مجلــة العلـوم الإنسانيــة والتطبيقيـــــة
Journal of Humanitarian and Applied Sciences
كلية الآداب والعلوم قصر خيار -جامعة المرقب
المجلد العاشر -العدد التاسع عشر -يونيو /2026

Citrus Lemon Extracts as Green Corrosion Inhibitors for Mild Steel in Saline Solutions

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Received Date: 06/ March / 2026 **Accepted Date** 27/ April/ 2026

Abstract

Corrosion of metals is a serious challenge for many industries. Green corrosion inhibitors offer an eco-friendly and biodegradable alternative to traditional chemicals. This study aimed to evaluate the effectiveness of *Citrus limon* leaf extract as a green inhibitor for mild steel corrosion in a neutral 3.5% NaCl saline solution. The plant was extracted using 80% ethanol, and inhibition efficiency was assessed by the weight loss method at different extract concentrations, temperatures (30–60 °C) and immersion times (4–72 h) The results showed that the extract had a maximum inhibition efficiency of 88.65%. The inhibition efficiency increased with higher extract concentration and longer immersion time but decreased with higher temperature, suggesting the formation of a protective layer on the metal surface. Based on these findings, *Citrus limon* extract has shown promising potential as a green corrosion inhibitor. Further research is recommended to elucidate the inhibition mechanisms and application conditions for practical use.

Keywords; Citrus Limon, Green Corrosion Inhibitors, Biodegradable, Mild Steel, Weight Loss, Saline Solutions.

حمضيات الليمون كمثبطات خضراء لتآكل الفولاذ الطري في محلول ملحي

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الملخص:

يُعدّ تآكل المعادن تحديًا خطيرًا للعديد من الصناعات. وتُقدّم مثبطات التآكل الصديقة للبيئة بديلاً صديقًا للبيئة وقابلًا للتحلل الحيوي للمواد الكيميائية التقليدية. هدفت هذه الدراسة إلى تقييم فعالية مستخلص أوراق الليمون كمثبط

صديق للبيئة لتآكل الفولاذ الطري في محلول ملحي متعادل بتركيز 3.5% من كلوريد الصوديوم. تم استخلاص النبات باستخدام الإيثانول بنسبة 80%، وقُيِّمت كفاءة التثبيط بطريقة فقدان الوزن عند تراكيز مختلفة للمستخلص، ودرجات حرارة (30–60 درجة مئوية)، وفترات غمر (4–72 ساعة). أظهرت النتائج أن المستخلص حقق أعلى كفاءة تثبيط بلغت 88.65%. وقد زادت كفاءة التثبيط مع زيادة تركيز المستخلص ومدة الغمر، ولكنها انخفضت مع ارتفاع درجة الحرارة، مما يشير إلى تكوّن طبقة واقية على سطح المعدن. بناءً على هذه النتائج، أظهر مستخلص الليمون إمكانات واعدة كمثبط صديق للبيئة للتآكل. يُوصى بإجراء المزيد من البحوث لتوضيح آليات التثبيط وشروط التطبيق للاستخدام العملي.

الكلمات المفتاحية: الليمون الحمضي، مثبطات التآكل الخضراء، قابلة للتحلل الحيوي، الفولاذ الطري، فقدان الوزن، محاليل ملحية.

