

Article

Improved Mechanical Performance and Green Corrosion Inhibition of Copper Matrix Composites Reinforced with *Crassostrea Madrasensis* via Powder Metallurgy and *Allium sativum* Extract

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Abstract

This paper explores the structural, mechanical, thermal, and electrochemical properties of copper matrix composites (CMCs) enhanced by *Crassostrea madrasensis* seashell powder, which were produced via powder metallurgy and resistance sintering. FESEM images showed a uniform distribution of bio-ceramic particles in the copper matrix composites (CMCs), leading to an improved microstructure and enhanced mechanical behavior. Mechanical tests showed that after incorporating 12 wt.% seashell powder, the average hardness increased to 56 HV, and compressive strength improved to 686 MPa. Density analysis showed a decrease in porosity, which was attributed to better particle diffusion during sintering. The corrosion resistance was evaluated using electrochemical techniques, including OCPT, Tafel polarization, EIS, LSV, and chronocoulometry, which were employed in 3.5 wt.% NaCl media with varying concentrations of the extract of *Allium sativum* (garlic) as a green inhibitor. Garlic-derived phytochemicals facilitated surface passivation, which was proven by shifts in potential, reduced corrosion rates, and minor charge transfer. The findings confirm that *Crassostrea madrasensis* bio-ceramic reinforcements and garlic extract-based corrosion inhibition provide a sustainable method for improving the performance and durability of copper matrix composites.

Keywords: copper matrix composites; seashell powder; bio-ceramic reinforcement; powder metallurgy; green corrosion inhibitor; garlic extract



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1. Introduction

As a result of their remarkable resistance to high thermal and electrical conductivity, corrosion and wear, and suitability for advanced engineering applications like electronics, heat sinks, machining, and biomedical components, copper matrix composites (CMCs) are the focus of extensive investigation [1–4]. Enhancing copper with hard ceramic particles or natural mineral-based fillers boosts its mechanical properties without sacrificing its inherent qualities. Traditional reinforcements include silicon carbide (SiC), fly ash, graphite and graphene [5–7], while recent efforts have explored sustainable options like seashells

and other biomineral sources [8]. The use of CMCs in thermal settings necessitates materials with improved thermal stability and conductivity.

Reinforcements such as fly ash, nano-TiC, and metallic glass have shown significant enhancements in thermal resistance and dimensional stability when exposed to heat [9–11]. Powder metallurgy offers economically viable and adaptable technique for making these composites, allowing a uniform distribution of reinforcement particles and a customizable microstructure. Studies have specified that process parameters like the sintering temperature, compaction pressure, and reinforcement loading significantly affect densification, grain refinement, and performance [12–15]. From a mechanical standpoint, natural shell-derived bio-ceramic fillers from *Crassostrea madrasensis* (oyster shell) provide hardness and brittleness similar to engineered ceramics. These bio-waste materials are primarily composed of crystalline calcium carbonate (CaCO_3) in the calcite form, which enhances load transfer efficiency and hardness [16–18].

Structural analyses through XRD and FTIR verified the phase purity and functionality of these materials [19–22]. Additionally, surface and microstructural examinations by using SEM, FESEM, and EDX demonstrated that bio-ceramic particles can be consistently distributed in copper matrix composites (CMCs), supporting strong interfacial bonding and crack resistance [23]. Research involving tungsten carbides, graphite nanoflakes, and nano-TiC as reinforcements has increased hardness and compressive strength, suggesting that bio-ceramic-based composites can fulfill the mechanical requirements of wear-resistant or load-bearing applications [24–26].

Moreover, the demand for corrosion-resistant materials in chloride and marine environments has driven the development of copper matrix composites (CMCs) with improved electrochemical performance. Electrochemical corrosion testing methods like OCPT, Tafel, EIS, LSV, and chronocoulometry offer a comprehensive understanding of corrosion mechanisms and protection efficiency [27–29]. Natural corrosion green inhibitors like *Allium sativum* (Garlic) extract have become popular because of their non-toxic, biodegradable, and adsorption-based inhibition mechanisms [30–33]. These inhibitors form protective films through sulfur-containing compounds like allicin, providing substantial resistance in saline environments. Studies have demonstrated the interaction between natural reinforcements and green inhibitors which enriched the corrosion resistance of copper matrix composites (CMCs) in severe conditions [34–39].

In this context, the current study focuses on the sustainable development of copper matrix composites reinforced with *Crassostrea madrasensis* seashell powder processed via powder metallurgy and resistance sintering [40]. The thermal behavior (TGA/DSC), microstructure (FESEM, EDX), mechanical strength (hardness, compression), machinability, corrosion resistance (electrochemical methods using garlic extract as a green inhibitor), and structural integrity of the composites were all assessed. This study combines the mechanochemical milling and resistance sintering of *Crassostrea madrasensis* seashell powder with comprehensive mechanical, thermal, and electrochemical evaluations that compare its performance to biogenic reinforcement. The purpose of this work is to show how marine bio-waste and plant-based inhibitors can be used to create high-performance, ecofriendly copper composites for a variety of uses.

2. Materials and Methods

2.1. Selection of Materials

Both powders of electrolytic copper and *Crassostrea madrasensis* seashell were used in the current investigation. The 45-micron mesh size electrolytic copper powder of EC1 (4 grades), which is commercially accessible, was acquired from M/s. Thirumangalam, Madurai, Tamil Nadu, India: The Metal Powder Company (P) Ltd. *Crassostrea madrasensis*

seashell powder, considered a natural ceramic, is widely accessible. Seashells (Figure 1) gathered from the Bay of Bengal shores near the Regional Station of CMFRI, Thoothukudi, Tamil Nadu, India, were powdered.

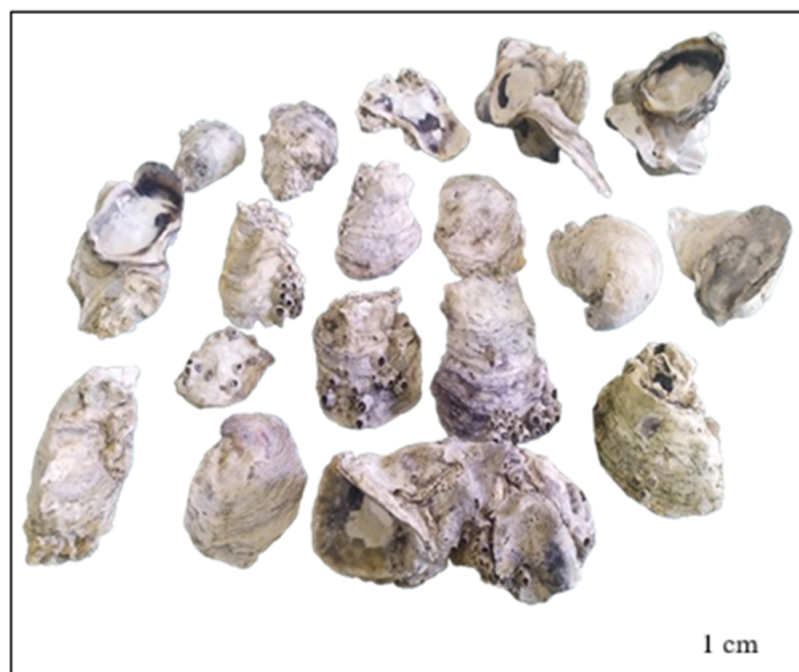


Figure 1. *Crassostrea madrasensis* seashell powder used as the raw material for CaCO_3 extraction.

Table 1 lists the ingredients of powdered *Crassostrea madrasensis* seashell. The elemental data were obtained through EDX. Five randomly selected sample sections were examined at a distance of 10 mm and an acceleration of 15 kV. Averaged atomic and weight percentages are represented by the reported values.

Table 1. Composition of *Crassostrea madrasensis* seashell powder (wt.%).

Element	O	Ca	C	Cl	Na	Mg	Si
wt.%	42.0	38.1	17.4	0.9	0.7	0.6	0.3

To make *Crassostrea madrasensis* seashell powder of uniform size, the coarse, unevenly grained particles were ball-milled under dry conditions at a 10:1 ball-to-powder ratio. A ball mill was used to grind the *Crassostrea madrasensis* seashells into a fine powder, which was subsequently sieved to less than 75 microns size. Its density was determined as 2.711 g/cm^3 , the melting point temperature was 850°C , and the particle size was below 75 microns [18,19]. Table 1 shows the composition of *Crassostrea madrasensis* seashell powder.

