Optimization of mild steel corrosion inhibition by water hyacinth and common reed extracts in acid media using factorial experimental design

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ABSTRACT

Aquatic macrophytes biomasses provide an opportunity of using their unwanted biomasses that cause ecological disturbance as green corrosion inhibitors. The extracts of water hyacinth (\textit{Eichhornia crassipes}) and common reed (\textit{Phragmites australis}) were prepared and assessed, for mild steel corrosion inhibition. The inhibitive effect has been investigated by electrochemical impedance spectroscopy and potentiodynamic polarization techniques. Increasing aquatic and ethanolic extract concentration of both plant extracts increased the inhibition efficiency (\% IE). The maximum IE was recorded 86.8 and 89.6\% for ethanolic extracts of water hyacinth and common reed. The corrosion current density ($i_{corr}$) was recorded as 0.534 and 0.369 mA cm$^{-2}$ for water hyacinth and common reed, respectively, at the maximum concentration. Theoretical fitting of isotherms, Langmuir, Florry–Huggins, and kinetic–thermodynamic models were analyzed to clarify the nature of adsorption behaviour. The \% IE of plants extract for mild steel corrosion was evaluated and optimized by $2^3$ full factorial experimental design. Three factors have been studied namely: extraction method, pH and extract dose. The optimum conditions were at low pH and high plant extract dose concentration especially with ethanolic extraction. The validation models were calculated with $R^2 \geq 0.986$. The effectiveness of the investigated green inhibitors was also verified using the response surface methodology (RSM).

1. Introduction

Corrosion phenomenon is one of the major issues in most industries because it affects the metallic substances which adversely influence the process efficiency and its economy (1). As mild steel is the widely used materials in industries and households due to low cost and mechanical strength, it is known to be heavily corroded in acidic medium. In various industries and applications, acid pickling is a common method for cleaning metallic surfaces and removing the former scaling layer on a substrate although it can cause undesirable corrosion as a side effect (2). Corrosion inhibitors are substances which could slow down or prevent the metal corrosion and those inhibitors are classified as inorganic and organic ones. It is worthing to mention that inorganic inhibitors are not used any longer because they contain harmful heavy metals, and their bio-toxicity (3). Consequently, organic corrosion inhibitors are used due to their simple use and effectiveness with small dosage (4, 5). These inhibitors possess aromatic rings and heteroatoms as sulfur (S), oxygen (O), and nitrogen (N), and these properties can cause the molecules to emit lone electron pairs, creating coordination bonds with the transition metal...
and causing chemical adsorption at the metal (6, 7). However, many synthetic organic inhibitors are progressively restricted and abandoned despite their effective due to their high cost, environmental toxicity, carcinogenicity as well as strict environmental regulations to be applied in industrial facilities (8, 9) because the discharged organic inhibitors can pollute the ecosystem.

Commonly used coatings are epoxy and acrylic. Epoxy could extend the shelf life of metals through creating a defensive barrier for the surfaces of the metals from water and oxygen. However, it contains pores which facilitate the corrosive materials to pass through the coating and causing corrosion (10). Acrylic is a poor solvent and chemical resistance. Both polymers coatings are degraded under sunlight or ultraviolet light (11). One of the ways to solve these issues is by adding the additives into the coating.

Green corrosion inhibitors are sustainable alternatives that can be derived from natural products such as plant extracts. Natural products are proved to be preferred as corrosion inhibitors in acidic media for steel in oil & gas industries (12). This could be due to their low cost of preparations and ease of application.

During the last few decades, environmental awareness for minimizing the use of chemical-based anti-corrosion inhibitors has been raised. Application of green chemistry principles is highly encouraged in research and industrial fields. Therefore, many research studies discuss the possibility of using natural occurring plant extracts as green corrosion inhibitors for metals in different aqueous media (8, 13, 14). There is still a limitation in the choice of the suitable solvent that could be used for extraction of the bioactive constituents from the plant biomass. According to Miralrio and Espinoza Vázquez (15) and Tamalmani and Husin (16), the solvent type has an influence on its diffusion into the plant tissues to solubilize and extract the bioactive constituents.

Plant extracts-based corrosion inhibitors have been successfully applied for steel in various medium. For instance, date palm leaves and seed extracts are studied as anti-corrosion for carbon steel corrosion in acidic medium (17). Used coffee grounds were used as inhibitor for C38 steel corrosion in a 1 M hydrochloric acid (HCl) medium (18). Citrus aurantium leaves extract was employed to inhibit the corrosion of mild steel in 1 M sulfuric acid (H2SO4). They found that the inhibition efficiency was reached 89% at 40°C (19). The inhibition of mild steel in 1 M phosphoric acid (H3PO4) was tested using apricot juice (20). Recently, aqueous extract of Betel leaves was used as anti-corrosion for Q235 steel and its efficiency was ~ 94% at 400 mg L−1 (21). It is obvious that there are different pickling solutions to study as acidic medium. Herein, we chose 0.5 M H2SO4 as a pickling solution. This is due to its better stability than the other acids because there is no volatility relative to HCl and HNO3. Furthermore, the chloride of HCl is very corrosive to metals and HNO3 is easily decomposed with increasing temperature (22). Most of these studies focused only on studying one factor at a time. Thomas et al. (23) tested the aqueous extract of kokum (Garcinia indica) fruit, as an inhibitor of mild steel in acidic medium, and they found that the efficiency reached 87% and 93% for 1 and 0.5 M HCl, respectively. However, few have used the factorial experimental design to evaluate the factors that affect the inhibition efficiency (% IE) of plant extracts on metal corrosion (24, 25).

In this context, water hyacinth (Eichhornia crassipes) and common reeds (Phragmites australis) were chosen as they are the dominant aquatic macrophytes in Lake Mariout that can be considered as promising green corrosion inhibitors. The reason is due to the presence of a variety of phytochemicals such as alkaloids, terpenoids, flavonoids, amino acids, and phenolic compounds, in the aqueous and ethanolic extracts of plant species (26, 27).

