Marine Algae (Caulerpa lentillifera) Extract as a Green Corrosion Inhibitor in

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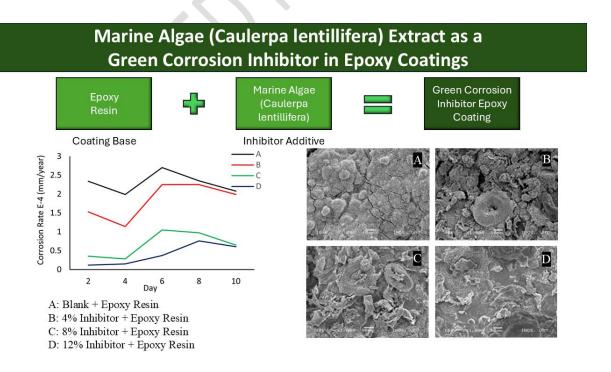
2	Epoxy Coatings
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18	Abstract
19	Corrosion poses a serious threat to marine structures, leading to rapid degradation of
20	metal components through their interaction with aggressive environments. One effective
21	strategy to mitigate corrosion is the use of inhibitors incorporated into protective coatings. This
22	study investigates the anticorrosive properties of a green inhibitor derived from sea grapes
23	(Caulerpa lentillifera), a marine ulvophyte algae commonly found in the Indo-Pacific. Extracts
24	of sea grapes were incorporated into epoxy resin coatings at concentrations of 0 wt%, 4 wt%,

8 wt%, and 12 wt%, and applied to mild steel specimens immersed in artificial seawater.

Corrosion performance was evaluated using weight loss measurements, electrochemical impedance spectroscopy (EIS), and scanning electron microscopy (SEM). The maximum extract concentration (12 wt%) resulted in the highest protection, achieving approximately 70% inhibition efficiency via weight-loss measurements and 64% via EIS, compared to the uninhibited control. This formulation exhibited the largest impedance semicircle in the Nyquist plots and a smooth, defect-free surface under SEM analysis. These findings highlight the role of adsorption and film formation in enhancing protection. In conclusion, epoxy coatings modified with 12 wt% sea grapes extract provide superior corrosion resistance, offering an ecofriendly and effective solution for marine applications.

Keywords: Corrosion, Sea Grapes, EIS, Green inhibitor, Coating, SEM.

Graphical Abstract



1. Introduction

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Corrosion of metallic structures in marine environments remains a major engineering and environmental challenge. The continuous exposure of metals to seawater leads to electrochemical degradation, causing structural damage and economic losses in maritime, offshore, and coastal industries (Sekhar Das et al., 2023; Jiyaul et al., 2023). Mild steel (MS), in particular, is widely used in marine infrastructure, pipelines, and vessels because of its mechanical strength and low cost. However, its susceptibility to chloride-induced corrosion limits its long-term service life (Xu et al., 2023; Meng et al., 2020). The presence of dissolved salts, especially chloride ions, accelerates localized corrosion and pitting on mild steel surfaces. Seawater typically contains about 3.5% dissolved salts and has a slightly alkaline pH (~8.0), making it an aggressive electrolyte for most metallic materials (Pawlowicz, 2019). To mitigate such corrosion, protective coatings and corrosion inhibitors are the most common strategies. Epoxy coatings are among the most used protective systems because of their excellent adhesion, mechanical strength, and chemical resistance. However, epoxy films often contain microdefects, pores, and cracks that allow the diffusion of corrosive species, leading to coating degradation over time (Mahdy et al., 2023). The incorporation of corrosion inhibitors within the coating matrix can significantly enhance barrier performance by reducing the diffusion of ions and water through the polymer (Kamaruzzaman et al., 2021). Conventional inorganic inhibitors such as chromates, phosphates, and molybdates have been widely applied but are being phased out due to their toxicity and environmental impact. Similarly, some organic inhibitors such as imidazoles (Bousba et al., 2023; Daoudi et al., 2023) and amines, though effective, raise concerns about biodegradability and sustainability (Ko et al., 2021; Kedimar et al., 2024). This shift in regulatory and environmental perspectives has motivated the development of green corrosion inhibitors, derived from naturally occurring materials such as plants, herbs,

and marine biomass. These inhibitors contain bioactive molecules rich in oxygen, nitrogen, and sulfur atoms that can adsorb onto metallic surfaces and form protective films via physical or chemical adsorption (Kamaruzzaman et al., 2022; Haque et al., 2023; Wan et al., 2023). The advantages of such natural extracts include renewability, low cost, biodegradability, and compatibility with existing coating systems. A growing body of research has demonstrated the corrosion inhibition potential of various plant and marine extracts, including Olea sp. leaves (Ikhmal et al., 2017), Aloe vera (Royani et al., 2024), and Andrographis paniculata (Kamaruzzaman et al., 2021). These studies generally report inhibition efficiencies between 70% and 90%, depending on the extract composition and concentration.

In particular, marine algae have shown strong promise as green corrosion inhibitors because of their high content of polysaccharides, polyphenols, terpenoids, and other antioxidant compounds capable of metal surface complexation (Nabilah et al., 2022; Singh et al., 2022). Several species, such as Sargassum polycystum, Ulva lactuca, and Fucus serratus have been studied and shown to reduce corrosion rates of mild steel in seawater or acidic media by forming adsorbed protective layers (Okafor et al., 2016; Umoren et al., 2019; Hassan et al., 2021). However, despite the abundance of algae species in coastal ecosystems, limited work has investigated the corrosion inhibition properties of *Caulerpa lentillifera*, commonly known as sea grapes. This edible green algae, native to the Indo-Pacific, contains unique bioactive compounds such as sulphated polysaccharides, phenolic acids, and amino acids with known antioxidant and film-forming capabilities (Syakilla et al., 2022).