2.2. Preparation of Powder

Mixing is essential for the powder metallurgy process. The mechanical alloying technique is a mixing method that provides equivalent distribution and is well suited to powder metallurgy methods. Electrolytic copper powder ($45 \mu\text{m}$, EC1) and *Crassostrea madrasensis* shells were taken in the required quantity. *Crassostrea madrasensis* seashells were cleansed with deionized water. Then, they were dehydrated at 60°C for up to 12 h and coarse-crushed. In a dry ball mill (Model: Pulverisette-6, Fritsch, Fellbach, Germany), the separate powders were ground up and combined with electrolytic copper. The weight

ratio of ball–powder was 10:1. The powder was milled at 300 rpm for 90 min in a moist medium with toluene mixed to stop the charge from oxidizing and clumping together. The milling process was performed under dry conditions in an ambient atmosphere to minimize agglomeration and ensure uniform particle refinement. A mini-ball mill (TWIN BOWL) operating at 426 rpm was used to grind the powder mixtures for 90 minutes. After the milling process, the shell powder was sieved to a particle size of $<75\ \mu\text{m}$ to ensure a uniform distribution [15]. By using the powder metallurgy method, composites were developed by reinforcing 12% of the copper matrix composites (CMCs) with powdered *Crassostrea madrasensis* seashell.

2.3. Characterization Studies

With the aid of XRD (Model: PW 1710, Philips, Amsterdam, The Netherlands) analysis [2,6], the stages of the raw materials were identified, and the dislocation density, lattice strain, and crystal size were computed. The distinctive bonds in Cu with the *Crassostrea madrasensis* seashell composite were identified by using FTIR analysis (Bruker, Model: Tensor 27, Bruker, Ettlingen, Germany) [11,16].

FESEM (Model: MERLIN Compact, ZEISS, Oberkochen, Germany) with an EDX analyzing system was used to evaluate the surface morphologies of the *Crassostrea madrasensis* seashell powder [31]. A Robo Cut Molybdenum Wire Cut Machine (Model: ROBO CUT H25, Mitsubishi Electric, Tokyo, Japan) was used to machine the sintered composite specimen to the necessary dimensions. Following that, the surface was prepared by polishing it in stages by using electro-coated silicon carbide waterproof emery sheets with grit sizes of P1000, CV371, and QB1. Using distilled water and alumina paste on a disk-polishing machine, the final mirror finishing was achieved.

Thermal Analysis

The thermal behavior of the copper and *Crassostrea madrasensis* seashell composite was investigated by Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (Model: Mettler Toledo Simultaneous Thermal Analyser, (Toledo, Greifensee, Switzerland). DSC can analyze the composite's melting, crystallization, and igniting characteristics. The thermal degradation behavior of copper with *Crassostrea madrasensis* seashell was analyzed by using a Thermal Gravimetric Analyzer (TGA). The thermal stability and degree of material deterioration are determined by the integral of TGA and derivative DSC curves [11,12,16].

2.4. Preparation of Composite

2.4.1. Powder Compaction

Cylindrical compacts of 50 mm diameter and 10 mm thickness were made. Powdered Cu–*Crassostrea madrasensis* seashell that had been ball-milled was used to make the compacts. After mixing the powder for 90 minutes in a ball mill, it was crushed with an appropriate punch and die-set on a 100-tonne hydraulic pressing machine (Model: BEMCO, Hydraulics Limited, Karnataka, India). For the specimen, a 300 MPa (corresponding to 60-tonnes) compacting pressure was applied progressively. Graphite was used as a lubricant on the punches and die. A small amount of graphite binder was added to the powder mixture to enhance the green strength [1,15]. Figure 2 shows the preparation of Cu–*Crassostrea madrasensis* seashell.

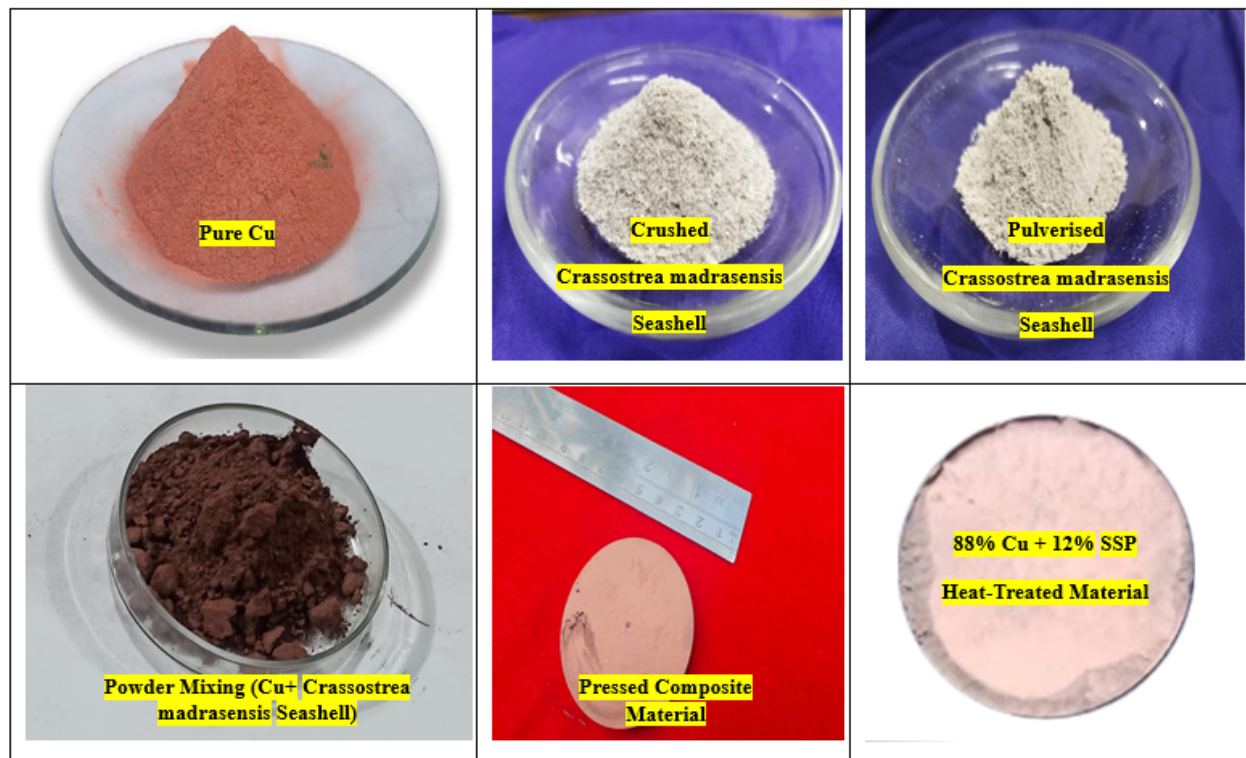


Figure 2. Preparation of Cu–Crassostrea madrasensis seashell.

2.4.2. Metal Sintering

After completion of the compaction, samples were placed in the furnace for electrical resistance sintering. The samples are heated for two hours in a furnace with an inert argon environment for preventing oxidation. Resistance sintering was performed at 800 °C for one hour under flowing argon (2 L per minute) in an electric muffle furnace with no external pressure [1]. The sintered samples were cooled by a water quenching process within the furnace as soon as the sintering schedule was finished. A fine wire brush was used to clean the preforms in the subsequent sintering process in order to examine the sintered sample's, bulk density, relative density, and apparent porosity. As per the Standards of ASTM B962-08 [24], density was determined by applying Archimedes' principle.

2.5. Mechanical Testing

In addition, the Vickers microhardness (HV) was determined by using a hardness tester (Model: FUTURE TECH/FM/PCPL000229, Future-Tech, Tokyo, Japan), following the ASTM E384:2022 [1] Test Method, as detailed in [5]. The hardness values were tested by using a Vickers microhardness tester under 300 g load and 15 s dwell period [9,11] conditions. As per ASTM E9 [4], compressive tests were performed by using a Universal Testing Machine (Model: 4106 Universal Testing Machine, SANS, Shandong, China) on sintered specimens of 10 mm × 10 mm × 8 mm [4–7]. The ultimate strength, yield strength, compressive strength and elongation were all computed [22,40].

2.6. Corrosion Testing

2.6.1. Preparation of Corrosion Inhibitor

Figure 3 illustrates the preparation of *Allium sativum* inhibitor (Garlic) extract. About 226 g of *Allium sativum* (Garlic) was cut into small pieces and steeped in water for half an hour, and then it was ground. After filtering, 150 mL of the solution mixture was obtained. The stock concentration corresponds to 1506.7 mg·L^{−1}. A blank Cu–Crassostrea madrasensis seashell composite specimen is placed in a beaker containing 150 mL of water

for 24 hours. Likewise, the specimens were soaked in the extraction of different amounts of *Allium sativum* (1 mL to 5 mL) for 24 h [32,33].



Fresh bulbs of garlic



Peeled garlic cloves



150 milliliters of the solution mixture

Figure 3. Preparation of *Allium sativum* inhibitor.

2.6.2. Corrosion Studies

A traditional three-electrode electrochemical cell (Model: chi650c, Sin Shill International Electrochemical Corrosion Tester, CH Instruments, Bee Cave, TX 78738, USA) was used for the analysis. Specimen underwent mechanical polishing, after which were cleaned with ethanol deionized water and then dehydrated before testing. A NaCl solution (3.5 wt.%) was utilized as the corrosive medium with varying amounts (1 mL to 5 mL) of *Allium sativum* (garlic) extract added to examine its inhibitory effect. Three electrode systems were used in the electrochemical experiments. They were saturated with calomel, platinum and a copper electrodes. In an electrochemical workstation, the observation of all the measurements was performed at room temperature.

