water molecules by inhibitor molecules leads to a reduction in local dielectric constant and/or an increase in the thickness of the electric double layer formed on the metal surface \((56, 57)\).

3.7. Electrochemical frequency modulation

EFM is a nondestructive corrosion test that can directly verify the corrosion current value without earlier knowledge of Tafel curves, and only with a low polarizing signal. These features of the EFM test make it a perfect application for online corrosion monitoring \((58)\).

The large strength of the EFM is the causality factors which give an internal check on the validity of EFM measurement. The causality factors CF-2 and CF-3 are computed from the frequency spectrum of the current responses. Figure 10 illustrates the frequency spectrum of the current response of pure Aluminum in 1.0 M H\(_2\)SO\(_4\) solution, involves not only the input frequencies, but also the frequency components which are the total, difference and multiples of the two input frequencies. The EFM inter-modulation spectrums of Al in 1.0 M H\(_2\)SO\(_4\) solution involving (50–300 ppm) of the \(B.\ muricata\) extract at 25°C is illustrated in Figure 10. The harmonic and inter-modulation peaks are obviously visible and are much higher than the background noise. The two large peaks, with an amplitude of about 200 µA, or the response to the 40 and 100 mHz (2 and 5 Hz) excitation frequencies. It is essential to remind that there is nearly no current response between the peaks (<100 mA). The gained EFM data were treated via two different models: complete

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**Figure 10.** Inter-modulation plots for the corrosion of Aluminum in 1.0 M H\(_2\)SO\(_4\) in the absence and presence of different concentrations of the \(B.\ muricata\) extract at 25°C.
diffusion control of the cathodic reaction and the “activation” model. For the latter, a set of three non-linear equations had been solved, supposing that the corrosion potential doesn’t change due to the working electrode polarization (59). The higher peaks are used to compute the corrosion current density ($i_{corr}$), the Tafel slopes ($\beta_{c}$ and $\beta_{a}$) and the causality factors (CF-2 and CF-3). At once, these electrochemical parameters are specified by Gary EFM140 software, and demonstrated in Table 6 signifying that this extract block the corrosion of Aluminum in 1.0 M H2SO4 through adsorption. The causal factors gained under different experimental conditions are approximately equivalent to the theoretical values (2 and 3) signifying that the gained data are verified a good quality (60). The inhibition efficiencies (IE%) raised by raising the examined extract concentrations and was calculated by the following equation:

$$\text{IE} \% = \left( 1 - \frac{i_{corr}}{i_{corr}^{\Theta}} \right) \times 100$$

(12)

Where $i_{corr}^{\Theta}$ and $i_{corr}$ are corrosion current densities in the absence and presence of the $B$. muricata extract, respectively.

3.8. Surface analysis by scanning electron microscopy

Figure 11 illustrates a SEM micrographs recorded for Polished aluminum samples (A) and exposed for 24 h in 1.0 M H2SO4 solution without extract (B) and treated with 300 ppm of the $B$. muricata extract (C) at 25°C. A micrograph of the polished aluminum surface before inundation in 1.0 M H2SO4 solution is illustrated in (Figure 10(A)). The photograph illustrates the surface is smooth and without any pits. The SEM micrographs of the corroded aluminum in the presence of 1.0 M H2SO4 solution are illustrated in (Figure 10(B)). The visual seen of these micrographs are a result of pits created owing to the contact of aluminum to the acid medium. Impact of the inhibitor addition 300 ppm on the aluminum in 1.0 M H2SO4 solution is illustrated in (Figure 10 (C)). The morphology in (Figure 10(C)) observes a coarse surface, characterization of regular corrosion of aluminum in acid, as reported previously (61,62). The corrosion doesn’t take place in the existence of the extract and therefore corrosion was blocked strongly when the extract molecules are present in the sulfuric acid medium, and the surface layer is very coarse. On the other hand, in the existence of 300 ppm of the $B$. muricata extract, there is much less damage on the aluminum surface, which advanced the inhibitory action. Furthermore, there is an adsorbed film which is created on aluminum surface presented in Figure 10(C). Finally, it might be deduced that the adsorbed film can mitigate the corrosion of Aluminum efficiently.