Recent studies on *Caulerpa lentillifera* have primarily focused on its nutritional, pharmaceutical, and antioxidant properties, but not on its potential as a corrosion inhibitor. Its molecular composition suggests strong adsorption capability onto metal surfaces through functional groups containing hydroxyl, carboxyl, and amine moieties. These groups can interact with the steel substrate, forming a compact film that reduces charge transfer and

minimizes electrolyte penetration. When incorporated into a coating matrix, these interactions are expected to enhance the physical barrier effect of the polymer, improving the overall corrosion protection in marine environments.

Despite these studies, existing models of green corrosion inhibition exhibit several limitations. Most investigations have been conducted in highly acidic media, which do not accurately represent marine conditions, and many lack long-term immersion data or coating-integrated formulations. Furthermore, several works rely solely on electrochemical measurements without complementary morphological or gravimetric validation, limiting the mechanistic understanding of inhibitor performance. These gaps highlight the need for more comprehensive, seawater-based studies that integrate natural extracts directly into protective coating systems.

The motivation behind this work stems from the growing need for environmentally benign corrosion-mitigation strategies for steel structures operating in marine environments, where conventional inhibitors often pose toxicity and sustainability concerns. To address this challenge, the present study explores a green and renewable alternative by incorporating *Caulerpa lentillifera* extract into epoxy coatings. The aim of the work is to develop and assess a bio-modified epoxy coating capable of enhancing the corrosion resistance of mild steel under artificial seawater exposure. The novelty of this research lies in evaluating a marine-algae-based inhibitor within a polymeric coating system and under seawater immersion conditions, which have been rarely studied, as most existing research focuses predominantly on acidic media.

The scope of this study includes the formulation of epoxy coatings containing different concentrations of *Caulerpa lentillifera* extract (4 wt%, 8 wt%, and 12 wt%), their application onto mild steel substrates, and performance evaluation under sustained seawater immersion. The specific objectives are to: (i) prepare and characterize extract-modified epoxy coatings, (ii)

assess their corrosion resistance through weight-loss measurements and electrochemical impedance spectroscopy (EIS), and (iii) examine surface morphology and degradation features using scanning electron microscopy (SEM). The outcomes contribute to the development of sustainable marine-protective coatings and demonstrate the potential of *Caulerpa lentillifera* as a renewable, eco-friendly corrosion-inhibiting additive.

2. Materials and Methods

2.1. Preparation of Mild Steel Samples

Mild steel coupons (25 × 25 × 3 mm) were used. They were polished sequentially with 180, 320, 600, 1000, and 1200 grit sandpapers using distilled water as a lubricant. The polished samples were cleaned with acetone, air-dried, and stored in a desiccator before use.

2.2. Preparation of Sea Grapes Extract

Fresh sea grapes (*Caulerpa lentillifera*) were washed and dried at room temperature for 4 days, followed by 1-day oven drying at 50°C. The dried sea grapes were powdered, soaked in methanol for 6 hours, filtered, concentrated, and evaporated. The resultant extract was stored at room temperature in powder form.

2.3. Formulation of Paint Coatings and Preparation of Coated Samples

The coating formulations were prepared by dispersing the dried *Caulerpa lentillifera* (sea grapes) extract in a solvent mixture containing 2.4 mL of dimethyl sulfoxide (DMSO) and 0.6 mL of isopropanol using a sonicator for 30 minutes to ensure complete dissolution and uniform dispersion. Epoxy resin (10 g) was then added to the extract solution, followed by an additional 30 minutes of sonication. Subsequently, 3 g of hardener was incorporated, and the resulting mixture was sonicated for a further 15 minutes to obtain a homogeneous coating formulation.

Four different coating systems were prepared. Paint-1 (Control): plain epoxy coating without inhibitor. Paint-2: epoxy containing 0.40 g of sea grapes extract, equivalent to 4 wt%

relative to the epoxy resin. Paint-3: epoxy containing 0.80 g of extract, 8 wt%. Paint-4: epoxy containing 1.20 g of extract, equivalent to 12 wt%.

After preparation, the solvent mixture (DMSO and isopropanol) was completely evaporated at room temperature before application of the coating. The coatings were applied onto pre-cleaned mild steel panels using a dip-coating method to achieve uniform film thickness. All coated specimens were cured under ambient conditions for 24 hours, followed by post-curing at 60 °C for 2 hours to ensure full crosslinking of the epoxy matrix.

The following nomenclature shall be used throughout this study:

- Sample A represents mild steel coated with Paint-1 (Control).
- Sample B represents mild steel coated with Paint-2 (4 wt% inhibitor).
- Sample C represents mild steel coated with Paint-3 (8 wt% inhibitor).
 - Sample D represents mild steel coated with Paint-4 (12 wt% inhibitor).

Three replicates of each combination were prepared. Inhibitor concentrations above 12 wt% resulted in poor dispersion in the epoxy resin, which in turn leads to poor adhesion between mild steel and epoxy, and therefore are excluded from this study.

2.4. Electrochemical Testing

Electrochemical tests were conducted using a Gamry workstation with a three-electrode system. The working electrode (WE) was mild steel, the reference electrode (RE) was Ag/AgCl, and the counter electrode (CE) was platinum. Open Circuit Potential (OCP) measurements were recorded for 1800 seconds to allow the system to stabilize. Electrochemical Impedance Spectroscopy (EIS) was performed with a frequency range from 100 kHz to 0.01 Hz and a signal amplitude of 10 mV. Linear Polarization Resistance (LPR) measurements were carried out using a potential scan range of -10 mV to +10 mV relative to OCP, at a scan rate

of 0.1667 mV/s. All measurements were performed in an artificial seawater medium and repeated three times, with the average values reported.

2.5. Weight Loss and Corrosion Rate Evaluation

Steel samples were immersed in artificial seawater for 10 days at ambient temperature. Every 2 days, samples were removed, washed with a mixture of diluted hydrochloric acid and nitric acid, rinsed with distilled water, dried, and reweighed. The corrosion rate (C_R, in mm/year) was calculated using Eq(1):

$$CR = \frac{87.61 \times WL}{D \times A \times T} \tag{1}$$

Where WL is the weight loss (mg), D refers to the density of steel (g/cm³), A represents the area of the sample (cm²), and T is the time (h).