The ingredients of the ethanolic extracts of water hyacinth. Those include, but not limited to, 1,2,4-Dihydroxyphenyl)2(4-methoxy-3-nitrophenyl) ethanone, pipradrol, 1H-pyrole, 1-phenyl, phytol, salicylic acids, vanillic acid, syringic acid, p-hydroxybenzoic acid, 4-methylresorcinol, catechol, pyrogallol, quinine, codeine, cytisine and thebaine (28, 29). Other scholars tackle the phytochemical screening of Phragmites australis ethanol extract and reported the presence of anti-oxidant ingredients such as; alkaloids, flavonoids, saponins and steroids (30, 31). Those ingredients include, but not limited to, C-glycosyl flavonones, swertiajaponin, isoswertiajaponin, 3′-O-gentiobioside and the 3′-O-glucoside of swertiajaponin, rhamnetin 3-O-rutinoside and rhamnetin 3-O-glucoside. Those phytomolecules possess a role in the protection of metals from corrosion through their electrostatic attractions with charged metals as well as metals vacant d-orbital and electrons of phytochemicals (32).

The aims of this study are (i) exploring the potentiality of using the extracts of two common aquatic macrophytes as green corrosion inhibitors for mild steel for the first time, (ii) depicting the effect of extract dose, extraction methods and pH on corrosion inhibition process to identify factors that may affect corrosion % IE, (iii) determining the optimal conditions for corrosion inhibition process as well as the interaction effects between factors using full factorial experimental design.
2. Materials and methods

2.1. Plant samples collection and preparation

Fresh plant samples of water hyacinth (E. crassipes) and common reeds (P. australis) were collected from Lake Mariout, Egypt, that situated along the Mediterranean coast of Egypt at latitude 31° 10' N and longitude 29° 55' E. After harvesting, the collected plant samples were rinsed with tap water many times to remove the dust and then washed with distilled water, dried in oven at 70°C till having constant dry weight (33).

2.2. Preparation of plant extracts

Aqueous and ethanol stock solutions of E. crassipes and P. australis were obtained by refluxing 5 g of dry plant in 200 mL of distilled water for 45 min and 250 mL of ethanol (95%) for 30 min, respectively. The refluxed solution was filtered to remove any residue of the plant. Two levels of the three studied factors were investigated for each plant extract namely: extraction method, pH and extract dose. Two levels of the three studied factors were applied potential signal amplitude around the rest potential. At a scan rate of 20 mV min⁻¹, polarization curves were measured. The results were collected using a three-electrode mode, with a graphite rod as the counter electrode and a saturated calomel electrode as the reference electrode. Mild steel rods were utilized to make the working electrode with the chemical composition (wt %): Fe = 96.86; Si = 0.35; Mn = 2.5; P = 0.04; S = 0.04; C = 0.21.

An epoxy resin was used to embed the mild steel samples in polytetrafluoroethylene rods, leaving only one surface uncovered. The exposed area (0.28 cm²) was mechanically polished with a succession of emery papers of variable grades, after which the samples were completely washed with distilled water, ethanol, and finally distilled water, just before insertion in the cell. Measurements were done at 30 ± 0.2°C.

The % IE is calculated using the following equation: The % IE were calculated from impedance measurements using Equation (1):

\[
\text{%IE} = \left[ \frac{R_{ct} - R_{ct0}}{R_{ct0}} \right] \times 100 \tag{1}
\]

where \( R_{ct0} \) and \( R_{ct} \) are the total resistances in the absence and presence of different plant extracts. The adsorption isotherms were also calculated based on the surface coverage degree (\( \theta \)) related to the inhibitor concentration (\( C \)) as illustrated in Equation (2) (Langmuir isotherm) and Equation (3) (Flory–Huggins). The kinetic–thermodynamic model was calculated using Equation (4):

\[
\left[ \frac{\theta}{1 - \theta} \right] = K_{ad} \times C_{inh} \tag{2}
\]

\[
K_{ad} \times C_{inh} = \frac{\theta}{x \left( 1 - \theta^x \right)} \tag{3}
\]

\[
\log \left[ \frac{\theta}{1 - \theta} \right] = \log K y \log C_{inh} \tag{4}
\]

where \( K_{ad} \) is the adsorption equilibrium constant (directly proportional to the % IE). \( C_{inh} \) is the inhibitor concentration in the solution. \( x \) is the number of the adsorbed water molecules replaced by one molecule of organic adsorbate. \( K \) is constant related to the adsorption binding constant.

2.4. Statistical optimization

The % IE of E. crassipes and P. australis extracts on mild steel corrosion was evaluated and optimized by \( 2^{3} \) full factorial experimental design. The statistical package MINITAB® 16 was used in this investigation.

Three factors have been investigated for each plant extract namely: extraction method, pH and extract dose. Two levels of the three studied factors were
Table 1. High and low levels of experimental factors for mild steel using *E. crassipes* extract.

| Experimental factor | Code | Low level (−1) | High level (+1) |
|---------------------|------|----------------|-----------------|
| Extraction solvent   | A    | Aqueous        | Ethanol (95%)   |
| pH                  | B    | 1              | 7               |
| Dose                | C    | 100 ppm        | 2000 ppm        |

Table 2. High and low levels of experimental factors for mild steel using *P. australis* extract.

| Experimental factor | Code | Low level (−1) | High level (+1) |
|---------------------|------|----------------|-----------------|
| Extraction solvent   | A    | Aqueous        | Ethanol (95%)   |
| pH                  | B    | 1              | 7               |
| Dose                | C    | 50 ppm         | 500 ppm         |

used, high level ‘+1’ and low level ‘−1’ (Tables 1 and 2). Eight batch experiments were formulated and done in triplicates at constant temperature (30°C). The metal area exposed to the aqueous environment was 0.2827 cm². Hydrogen concentration ion (pH) was adjusted to 1 using 0.5 M H₂SO₄ while to 7 using 0.5 M NaCl for each extract concentration.