3.9. Surface analysis by atomic force microscopy

Atomic force microscopy technique is very significant to confirm the efficiency of the extract on the

Table 6. EFM electrochemical kinetic parameters for Aluminum in 1.0 M H2SO4 in the absence and presence of different concentrations of the $B$. muricata extract at 25°C.

| Conc. (ppm) | $i_{corr}$ (µA) | $\beta_{c}$ (mV dec$^{-1}$) | $\beta_{a}$ (mV dec$^{-1}$) | CF-2 | CF-3 | %IE | $\Theta$ |
|------------|----------------|-----------------|-----------------|------|------|-----|-----|
| 1.0 M H2SO4| 31.6           | 119             | 138             | 2.1  | 3.2  | –   | –   |
| 50         | 7.2            | 102             | 121             | 1.8  | 2.8  | 77.2| 0.772|
| 100        | 5.3            | 79              | 79              | 1.9  | 3.1  | 83.2| 0.832|
| 150        | 4.8            | 89              | 96              | 1.8  | 3.2  | 84.8| 0.848|
| 200        | 4.5            | 68              | 82              | 1.9  | 2.9  | 85.8| 0.858|
| 250        | 3.9            | 59              | 71              | 1.7  | 2.8  | 87.7| 0.877|
| 300        | 3.2            | 62              | 65              | 1.8  | 3.1  | 89.8| 0.898|

Figure 11. SEM micrographs of aluminum surface (A) before of inundation in 1.0 M H2SO4, (B) after 24 h of inundation in 1.0 M H2SO4 and (C) after 24 h of inundation in 1.0 M H2SO4 + 300 ppm of the $B$. muricata extract at 25°C.
corrosion of Aluminum. The AFM technique gives roughness data for different surfaces which make this powerful method. The images produced by this method could be used to differentiate between several Aluminum surfaces easily (63,64). The 3D images for furbished Aluminum surface (standard specimen), Aluminum immersed in 1.0 M H₂SO₄ containing 300 ppm from the investigating B. muricata extract were shown in (Figure 12). Roughness data for different Aluminum surfaces are listed in the following (Table 7). The roughness data give clear indication that the Aluminum surface appears smoother owing to the inhibitor adsorption on the Aluminum and forming the protective layer (65).

### 3.10. Mechanism of the corrosion inhibition

The adsorption features of plant extract molecules can be qualified via two major interactions: physisorption or chemisorptions or both of them. Generally, physisorption needs the existence of both, the electrically charged metal surfaces and charged species in medium. The metal surface charge is owing to the

| Specimen | Average roughness (Sₐ) (nm) |
|----------|-----------------------------|
| (A)      | 33.2                        |
| (B)      | 433.5                       |
| (C)      | 62.4                        |

Table 7. AFM roughness data of aluminum surface immersed for 24 h at 25°C.

Figure 12. Three-dimensional (3D) AFM micrographs of aluminum surface (A) before of inundation in 1.0 M H₂SO₄, (B) after 24 h of inundation in 1.0 M H₂SO₄ and (C) after 24 h of inundation in 1.0 M H₂SO₄ + 300 ppm of the B. muricata extract at 25°C.
electric field presenting at the metal/solution interface. In contrast, chemisorption process needs charge sharing or charge transfer from the inhibitor molecules to the metal surface to create a co-ordination bond. This is probable in the case of a positive as well as a negative charge on the surface. The existence of a transition metal, involving vacant, low-energy electron orbital’s (Al\(^{+}\) and Al\(^{3+}\)) and an inhibitor with molecules having comparatively loosely bound electrons or heteroatoms’s with a lone pair of electrons are essential for the inhibiting achievement (66). In general, two types of mechanisms of inhibition are suggested, one was the electrostatic attraction between charged molecules and charged metal and the other was the co-ordination of the unshared pairs of electrons on the different molecules involved in the \(B.\ muricata\) extract to the metal atom, and the \(\pi\)-electrons of the extract molecules play an important role on the co-ordination process and adsorption process (67–69).