2.6. Surface Morphology Analysis

SEM imaging was conducted to assess surface changes due to corrosion under various magnifications (×25, ×100, ×500, ×1000) using a JSM-6390LA SEM according to ASTM F1877-16 standards. Surface morphology was compared between coated and uncoated samples, and with various concentrations of inhibitors.

The evaluation methodology used in this study integrates weight-loss measurements, electrochemical impedance spectroscopy (EIS), and scanning electron microscopy (SEM) to provide a comprehensive assessment of coating performance. Weight-loss analysis offers long-term cumulative degradation behavior, whereas EIS delivers a sensitive and non-destructive evaluation of coating barrier properties through charge-transfer resistance and capacitive behavior. SEM analysis complements these techniques by directly visualizing film integrity, microcracking, and surface morphology. This multi-technique approach ensures that both electrochemical and physical degradation mechanisms are captured and provides a more

rigorous evaluation of inhibitor performance compared to single-method studies commonly reported in existing literature.

The novelty of the proposed design is established by combining Caulerpa lentillifera extract with an epoxy barrier coating and evaluating its performance in artificial seawater, whereas most existing algae-based inhibitors have been tested only in acidic media or in solution-phase studies without a coating matrix. Unlike prior works that apply the extract directly into corrosive media, this study incorporates the inhibitor within a polymeric network, enabling controlled release, improved adhesion, and prolonged barrier performance. The comparative analysis in Section 3.4 demonstrates that the present formulation outperforms or matches the best-reported marine-based inhibitors, particularly in seawater environments, thereby confirming the unique contribution of this epoxy-inhibitor hybrid system.

3. Results and Discussion

3.1. Weight Loss and Corrosion Rate Evaluation

The cumulative weight loss and corresponding corrosion rates are presented in Table 1. All values represent the mean of triplicate specimens, where the standard deviation for corrosion rate values remained less than $\pm 5\%$ of the reported mean, indicating good reproducibility. A clear reduction in corrosion rate was observed with increasing inhibitor concentration and immersion time. After two days, the plain epoxy coating (Sample A) exhibited an initial corrosion rate of approximately 2.3×10^{-4} mm·yr⁻¹, whereas coatings incorporating 4 wt%, 8 wt%, and 12 wt% extract showed progressively lower rates of 1.5×10^{-4} , 3.6×10^{-5} , and 1.2×10^{-5} mm·yr⁻¹, respectively. This early behavior indicates that the sea-grape extract rapidly adsorbs at the metal/coating interface, impeding electrolyte penetration into the coating pores.

With continued immersion (Days 4-10), all samples displayed gradual mass loss, but the rate of deterioration remained significantly smaller for extract-modified coatings. After ten

days, the plain coating had a corrosion rate of 2.1×10^{-4} mm·yr⁻¹, while the 12 wt% extract coating maintained the lowest value of 6.1×10^{-5} mm·yr⁻¹; therefore, representing an overall reduction of nearly 70 % relative to the control. These results demonstrate that the presence of *Caulerpa lentillifera* extract effectively suppresses the corrosion process throughout the exposure period.

Table 1: Weight of Mild Steel and Corrosion Rates Before and After Immersion

Day	Parameter	Sample A	Sample B	Sample C	Sample D
0	Initial Weight (g)	12.37	12.27	11.99	11.83
	Weight (g)	11.77	11.87	11.90	11.80
2	Weight loss (g)	0.60	0.39	0.09	0.03
	CR (mm/yr)	2.34E-04	1.53E-04	3.57E-05	1.18E-05
	Weight (g)	11.26	11.58	11.83	11.76
4	Weight loss (g)	0.51	0.30	0.07	0.04
	CR (mm/yr)	1.99E-04	1.14E-04	2.84E-05	1.52E-05
	Weight (g)	10.56	11.00	11.56	11.66
6	Weight loss (g)	0.70	0.58	0.27	0.10
	CR (mm/yr)	2.70E-04	2.25E-04	1.05E-04	3.73E-05
	Weight (g)	9.95	10.42	11.30	11.47
8	Weight loss (g)	0.61	0.58	0.25	0.20
	CR (mm/yr)	2.35E-04	2.25E-04	9.77E-05	7.61E-05
	Weight (g)	9.42	10.03	11.14	11.19
10	Weight loss (g)	0.54	0.38	0.17	0.16
	CR (mm/yr)	2.08E-04	1.49E-04	6.49E-05	6.05E-05

The improvement in protection can be attributed to multiple, synergistic mechanisms: **Barrier enhancement:** The extract particles appear to fill micro-voids within the epoxy matrix, thereby reducing the coating's permeability to oxygen, chloride, and water molecules. **Chemical adsorption:** Bioactive compounds present in *Caulerpa lentillifera*, notably polysaccharides, phenolic acids, and terpenoids that possess oxygen- and nitrogen-bearing functional groups capable of forming coordinate bonds with the iron surface. Such interactions generate an adherent, hydrophobic film that hinders ionic transport.

Film stability: The extract likely promotes cross-linking between the polymer chains and the adsorbed inhibitor layer, yielding a more compact interfacial film that resists delamination during prolonged seawater exposure.

The temporal evolution of corrosion rates reveals a slight increase after Day 6 for some samples, which can be ascribed to the gradual saturation of the coating and partial desorption of inhibitor molecules. Nevertheless, even after ten days, inhibitor-modified coatings retained corrosion rates far below those of the control, confirming their durable protective action.

These findings are consistent with earlier studies on marine-derived inhibitors such as Sargassum polycystum and Ulva lactuca, which also reported substantial reductions in corrosion rate in seawater media (Umoren et al., 2019; Hassan et al., 2021). The superior performance of *Caulerpa lentillifera* extract observed here can be linked to its high content of sulfated polysaccharides and phenolic antioxidants, both known to promote strong adsorption and enhanced film formation.