The response variable % IE was fitted by the following equation:

\[ Y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_1x_2 + a_5x_2x_3 + a_6x_1x_3 + a_7x_1x_2x_3 \]  

(5)

where \( Y \): estimate of the response, \( A \): constant term, \( a \): coefficients and \( x \): experimental factors. The studied experiments were done in triplicates and random order to minimize the effect of errors. Furthermore, response surface methodology (RSM) was conducted to examine the optimum factors for % IE of mild steel corrosion.

3. Results and discussion

3.1. Electrochemical impedance spectroscopy (EIS) measurements

The purpose of EIS is to investigate the concentration effect of the investigated green inhibitors on the impedance behaviour of mild steel in 0.5 M H₂SO₄. Figures 2 and 3 represent Nyquist plots for mild steel in 0.5 M H₂SO₄ solution in the absence and presence of different concentrations of aqueous and ethanol extracts of *E. crassipes* and *P. australis*. The resultant Nyquist plots for the investigated plant species manifest only one depressed capacitive semicircle. This behaviour can be discussed on the basis of the presence of charge transfer resistance \( R_{ct} \) associated with the effect of ionic double-layer capacitance \( C_{dl} \).

It is notable that the diameter of semicircles was higher in the presence of inhibitor compared to in their absence. Furthermore, there was an increment in the semicircles diameters indicated that increasing extract concentration increases the \( R_{ct} \) and the % IE which indicates that the investigated extracts act as good corrosion inhibitor. However, the decrease of the double-layer capacitance \( C_{dl} \) indicates that *E. crassipes* and *P. australis* aqueous and ethanol extracts decrease the rate of corrosion of mild steel in acidic medium. Those findings are supported by Verma et al. (34) and Iroha and Hamilton-Amachree (35) who tested *Holoptelea integrifolia* leaf extract and *Balanites aegyptiaca* seed extract, respectively, for mild steel corrosion in 1 M HCl.

The obtained values of the electrochemical parameters with various concentrations of *E. crassipes* and *P. australis* aqueous and ethanol extracts as well as % IE are given in Tables 3 and 4. The increment of \( R_{ct} \) and decrement of \( C_{dl} \) with increasing the concentration of both extracts, suggesting the increased adsorption of the extract bioactive constituents on the steel surface, leading to better protection of the mild steel. With increasing inhibitor concentration, the covered area of steel surface by the inhibitor increased. This could reduce or prevent the charge transfer from the steel to the solution (36).

It is noting that the ethanolic extracts of both plant biomasses possess better % IE than the aqueous extracts. The process of extraction is mainly to extract bioactive constituents from the studied plant biomass (37, 38). Ethanolic extract of both plant species have more phytoconstituents that will inhibit the corrosion of mild steel opposed to aqueous extract. The maximum % IE of ethanolic extracts of *E. crassipes* and *P. australis* reached 86.8% and 89.6%, respectively. This finding is concomitant with Chen et al. (39). It is also revealed that through the EIS measurements, *Matricaria aurea* showed potent anticorrosive activity for mild steel with IE = 94% in 1 M HCl (32).

3.2. Polarization measurements

Figures 4 and 5 show the influence of aqueous and ethanol extracts of *E. crassipes* and *P. australis* on the polarization curves of mild steel in 0.5 M H₂SO₄ solution. It is shown that when the concentration of the extracts increased, the corrosion current density \( i_{corr} \) values shifted more to the positive values. Similar observations were obtained when the extract of *Crataevaudansonii* was utilized as a green inhibitor for mild steel in acidic medium (1.75 M HCl) by Olarewaju et al. (40).

Corrosion parameters (Tables 5 and 6) were calculated using cathodic and anodic potential against current density characteristics in the Tafel potential
The values of the corrosion current density \(i_{corr}\), extrapolation of cathodic, and anodic Tafel lines (slopes; \(\beta_a\) and \(\beta_c\)), and the corrosion potential \(E_{corr}\) are presented in Tables 3 and 4 for the steel surface before and after the addition of various concentrations of the investigated plant extracts. Furthermore, the % IE of plant extracts increased with increasing their concentrations. This is in similarity with what was detected by Umoren et al.\(^{(41)}\) on using *Sida acuta* for inhibiting the corrosion of mild steel in H\(_2\)SO\(_4\) media and Ríos et al.\(^{(42)}\) who used *Agaviodeae* extract for the corrosion inhibition of mild steel in 1 M HCl. Furthermore, Soltani and Khayatkashani\(^{(43)}\) investigated the inhibitive action of leaf extract of *Gundelia tournefortii* on mild steel corrosion in 2.0 M HCl and 1.0 M H\(_2\)SO\(_4\) solutions and found the similar observation with increasing the inhibitor concentrations due to the adsorption of the inhibitor molecules on the metal surface.

It is observed that the presence of aqueous and ethanol extract of *E. crassipes* and *P. australis* affect both the cathodic and anodic Tafel lines indicating that both aqueous and ethanol extracts act as mixed type inhibitors. Consequently, the adsorption of inhibitors occurs more likely at both cathodic and anodic sites. This conclusion is concurrent with Cang et al.\(^{(44)}\) who studied the use of *P. australis* leaves extract as a green corrosion inhibitor for steel in 0.5 M H\(_2\)SO\(_4\).

### 3.3. Adsorption isotherms

Adsorption of inhibitor molecules on metal surface involves the removal of adsorbed water molecules through a displacement reaction. This reaction is subjected to the solvation energy of the inhibitor. So that, as the size of the inhibitor molecule increases, its solubility decreases while its adsorbability increases. This is
consistent with the increasing inhibitive efficiency observed at constant concentrations with the increasing molecular size in a series of related compounds.

To learn the adsorption characteristics of the investigated green inhibitors on the metal surface, Langmuir, Flory–Huggins and kinetic–thermodynamic models were applied to fit the experimental results of aqueous and ethanol extract of *E. crassipes* and *P. australis* on mild steel.

Figure 6 shows the application of Langmuir, Flory Huggins and kinetic–thermodynamic models to fit the corrosion inhibition effect of aqueous and ethanol extract of *E. crassipes* and *P. australis*. The parameters acquired from these models are represented in Table 7.