The following methods were applied: open-circuit potential–time (OCPT) to assess corrosion tendency over a 600-second immersion period; Tafel polarization to determine the corrosion rate (CR), corrosion current density (i_{corr}), and inhibition efficiency (IE%); electrochemical impedance spectroscopy (EIS) to evaluate impedance behavior and to charge transfer resistance at various inhibitor concentrations; linear sweep voltammetry (LSV) to analyze current potential response and estimate inhibition effectiveness based on current suppression; and chronocoulometry (CC) to measure total charge transfer over time, which indicates inhibitor adsorption behavior. Measured volumes to the 3.5 wt.% NaCl electrolyte was added to make the media. To confirm accuracy and reproducibility, entirely tests were conducted in triplicate [31–33].

3. Experimental Results and Discussion

3.1. *Crassostrea Madrasensis* Seashell

3.1.1. X-Ray Diffraction (XRD)

The *Crassostrea madrasensis* seashell XRD pattern (Figure 4) shows distinct, pointed peaks that point to a highly crystalline structure. Calcite, the maximum common crystalline form of calcium carbonate (CaCO_3 , PDF No. 05-0586), is characterized by the most pronounced peak, which is seen at $2\theta = 29.4^\circ$, or the (014) plane. The formation of calcite phases is further proved through other peaks seen at 2θ values, including 23.1° (012), 31.4° (006), 36.0° (110), 39.4° (113), 43.2° (022), 47.5° (024) and 48.5° (116). Minor peaks at higher angles 55.7° (120), 57.4° (122), 60.7° (124), 64.8° (031), and 65.6° (032) could be secondary calcium carbonate (CaCO_3) polymorphs similar to vaterite or aragonite or trace impurities. The

pattern, which is dominated by the (014) calcite phase with high crystallinity, is typical of molluscan shells, which strongly confirms the shell's biogenic origin. The minimal amorphous content is confirmed by the broad, low-intensity background at the wavelength of 1.54060 Å (Cu K α radiation), which was employed for the analysis.

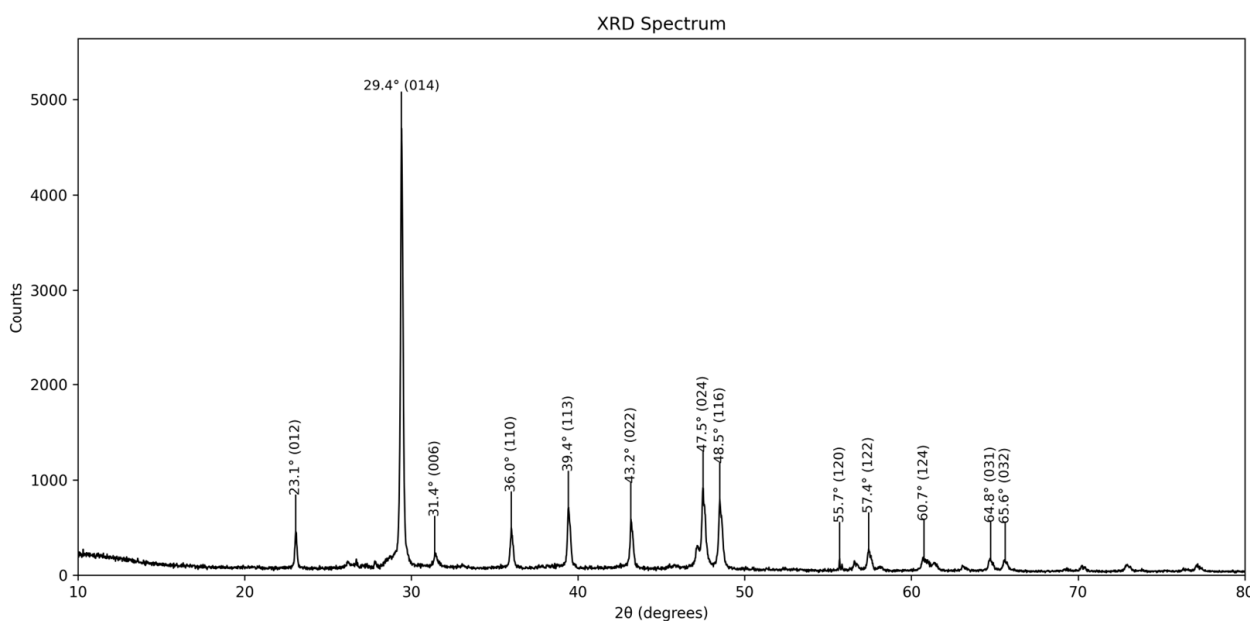


Figure 4. XRD of *Crassostrea madrasensis* seashell.

The diffraction peaks in Figure 4 were matched with JCPDS standards 29-4698 (calcium hydroxide) and 47-916 (calcium carbonate). As a result, *Crassostrea madrasensis* seashell powder is a simple alternative to inorganic calcium carbonate when it comes to electrolytic copper reinforcement. *Crassostrea madrasensis* seashell powder is an easily accessible natural and organic ceramic substance. Hence, in this work, *Crassostrea madrasensis* powder was employed as a reinforcement [16,17].

3.1.2. FTIR

Key vibrational bands that are indicative of calcium carbonate (CaCO₃) and the organic matrix components prevalent in biogenic shells are visible in the FTIR spectrum of the seashell *Crassostrea madrasensis*, as shown in Figure 5. The presence of calcite is proved by a strong absorption band at about 1481 cm^{−1} with shoulder peaks at 1443 cm^{−1} and 1396 cm^{−1}. The presence of the calcite phase is confirmed by the distinctive peaks in the FTIR spectrum of the seashell-derived CaCO₃ that correspond to carbonate (CO₃^{2−}) vibrations at about 712, 875, and 1420 cm^{−1}. The out-of-plane bending mode (ν_2) of CO₃^{2−} is responsible for the sharp band seen at about 880 cm^{−1}, while in-plane bending vibrations (ν_4) are responsible for the peaks at 710 cm^{−1} in addition to 617 cm^{−1}, which further supports the carbonate structure. The occurrence of O–H elongating vibrations, which are usually linked in absorbed water and hydroxyl groups, is suggested by broad bands in the ~3395–3881 cm^{−1} range. C–H stretching is represented by peaks at 2963 cm^{−1} and 2870 cm^{−1}, which show that the shell matrix contains organic components like proteins or lipids. Furthermore, trace organic components referring to remnants of the natural biopolymer matrix (conchiolin proteins and polysaccharides) embedded in the biogenic CaCO₃ lattice of the oyster shell or phosphate/silicate impurities may be responsible for the small peaks at 1080 cm^{−1}, 1034 cm^{−1}, and 810 cm^{−1} [12,16,19].

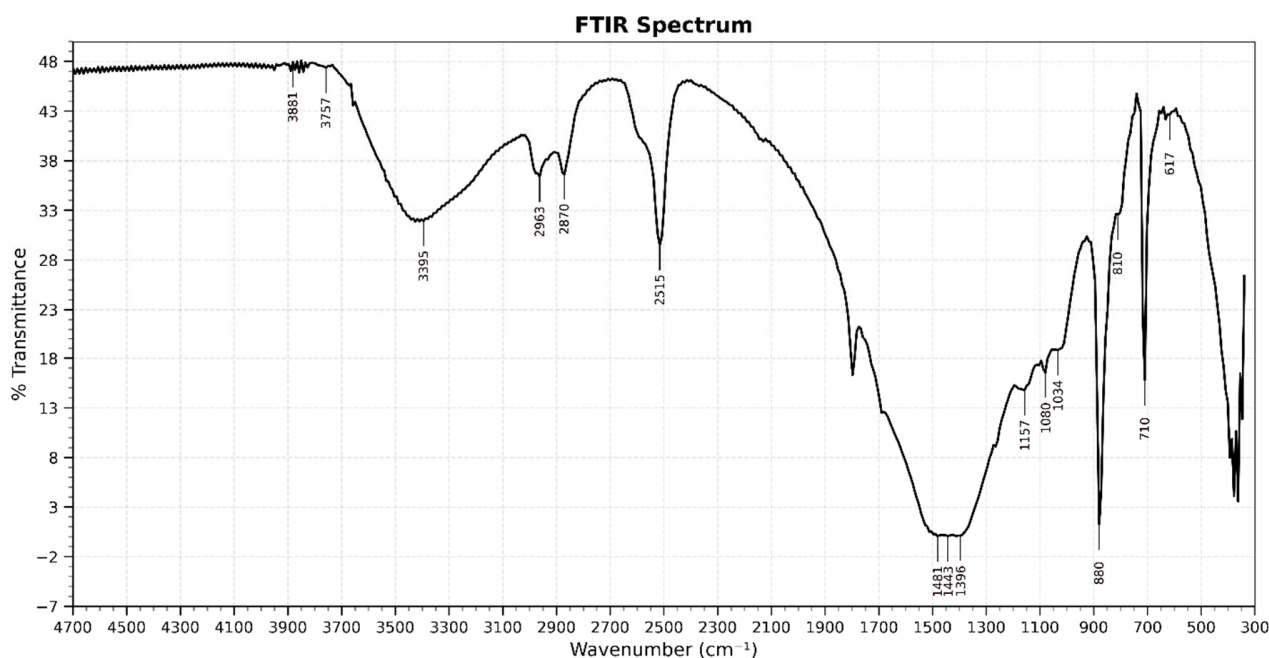


Figure 5. FTIR of *Crassostrea madrasensis* seashell powders.