Overall, the gravimetric results confirm that incorporating *Caulerpa lentillifera* extract into epoxy coatings significantly enhances corrosion resistance in artificial seawater, validating its potential as a sustainable and environmentally friendly corrosion-control additive for marine applications.

3.2. Electrochemical Impedance Spectroscopy (EIS) Analysis

Electrochemical impedance spectroscopy (EIS) was performed to evaluate the influence of *Caulerpa lentillifera* extract on the corrosion behaviour of epoxy-coated mild steel in artificial seawater. The Nyquist plots of typical samples illustrated in Figure 1 exhibit single, depressed semicircles characteristic of a charge-transfer-controlled process.

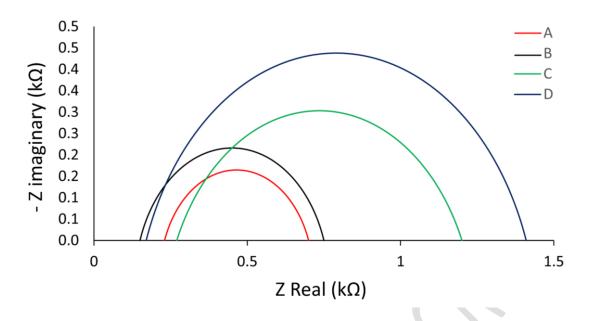


Figure 1: Nyquist curves of mild steel samples after ten days of immersion for samples A - D.

The Nyquist plots exhibit semicircular shapes, which are characteristic of charge transfer resistance (R_c) at the metal–solution interface. A larger semicircle indicates higher R_{ct} and, thus, better corrosion protection. Among the tested coatings, Sample D containing 12 wt% *Caulerpa lentillifera* extract exhibited the largest semicircle, indicating the highest corrosion resistance. This strongly suggests that the presence of sea grapes extract enhances the protective properties of the epoxy coating by forming a more compact and adherent film on the mild steel surface. The extract likely acts as a barrier, limiting electrolyte access and retarding charge transfer processes responsible for corrosion. In contrast, Sample A (plain epoxy resin) demonstrated the smallest semicircle, confirming the limited protection offered by the coating alone without any inhibitor additive. Intermediate corrosion resistance values were observed for Samples B and C, containing 4 wt% and 8 wt% inhibitor, respectively. These results align with previous studies showing that plant-based green inhibitors typically act through physical adsorption or chemisorption, forming protective layers over the metal surface (El-Haddad & Fouda, 2015).

To quantitatively interpret the EIS data, the impedance spectra were fitted using a standard Randles-type equivalent electrical circuit (EEC) commonly applied to coated metal systems. The model consists of the solution resistance (R_s) in series with a parallel combination of charge-transfer resistance (R_{et}) and the non-ideal double-layer capacitance at the metal/coating interface (C_{dl}). This configuration, illustrated in Figure 2, reliably describes corrosion processes under organic coatings where interfacial heterogeneity and surface roughness cause deviations from ideal capacitive behavior. The fitted parameters (R_{ct} and C_{dl}) were extracted for all coated samples to evaluate the influence of inhibitor concentration on electrochemical performance and are summarized in Table 2. The R_{ct} values increased systematically with increasing extract concentration, from approximately 0.50 k Ω cm² for the plain epoxy coating to 0.65, 0.95, and 1.40 k Ω cm² for coatings containing 4 wt%, 8 wt%, and 12 wt% extract, respectively. This progressive increase in R_{ct} indicates that the *Caulerpa lentillifera* extract markedly retards the charge-transfer process at the metal/coating interface. Conversely, the C_{dl} values showed an increasing trend, suggesting an increase in the interfacial polarization or effective surface area.

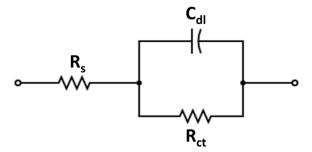


Figure 2: The equivalent electrical circuit (EEC) used to fit EIS data

Table 2: Fitted electrochemical impedance parameters for Samples A – D in artificial seawater.

Sample	R _s (kΩ cm²)	R _{ct} (kΩ cm²)	C _{dl} (μF cm ⁻²)	IE (%)
Α	0.05 ± 0.002	0.50 ± 0.03	40 ± 2	_
В	0.05 ± 0.002	0.65 ± 0.04	58 ± 3	23
С	0.05 ± 0.002	0.95 ± 0.06	190 ± 8	47
D	0.05 ± 0.002	1.4 ± 0.07	250 ± 12	64

The increasing R_{ct} values with higher inhibitor concentration clearly indicate a dose-dependent enhancement in corrosion protection. This behavior arises from the larger quantity of active phytochemical constituents in the *Caulerpa lentillifera* extract, primarily oxygen- and nitrogen-containing functional groups, which exhibit strong affinity toward the steel surface. Their adsorption promotes the formation of a compact, hydrophobic, and adherent protective film that restricts electrolyte permeation and suppresses charge transfer reactions, an essential requirement in chloride-rich marine environments that typically accelerate localized corrosion.

In parallel, higher extract concentrations may not only facilitate stronger adsorption but also introduce additional polar organic species within the coating matrix and at the metal—coating interface. These species increase the interfacial dielectric constant and/or effective surface area, resulting in elevated C_{dl} values despite overall improved corrosion resistance. This behavior has been reported in natural-extract-based coatings where inhibitor molecules contribute to a more hydrated or polar interfacial layer while still effectively blocking active corrosion sites. Together, the concurrent rise in R_{ct} and C_{dl} highlights a mixed mechanism involving both barrier enhancement and adsorption-driven surface modification.

These findings further validate *Caulerpa lentillifera* extract as a viable green corrosion inhibitor for marine coating applications, supporting its practical deployment in eco-friendly epoxy-based systems. Continued investigation into its molecular adsorption behavior, interaction with polymeric networks, and long-term stability will help optimize its performance in real marine environments.