**Figure 3.** Nyquist plots for mild steel in 0.5 M H$_2$SO$_4$ without and with (a) aqueous extract and (b) ethanol extract of *P. australis*.

**Table 3.** Impedance parameters for aqueous and ethanol extracts of *E. crassipes* with different concentrations in 0.5 M H$_2$SO$_4$ based on Nyquist plots.

| Conc. (mg L$^{-1}$) | $R_s$ (ohm cm$^2$) | $C_{dl}$ (µF cm$^{-1}$) | $R_{ct}$ (ohm cm$^2$) | % IE | $R_s$ (ohm cm$^2$) | $C_{dl}$ (µF cm$^{-1}$) | $R_{ct}$ (ohm cm$^2$) | % IE |
|---------------------|------------------|-----------------|------------------|-----|------------------|-----------------|------------------|-----|
| 0                   | 1.247            | 3.387 E-04      | 12.3             | 0.0 | 1.247            | 3.387 E-04      | 12.3             | 0.0 |
| 100                 | 1.310            | 3.164 E-04      | 16.6             | 25.9| 1.450            | 3.668 E-04      | 14.7             | 16.3|
| 500                 | 1.253            | 2.190 E-04      | 35.5             | 65.3| 1.478            | 3.001 E-04      | 16.9             | 27.2|
| 1200                | 1.645            | 1.333 E-04      | 49.1             | 74.9| 1.879            | 1.592 E-04      | 61.4             | 79.9|
| 1500                | 1.212            | 1.603 E-04      | 55.6             | 77.8| 1.882            | 1.399 E-04      | 68.9             | 82.1|
| 1800                | 1.374            | 1.651 E-04      | 58.3             | 78.9| 1.977            | 1.455 E-04      | 89.3             | 86.2|
| 2000                | 1.524            | 1.530 E-04      | 61.7             | 80.0| 2.070            | 1.320 E-04      | 93.7             | 86.8|
It is apparent that Langmuir model is applicable to fit the data of both *E. crassipes* and *P. australis* ethanol extract indicating ideal behaviour in the adsorption process of these extracts on the mild steel surface. It is found that the inhibitive action of *Gundelia tournefortii* leaves extract on mild steel corrosion followed Langmuir adsorption isotherm and the % IE was 93% and 90% at 150 ppm in 2.0 M HCl and 1.0 M H$_2$SO$_4$, respectively (43). However, Langmuir model is obviously not applicable to fit the data of the aqueous extract of both *E. crassipes* and *P. australis* in this work.

The efficiency of a given inhibitor is basically a function of the magnitude of its binding constant (K), large value of K indicates better and stronger interaction, whereas small value of K means that the interaction between the inhibitor molecules and the metal is weaker. Therefore, according to the numerical values

| Conc. (mg L$^{-1}$) | $R_s$ (ohm cm$^2$) | $C_{dl}$ (µF cm$^{-1}$) | $R_{ct}$ (ohm cm$^2$) | % IE | $R_s$ (ohm cm$^2$) | $C_{dl}$ (µF cm$^{-1}$) | $R_{ct}$ (ohm cm$^2$) | % IE |
|---------------------|--------------------|-------------------------|-----------------------|-----|-------------------|-------------------------|-----------------------|-----|
| 0                   | 1.247              | 3.387 E-04              | 12.3                  | 0.0 | 1.247             | 3.387 E-04              | 12.3                  | 0.0 |
| 50                  | 1.077              | 3.128 E-04              | 16.3                  | 24.5| 1.280             | 3.462 E-04              | 14.1                  | 12.7|
| 100                 | 1.350              | 2.348 E-04              | 29.9                  | 58.8| 1.311             | 2.301 E-04              | 26.9                  | 54.2|
| 200                 | 1.089              | 1.994 E-04              | 42.4                  | 70.9| 1.465             | 1.457 E-04              | 56.8                  | 78.3|
| 400                 | 1.063              | 1.256 E-04              | 60.0                  | 79.5| –                 | –                       | –                     | –   |
| 500                 | 8.398              | 1.336 E-04              | 66.9                  | 81.3| 1.989             | 1.207 E-04              | 81.7                  | 84.9|
| 800                 | –                  | –                       | –                    | –   | 3.893             | 1.172 E-04              | 119.4                 | 89.6|

**Table 4.** Impedance parameters for aqueous and ethanol extracts of *P. australis* with different concentrations in 0.5 M H$_2$SO$_4$ based on Nyquist plots.

Figure 4. Polarization curves of the Tafel plots for (a) aqueous extract and (b) ethanol extract of *E. crassipes* with different concentrations in 0.5 M H$_2$SO$_4$. 
of K, the % IE of ethanol extract of P. australis is greater than that of E. crassipes.

The values of the size parameter (\(x\)) for aqueous and ethanol extracts of P. australis in addition to aqueous extract of E. crassipes obtained by applying Flory–Huggins model indicate that the adsorbed species can displace more than one water molecule on mild steel surface. However, the value of \(x\) for E. crassipes ethanol extract indicates that more than one adsorbed species can displace only one water molecule.

Kinetic–thermodynamic model is also found to fit the obtained data of the investigated plant extracts. The slope of \(y\) and intercept of log \(K\) can be calculated with a plot of log \(\theta / (1 - \theta)\) versus log \(C_{\text{inh}}\) as shown in Figure 6(e, d). The values of active sites occupied by inhibitor molecules (1/\(y\)) are calculated using Equation

\[
\log \frac{C_{\text{inh}}}{1 - C_{\text{inh}}} = \log K + \log y
\]

Table 5. Potentiodynamic polarization parameters for aqueous and ethanol extracts of E. crassipes with different concentrations in 0.5 M H\(_2\)SO\(_4\).