3.1.3. FESEM and EDX Analysis

FESEM was used to observe the morphologies of *Crassostrea madrasensis* seashell powders. As seen in Figure 6, the powdered *Crassostrea madrasensis* seashell displayed as ill-defined morphologies with particle sizes varying from 2 to 20 μm . After the milling process, the average particle size was $8.6 \pm 3.2 \mu\text{m}$, which indicates moderately small fragmentation in accordance with a quantitative particle size distribution derived from over 300 particles assessed by using image analysis. Peaks from carbon and oxygen may be seen in the FESEM-EDX spectrum analysis of powdered *Crassostrea madrasensis* seashell (Figure 7) [31].

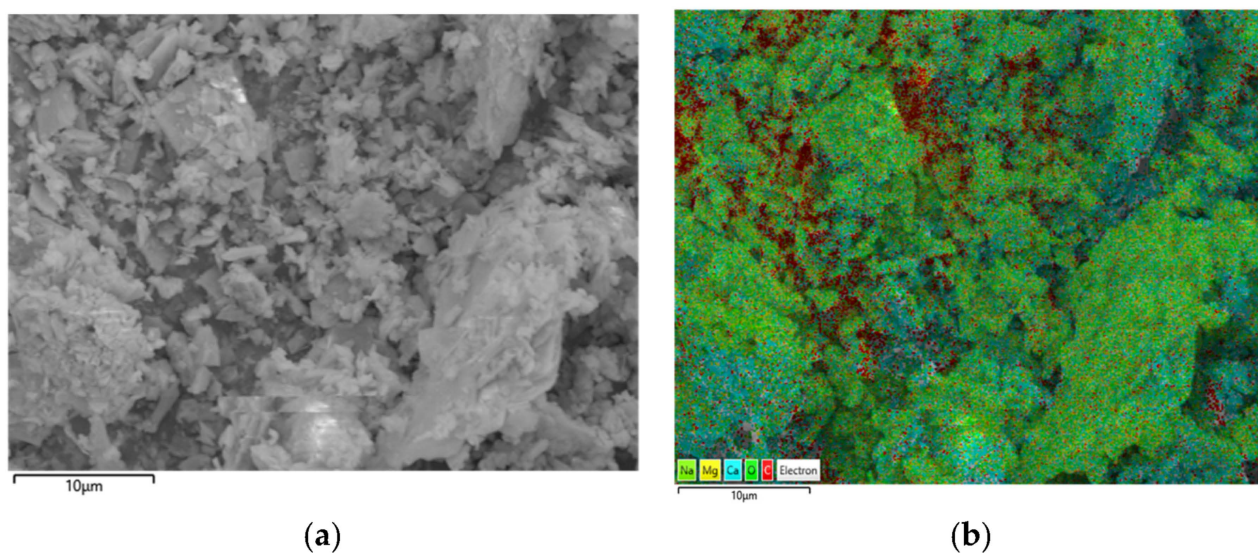


Figure 6. FESEM image of *Crassostrea madrasensis* seashell powder. (a) Surface morphology; (b) Elemental mapping showing the distribution.

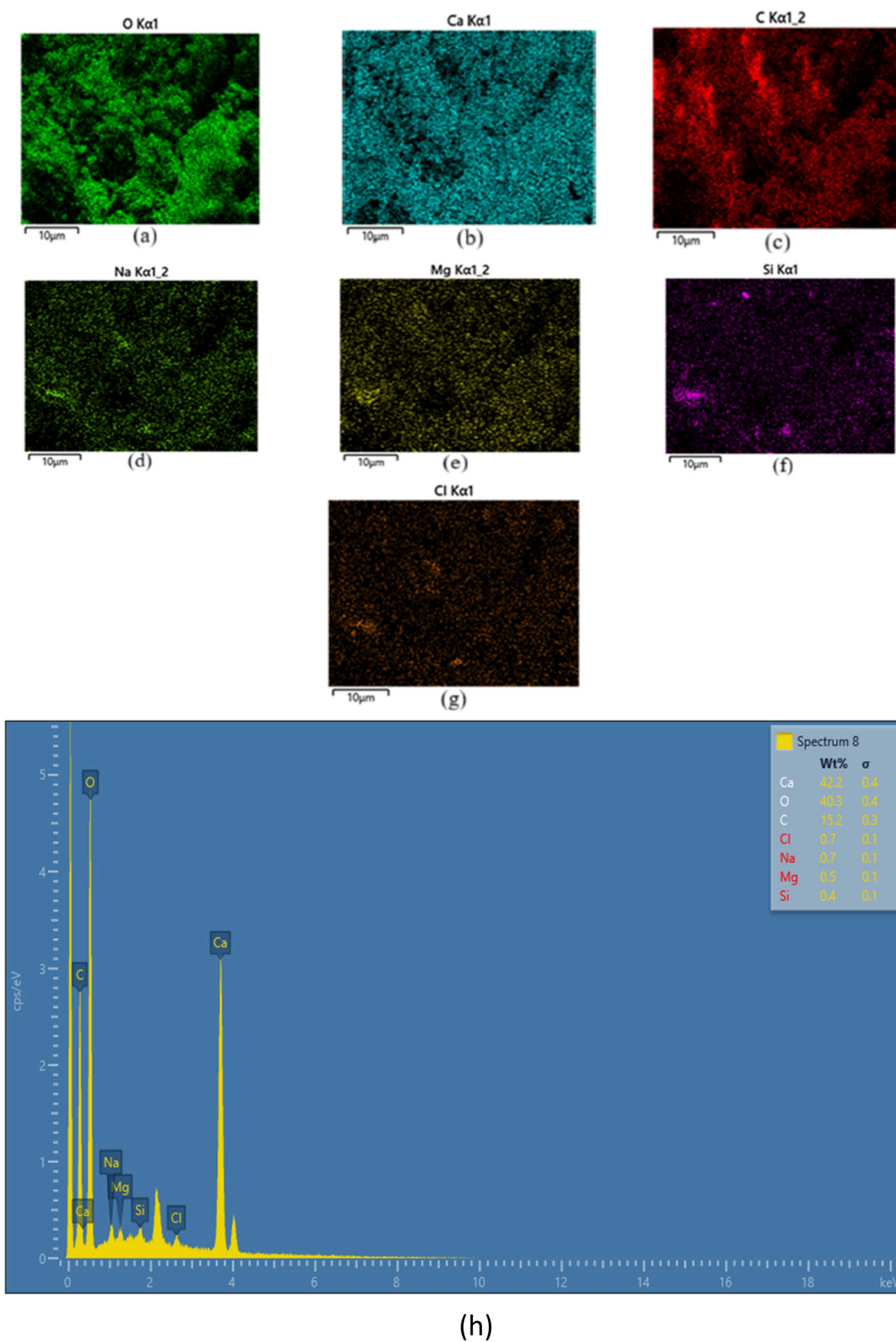


Figure 7. *Crassostrea madrasensis* seashell powder—Energy Dispersive X-ray Spectroscopy. (a) O mapping; (b) Ca mapping; (c) C mapping; (d) Na mapping; (e) Mg mapping; (f) Si mapping; (g) Cl mapping; (h) EDS spectrum.

The elemental composition (Table 2) of the *Crassostrea madrasensis* seashell was further validated by EDX analysis. The preponderance of calcium carbonate was confirmed by the major peaks for Ca, C, and O (42.2 wt.%, 15.2 wt.%, and 40.3 wt.%, respectively). There were also trace amounts of minor elements, including Na, Mg, and Si (<1 wt.% each), which could have come from exposure to the environment or marine origin. This spectrum's lack of a Cu peak confirmed that the analyzed region consisted of the seashell reinforcement rather than the copper matrix.

Table 2. Elemental composition of seashell-derived CaCO_3 particle (EDX Spectrum 8).