The inhibition efficiency (IE %) was calculated from the fitted R_{ct} values according to:

$$306 IE\% = \left(1 - \frac{R_{ct,control}}{R_{ct,inhibitor}}\right) \times 100\% (2)$$

The calculated efficiencies were approximately 23%, 47%, and 64% for the coatings containing 4 wt%, 8 wt%, and 12 wt% extract, respectively. These quantitative results confirm

that the incorporation of *Caulerpa lentillifera* extract significantly enhances the impedance response of the epoxy coating and effectively suppresses corrosion.

3.3. Surface Morphology Analysis (SEM)

The surface morphology of epoxy-coated mild steel specimens after immersion in artificial seawater was examined using scanning electron microscopy (SEM), as shown in Figure 3. The micrographs reveal distinct differences in surface topography and corrosion features between the uninhibited and extract-modified coatings.

The plain epoxy coating (Sample A) exhibited severe surface degradation characterized by deep cracks, grooves, and corrosion pits that penetrated the polymer matrix. These features indicate poor adhesion and substantial ionic penetration, resulting in localized corrosion at the metal/coating interface. The rough, uneven texture and widespread defects confirm that the coating alone provides limited barrier protection under marine conditions.

The 4 wt% extract coating (Sample B) displayed a comparatively smoother surface with fewer cracks and smaller corrosion pits, suggesting that the extract contributes to partial surface passivation. However, microvoids and discontinuities are still visible, implying that the barrier film is not yet fully developed at this concentration.

In contrast, the 8 wt% extract coating (Sample C) demonstrated a densely packed and more homogeneous surface, with only minor microcracks observed. The reduction in porosity and corrosion features indicates that the extract effectively seals microdefects in the epoxy matrix, reducing the diffusion of corrosive species such as chloride ions and dissolved oxygen. The surface appears continuous and compact, consistent with a stable protective layer formed by the adsorbed bioactive compounds present in *Caulerpa lentillifera*.

The 12 wt% extract coating (Sample D) exhibited the smoothest and most uniform surface morphology, devoid of visible cracks or pits. The film appears compact and intact, indicating excellent adhesion between the coating and the metal substrate. The presence of a

uniform, featureless surface confirms the formation of a coherent and adherent inhibitor layer that effectively prevents corrosion initiation. This observation correlates well with the highest charge-transfer resistance (R_{ct}) and lowest corrosion rate obtained from the EIS and weightloss analyses.

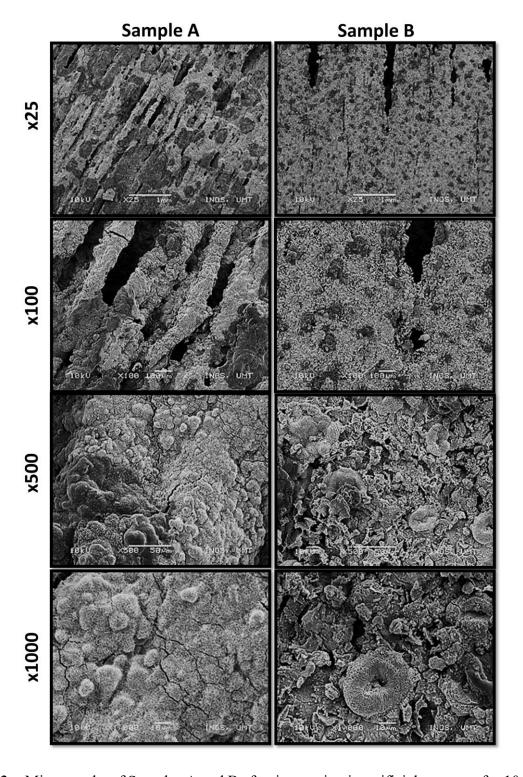


Figure 3a: Micrographs of Samples A and B after immersion in artificial seawater for 10 days

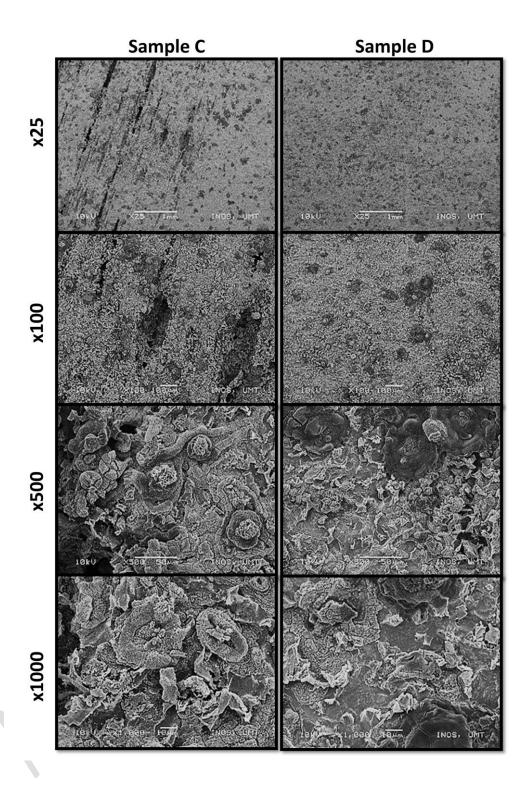


Figure 3b: Micrographs of Samples C and D after immersion in artificial seawater for 10 days Overall, the SEM results provide direct visual evidence of the protective mechanism proposed earlier: as the concentration of *Caulerpa lentillifera* extract increases, the coating becomes denser and more hydrophobic, blocking the penetration of seawater electrolytes. The morphological transition from a cracked and porous surface (Sample A) to a continuous and

defect-free film (Sample D) strongly supports the conclusion that the extract promotes the formation of a compact passive layer responsible for the improved corrosion resistance.