| Conc. (mg L\(^{-1}\)) | \(-E_{\text{corr}}\) (mV) | \(\beta_a\) (mV dec\(^{-1}\)) | \(\beta_c\) (mV dec\(^{-1}\)) | \(i_{\text{corr}}\) (mA cm\(^{-2}\)) | % IE | \(-E_{\text{corr}}\) (mV) | \(\beta_a\) (mV dec\(^{-1}\)) | \(\beta_c\) (mV dec\(^{-1}\)) | \(i_{\text{corr}}\) (mA cm\(^{-2}\)) | % IE |
|----------------------|--------------------------|-----------------|-----------------|-----------------|-----|--------------------------|-----------------|-----------------|-----------------|-----|
| 0                    | 523                      | 173             | 89              | 3.966           | 0   | 523                      | 173             | 89              | 3.966           | 0   |
| 100                  | 507                      | 184             | 77              | 3.044           | 23  | 519                      | 182             | 101             | 3.432           | 13  |
| 500                  | 497                      | 140             | 81              | 1.477           | 62  | 520                      | 174             | 56              | 2.818           | 28  |
| 1200                 | 505                      | 152             | 87              | 1.265           | 68  | 495                      | 141             | 94              | 0.873           | 77  |
| 1500                 | 502                      | 136             | 110             | 0.972           | 75  | 497                      | 134             | 80              | 0.727           | 81  |
| 1800                 | 491                      | 126             | 93              | 0.868           | 78  | 494                      | 130             | 73              | 0.594           | 85  |
| 2000                 | 501                      | 131             | 75              | 0.778           | 80  | 496                      | 134             | 91              | 0.534           | 86  |

Note: dec = decade.
Table 6. Potentiodynamic polarization parameters for aqueous and ethanol extracts of *P. australis* with different concentrations in 0.5 M H$_2$SO$_4$.

| Conc. (mg L$^{-1}$) | $E_{corr}$ (mV) $\beta_a$ (mV dec$^{-1}$) $\beta_c$ (mV dec$^{-1}$) $i_{corr}$ (mA cm$^{-2}$) | $E_{corr}$ (mV) $\beta_a$ (mV dec$^{-1}$) $\beta_c$ (mV dec$^{-1}$) $i_{corr}$ (mA cm$^{-2}$) | % IE $E_{corr}$ (mV) $\beta_a$ (mV dec$^{-1}$) $\beta_c$ (mV dec$^{-1}$) $i_{corr}$ (mA cm$^{-2}$) | % IE |
|-------------------|---------------------------------|---------------------------------|---------------------------------|--------|
| 0                 | 523 173 89 3.966 0               | 523 173 89 3.966 0               | 0.0                              | 0.0    |
| 50                | 482 144 57 2.816 28.9            | 518 159 89 2.627 33.7            | 50.0                             | 50.0   |
| 100               | 498 155 65 2.173 45.2            | 509 145 79 1.793 54.7            | 50.0                             | 50.0   |
| 200               | 497 131 67 1.480 62.6            | 502 149 82 1.127 67.0            | 50.0                             | 50.0   |
| 400               | 495 133 73 1.091 72.4            | –– –– –– 0.0 0.0 0.0            | 50.0                             | 50.0   |
| 500               | 498 123 97 0.790 80.0            | 493 151 85 0.900 77.3            | 50.0                             | 50.0   |
| 800               | –– –– –– –– –– –– –– –– –– –– –– | 491 125 108 0.369 90.6          | 50.0                             | 50.0   |

Figure 6. Linear fitting plots of (a) Langmuir isotherm for the ethanol extract of *E. crassipes* and *P. australis*, (b, c) Flory–Huggins model, (d, e) kinetic–thermodynamic model for the aqueous and ethanol extracts of *E. crassipes* and *P. australis* obtained from impedance measurements for mild steel in 0.5 M H$_2$SO$_4$.
Table 7. Linear fitting parameters of *E. crassipes* and *P. australis* according to the Langmuir, Flory–Huggins and kinetic–thermodynamic models.

| Extraction method | Plant biomass | Langmuir \( K_{x} \) [L mg\(^{-1}\)] | Flory–Huggins | Kinetic–thermodynamic |
|-------------------|---------------|-------------------------------------|---------------|-----------------------|
| Aqueous           | *E. crassipes* | –                                   | 12.460        | 2.139                 |
|                   | *P. australis* | –                                   | 25.102        | 1.612                 |
| Ethanol           | *E. crassipes* | 3.568                               | 1.1029        | 0.384                 |
|                   | *P. australis* | 10.611                              | 16.404        | 1.353                 |

(4) in Table 6. The 1/y values > 1 indicated that a single inhibitor molecule will occupy more than one active site. Whereas the 1/y values less than or nearly equal 1 revealed the formation multilayers of the inhibitor on the mild steel surface and each molecule occupied one active site. The number of active sites occupied by a single inhibitor molecule (1/y) was different to the size parameter (x) for all plant extracts. The %IE order of different plant extract based on the values of \( K \) is different from that obtained from Flory–Huggins model.

3.4. Statistical optimization

The results for corrosion %IE of aqueous and ethanol extract of *E. crassipes* and *P. australis* for mild steel corrosion in acidic and neutral media are shown in Table 8.

The effects, regression coefficients and the associated standard errors for inhibition of mild steel corrosion are shown in Tables 9 and 10. Main factors and their interactions were significant at 5% of probability level (\( P < 0.5 \)). The main effects of factors (A, B, C) represent deviations of the average between high and low levels for each one of them. Variation in pH (B) from high to low level resulted in 50% and 49% increase in the corrosion %IE of mild steel when using *E. crassipes* and *P. australis* extract respectively. Moreover, variation in extract dose (C), from low to high increased the corrosion %IE of mild steel by 29.5% and 31%, respectively.

The interaction of (pH and dose) indicated that decreasing the pH level enhance the %IE at low and high extract dose compared with high pH level that showed a negative response. At high extract dose of *E. crassipes* extract (2000 ppm), %IE reached 86% and 80% when using ethanol and aqueous extract, respectively. On using high dose of *P. australis* (500 ppm), %IE reached 84% and 81% when using ethanol and aqueous extract, respectively.

The interaction of (Ex. solvent and dose) indicated that using ethanol extract of *E. crassipes* and *P. australis* at high dose increases the %IE compared with the use of aqueous extract. At high dose (2000 ppm) of *E. crassipes* ethanol extract, the %IE increases from 80% to 86% and the use of high dose (500 ppm) of *P. australis* ethanol extract increases the %IE from 81% to 84% at pH = 0.3.