I. Introduction

Corrosion inhibitors derived from plant extracts offer a promising avenue for developing green and renewable corrosion protection solutions due to their wide availability, cost-effectiveness, low toxicity, high efficiency, and ease of degradation. Several plant extracts, such as those from fruits, leaves, stems, flowers, and roots, have been identified as effective corrosion inhibitors with advantages including eco-friendliness, abundance, and low toxicity (Wang et al, 2023). These inhibitors have gained significant attention in the field of corrosion protection for metals and alloys (Wang et al., 2023). Studies have shown that plant extracts like those from *Papaya*, *Poinciana pulcherrima*, *Cassia occidentalis*, and *Datura stramonium* seeds, as well as *Calotropis procera*, have demonstrated high efficiency in reducing the corrosion of steel in acidic environments (Rani & Basu, 2011). Additionally, extracts from plants such as *Moringa oleifera*, *Matricaria aurea*, *Citrus aurantium* leaves, and *Aerva lanata* have been identified as effective inhibitors for various metals, showcasing their potential as corrosion inhibitors (Jebaraj et al, 2022; Khan et al, 2019; Dakhil et al, 2018; V et al, 2018). The utilization of green inhibitors, such as *Moringa oleifera* leaf extract, has shown promise in inhibiting corrosion in magnesium, further emphasizing the potential of plant-derived inhibitors in corrosion protection (Jebaraj et al, 2022). The use of natural inhibitors from plant extracts is seen as an economic, safe, and environmentally friendly approach for protecting metals from corrosion processes (Elshahawi et al, 2022). Research efforts have focused on extracting organic compounds from plants to develop organic corrosion inhibitors, which not only hold scientific value but also practical significance (Jia et al, 2023). Numerous plant extracts, including *Tamarindus indica*, have been explored for their effectiveness as metal corrosion inhibitors, especially in acid cleaning processes, aligning with the trend towards environmentally friendly corrosion protection methods (Nasser & Masmali, 2022). Studies have highlighted the application of plant extracts as corrosion inhibitors for mild steel, showcasing the potential of natural compounds in inhibiting corrosion processes (Chigondo & Chigondo, 2016). Extracts from plants, like *Prunus dulcis* seeds, have demonstrated active inhibition of metal corrosion, positioning plant extracts as viable alternatives to synthetic inhibitors (Oshomogho et

al, 2020). Additionally, *Coconut dust* extract has been investigated as a pitting corrosion inhibitor for reinforcing steel in concrete, indicating the wide-ranging applications of plant extracts in corrosion protection (Cao et al, 2023). The use of plant extracts as corrosion inhibitors is not a new concept, with research dating back to earlier studies that have explored the inhibitive properties of natural extracts on metals like carbon steel in different corrosive media (Singh et al, 2012). These extracts have been found to contain organic substances such as alkaloids, flavonoids, triterpenoids, tannins, phenols, and amino acids, among others, which contribute to their corrosion inhibiting abilities (Nnanna et al, 2012). Furthermore, the adsorption of these organic compounds on metal surfaces forms protective layers that prevent corrosion, highlighting the potential of plant extracts as eco-friendly alternatives to synthetic inhibitors (Katuwal et al, 2020). Generally, the use of plant extracts as corrosion inhibitors offers a sustainable and environmentally friendly approach to mitigating corrosion in various industries. These natural inhibitors not only provide effective corrosion protection but also align with the growing emphasis on green and renewable technologies in corrosion prevention strategies.

To explore the potential of *Citrus limon* extract as a green inhibitor for mild steel corrosion in a saline solution, various studies on the corrosion inhibition properties of plant extracts on mild steel can be examined. *Citrus limon*, commonly known as lemon, has been investigated for its antioxidant, antimicrobial, larvicidal, and corrosion inhibition effects. Research has indicated that *Citrus limon* extracts exhibit significant antioxidant potential (Riaz et al, 2022), antimicrobial properties (G et al, 2021), and larvicidal activity (Grace et al, 2020). These characteristics suggest that *Citrus limon* extract may have the ability to inhibit corrosion by neutralizing reactive oxygen species and displaying antimicrobial effects. Moreover, investigations on other plant extracts such as *Prunus dulcis* (Pal et al., 2018), *Caryota urens* (Vadivu et al, 2017), and *Clematis gouriana* (Mayakrishnan et al, 2011) have demonstrated their efficacy as green inhibitors for mild steel corrosion. These studies highlight the promise of plant extracts as corrosion inhibitors, providing further support for considering *Citrus limon* extract in this capacity. Overall, the extensive research on *Citrus limon* extract emphasizes its diverse properties, ranging from corrosion inhibition to antimicrobial, antioxidant, larvicidal, and pharmaceutical activities. Therefore, the present study aims to investigate the corrosion inhibition potential of *Citrus limon* leaf extract on mild steel in a 3.5% NaCl solution using the weight loss method, and to evaluate the influence of inhibitor concentration, immersion time, and temperature on its efficiency.

II. Materials and methods

Test solution

NaCl & distilled water were used to prepare the aggressive solution (3.5% NaCl) for all experiments in the absence and presence of different concentrations of plant extracts (Saedah, 2014).

Plant collection, authentication, drying and grinding

Citrus limon leaves was collected by hand randomly from the northwestern part of Libya (Mashrue Alhadba and Farm of Faculty of Agriculture - University of Tripoli). The plant specimen was taxonomically identified at botany department-faculty of

science-university of Tripoli, Tripoli, Libya. Plant collected was rinsed under running water to remove any dust or dirt, then dried in shade & at room temperature until dried out completely, after that it was milled by an electric mill.