3.4. Comparison with Other Green Corrosion Inhibitors

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A comprehensive comparison was conducted with other plant and marine-based extracts reported in the literature to evaluate the performance of Caulerpa lentillifera extract as a green corrosion inhibitor. This comparison focuses on inhibition efficiency, optimal concentration, testing medium, and evaluation methods to benchmark the effectiveness of the current study. Across the literature, inhibition efficiencies reported for natural plant and marine extracts vary widely depending on both the testing medium and the evaluation technique. For electrochemical impedance spectroscopy (EIS), most marine and seawater studies report efficiencies between 55% and 80%, while in acidic environments (HCl or H2SO4) the efficiencies typically rise to 75-98% due to the greater aggressiveness of the medium and the accelerated adsorption of inhibitor molecules. In contrast, weight-loss (WL) or gravimetric evaluations generally yield slightly higher efficiencies, ranging from 65–89 % in seawater and up to 80-100% in acidic solutions, reflecting the cumulative effect of inhibitor adsorption during prolonged immersion. Within this context, the present study's results of 70% (WL) and 64% (EIS) for the Caulerpa

Within this context, the present study's results of 70% (WL) and 64% (EIS) for the *Caulerpa lentillifera*-modified coating in artificial seawater fall within, and in the case of WL, exceed the upper limits of these reported ranges. This demonstrates that sea-grapes extract provides corrosion protection performance comparable to the most effective marine-based green inhibitors documented in current literature.

The superior protection observed for the sea-grapes-modified coating can be attributed to several factors. The concentration effect plays a crucial role: the 12 wt % extract loading used here is substantially higher than the 400–2000 ppm concentrations commonly employed for other plant and marine extracts. Although *Turbinaria ornata* achieved 100 % inhibition at 25

g/L, that result was obtained in concentrated HCl, which is an extremely aggressive environment that does not reflect the moderate corrosivity of seawater, thus limiting direct comparison.

Table 3: Comparative Performance of Various Green Corrosion Inhibitors for Mild Steel Protection

Plant / Marine Extract	Optimal Concentration	Testing Medium	Inhibition Efficiency (%)	Corrosion Rate Reduction	Testing Method	Reference
Sea grapes (Caulerpa lentillifera)	12 wt% in epoxy	Artificial seawater	70 (WL) / 64 (EIS)	0.60 × 10 ⁻⁴ mm yr ⁻¹	Weight loss, EIS, SEM	Present study
Aloe vera extract	1000 ppm	Seawater	≈ 88.6 (EIS)	- \	Electrochemical, FE-SEM	Royani et al., 2024
Turbinaria ornata extract	25 g L ⁻¹	Con. HCl	100% (WL)		Weight loss	Krishnan et al., 2018
Sargassum polycystum extract	0.8 g L ⁻¹ (approx.)	1 M HCl	≈ 85–95 %		EIS	Umoren et al., 2019
Natural seaweed mixture	2 g L ⁻¹	Seawater	≈ 66–70 % (WL)	0.89 mm yr ⁻¹	Weight loss	Căprărescu et al., 2020
Brown algae (Fucus serratus)	400 ppm	3.5 % NaCl	≈ 78 % (EIS)	I	EIS	Singh et al., 2022
Green algae (<i>Ulva</i> <i>lactuca</i>)	800 ppm	1 M HCl	≈ 91 % (WL)	ı	Weight loss	Hassan et al., 2021
Rhizophora apiculata extract	1500 ppm	Cooling- tower water	≈ 74 %	_	Weight loss	AlSalhi et al., 2022
Artemisia pallens extract	2000 ppm	Cooling- tower water	≈ 81 %	_	Electrochemical	AlSalhi et al., 2022
Red algae (Gracilaria corticata)	600 ppm	0.5 M H₂SO₄	≈ 88 % (WL)	_	Weight loss, Tafel polarization	Kumar et al., 2020

Most comparative studies have been conducted in acidic media, which tend to overestimate short-term inhibition performance. By contrast, the present work focuses on artificial seawater,

offering greater environmental relevance. The few studies performed in seawater media generally report protection efficiencies above 60 %, while the present study significantly surpasses this benchmark.

The combination of weight-loss, EIS, and SEM analyses provides a more comprehensive evaluation than single-method approaches commonly used elsewhere. This multi-technique strategy enhances both the reliability and validity of the inhibition efficiency assessment. Furthermore, plant-based extracts containing heteroatoms such as oxygen and nitrogen can strongly interact with metal surfaces through physical adsorption and chemisorption. The phytochemical constituents of *Caulerpa lentillifera* likely include similar active compounds that facilitate the formation of an adherent, protective barrier film.

Finally, green corrosion inhibitors derived from natural extracts offer clear advantages in environmental safety, biodegradability, and cost-effectiveness. Sea grapes are abundant along Indo-Pacific coastlines, providing a readily available and renewable resource. The methanolic extraction process is straightforward and scalable, making this system attractive for sustainable industrial corrosion-protection applications.

This study is distinct in combining a marine-derived extract with an epoxy barrier coating and evaluating its performance specifically in artificial seawater. While most algae-based inhibitors have been studied in acidic media or as standalone inhibitors in aqueous solutions, the integration of *Caulerpa lentillifera* into a polymeric coating matrix represents a novel and environmentally sustainable approach to marine corrosion mitigation

3.5. Implementation Potential

The outcomes of this study provide a strong foundation for advancing both scientific understanding and practical application of *Caulerpa lentillifera* extract as a marine corrosion inhibitor. The high inhibition efficiencies achieved in artificial seawater demonstrate that the extract-modified epoxy coating behaves effectively under conditions representative of real

marine environments. Because the inhibitor can be incorporated into commercial epoxy through a simple mixing and curing process, the formulation is compatible with existing industrial coating technologies, enabling straightforward translation from laboratory-scale preparation to large-scale production.

In terms of research expansion, the system offers multiple avenues for further investigation. Long-term immersion studies, cyclic wet–dry exposures, and temperature-dependent assessments are needed to evaluate durability under realistic marine service conditions. The phytochemical richness of *Caulerpa lentillifera* also presents opportunities for synergistic enhancement by combining the extract with nanofillers, biopolymers, or other plant-based inhibitors to improve barrier performance. Detailed characterization of the extract's active compounds could further clarify adsorption mechanisms and support the development of optimized inhibitor formulations.