The inhibition efficiency is clearly dependent upon the power of adsorption and is influenced by the number of adsorption sites, charge density, molecular size, the interaction mode with the metal surface and the formation extent of metallic complexes (70). Finally, the investigated molecules form the \(B.\ muricata\) extract may be adsorbed on Aluminum surface. While, it is well known that the Al surface is negatively charged in acid medium (71,72), thus, it is easier for the donor molecules to move toward the negatively charged Al surface via the electrostatic attraction. In case of adsorption, this involve the substitution of water molecules from the Al surface and sharing electrons between the hetero-atoms and Al. Also, the inhibitor molecules can adsorb on Al surface on the basis of donor-acceptor interactions between \(\pi\)-electrons of aromatic rings and vacant p-orbitals of Aluminum atoms. Therefore, we can deduce that the inhibition of Al corrosion in H\(_2\)SO\(_4\) is largely due to electrostatic interaction. As a result, the \(B.\ muricata\) extract favored blocking both anodic and cathodic corrosion processes at higher temperatures as illustrated in (Figure 13).

**Figure 13.** Potential adsorption process of one protonated compound from the \(B.\ muricata\) extract on Aluminum in 1.0 M H\(_2\)SO\(_4\).

**Figure 14.** Comparison of inhibition efficiency (IE\%) resulted from experimental methods for corrosion of aluminum in 1.0 M H\(_2\)SO\(_4\) involving 300 ppm of the \(B.\ muricata\) extract at 25°C.
4. Conclusion

From the above gained experimental data, we are derived:

1. The *B. muricata* extract illustrates a good achievement as eco-friendly inhibitor for dissolution of aluminum in 1.0 M H$_2$SO$_4$. 

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**Scheme 1.** Schematic representation of the *B. muricata* leaves extract.

**Scheme 2.** Chemical structure of selected main compounds in the *B. muricata* leaves extract.

| Compounds | Molecular weight | Active center | Chemical formula |
|-----------|-----------------|---------------|-----------------|
| ![Chemical structure 1](image1) | 790.88 g/mol | 13O | C$_{42}$H$_{68}$O$_{13}$ |
| ![Chemical structure 2](image2) | 580.5 g/mol | 15O | C$_{25}$H$_{28}$O$_{15}$ |
| ![Chemical structure 3](image3) | 592.55 g/mol | 14O | C$_{25}$H$_{32}$O$_{14}$ |
(2) The results gained from weight loss method demonstrated that the inhibiting action improved with the improvement of the B. muricata extract concentrations and reduces with the rising in temperatures.

(3) Double layer capacitances reduce related to blank solution when the plant extract is added. This fact approved the adsorption of plant extract molecules on the aluminum surface.

(4) The B. muricata extract blocks the corrosion process by creating an adsorbed film on the aluminum surface which following Temkin adsorption isotherm.

(5) The inhibition efficiency estimated by weight loss, potentiodynamic polarization, EIS and EFM techniques are raised by rising The B. muricata extract concentrations and in a good agreement with gained from weight loss method (Figure 14).

Disclosure statement
No potential conflict of interest was reported by the authors.