For better evaluation of each factor and its interaction, the plot of normal probability of the standardized

Table 8. Experimental factorial design results for inhibition efficiency of mild steel corrosion.

| Factors | Average (% IE) |
|---------|---------------|
| Ex. Sol. (A) | pH (B) | Dose (C) | *E. crassipes* | *P. australis* |
| −1       | −1       | −1       | 25           | 24           |
| −1       | −1       | 1        | 80           | 81           |
| −1       | 1        | −1       | 0            | 0            |
| 1        | 1        | 1        | 0            | 0            |
| 1        | 1        | 1        | 16           | 12           |
| 1        | 1        | 1        | 86           | 84           |
| 1        | 1        | −1       | 0            | 0            |
| −1       | 1        | 0        | 0            | 0            |

Notes: A: extraction solvent (Ex. Sol.); B: hydrogen ion concentration (pH); C: extract dose; %IE: inhibition efficiency; 1: high level; −1: low level.

Table 9. Statistical parameters for full 2\(^{3}\) factorial design of inhibition efficiency of mild steel corrosion using *E. crassipes*.

| Term             | Effect | Regression coefficients | Standard errors | \( T \) | \( P \) |
|------------------|--------|-------------------------|-----------------|--------|-------|
| Constant         |        |                         | 27.03           | 1.005  | 26.89 | 0.000 |
| Ex. Solvent      |        | −2.77                   | −1.38           | 1.005  | −1.38 | 0.188** |
| pH               |        | −50.07                  | −25.03          | 1.005  | −24.90| 0.000** |
| Dose             |        | 29.57                   | 14.78           | 1.005  | 14.71 | 0.000** |
| Interaction of two factors |        |                         |                  |        |       |
| Ex. Solvent*pH   |        | −1.23                   | −0.62           | 1.005  | −0.61 | 0.548*** |
| Ex. Solvent*Dose |        | 5.80                    | 2.90            | 1.005  | 2.89  | 0.011** |
| pH*Dose          |        | −33.57                  | −16.78          | 1.005  | −16.70| 0.000** |
| Interaction of three factors |        |                         |                  |        |       |
| Ex. Solvent*pH*Dose |    | −1.80                  | −0.90           | 1.005  | −0.90 | 0.384*** |

Notes: A: extraction solvent; B: pH; C: extract dose; T: t-test; P: probability values.
** Significant factor(s).
*** Insignificant factor(s).
effects for the studied corrosion inhibition by aqueous and ethanol extract of *E. crassipes* and *P. australis* were conducted (Figure 7(a, b)). Factors and the interactions between them which were represented as a square were significant. In addition, the plot indicated the direction of the studied factors’ effects whether positive, right

**Table 10.** Statistical parameters for full $2^{3}$ factorial design of inhibition efficiency of mild steel corrosion using *P. australis*.

| Term                  | Effect | Regression coefficients | Standard errors | $T$  | $P$  |
|-----------------------|--------|-------------------------|-----------------|------|------|
| Constant              | 25.91  | 0.5364                  | 48.30           | 0.000|      |
| Ex. Solvent           | −0.78  | −0.39                   | 0.5364          | −0.72| 0.481***|
| pH                    | −49.71 | −24.85                  | 0.5364          | −46.33| 0.000**|
| Dose                  | 31.11  | 15.55                   | 0.5364          | 28.99| 0.000**|
| Interaction of two factors | | | | |
| Ex. Solvent*pH        | 2.89   | 1.45                    | 0.5364          | 2.70 | 0.016** |
| Ex. Solvent*Dose      | 2.54   | 1.27                    | 0.5364          | 2.37 | 0.031** |
| pH*Dose               | −33.23 | −16.61                  | 0.5364          | −30.97| 0.000** |
| Interaction of three factors | | | | |
| Ex. Solvent*pH*Dose   | −4.66  | −2.33                   | 0.5364          | −4.34| 0.001***|

Notes: A: extraction solvent; B: pH; C: extract dose; T: t-test; $P$: probability values.

**Significant factor(s).**

*** Insignificant factor(s).

![Figure 7.](image)

(a) Normal probability plot of the standardized effects for inhibition efficiency of mild steel corrosion using (a) *E. crassipes* extract and (b) *P. australis* extract.
side of the line, or negative, left side of the line. Non-significant factors were represented as a circle.

The Pareto chart of the standardized effects for corrosion inhibition of mild steel by aqueous and ethanol extract of *E. crassipes* and *P. australis* at $\alpha = 0.05$ is shown in Figure 8(a, b). The line of $t$-value is the reference line that test the effect of the studied factors is zero in hypothesis. When the studied factors exceeded the line of $t$-value; 2.12, these factors are significant. The results of % IE of mild steel corrosion as in Table 8 and Figure 8 demonstrated the order of the factors that affecting the inhibition of mild steel corrosion in descending order. The results indicated that the factor pH has the largest effect on corrosion inhibition of mild steel. It was noticed that the response increases when this factor is changed from high level to low level. The second and third factors effect are pH*Dose and Dose, respectively.

The analysis of variance (ANOVA) (Tables 11 and 12) for the factorial design $2^3$ shows the significant factors and interactions on the % IE of *E. crassipes* and *P. australis* extracts on mild steel corrosion. In case of using *E. crassipes* extract as corrosion inhibitor, factor pH, Dose, two-way interaction pH*Dose and Ex. Solvent*Dose are significant at 5% of probability level ($P < 0.05$). While, factor Ex. Solvent, two-way interactions Ex. Solvent*pH and three-way interaction are insignificant. On using *P. australis* extract, the only insignificant factor is Ex. Solvent otherwise, all factors and their interactions are significant at 5% of probability level ($P < 0.05$).

**Figure 8.** Pareto chart of the standardized effects for inhibition efficiency of mild steel corrosion using *E. crassipes* extract and *P. australis* extract. Line represents t-test value at 95%.
Validation models are illustrated in Figure 9 that present the relationship between the observed and calculated corrosion % IE of mild steel using both green corrosion inhibitors with R² = 0.986 for *E. crassipes* and R² = 0.996 for *P. australis*.