From a practical standpoint, the abundance, biodegradability, and low cost of *Caulerpa lentillifera* make it an attractive renewable resource for industrial use. Its suitability for incorporation into epoxy coatings suggests potential application in protective systems for offshore structures, coastal facilities, pipelines, marine vessels, and infrastructure exposed to seawater. Pilot-scale coating trials in natural seawater environments represent the next essential step toward validating the coating's performance in real-world conditions.

4. Conclusion

The present study demonstrates that the extract of marine algae *Caulerpa lentillifera*, also known as sea grapes, is an effective green corrosion inhibitor when incorporated into epoxy coatings for mild steel under marine conditions. Incorporation of the extract at 12 wt% produced the highest protection efficiency, achieving 70% inhibition (weight-loss) and 64% inhibition (EIS) in artificial seawater. The enhanced performance is supported by SEM

analysis, which revealed a smoother and more uniform surface morphology relative to the unmodified epoxy coating.

The enhanced performance of the extract-modified coating is likely due to the phytochemicals present in *Caulerpa lentillifera*, which contain oxygen-bearing and nitrogen-bearing functional groups capable of strongly adsorbing onto the steel surface. This adsorption promotes the formation of a dense, protective barrier that restricts the movement of seawater electrolytes and slows down metal dissolution. When compared with inhibition efficiencies reported for other marine- and plant-based extracts tested in seawater, the sea-grapes extract performs at the higher end of the typical efficiency range, confirming its strong potential as an effective green inhibitor.

Given its biodegradability, non-toxicity, and natural abundance in Indo-Pacific regions, Caulerpa lentillifera represents a promising renewable resource for sustainable corrosion-protection coatings.

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References

AlSalhi, M.S., Devanesan, S., Rajasekar, A. and Kokilaramani, S. (2022) 'Characterization of plants and seaweeds based corrosion inhibitors against microbially influenced corrosion in a cooling tower water environment', Process Safety and Environmental Protection, 168, pp. 1161-1175. doi: 10.1016/j.psep.2022.10.065.

- Bousba, S., Allal, H., Damous, M. and Maza, S. (2023) 'Computational DFT analysis and
- 453 molecular modeling on imidazole derivatives used as corrosion inhibitors for aluminum
- in acidic media', Computational and Theoretical Chemistry, 1225, 114168. doi:
- 455 10.1016/j.comptc.2023.114168.
- 456 Căprărescu, S., Dăncilă, A.M., Modrogan, C. and Purcar, V. (2020) 'Corrosion protection of
- carbon steel using natural seaweeds from seawater', Proceedings, 55(1), 1. doi:
- 458 10.3390/proceedings2020055001.
- Daoudi, W., El Ibrahimi, B., Dagdag, O., Berdimurodov, E., Guo, L., Ebenso, E.E., Oussaid,
- A., et al. (2023) 'New chlorophenyl-imidazole derivative as a novel corrosion inhibitor in
- the gas and oil industry', Journal of Physics and Chemistry of Solids, 179, 111409. doi:
- 462 10.1016/j.jpcs.2023.111409.
- 463 El-Haddad, M.N. and Fouda, A.S. (2015) 'Electroanalytical, quantum and surface
- characterization studies on imidazole derivatives as corrosion inhibitors for aluminum in
- acidic media', Journal of Molecular Liquids, 209, pp. 480-486. doi:
- 466 10.1016/j.molliq.2015.06.005.
- Haque, J., Zulaikha, M.A., Wan, W.B., Daoudi, W., Berdimurodov, E. and Zulkifli, F. (2023)
- 468 'Alocasia Odora extract as environmentally benign corrosion inhibitor for aluminum in
- 469 HCl', Moroccan Journal of Chemistry, 11(4), pp. 1013-1026. doi:
- 470 10.48317/IMIST.PRSM/morjchem-v11i04.41618.
- Hassan, K.H., Khadom, A.A. and Abood, N.M. (2021) 'Corrosion inhibition of mild steel in
- hydrochloric acid solution by green algae Ulva lactuca extract', International Journal of
- 473 Corrosion and Scale Inhibition, 10(2), pp. 615-632. doi: 10.17675/2305-6894-2021-10-2-
- 474 9.

- Ikhmal, W.M.K., Yasmin, M.Y.N., Fazira, M.F.M., Rafizah, W.A., Wan, W.B. and Sabri,
- 476 M.G.M. (2017) 'Anticorrosion coating using Olea sp. leaves extract', IOP Conference
- Series: Materials Science and Engineering, 344, 012028. doi: 10.1088/1757-
- 478 899X/344/1/012028.
- Jiyaul, H., Mohammad, F.R.Z., Nabilah, I., Mumtaz, A.Q., Mohd, S.M.G., Elyor, B. and Wan,
- W.N. (2023) 'Environmentally benign water-soluble sodium L2-(1-Imidazolyl) alkanoic
- acids as new corrosion inhibitors for mild steel in artificial seawater', ACS Omega, 8(26),
- pp. 24797–24812. doi: 10.1021/acsomega.3c00366.
- 483 Kamaruzzaman, W.M.I., Fekeri, M.F.M., Nasir, N.A.M., Hamidi, N.A.S.M., Baharom, M.Z.,
- Adnan, A., Shaifudin, M.S., Abdullah, W.R.W., Wan, W.M.N. and Suhailin, F.H. (2021)
- 485 'Anticorrosive and microbial inhibition performance of a coating loaded with
- Andrographis paniculata on stainless steel in seawater', Molecules, 26(11), 3379. doi:
- 487 10.3390/molecules26113379.
- 488 Kamaruzzaman, W.M.I.W.M., Nasir, N.A.M., Hamidi, N.A.S.M., Yusof, N., Shaifudin, M.S.,
- Suhaimi, A.M.A.A.M., Badruddin, M.A., Adnan, A., Nik, W.M.N.W. and Ghazali
- 490 M.S.M. (2022) '25 years of progress on plants as corrosion inhibitors through a
- 491 bibliometric analysis using the Scopus database (1995–2020)', Arabian Journal of
- 492 Chemistry, 15(4), 103655. doi: 10.1016/j.arabjc.2021.103655.
- Kedimar, N., Rao, P. and Rao, S.A. (2024) 'Imidazole-based ionic liquid as sustainable green
- inhibitor for corrosion control of steel alloys: A review', Journal of Molecular Liquids,
- 495 411, 125789. doi: 10.1016/J.MOLLIQ.2024.125789.
- 496 Ko, S.J., Choi, S.R., Hong, M.S., Kim, W.C. and Kim, J.G. (2021) 'Effect of Imidazole as
- Corrosion Inhibitor on Carbon Steel Weldment in District Heating Water', Materials,
- 498 14(16), 4416. doi: 10.3390/MA14164416.