Element	wt. %	$\pm(\sigma)$	Atomic %	Observations
Ca	42.2	0.4	22.8	CaCO_3 primary component
O	40.3	0.4	55.9	Oxygen bonded to carbonate group
C	15.2	0.3	20.6	Possibly from carbonate coating
Cl	0.7	0.1	0.2	Trace impurity (residual salt)
Na	0.7	0.1	0.3	Trace impurity (biogenic origin)
Mg	0.5	0.1	0.2	Minor substitution in Ca lattice
Si	0.4	0.1	0.1	Potential contamination
Total	100.0	—	100.0	—

A homogeneous geographical distribution of Ca and Cu without significant agglomeration was confirmed by EDX mapping, which was conducted across five randomly chosen locations to guarantee microstructural homogeneity. A well-dispersed reinforcement phase was indicated by the local composition standard deviation, which was within ± 2 weight percent across these locations. The obtained FESEM and EDX results confirm a uniform elemental distribution and effective interfacial bonding of copper and the reinforcement *Crassostrea madrasensis* [1,25,28].

3.2. *Crassostrea Madrasensis* Seashell Reinforced Copper Matrix Composite

3.2.1. X-Ray Diffraction (XRD)

High crystallinity is shown in Figure 8 by the multiple distinct and strong peaks in the copper-incorporated *Crassostrea madrasensis* seashell's X-ray diffraction (XRD) pattern. The characteristic diffraction peaks detected 2θ values at 23.1° , 26.7° , 31.5° , 39.4° , 43.3° , 47.5° , 50.5° and 74.1° that correspond to the (012), (110), (006), (113), (009), (202), (025) and (035) planes of calcite, respectively, as indexed from the standard JCPDS card No. 05-0586. The strong intensity of the (104) reflection indicates the highly crystalline nature of the sample. For calcite, no discernible changes in peak location were found, suggesting that copper is probably surface bound or interstitial rather than being substituted into the CaCO_3 lattice. The retention of calcite peaks and the enhanced intensity of the metallic copper peaks, compared to the undoped shell, verify that copper was deposited without causing any damage to the biomineral crystalline structure. A successful functionalization is indicated by this dual phase pattern (calcite + Cu^0), which is appropriate for improved catalytic or antibacterial applications [12,16].

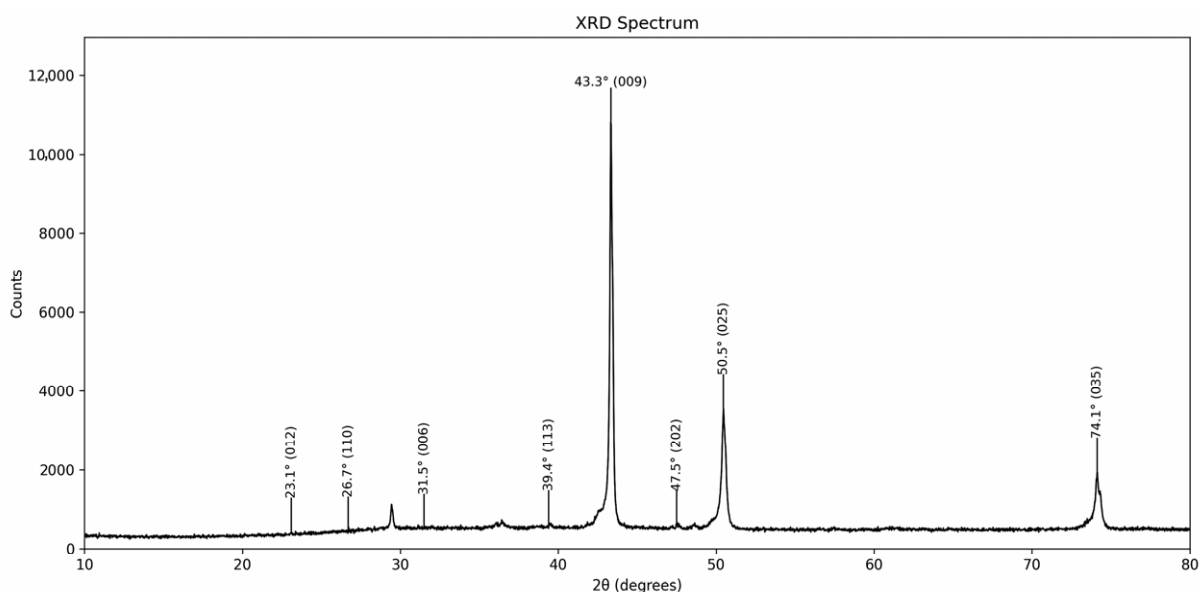


Figure 8. X-ray diffraction—copper with *Crassostrea madrasensis* seashell reinforcement.

3.2.2. FTIR

The FTIR profile confirms that the shell is mostly made of calcite and contains trace amounts of organic macromolecules that are necessary for biomineralization and shell integrity, as shown in Figure 9. The copper-treated *Crassostrea madrasensis* seashell's FTIR spectrum shows clear vibrational bands that shed light on the structural changes and chemical functions brought about by the copper addition. The O–H stretching vibrations from absorbed water, which are frequently found on biogenic calcium carbonate surfaces, are represented by the broad absorption band seen at around 3395 cm^{-1} and 3117 cm^{-1} .

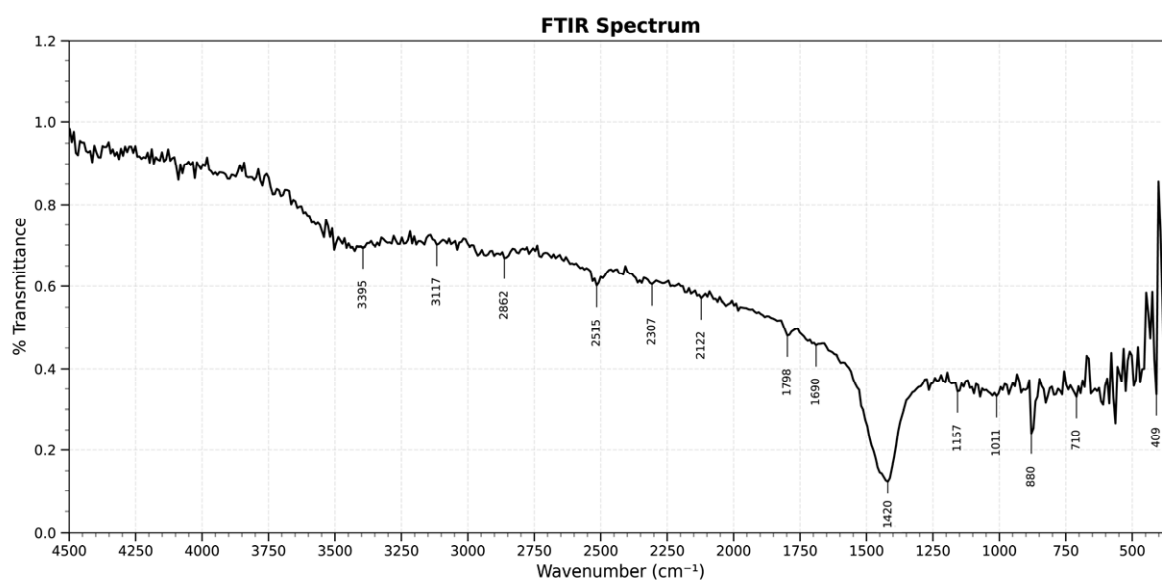


Figure 9. Copper with *Crassostrea madrasensis* seashell reinforcement.

C–H stretching vibrations are shown by the peaks at 2862 cm^{-1} , which indicate the presence of organic macromolecules like proteins or polysaccharides that were left over from the initial shell matrix. The band at 2515 cm^{-1} is notable, since it is indicative of Ca–OH bonds and shows that the carbonate lattice is still intact after doping. Around 1420 cm^{-1} (asymmetric CO_3^{2-} stretching, ν_3), 1157 cm^{-1} (maybe from C–O or phosphate groups), and $710\text{--}880\text{ cm}^{-1}$ (CO_3^{2-} bending, ν_4 and ν_2), important carbonate-related

vibrations are visible. The decrease in transmittance intensity in this low-frequency region further supports the possibility that lattice vibrations or potential metal–oxygen (Cu–O) interactions are indicated by the peak at 409 cm^{-1} .

Additional shoulders at 2307 cm^{-1} , 2122 cm^{-1} , and mid-band shifts, when compared to the undoped shell, indicate new bond environments that may be caused by Cu^{2+} interactions with carbonate or proteinaceous sites. This suggests that copper may be adsorbed or partially coordinated within the shell's organic–inorganic matrix. Copper was consolidated around the CaCO_3 particles during sintering without causing any harm to the biomineral crystalline structure, as evidenced by the retention of calcite peaks and the intensification of metallic Cu peaks [3,6,12,16,19].

3.2.3. Thermal Analysis

The thermal stabilities of the sintered copper-loaded *Crassostrea madrasensis* seashell powder composite were studied by TGA and DSC techniques. The TGA–DSC curves in Figure 10 display discrete mass change regions that correlate to oxidation, carbonate breakdown, organic matter breakdown, and moisture release. The release of surface-bound water seen in the DSC endotherm is compatible with the evaporation of physically adsorbed and weakly bound moisture, which is represented by a slight weight loss ($\approx 0.9\%$) up to roughly $180\text{ }^\circ\text{C}$. The sample then stays almost steady up to $220\text{ }^\circ\text{C}$ before gradually losing weight up to about $380\text{ }^\circ\text{C}$, which is explained by the breakdown of leftover organic matter and biopolymer residues, which were passed down from the shell matrix.