Factorial experimental design is commonly used in experiments involving a number of factors where it is necessary to study the joint effect of the factors on a response (45–47). This design allows the concurrent study of the effects of factors levels that may have on the optimization of the corrosion inhibition process with less number of experiments (48).

In factorial experimental design, if a coefficient of any of the investigated factors is large, then the corresponding experimental variable has a big influence on the response. If the coefficient is small, then it has only a small influence on the response.

In this work, the largest effect of the main factors in corrosion inhibition of mild steel by *E. crassipes* and *P. australis* extracts is attributed to hydrogen ion

| Source              | DF | Seq SS | Adj SS | Adj MS | F    | P    |
|---------------------|----|--------|--------|--------|------|------|
| Main effects        | 3  | 20331.1| 20331.1| 6777.0 | 279.48| 0.000|
| Ex. solvent         | 1  | 45.9   | 45.9   | 45.9   | 1.89 | 0.188**|
| pH                  | 1  | 15040.0| 15040.0| 15040.0| 620.24| 0.000**|
| Dose                | 1  | 5245.1 | 5245.1 | 5245.1 | 216.31| 0.000**|
| 2-Way interactions  | 3  | 6971.3 | 6971.3 | 2323.8 | 95.83 | 0.000**|
| Ex. Solvent*pH      | 1  | 9.1    | 9.1    | 9.1    | 0.38 | 0.548***|
| Ex. Solvent*Dose    | 1  | 201.8  | 201.8  | 201.8  | 8.32 | 0.011**|
| pH*Dose             | 1  | 6760.3 | 6760.3 | 6760.3 | 278.79| 0.000**|
| 3-Way interactions  | 1  | 19.4   | 19.4   | 19.4   | 0.80 | 0.384***|
| Ex. Solvent*pH*Dose | 1  | 19.4   | 19.4   | 19.4   | 0.80 | 0.384***|
| Residual error      | 16 | 388.0  | 388.0  | 24.2   |      |      |
| Pure error          | 16 | 388.0  | 388.0  | 24.2   |      |      |
| Total               | 23 | 27709.8|        |        |      |      |

Notes: DF: degree of freedom; Seq SS: sequential sum of squares; Adj MS: adjacent mean square; F: F-test; P: probability values.
** Significant factor(s).
*** Insignificant factor(s).

| Source              | DF | Seq SS | Adj SS | Adj MS | F    | P    |
|---------------------|----|--------|--------|--------|------|------|
| Main effects        | 3  | 20635.5| 20635.5| 6878.5 | 995.92| 0.000|
| Ex. solvent         | 1  | 3.6    | 3.6    | 3.6    | 0.52 | 0.481***|
| pH                  | 1  | 14825.5| 14825.5| 14825.5| 2146.55| 0.000**|
| Dose                | 1  | 5806.4 | 5806.4 | 5806.4 | 840.69| 0.000**|
| 2-Way interactions  | 3  | 6712.3 | 6712.3 | 2237.4 | 323.95| 0.000|
| Ex. Solvent*pH      | 1  | 50.2   | 50.2   | 50.2   | 7.26 | 0.016**|
| Ex. Solvent*Dose    | 1  | 38.8   | 38.8   | 38.8   | 5.61 | 0.031***|
| pH*Dose             | 1  | 6623.4 | 6623.4 | 6623.4 | 958.99| 0.000**|
| 3-Way interactions  | 1  | 130.2  | 130.2  | 130.2  | 18.85 | 0.001|
| Ex. Solvent*pH*Dose | 1  | 130.2  | 130.2  | 130.2  | 18.85 | 0.001***|
| Residual error      | 16 | 110.5  | 110.5  | 6.9    |      |      |
| Pure error          | 16 | 110.5  | 110.5  | 6.9    |      |      |
| Total               | 23 | 27588.5|        |        |      |      |

Notes: DF: degree of freedom; Seq SS: sequential sum of squares; Adj MS: adjacent mean square; F: F-test; P: probability values.
** Significant factor(s).
*** Insignificant factor(s).

Figure 9. Validation model of corrosion inhibition efficiency of mild steel using (a) *E. crassipes* extract and (b) *P. australis* extract.
concentration (pH). Potential-pH equilibrium for metals with the different surrounding media, steel is subjected to uniform corrosion effect in low pH (acidic) media. While at higher pH (6–7), a layer of ferrous hydroxide Fe(OH)$_2$ that will be covered by a more stable layer of magnetite Fe$_3$O$_4$ is formed on iron surface which prevent the corrosion effect except at unprotected areas leading to localized corrosion.

$$\text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{H}^+ \quad (3)$$

$$3\text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + 2\text{H}^+ + 2\text{e} \quad (4)$$

$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (5)$$

$$3\text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + \text{H}_2 \quad (6)$$

Results obtained from this study show that the % IE of mild steel corrosion by $E. \text{crassipes}$ and $P. \text{australis}$ extract increased as the pH level decreased. This is due to the formation of a protective layer formed by the adsorption of $E. \text{crassipes}$ and $P. \text{australis}$ extract on steel surface that prevented the attack of H$^+$ ion and the dissolution of the metal. On the other hand, plant extracts couldn’t inhibit the formation of ferrous hydroxide layer on steel surface in the neutral media (i.e. high pH level).

Valladares-Cisneros et al. (49) and Thiruvengadam et al. (24) concluded that the increase of % IE is due to the adsorption of the plant extract active ingredients on steel surface forming a protective layer that inhibit metal corrosion by the surrounding acidic environment.

The significant factor in corrosion inhibition of mild steel by $E. \text{crassipes}$ and $P. \text{australis}$ extracts is attributed to the dose of plant extract. Results show that the % IE of mild steel corrosion by $E. \text{crassipes}$ and $P. \text{australis}$ extract increase as the plant extract dose increase. Through applying adsorption models, the size parameter $x$ for aqueous and ethanol extracts of $P. \text{australis}$ in addition to aqueous extract of $E. \text{crassipes}$ indicates that the adsorbed species can displace more than one water molecule on mild steel surface. Therefore, it may be discussed that increasing plant extract dose will displace more water molecules from steel surface leading to better % IE.