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References
[1] Khadraoui, A.; Khelf, A.; Hachama, K.; Mehdaoui, R. Thymus Algeriensis Extract as a new eco-Friendly Corrosion Inhibitor for 2024 Aluminium Alloy in 1M HCl Medium. J. Mol. Liq. 2016, 214, 293–297. doi:10.1016/j.molliq.2015.12.064.
[2] Demian, I.N.; Ukaga, I; Ikenna, O.B.; Oguzie, E.E.; Oguzie, K.L.; Ibi, N. Natural Products for Materials Protection: Corrosion Protection of Aluminium in Hydrochloric Acid by Kola Nitida Extract. J. Mol. Liq. 2016, 219, 417–424. doi:10.1016/j.molliq.2016.03.049.
[3] Chaubey, N.; Singh, V.K.; Quraishi, M.A. Papaya Peel Extract as Potential Corrosion Inhibitor for Aluminium Alloy in 1 M HCl: Electrochemical and Quantum Chemical Study. Ain Shams Eng. J. (ASEJ). 2018, 9 (4), 1131–1140. doi:10.1016/j.asej.2016.04.010.
[4] Nathiya, R.S.; Vairamuthu, R. Evaluation of Dryopteris Cochleata Leaf Extracts as Green Inhibitor for Corrosion of Aluminium in 1 M H2SO4. Egypt. J. Petrol. 2017, 26, 313–323. doi:10.1016/j.ejpe.2016.05.002.
[5] Abiola, O.K.; Otaigbe, J.O.E. Effect of Common Water Contaminants on the Corrosion of Aluminium Alloys in Ethylene Glycol–Water Solution. Corros. Sci. 2008, 50, 242–247. doi:10.1016/j.corsci.2007.06.013.
[6] Yazdзад, A.R.; Shahrabi, T.; Hosseini, M.G. Inhibition of 3003 Al Alloy Corrosion by Propargyl Alcohol and Tartrate Ion and Their Synergistic Effects in 0.5% NaCl Solution. Mater. Chem. Phys. 2008, 109, 199–205. doi:10.1016/j.matchemphys.2007.11.012.
[7] Awad, M.K.; Metwally, M.S.; Soliman, S.A.; El-Zomrawy, A.A.; Bedair, M.A. Experimental and Quantum Chemical Studies of the Effect of Poly Ethylene Glycol as Corrosion Inhibitors of Aluminium Surface. J. Ind. Eng. Chem. 2014, 20, 796–808. doi:10.1016/j.jiec.2013.06.009.
[8] Ehsani, A.; Nasrollahzadeh, M.; Mahjani, M.G.; Moshtrefi, R.; Mostaanzadeh, H. Electrochemical and Quantum Chemical Investigation of Inhibitory of 1,4-Ph(OX)2(Ts)2 on Corrosion of 1005 Aluminum Alloy in Acidic Medium. J. Ind. Eng. Chem. 2014, 20, 4363–4370. doi:10.1016/j.jiec.2014.01.045.
[9] Chaubey, N.; Savita; Singh, V.K.; Quraishi, M.A. Corrosion Inhibition Performance of Different Bark Extracts on Aluminium in Alkaline Solution. J. Assoc. Arab Univ. Basic Appl. Sci. 2017, 22, 38–44. doi:10.1016/j.jaubas.2015.12.003.
[10] Deyab, M.A. Corrosion Inhibition of Aluminum in Biodiesel by Ethanol Extracts of Rosemary Leaves. J. Taiwan Inst. Chem. Eng. 2016, 58, 536–541. doi:10.1016/j.jctie.2015.06.021.
[11] Singh, A.; Ahamad, I.; Quraishi, M.A. Piper Longumextract as Green Corrosion Inhibitor for Aluminium in NaOH Solution. Arab. J. Chem. 2016, 9, S1584–S1589. doi:10.1016/j.arabjc.2012.04.029.
[12] Ummore, S.A.; Obot, I.B.; Israel, A.U.; Asuquo, P.O.; Solomon, M.M.; Eduok, U.M.; Udoh, A.P. Inhibition of Mild Steel Corrosion in Acidic Medium Using Coconut Coir Dust Extracted From Water and Methanol as Solvents. J. Ind. Eng. Chem. 2014, 20, 3612–3622. doi:10.1016/j.jiec.2013.12.056.
[13] Deng, S.; Li, X. Inhibition by Jasminum Nudiflorum Lindl. Leaves Extract of the Corrosion of Aluminium in HCI Solution. Corros. Sci. 2012, 64, 253–262.
[14] Abd-El-Nab, B.A.; Abdullahaf, O.A.; El-Kshlan, H.M.; Khamis, E.; Abd-El-Fatah, M.A. Effect of Alkaline Etching on the Inhibition of the Acidic Corrosion of Aluminium by Lajpurn Extract. Port. Electrochim. Acta 2015, 33, 1–11. doi:10.4152/pea.201501001.
[15] Jain, T.; Chowdhary, R.; Mathur, S.P. Electrochemical Behavior of Aluminum in Acidic Media. *Mater. Corros.* **2006**, *57*, 422–426. doi:10.1002/maco.200503913.

[16] Njoku, D.I.; Onuoha, G.N.; Oguzie, E.E.; Oguzie, K.L.; Egbedina, A.A.; Alshawabkeh, A.N. *Nicotiana Tabacum* Leaf Extract Protects Aluminium Alloy AA3003 From Acid Attack. *Arab. J. Chem.* in press, doi:10.1016/j.arabjc.2016.07.017.

[17] Chaubey, N.; Yadav, D.K.; Singh, V.K.; Quraishi, M.A. A Comparative Study of Leaves Extracts for Corrosion Inhibition Effect on Aluminium Alloy in Alkaline Medium. *Ain Shams Eng. J.* **2017**, *8*, 673–682. doi:10.1016/j.asej.2015.08.020.