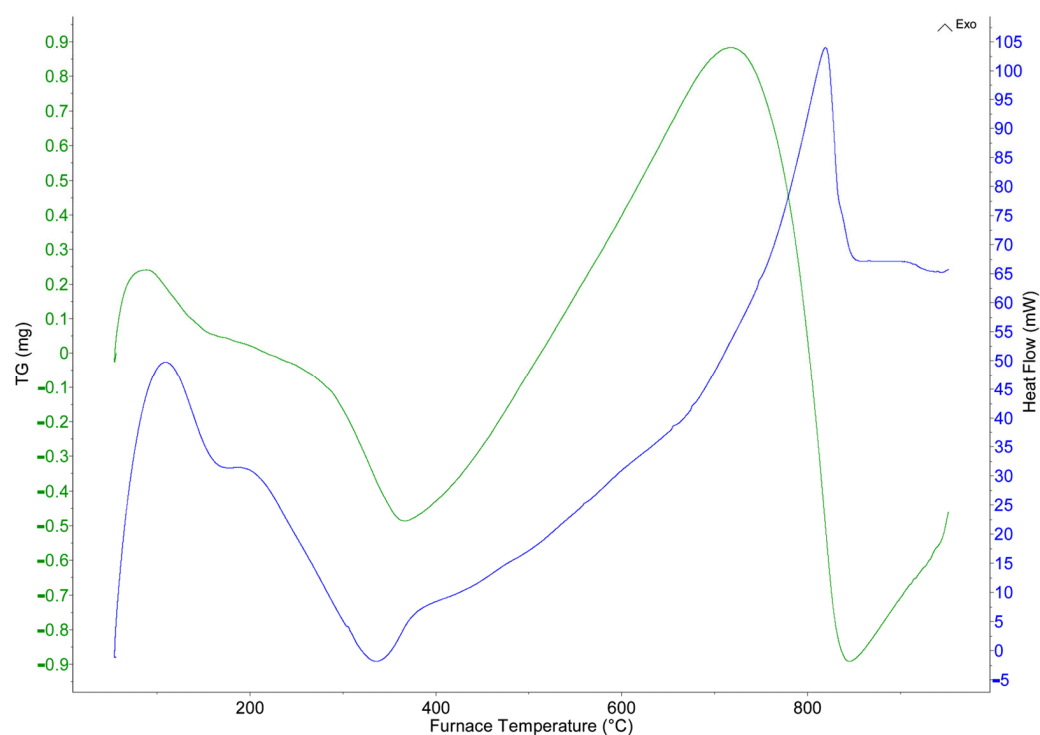


Figure 10. TGA/DSC analysis curve of copper with *Crassostrea madrasensis* seashell powder.

Up to $600\text{ }^\circ\text{C}$, the sample shows good thermal stability with no discernible mass change. Sometimes, between $450\text{ }^\circ\text{C}$ and $600\text{ }^\circ\text{C}$, a small weight gain ($\sim 0.3\%$) is seen. This could be because copper partially oxidizes to cuprous or cupric oxide in an argon environment that is flowing and contains trace oxygen. Then, a mass gain is detected in the range of around $650\text{--}700\text{ }^\circ\text{C}$, corresponding to the formation of oxides. After $800\text{ }^\circ\text{C}$, a strong endothermic peak is observed in the DSC curve, associated with a major weight reduction ($\approx 0.8\%$), corresponding to the calcination of calcium carbonate. This reaction

is typical of CaCO_3 from *Crassostrea madrasensis* seashell and verifies the onset of the CaCO_3 decomposition stage. After this point, up to around 820°C , another mass loss happens, which is likely due to volatilization or decomposition in another component. The Cu– CaCO_3 composite exhibits structural integrity and thermal stability across the majority of the practical temperature ranges, as evidenced by the overall mass change ($\sim 2\text{--}3\%$) and stable baseline below 700°C [5,11,12,16].

3.2.4. Optical Microstructure (OM) Characterization

The existence of *Crassostrea madrasensis* seashell particulates was confirmed in optical micrographs. The presence of *Crassostrea madrasensis* seashell lowers the grain size. Figure 11a,b represent the optical microscopy images of pure copper and copper matrix composites. To accurately define grain boundaries, both micrographs were re-etched for 15 s using a $\text{FeCl}_3\text{--HCl}$ solution (ASTM E407 [5]). An average grain size of $28 \pm 3\ \mu\text{m}$ for pure Cu and $19 \pm 2\ \mu\text{m}$ for the Cu– CaCO_3 composite was found by quantitative grain size analysis using the linear-intercept method (ASTM E112 [15]), demonstrating significant grain refinement brought on by the biogenic reinforcement. By dispersing on the surface of the resulting flake composite powders or copper powders, the *Crassostrea madrasensis* seashell impeded grain boundary movement and constrained copper grain growth during sintering [5,11,15].

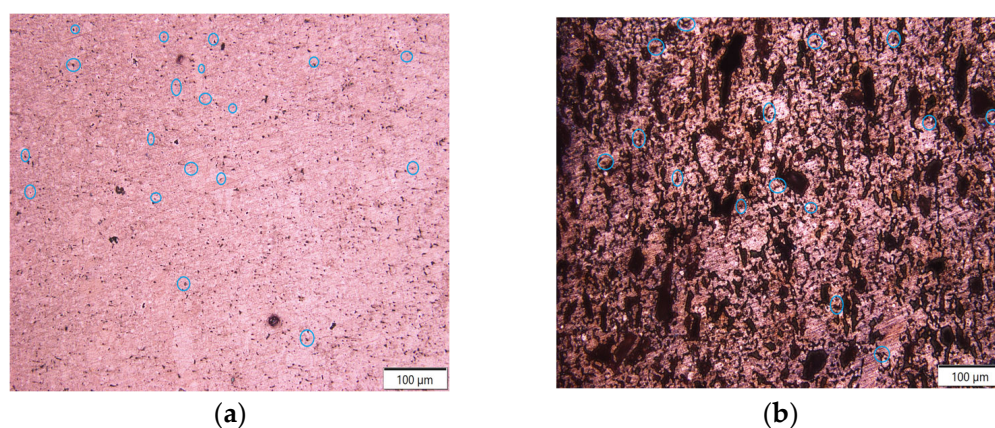


Figure 11. (a) Pure copper, (b) copper–*Crassostrea madrasensis* seashell.

3.2.5. Density and Porosity Characteristics

Density and porosity are the most critical characteristics of materials for the powder metallurgy method. During sintering, the mechanical properties are directly impacted by the porosity percentage. The primary factor influencing density is the sintering temperature. Furthermore, issues including improper material component mixing and post-sintering shrinking can result in voids and pores. The composite specimens' theoretical, bulk, relative density, and apparent porosity were determined. The theoretical density of the 88 wt.% Cu + 12 wt.% seashell composite was calculated by using component densities ($\rho_{\text{Cu}} = 8.96\ \text{g/cm}^3$, $\rho_{\text{shell}} = 2.71\ \text{g/cm}^3$), yielding $7.0186\ \text{g/cm}^3$. With a measured relative density of 77.0%, the corresponding bulk density is $5.4043\ \text{g/cm}^3$, indicating an apparent porosity of approximately 23%.

$$\rho_{th} = \frac{1}{\left(\frac{\omega_{\text{Cu}}}{\rho_{\text{Cu}}} + \frac{\omega_{\text{shell}}}{\rho_{\text{shell}}}\right)} = \frac{1}{\left(\frac{0.88}{8.96} + \frac{0.12}{2.711}\right)} = 7.0186\ \text{g/cm}^3$$

Meanwhile, there was a discernible decrease in the apparent porosity. This is because particle diffusion is affected by the sintering temperature, which is important in understand-

ing these processes. The diffusion rate is increased by raising the sintering temperature, which permits particle interactions and promotes grain development while reducing pore volume. The 12 wt.% Cu–CaCO₃ composite demonstrates measurable strengthening and corrosion resistance by confirming the beneficial effect of biogenic reinforcement [7,14,24].

3.2.6. Mechanical Properties

Effect of Crassostrea Madrasensis Seashell Powder Addition on HARDNESS

The porosity ratio and sintering temperature have a major impact on hardness in copper matrix composites (CMCs). Moreover, the reinforcing particles that are added have a direct effect on the hardness of copper matrix composites. Vickers microhardness testing was performed to describe different regions ($n = 3$) of the sample surface in order to assess the mechanical qualities of the pure copper–Crassostrea madrasensis seashell composite. The bulk composites made by resistance sintering the powdered copper–Crassostrea madrasensis seashell composite had an average hardness of 56.0 ± 3.0 HV. Vickers microhardness levels fluctuated due to the variable levels of precipitation seen at different areas in the surface of the samples during the method. This fluctuation is explained by the ceramic particles in the Crassostrea madrasensis seashell powder's intrinsic hardness and brittleness. These precipitated particles influence the composite's overall hardness by promoting localized resistance to indentation.