Plant extraction

The powdered plant was refluxed in 80% ethanol using the reflux apparatus for three hours, the ethanolic extract was filtered using filter paper and the resulted filtrate was concentrated using a rotary evaporator finally dried in the oven at 60 °C for 24 hours and stored in small jars at 2°C until use. At the time of an experiment, plant extract's test solutions were prepared from stock extract at concentrations of 800, 400, 200, 100 ppm using 3.5% NaCl solution (Qiang et al., 2018).

Phytochemical screening

Citrus limon leaves extract was subjected to Dragendrof's, Mayer's, Wagner's tests to detect the presence of Alkaloids, Shinoda, Alkaline reagent test to detect flavonoids, Keller-Killiani test for glycosides, Ferric Chloride test for phenolic compounds and tannins, Ninhydrin, Millon's test for amino acids, Biuret test for proteins, Libermann-Burchard, Salkowski's test to detect sterols and triterpenoids, Fehling's, Molisch, Benedict's to detect carbohydrates, Froth test for saponins, test for oils and fats, tests for organic acids and inorganic acids (Raj V. N. *et al*., 2017).

Sample preparation

The metal used for this study was mild steel, it was a rod with an average length of 4.0 cm and a diameter of 1.1 cm for weight loss method. The specimen surface was ground with emery paper (down to 600), washed with distilled water, degreased with acetone and dried with a stream of air. The sample was analyzed using FONDARY MASTER PRO instrument (optical emission spectrometer) at the high vocational center of casting (Al – Sayeh, Tripoli – Libya), The results of the analysis describe the chemical composition of the steel as follow (wt %):

Element	C	Si	Mn	S	P	Cr	Fe
Wt%	0.178	0.303	0.546	0.0127	0.0086	0.0127	Balance

Corrosion rate measurement

Weight loss (gravimetric) method

After the length, diameter and weight measurement of the mild steel specimens by using vernier caliper and analytical balance respectively, the specimens were completely immersed in 50ml of the test solution of 3.5% NaCl in the presence and absence of different concentrations of the inhibitor at different temperature (30, 50, 60 °C). The specimens were removed from the test solutions after 4, 24, 48, 72 hours, washed immediately with distilled water, degreased with acetone and dried with a stream of air then re-weighed again. The weight loss data was obtained from the difference in weight of the specimens before and after the experiment.
The corrosion rate (CR) was calculated from

$$CR = \frac{WL}{At}$$

Where WL is weight loss in gram, A is the specimen surface area in cm^2 and t which is the immersion period in hours.

The inhibition efficiencies (%I) for the corrosion of mild steel in 3.5% NaCl containing a different concentration of inhibitor were calculated using:

$$\%I = \left(\frac{CR_{blank} - CR_{inh}}{CR_{blank}}\right) x100$$

Where CR_{blank} and CR_{inh} are the corrosion rate in the absence and presence of the inhibitor, respectively.

III. Results and discussion

Phytochemical screening

The phytochemical screening confirms that *C. limon* extract contains alkaloids, flavonoids, glycosides, phenolic compounds, tannins, amino acids, proteins, sterols, triterpenoids, carbohydrates, saponins, and organic acids.

It's interesting that some of the chemical molecules listed above have antioxidant properties. Some examples of antioxidants are the flavonoid and the phenolic compounds. Previous studies have shown that tannins and some antioxidant compounds in plant extracts can stop steel from rusting in acidic environments (Oguzie, 2007; Oguzie, 2008; Eddy & Ebenso, 2008). Tannins, triterpenoids, flavonoids, amino acids, alkaloids, saponins, phenols, and glycosides are some of the organic compounds that have been found in plant and leaf extracts that can stop corrosion in corrosive media (Cao et al., 2023; Chigondo & Chigondo, 2016); (Dakhil et al., 2018); (Katuwal et al., 2020).

Inhibition efficiency

The results show that the inhibition efficiency of *Citrus limon* plant extract was 88.65%. That means our plant extract can acts as a good corrosion inhibitor in 3.5% NaCl media. That is due to the adsorption of some phytochemical compounds of the plant extract on the surface of the mild steel, more specifically the heteroatoms present in the phytochemical compounds will bind to the iron and change the charge density of mild steel resulting in retardation of cathodic and anodic reaction.