[18] Al-Moubarak, A.H.; Al-Howiti, A.A.; Al-Dailami, M.M.; Enas, A. The A-Ghalmi role of Aqueous Extract of Celery (*Apium Gravoleons*) Leaves Against the Corrosion of Aluminium/Sodium Hydroxide Systems. *J. Environ. Chem. Eng.* **2017**, *5*, 4149–4205. doi:10.1016/j.jece.2017.08.015.

[19] Mary Anbarasi, C.; Divya, G. A Green Approach to Corrosion Inhibition of Aluminium in Acid Medium Using *Azwain* Seed Extract. *Mater. Today Proc.* **2017**, *4*, 5190–5200.

[20] Xhanari, K.; Fingsar, M.Z.; Hrncli, M.K.; Mauer, U. Zeljko Knez and Bujar Seitz Green Corrosion Inhibitors for Aluminium and its Alloys: a Review. *RSC Adv.* **2017**, *7*, 27299–27330. doi:10.1039/C7RA03944A.

[21] Ebenso, E.E. Synergistic Effect of Halide ions in the Corrosion Inhibition of Aluminium in H2SO4 Using 2-Acetylphenophiazine. *Mater. Chem. Phys.* **2003**, *79*, 58–70. doi:10.1016/S0254-0584(02)00446-7.

[22] Okafor, P.C.; Osabor, V.I.; Ebenso, E.E. Eco-friendly Corrosion Inhibitors: Inhibitive Action of Ethanol Extracts of *Garcinia Kola* for the Corrosion of Mild Steel in H2SO4 Solutions. *Pigment Resin Tech.* **2007**, *36*, 299–305. doi:10.1108/03699420710820414.

[23] Vem, D.K.; Fahmida, K.; Bahadur, I.; Salman, M.; Quraishi, M.A.; Verma, C.; Ebenso, E.E. Inhibition Performance of *Glycine max*, *Cuscuta Re* max, and *Spirogyra* Extracts for *Ananas Sativum* as Green Corrosion Inhibitor for Aluminium in Hydrochloric Acid Solutions. *Green Chem. Lett. Rev.* **2010**, *3*, 61–68. doi:10.1080/175182090350253.

[24] Unarvez, L.; Cano, E.; Bastidas, D.M. 3-Hydroxybenzoic Acid as AISI 316L Stainless Steel Corrosion Inhibitor in a H2SO4 Solution. *J. Appl. Electrochem.* **2005**, *35*, 499–506. doi:10.1007/s10800-005-0291-1.

[25] Shaker, K.H.; Al Jubiri, S.M.; El-hady, F.K.A.; Al-Sehemi, A.G. New Compounds From Bassia Muricata and Fagonia Indica. Int. J. Pharm. Sci. Res. Rev. **2013**, *23*, 231–236.

[26] ASTM G1-03(2017)e1 *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens*; ASTM International: West Conshohocken, PA, 2017.

[27] Prabhu, R.A.; Venkatesha, T.V.; Shanbhag, A.V. Carmine and Fast Green as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution. *J. Iran. Chem. Soc.* **2009**, *6*, 353–363.

[28] Fouda, A.E.; Ahmed, A.; Emad, E. Thiozole Derivatives as Corrosion Inhibitors for C-Steel in Sulphuric Acid Solution. *Eur. J. Chem.* **2010**, *1*, 312–318. doi:10.5155/eurjchem.1.4.312.318.105.

[29] Fouda, A.S.; Shalabi, K.; Idress, A.A. Thymus Vulgarise Extract as Nontoxic Corrosion Inhibitor for Copper and α-Brass in 1 M HNO3 Solutions. *Int. J. Electrochem. Sci.* **2014**, *9*, 5126–5154.

[30] Fouda, A.E.-A.S.; El-Katori, E.E.; Al-Mhyawi, S. Methanol Extract of Slanum Nigrum as Eco-Friendly Corrosion Inhibitor for Zinc in Sodium Chloride Polluted Solutions. *Int. J. Electrochem. Sci.* **2017**, *12*, 9104–9120. doi:10.20964/2017.10.64.

[31] Mu, G.N.; Zhao, T.P.; Liu, M.; Gu, T. Effect of Metallic Cations on Corrosion Inhibition of an Anionic Surfactant for Mild Steel. *Corrosion* **1996**, *52*, 853–856. doi:10.5006/1.3292077.