Table 3 summarizes the estimated average $\pm$ SD values and specific hardness readings.

Table 3. Vickers microhardness (HV) of Pure Cu and Cu–Crassostrea madrasensis seashell composites.

Composition	Hardness (HV)	Average $\pm$ SD (HV)	Improvement (%)
100% Pure Cu	57, 54, 51	54.0 ± 3.0	–
88% Cu + 12% Seashell	53, 59, 56	56.0 ± 3.0	3.7

Based on the initial hardness and density investigations, which showed near-optimal particle dispersion without severe agglomeration or porosity, the 12 wt.% CaCO₃ reinforcement level was chosen. Higher loadings (>16 wt.%) led to weak interparticle bonding and poor compaction, while lower loadings (<8 wt.%) only slightly strengthened the material. Consequently, 12 wt.% was chosen as a balanced composition that produced reliable mechanical performance and densification. This demonstrates how adding a small amount of Crassostrea madrasensis seashell powder increases hardness. This might be due to the Orowan strengthening mechanism initiated by the dispersed, incoherent seashell particles. The voids created by inhomogeneous consolidation may also be responsible for the abrupt drop in hardness. It was determined that the microhardness of the composite exhibited a negative correlation with precipitation-free regions, while a positive correlation was observed with eutectic structures. Resistance sintering with Crassostrea madrasensis seashell improved the overall hardness of the composite by 3.7% compared to pure copper (54.0 ± 3.0 HV) [21,24].

Effect of Crassostrea Madrasensis Seashell Powder Addition on Compressive Strength

The compressive characteristics of the copper–Crassostrea madrasensis sea shell composite, with a 12 wt.% reinforcement, were assessed by using a universal testing machine following ASTM E9-19 standards [6]. A compressive test sample with a length of 10.15 mm, a height of 8.90 mm, and a cross-sectional area of 90.34 mm² was examined, and the resulting stress–strain curve is depicted in Figure 12. The graph shows an initial linear elastic phase, which is followed by a brief yield plateau and subsequent strain hardening, indicating a gradual resistance to plastic deformation. The composite material demonstrated a

yield strength of 270 MPa at a 0.2% offset strain and an ultimate compressive strength of 686 MPa, confirming its strong load-bearing capability.

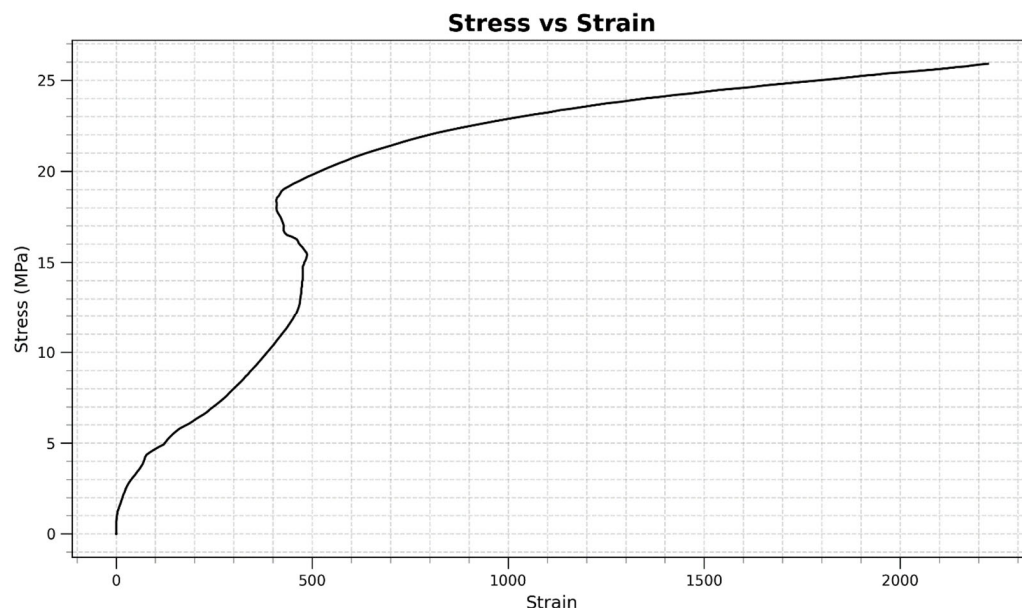


Figure 12. Stress–strain curve of the copper–*Crassostrea madrasensis* seashell composite.

The continuous increase in stress after yielding highlights the composite's capacity to undergo plastic deformation while retaining structural integrity. The improved strength and ductility are attributed to the even distribution of bio-ceramic *Crassostrea madrasensis* particles, which hinder dislocation movement and enhance interfacial bonding within the copper matrix. Also, the occurrence of bio-ceramic phases has heightened the matrix's resistance to localized deformation, resulting in improved mechanical performance. These results indicate that incorporating 12 wt.% *Crassostrea madrasensis* shell powder not only strengthens the copper matrix but also allows the composite to endure higher compressive loads with enhanced ductility, making it a suitable option for structural applications requiring resistance to compressive stresses [1,22].

3.2.7. Corrosion Studies: Electrochemical Corrosion Testing Techniques Open-Circuit Potential–Time (OCPT)

Figure 13 shows that during a 600-second immersion period, the open-circuit potential–time (OCPT) analysis provides insight into the corrosion behavior and thermodynamic stability of the copper–*Crassostrea madrasensis* sea shell composite in the occurrence of *Allium sativum* (Garlic) extract [26,27]. Table 4 shows the shift in OCPT values with increasing volumes of garlic extract in a 100 mL NaCl solution. In the control sample (0 mL garlic), the final OCPT values from -0.194 V to -0.212 V, corresponding to an OCPT shift of -0.018 V, indicate active corrosion. With the gradual addition of garlic extract (from 1 mL to 5 mL), a progressive reduction in the negative shift was observed [33]. The OCPT shift at 1 mL garlic was -0.014 V, and the inhibitory efficiency (IE) was about 22%. With efficiencies of about 56% and 67%, respectively, further increases to 2 mL and 3 mL garlic decreased the shift to -0.008 V and -0.006 V. The OCPT shift was reduced to -0.002 V at 4 mL of garlic extract, resulting in an efficiency of around 89%. Interestingly, the OCPT showed a tiny positive shift ($+0.002$ V) at 5 mL garlic, which corresponds to almost 100% inhibitory efficiency. These compounds likely form a protective film that delays electrochemical reactions and enhances corrosion resistance [31,33]. The gradual positive shift indicates that the garlic extract acts as an anodic inhibitor, improving the

system's thermodynamic stability by suppressing the metal dissolution process. The most significant protection is seen at 5 mL garlic concentration, confirming optimal inhibition under these conditions [27,33].