The effect of immersion time on the inhibition efficiency at different plant extract concentrations is presented in Figure 1. In this graph, the curves represent the relationship between **Immersion Time (hour)** on the x-axis and **Inhibition Efficiency (%)** on the y-axis for extract on mild steel.

The graph in Figure 1 shows multiple curves, representing **Inhibition Efficiency** at different immersion times and concentrations. It's clearly showing positive correlation with concentration. All curves show a steep upward trend initially, meaning that as you add more *Citrus limon* extract, the protection against corrosion increases significantly. The different colored lines/curves (e.g., the red squares vs.

green triangles) represent different *Citrus limon* extract concentrations. The higher curves indicate that **higher** *Citrus limon* extract concentrations result in higher inhibition efficiency. As can be seen in the Figure 1 where the yellow curve represents the 800 ppm of the extract concentration showed the highest inhibition efficiency around 90% after 72 hours of immersion time. This is because the inhibitor molecules have more time to organize into a stable, dense protective layer on the steel surface. Conversely, the lowest extract concentration (blue curve) displayed a decrease in the inhibition efficiency. The curves prove that both a **higher concentration** and **more time** allow the inhibitor molecules to form a more effective barrier against the corrosive medium.

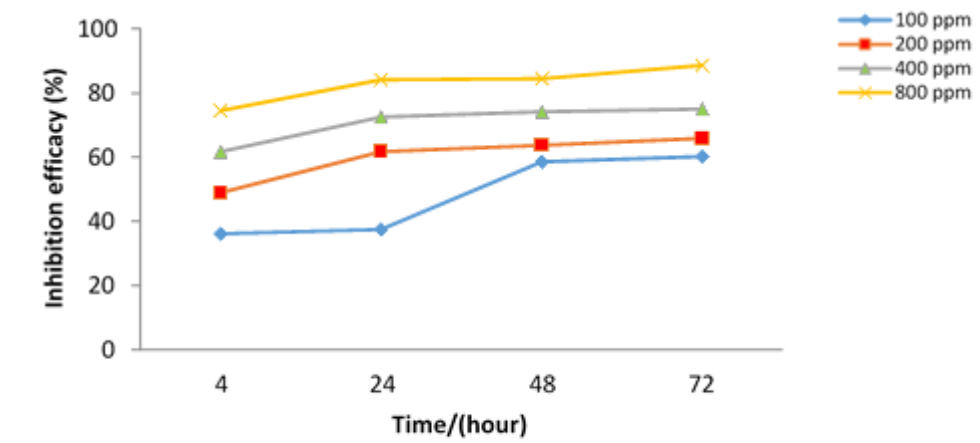


Figure 1. Effect of inhibitor concentration on protection efficiency on mild steel.

Hence, the inhibition efficiency of *C. limon* plant extract increases with the increase of its concentration and immersion time as shown in [Figure 1]. These findings are aligned with several previous studies, for instance, a study that was performed by Onuegbu *et al*. showed the use of *Citrus* peels as inhibitor in corrosive media of mild steel obtained 90.3 % inhibition efficiency from the use of *Citrus* peels inhibitor concentration of 900 ppm for mild steel in 1M HCl medium (Onuegbu *et al*., 2013; Patel *et al*., 2018).

The effect of temperature on the inhibition efficiency is presented in [Figure 2]. The graph is showing the "Effect of temperature on inhibition efficiency" typically plots **Temperature** (on the x-axis) against **Inhibition Efficiency (%)** (on the y-axis). It demonstrates that the inhibition efficiency of the *C. limon* plant extract decreases with the increase of temperature (as the temperature rises, the "inhibition efficiency" decreases). The highest IE (80-90%) was obtained using 800 ppm of *Citrus limon* extract concentration at various temperatures. The IE was around 90% at 30 °C while IE decreased by around 10% to 80% when the temperature increased to 60 °C On the other hand, when *Citrus limon* extract concentration reduced to 100 ppm, the inhibition efficiency dropped down to 60% at 30°Cand to lower percentage 20% at 60°C Since lemon extract is rich in ascorbic acid and citric acid, these organic compounds contain oxygen atoms that "stick" to the surface of the mild steel. The graph would be the visual proof of how well that "sticky" protective layer holds up when the heat is turned up. These findings are very close to the ones that were

achieved by Aboubi *et al.* (Aboubi *et al.*, 2025). In their study, they were investigating the performance of three Citrus limon extracts collected from three different regions in Morocco, as green corrosion inhibitors to protect mild steel in 1M HCl medium. However, in the current work, a neutral solution of 3.5% sodium chloride (NaCl) has been used instead of 1M HCl medium.