[32] Parr, R.G.; Donnelly, R.A.; Levy, M.; Palke, W.E. Electronegativity: The Density Functional Viewpoint. *J. Chem. Phys.* **1978**, *68*, 3801–3807. doi:10.1063/1.436185.

[33] Bentiss, F.; Traisnel, M.; Lagrenee, M. The Substituted 1,3,4-Oxadiazoles: a new Class of Corrosion Inhibitors of Mild Steel in Acidic Media. *Corros. Sci.* **2000**, *42*, 127–146. doi:10.1016/S0010-938X(99)00049-9.

[34] Fouda, A.S.; Elewady, G.Y.; Shalabi, K.; Abd El-Aziz, H.K. Alcamines as Corrosion Inhibitors for Reinforced Steel and Their Effect on Cement Based Materials and Mortar Performance. *RSC Adv.* **2015**, *5*, 36957–36968. doi:10.1039/C5RA0071H.

[35] El-Askalany, A.H.; Mostafa, S.I.; Shalabi, K.; Eid, A.M.; Shaaban, S. Novel Tetrazole-Based Symmetrical Diselenides as Corrosion Inhibitors for N80 Carbon Steel in 1 M HCl Solutions: Experimental and Theoretical Studies. *J. Mol. Liq.* **2016**, *223*, 497–508. doi:10.1016/j.molliq.2016.08.088.

[36] Abdallah, Y.M.; Hassan, H.M.; Shalabi, K.; Fouda, A.S. Effects of Arctostaphylos uva-Ursi Extract as Green Corrosion Inhibitor for Cu10Ni Alloy in 1 M HNO3. *Int. J. Electrochem. Sci.* **2014**, *9*, 5073–5091.

[37] Bockris, J.O.; Swinkels, D.A.J. Adsorption of n-Decylamine on Solid Metal Electrodes. *J. Electrochem. Soc.* **1964**, *111*, 736–743. doi:10.1149/1.2426222.

[38] Ating, E.I.; Umoren, S.A.; Udousoro, I.I.; Ebenso, E.E.; Udoh, A.P. Leaves Extract of *Ananas Sativum* as Green Corrosion Inhibitor for Aluminium in Hydrochloric Acid Solutions. *Green Chem. Lett. Rev.* **2010**, *3*, 61–68. doi:10.1080/175182090350253.

[39] Narvez, L.; Cano, E.; Bastidas, D.M. 3-Hydroxybenzoic Acid as AISI 316L Stainless Steel Corrosion Inhibitor in a H2SO4–HF–H2O2 Pickling Solution. *J. Appl. Electrochem.* **2005**, *35*, 499–506. doi:10.1007/s10800-005-0291-1.

[40] Li, X.H.; Deng, S.D.; Fu, H. Synergism Between red Tetrazolium and Uricol on the Corrosion of Cold Rolled Steel in H2SO4 Solution. *Corros. Sci.* **2009**, *51*, 1344–1355. doi:10.1016/j.corsci.2009.03.023.

[41] Albrimi Y., A.; Addi, A.A.; Douch, J.; Souto, R.M.; Hamdani, M. Inhibition of the Pitting Corrosion of 304 Stainless Steel from 0.5 M Hydrochloric Acid Solution by Hectamolybdate Ions. *Corros. Sci.* **2015**, *90*, 522–528. doi:10.1016/j.corsci.2014.10.023.

[42] Goulart, C.M.; Esteves-Souza, A.; Martinez-Huitle, C.A.; Rodrigues, C.J.F.; Maciel, M.A.M.; Echevarria, A. Experimental and Theoretical Evaluation of Semicarbazones and Thiosemicarbazones as Organic Corrosion Inhibitors. *Corros. Sci.* **2013**, *67*, 281–291. doi:10.1016/j.corsci.2012.10.029.

[43] Amin, M.A.; Ibrahim, M.M. Corrosion and Corrosion Control of Mild Steel in Concentrated H2SO4 Solutions by a Newly
Synthesized Glycine Derivative. *Corros. Sci.* 2011, 53, 873–885. doi:10.1016/j.corsci.2010.10.022.

[44] Fiori-Bimbi, M.V.; Alvarez, P.E.; Vaca, H.; Gervasi, C.A. Corrosion Inhibition of Mild Steel in HCL Solution by Pectin. *Corros. Sci.* 2015, 92, 192–199. doi:10.1016/j.corsci.2014.12.002.