In this study, the corrosion inhibition of mild steel using $P. \text{australis}$ extract was better than that of $E. \text{crassipes}$ in respect to the concentration dose used. In other words, % IE that is achieved by using 500 ppm of $P. \text{australis}$ extract required about 2000 ppm of $E. \text{crassipes}$ to nearly reach the same % IE. Therefore, considering the use of natural resources, $P. \text{australis}$ extract was more efficient than $E. \text{crassipes}$ extract.

Moreover, validation models for % IE of mild steel by $E. \text{crassipes}$ and $P. \text{australis}$ extracts demonstrated that the observed values (experimental) were set closely to calculated values (model). Hence, these models could suggest a normal distribution for the suitability of the models for the present study.

RSM is used for closer inspection of the relationship between the studied factors and the response variable in the corrosion inhibition process. Results demonstrated by response surface plots were concomitant with those obtained by factorial experimental design for both metals.

Optimal conditions for the corrosion % IE of plant extracts, $E. \text{crassipes}$ and $P. \text{australis}$, on mild steel corrosion are illustrated using the response surface plot (Figure 10). Each plot includes two variables, and the third one is presented as a constant because extraction solvent parameter is categorial variable. Both extracts are best functioning at low level of the factor pH and high level of the factor dose. The regression equations of % IE, derived from RSM, are presented below for aqueous and ethanol extracts of $E. \text{crassipes}$ and $P. \text{australis}$.

$E. \text{crassipes}$

Aqueous extract %IE = 23.10 – 1.95 pH + 0.036 Dose
− 0.0058 pH * Dose

Ethanol extract %IE = 15.57 – 2.36 pH + 0.042 Dose − 0.0058 pH * Dose

$P. \text{australis}$

Aqueous extract %IE = 16.84 – 1.99pH + 0.162 Dose − 0.024 pH * Dose

Ethanol extract %IE = 9.10 – 1.04 pH + 0.173 Dose − 0.0245 pH * Dose

The % IE of $E. \text{crassipes}$ and $P. \text{australis}$ extract on the corrosion of mild steel and zinc obtained by the present study were compared with those recorded in most of the previously available literature (Table 13).

4. Conclusions

This work outcomes show that $E. \text{crassipes}$ and $P. \text{australis}$ aqueous and ethanol extracts can be effectively used as green corrosion inhibitors for mild steel in acidic (0.5 M H$_2$SO$_4$) and neutral (0.5 M NaCl) media. $E. \text{crassipes}$ and $P. \text{australis}$ extracts are classified as mixed type inhibitors for mild steel corrosion. Ethanol extract of both $E. \text{crassipes}$ and $P. \text{australis}$ acquire ideal
adsorption behavior on mild steel surface in acidic medium according to Langumir model. The corrosion inhibitive capability of *E. crassipes* and *P. Australis* ethanolic extracts increased with increasing their concentrations, and the highest IE (89.6%) was achieved at 0.464 mM. On the contrary, aqueous extract of *E. crassipes* and *P. australis* showed non-ideal behaviour when applying the same model. The binding constant (K) values obtained from Flory–Huggins/kinetic–thermodynamic model demonstrate that the inhibitory efficiency of ethanol extract of *P. australis* is greater than that of *E. crassipes* for mild steel corrosion.

The factorial experiment design approach is a reliable way for determining the influence of studied parameters on response factors. Results obtained from the $2^{3}$ factorial design and the ANOVA show that the largest effect of the main factors in corrosion inhibition of mild steel by *E. crassipes* and *P. australis* extracts is attributed to hydrogen ion concentration (pH) then, followed by the dose of plant extract (dose). The interaction effect of pH*Dose and Ex. Sol.*Dose have a significant influence on the inhibition of mild steel corrosion by *E. crassipes* extract at 5% of probability level ($P < 0.05$). While, the interaction effect of pH*Dose, Ex. Sol.*pH*Dose, Ex. Sol.*pH and Ex. Sol.*Dose have significant influence on the inhibition of mild steel corrosion by *P. australis* extract at 5% of probability level ($P < 0.05$).

RSM used successfully for optimizing the % IE of mild steel corrosion by *E. crassipes* and *P. australis* extract in aqueous environment. Both extracts are best functioning in acidic medium and at high plant extract dose. The observed values (experimental) were set closely to calculated values (model) that allowed suggesting a

Table 13. Comparison of inhibition efficiency (% IE) of green inhibitors for mild steel corrosion in acidic medium between the current work and literature.

| Green inhibitors                     | % IE | References |
|-------------------------------------|------|------------|
| Loquat leaf extract                  | 42   | (50)       |
| *Gundelia tournefortii* extract      | 90   | (43)       |
| *Ilex paraguariensis* extract        | 91   | (51)       |
| *Cynara scolymus* extract           | 89   | (49)       |
| Tobacco rob extract                  | 85.8 | (14)       |
| Green tea extract                    | 87   | (52)       |
| *Citrus aurantiifolia*               | 96.4 | (53)       |
| Tamarind shell tannin methanol extract | 87.7 | (54)      |
| Tamarind shell tannin acetone extract | 86.3 |          |
| *Arbutus unedo* extract             | 91.7 | (9)        |
| *Thevetia peruviana* flower extract  | 91.2 | (8)        |
| *Eichhornia crassipes* aqeous extract | 80  | This work |
| *Eichhornia crassipes* ethanol extract | 86.8 |          |
| *Phragmites australis* aqeous extract | 81  |           |
| *Phragmites australis* ethanol extract | 89.6 |          |

Figure 10. Response surface plots showing the effect of hydrogen ion concentration (pH) and extract dose on % IE of mild steel corrosion using (a) *E. crassipes* extract and (b) *P. australis* extract.
normal distribution from the normal probability plot of predicted % IE for mild steel.

Disclosure statement
No potential conflict of interest was reported by the author(s).

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