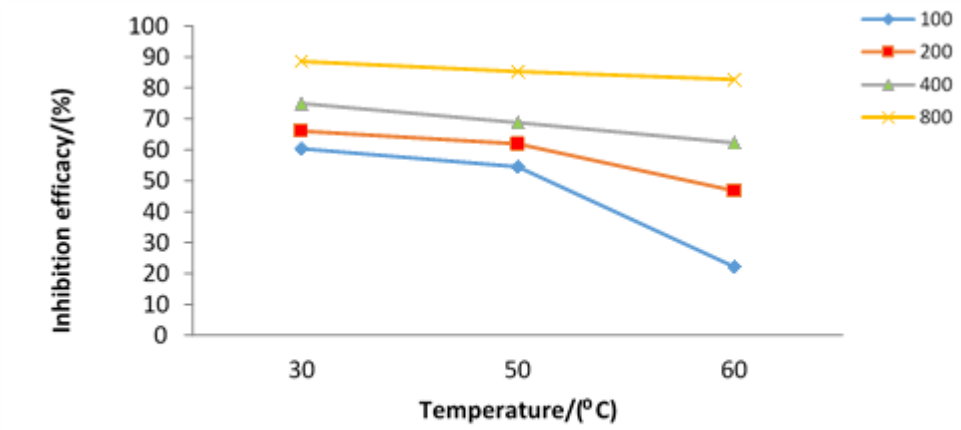


Figure 2 Effect of temperature on the inhibition efficiency of Citrus limon plant extract on mild steel.

Corrosion rate

The effect of concentration and immersion time on the corrosion rate is presented in [Figure 3]. In this graph, the x-axis represents the duration the metal is left in the solution (Immersion Time), and the y-axis represents the speed at which the metal is losing mass (Corrosion Rate). The results show that the corrosion rate decreases with the increase of inhibitor concentration and immersion time. In Figure 3, we can see the lines/curves for both the "presence" and "absence" of the plant extract:

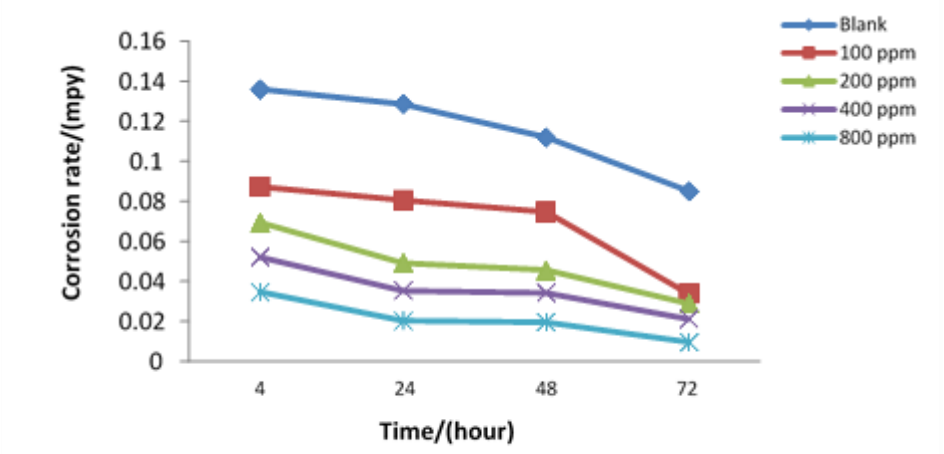


Figure 3. Effect of immersion time on the corrosion rate of mild steel in the presence and absence of plant extract.

1. **Without extract (Control/ blank):** The corrosion rate remains high or may even increase as the NaCl solution attacks the unprotected metal.

2. **With plant extract:** The curve illustrates a sharp or steady downward slope, indicating that as time passes, the inhibitor becomes more effective at shielding the steel.

It's noteworthy that the corrosion rate also decreases when the concentration of the inhibitor is increased, suggesting that both time and the amount of extract used work together to protect the metal. This observation is consistent with the findings by (Okunzuwa & Okunzuwa, 2023) using *Citrus sinensis* extract as a green inhibitor for mild steel in 1M HCl solution at different concentrations.