[45] Putliova I.K.; Balezin S.A.; Barasanik Y.P. Oxford: Pergamon Press, 1960.

[46] Saliyan, V.R.; Adhikari, A.V. Inhibition of Corrosion of Mild Steel in Acid Media by N’-Benzylidene-3-(Quinolin-4-Ylthio)Propanohydrazone. *Bull. Mater. Sci.* 2007, 31, 699–711.

[47] Oguzie, E.E.; Li, Y.; Wang, F.H. Effect of 2-Amino-3-Mercaptopropanoic Acid (Cysteine) on the Corrosion Behaviour of low Carbon Steel in Sulphuric Acid. *Electrochim. Acta* 2007, 53, 909–914. doi:10.1016/j.electacta.2007.07.076.

[48] El-Katori, E.E.; Al Angari, Y.M. Electrochemical and Theoretical Evaluation on the Corrosion Inhibition of Carbon Steel by Organic Selenides in Acidic Medium. *Int. J. Electrochem. Sci.* 2018, 13, 4319–4337. doi:10.20964/2018.05.05.

[49] Fouda, A.S.; Shahabi, K.; Idress, A.A. *Ceratonia Siliqua* Extract as a Green Corrosion Inhibitor for Copper and Brass in Nitric Acid Solutions. *Green Chemistry Letters And Reviews* 2015, 8, 17–29. doi:10.1080/17518253.2015.1073797.

[50] Kosari, A.; Moayed, M.H.; Davoodi, A.; Parviz, R.; Momeni, M.; Eshghi, H.; Moradi, H. Electrochemical and Quantum Chemical Assessment of two Organic Compounds From Pyridine Derivatives as Corrosion Inhibitors for Mild Steel in HCl Solution Under Stagnant Condition and Hydrodynamic Flow. *Corr. Sci.* 2014, 78, 138–150. doi:10.1016/j.corros.2013.09.009.

[51] Biswas, A.; Pal, S.; Udayabhanu, G. Experimental and Theoretical Studies of Xanthan gum and its Graft co-Polymer as Corrosion Inhibitor for Mild Steel in 15% HCl. *Appl. Surf. Sci.* 2015, 353, 353–361. doi:10.1016/j.apsusc.2015.06.128.

[52] Eddy, N.O.; Odoemelam, S.A.; Amo, I.N. Ethanol Extract of *Ocimum Gratissimum* as a Green Corrosion Inhibitor for the Corrosion of Mild Steel in *H*2*SO*4. *Green Chemistry Letters and Reviews* 2010, 3, 165–172. doi:10.1080/1751825100364428.

[53] Macdonald, J.R.; Johanson, W.B.; Macdonald, J.R. (Eds.). Fundamentals of Impedance Spectroscopy, Chapter 1; John Wiley & Sons: New York, 1987; p. 1.

[54] Mertens, S.F.; Xhoffer, C.; Decooman, B.C.; Temmerman, E. Short-term Deterioration of Polymer-Coated 55% Al–Zn 1. Behavior of Thin Polymeric Films. *Corrosion* 1997, 53, 381–388.

[55] Lagrenée, M.; Mernari, B.; Bouanis, M.; Traisnel, M.; Bentiss, F. Study of the Mechanism and Inhibiting Efficiency of 3,5-bis(4-Methylthiophenyl)-1H,1,2,4-Triazole on Mild Steel Corrosion in Acidic Media. *Corros. Sci.* 2002, 44, 573–588. doi:10.1016/S0010-938X(01)00075-0.

[56] Bentiss, F.; Lagrenée, M.; Traisnel, M. 2,5-Bis(n-Pyridyl)-1,3,4-Oxadiazoles as Corrosion Inhibitors for Mild Steel in Acidic Media. *Corrosion* 2000, 56, 733–742. doi:10.5006/1.3280577.

[57] Abdel--Rehim, S.S.; Khaleed, K.F.; Abd-Elshefi, N.S. Electrochemical Frequency Modulation as a new Technique for Monitoring Corrosion Inhibition of Iron in Acid Media by new Thiourea Derivative. *Electrochim. Acta* 2006, 51, 3269–3277. doi:10.1016/j.electacta.2005.09.018.