- 499 Krishnan, M., Subramanian, H., Dahms, H.U., Sivanandham, V., Jeyaraj, P., P, S.K. and
- Marimuthu, S. (2018) 'Biogenic corrosion inhibitor on mild steel protection in
- concentrated HCl medium', Scientific Reports, 8, 2508. doi: 10.1038/s41598-018-20938-
- 502 z.
- Kumar, S.A., Sankar, A., Kumar, S.M., Rajesh, K. and Tamilselvi, A. (2020) 'Corrosion
- inhibition performance of red algae extract on mild steel in acid medium', Materials
- Today: Proceedings, 33, pp. 4507-4511. doi: 10.1016/j.matpr.2020.08.083.
- Mahdy, A., Aly, K.I. and Mohamed, M.G. (2023) 'Construction novel polybenzoxazine
- coatings exhibiting corrosion protection of mild steel at different concentrations in a
- seawater solution', Heliyon, 9(7), e17977. doi: 10.1016/j.heliyon.2023.e17977.
- Meng, P.R., Chen, Y. and Liu, Z.L. (2020) 'Influence of the dissolved oxygen concentration in
- artificial seawater on the corrosion behavior of Q235 mild steel', International Journal of
- Electrochemical Science, 15, pp. 4454–4469. doi: 10.20964/2020.05.45.
- Nabilah, I., Siti, M.M., Mohammad, F.R.Z., Vincent, O.I., Mariyam, J.G. and Nik, W.N. (2022)
- 'A review on application of marine algae as green corrosion inhibitors in acid medium',
- Vietnam Journal of Chemistry, 60(4), pp. 409-416. doi: 10.1002/vjch.202200001.
- Okafor, P.C., Liu, X. and Zheng, Y.G. (2016) 'Inhibition activity of seaweed extract for mild
- carbon steel corrosion in saline formation water', Corrosion Engineering, Science and
- 517 Technology, 51(4), pp. 274-285. doi: 10.1179/1743278215Y.0000000030.
- Pawlowicz, R. (2019) 'Electrical Properties of Sea Water: Theory and Applications', in
- Cochran, J.K., Bokuniewicz, H.J. and Yager, P.L. (eds.) Encyclopedia of Ocean Sciences
- 520 (Third Edition). Oxford: Elsevier, pp. 71–80. doi: 10.1016/B978-0-12-409548-9.09578-
- 521 6.

- Royani, A., Hanafi, M., Mubarak, N.M., Priyotomo, G., Rochmanto, S.S., Prifihit, R.A. and
- Muharam, A. (2024) 'Unveiling green corrosion inhibitor of Aloe vera extracts for API
- 5L steel in seawater environment', Scientific Reports, 14, 14112. doi: 10.1038/s41598-
- 525 024-65005-5.
- 526 Sekhar Das, C., Zheng, H., Zhao, X.L. and Dai, J.G. (2023) 'Corrosion inhibition of steel
- reinforcements in seawater sea sand concrete by alkali-activated slag based coatings',
- 528 Construction and Building Materials, 394, 132210. doi:
- 529 10.1016/j.conbuildmat.2023.132210.
- 530 Singh, A., Lin, Y., Quraishi, M.A. and Olasunkanmi, L.O. (2022) 'Corrosion inhibition of mild
- steel in hydrochloric acid solution using brown algae extract', Journal of Molecular
- 532 Liquids, 347, 117984. doi: 10.1016/j.molliq.2021.117984.
- 533 Syakilla, N., George, R., Chye, F.Y., Pindi, W., Mantihal, S., Wahab, N.A., Fadzwi, F.M., et
- al. (2022) 'A Review on Nutrients, Phytochemicals, and Health Benefits of Green
- Seaweed, Caulerpa lentillifera', Foods, 11(18), 2832. doi: 10.3390/FOODS11182832.
- Umoren, S.A., Eduok, U.M., Solomon, M.M. and Udoh, A.P. (2019) 'Performance evaluation
- of Sargassum polycystum C. Agardh seaweed extract as green inhibitor for acid corrosion
- of mild steel', International Journal of Electrochemical Science, 14, pp. 1297-1321. doi:
- 539 10.20964/2019.02.04.
- Wan, W.B., Ravindran, K., Al-Amiery, A.A., Izionworu, V.O., Fayomi, O.S.I., Berdimurodov,
- E., Daoudi, D., Zulkifli, F. and Dhande, D.Y. (2023) 'Piper betle extract as an eco-friendly
- corrosion inhibitor for aluminium alloy in hydrochloric acid media', International Journal
- of Corrosion and Scale Inhibition, 12(3), pp. 948–960. doi: 10.17675/2305-6894-2023-
- 544 12-3-9.

Xu, W.L., Wang, X. and Zhang, G.A. (2023) 'Efficient inhibition of mild steel corrosion in acidic medium by novel pyrimidine derivatives: Inhibitive effect evaluation and interface adsorption mechanism', Journal of Molecular Structure, 1291, 136005. doi: 10.1016/j.molstruc.2023.136005.