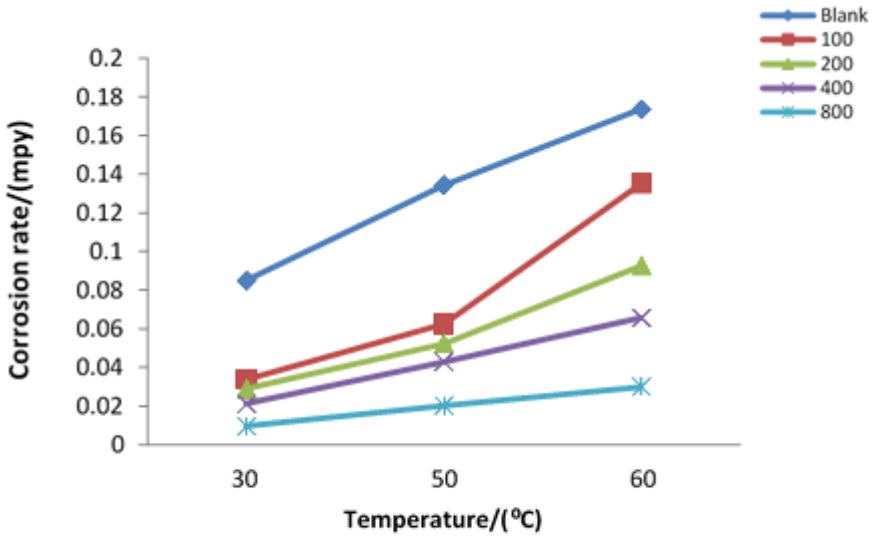


Figure 4. Effect of temperature on the corrosion rate of mild steel in the presence and absence of plant extract.

The effect of temperature on the corrosion rate is presented in [Figure 4]. Based on this graph the relationship between temperature and the corrosion rate of mild steel is characterized by a direct correlation. As expected, the inhibition efficiency increases with increase in *Citrus aurantium* extract concentration as a further indicative that various plant extracts are effective in inhibiting corrosion. In a different study that was conducted by Patel *et al*. (Patel *et al*, 2018) reveals that *Citrus aurantium* extract is a good inhibitor for the corrosion of mild steel in 0.05 M sulphuric acid medium. In which, the results showed that the corrosion rate (CR) increased with increase in the immersion time and temperature (°C) while inhibition efficiency (IE%) of inhibitors decreased with the rise in immersion time (hour) as well as the rise in temperature (Patel *et al*, 2018).

The results indicate that the corrosion rate increases as the temperature rises. Generally, higher temperatures provide more energy to the reacting molecules, accelerating the chemical reactions that lead to metal degradation. Nevertheless, in the absence of plant extract (Control), the metal surface is fully exposed to the corrosive medium leading to a rapid and steep increase in the corrosion rate.

C. Limon extract has shown to have promising results as a green inhibitor for the corrosion of mild steel in saline solutions. Thus, this study established the

corrosion inhibition performance of *Citrus limon* extract as a corrosion inhibitor of mild steel in 3.5% NaCl solution. The knowledge acquired from this work will be useful in applying an eco-friendly solution to the mild steel corrosion issue, which consequently will contribute to a greener and cleaner environment. However, more work is needed to fully understand the mechanisms and make the application and concentration optimal for practical use and at several ecological conditions.

Conclusion

This study has dealt with *Citrus limon* plant extract and based on the results the following conclusions have been drowned:

- The major phytochemical groups of *C. limon* plant extract has been identified but the corrosion test was carried out without group separation.
- *C. limon* extract exhibit a good corrosion inhibition efficiency for mild steel in 3.5% NaCl solution. Remarkably, the *Citrus Limon* extract showed a strong corrosion inhibition effect (88.65%).
- The protection efficiency of mild steel by *C. limon* plant extract has increased upon immersion time and inhibitor concentration but has decreased with the increase of temperature.
- Acceptable corrosion rates of mild steel were recorded under the inhibition of *C. limon* plant extract.
- Finally, while the corrosion rate still increases with temperature even when the plant extract is present, it does so at a much slower pace compared to the unprotected metal (Control). To ensure the sustainability and dependability of this natural corrosion inhibitor, future studies should investigate the inhibitor's performance under various environmental conditions.

Conflict of interest statement

We declare that we have no conflict of interest.

This research did not receive any specific grant from funding agencies in the public, commercial, or not-profit-sectors.

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