[58] Bosch, R.W.; Hubrecht, J.; Bogaerts, W.F.; Syrett, B.C. Electrochemical Frequency Modulation: A New Electrochemical Technique for Online Corrosion Monitoring. *Corrosion* 2001, 57, 60–70. doi:10.5006/1.3290331.

[59] Bentiss, F.; Bouanis, M.; Mernari, B.; Traisnel, M.; Vezin, H.; Lagrenee, M. Understanding the Adsorption of 4H-1,2,4-Triazole Derivatives on Mild Steel Surface in Molar Hydrochloric Acid. *Appl. Surf. Sci.* 2007, 253, 3696–3704. doi:10.1016/j.apsusc.2006.08.001.

[60] Shalabi, K.; Abdallah, Y.M.; Fouda, A.S. Corrosion Inhibition of Aluminum in 0.5 M HCl Solutions Containing Phenyl Sulfonylacetophenoneazo Derivatives. *Res. Chem. Intermed.* 2015, 41, 4687–4711. doi:10.1007/s11164-014-1561-5.

[61] Li, Y.; Zhao, P.; Liang, Q.; Hou, B. Berberine as a Natural Source Inhibitor for Mild Steel in 1 M H2SO4. *Appl. Surf. Sci.* 2005, 252, 1245–1253. doi:10.1016/j.apsusc.2005.02.094.

[62] Biswas, A.; Pal, S.; Udayabhanu, G. Experimental and Theoretical Studies of Xanthan gum and its Graft co-Polymer as Corrosion Inhibitor for Mild Steel in 15% HCl. *Appl. Surf. Sci.* 2015, 353, 173–183. doi:10.1016/j.apsusc.2015.06.128.

[63] Joseph Raj, X.; Nishimura, T. Investigation of the Surface Potential on Iron Nanoparticles During the Corrosion by Atomic Force Microscopy (AFM) and Kelvin Probe Force Microscopy (KFM). *Int. J. Electrochem. Sci.* 2014, 9, 2090–2100.

[64] Wang, B.; Du, M.; Zhang, J.; Gao, C.J. Electrochemical and Surface Analysis Studies on Corrosion Inhibition of Q235 Steel by Imidazoline Derivative Against CO2 Corrosion. *Corros. Sci.* 2011, 53, 353–361. doi:10.1016/j.corsci.2010.09.042.

[65] Rajendran, S.; Thangavelu, C.; Annamalai, G. Inhibition of Corrosion of Aluminium in Alkaline Medium by Succinic Acid in Conjunction with Zinc Sulphate and Diethylene Triamine Penta (Methylene Phosphonic Acid). *J. Chem. Pharm. Res.* 2012, 4, 4836–4844.

[66] Brusic, V.; Frisch, M.A.; Eldridge, B.N.; Novak, F.P.; Kauman, F.B.; Rush, B.M.; Frankel, G.S. Copper Corrosion With and Without Inhibitors. *J. Electrochem. Soc.* 1991, 138, 2253–2259. doi:10.1149/1.2085957.

[67] Antonijevic, M.M.; Petrovic, M.B. Copper Corrosion Inhibitors. A Review. *Int. J. Electrochem. Sci.* 2008, 3, 1–28.

[68] Anand, R.R.; Hurd, R.M.; Hackerman, N. Adsorption of Monomeric and Polymeric Amino Corrosion Inhibitors on Steel. *J. Electrochem. Soc.* 1965, 112, 138–144.

[69] Bordeaux, J.J.; Hackerman, N. Adsorption From Solution of Strytoric Acid on Iron: Effect on Electrode Potential. *J. Phys. Chem.* 1957, 61, 1323–1327. doi:10.1021/j150556a014.

[70] Fouda, A.S.; Moussa, M.N.; Taha, F.I.; Elneanaa, A.I. The Role of Some Thiosemicarbazide Derivatives in the Corrosion Inhibition of Aluminium in Hydrochloric Acid. *Corros. Sci.* 1986, 26, 719–726. doi:10.1016/0010-938X(86)90035-1.

[71] Desai, M.N. Corrosion Inhibitors for Aluminium Alloys. *Mat. Corros.* 1972, 23, 475–482. doi:10.1002/maco.19720230605.

[72] Vijh, A.K. Electrolytic Hydrogen Evolution Reaction on Aluminium in Acidic Solutions. *J. Phys. Chem.* 1968, 72, 1148–1156. doi:10.1021/j100850a012.