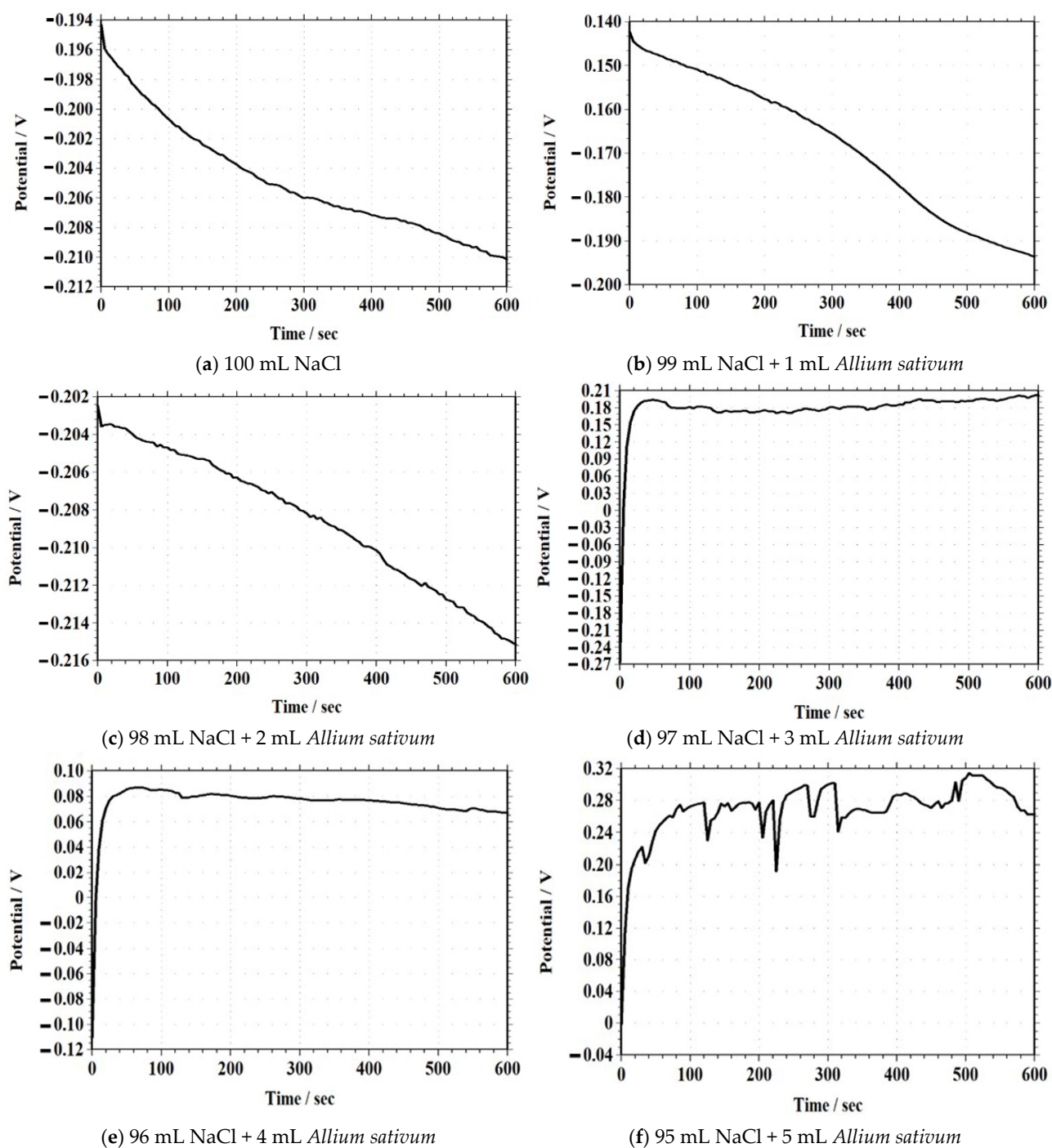


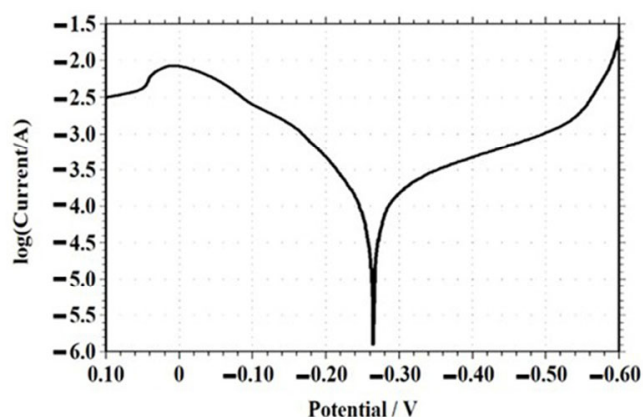
Figure 13. Open-circuit potential–time (OCPT) plots for various concentrations of *Allium sativum* (Garlic) extract.

Tafel Polarization

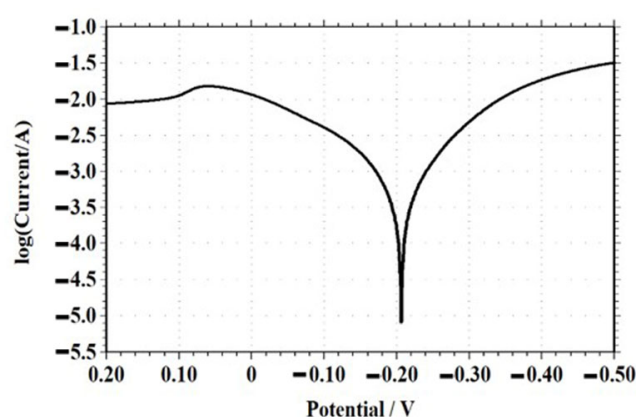
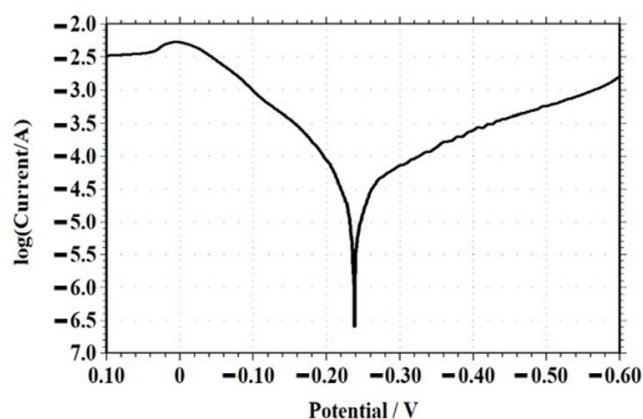
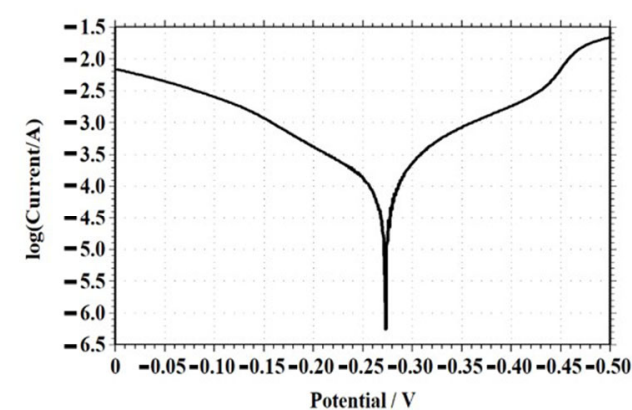
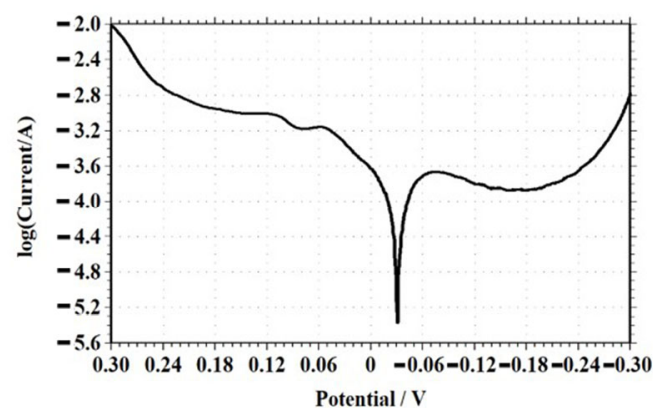
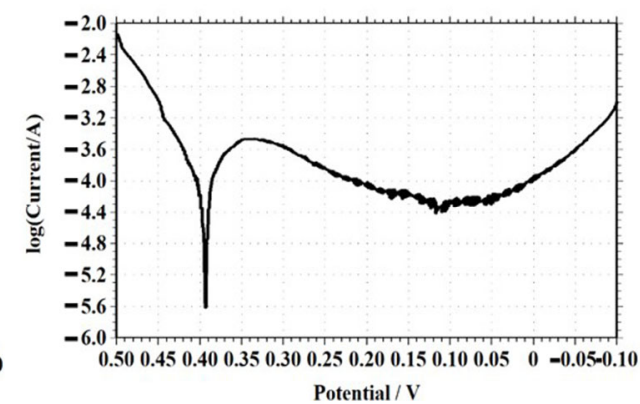
Figure 14 shows the electrochemical corrosion behavior of Cu–seashell composites in a 100 mL NaCl solution with different amounts of *Allium sativum* (Garlic) extract. Tafel polarization analysis was taken for calculating the inhibition efficiency and corrosion rate (CR) of copper–*Crassostrea madrasensis* sea shell composite in a NaCl (3.5 wt.%) with various *Allium sativum* extract concentrations [27,28,31].

Table 4. OCPT for various concentrations of *Allium sativum* (Garlic) extract over 600 s immersion.

Sample	Garlic Extract (mL)	Initial OCPT (V)	Final OCPT (V)	OCPT Shift (V)
100 mL NaCl (Control)	0	−0.194	−0.212	−0.018
99 mL NaCl + 1 mL Garlic	1	−0.196	−0.210	−0.014
98 mL NaCl + 2 mL Garlic	2	−0.198	−0.206	−0.008
97 mL NaCl + 3 mL Garlic	3	−0.199	−0.205	−0.006
96 mL NaCl + 4 mL Garlic	4	−0.200	−0.202	−0.002
95 mL NaCl + 5 mL Garlic	5	−0.202	−0.200	+0.002



(a) 100 mL NaCl

(b) 99 mL NaCl + 1 mL *Allium sativum*(c) 98 mL NaCl + 2 mL *Allium sativum*(d) 97 mL NaCl + 3 mL *Allium sativum*(e) 96 mL NaCl + 4 mL *Allium sativum*(f) 95 mL NaCl + 5 mL *Allium sativum***Figure 14.** Tafel polarization curves plots for various concentrations of *Allium sativum* (garlic) extract.

The results are summarized in Table 5. The blank sample (0 mL garlic) showed a corrosion rate of 0.0339 mpy, serving as the baseline. With the gradual addition of garlic extract, the corrosion rate decreased systematically. At 1 mL, 2 mL, 3 mL and 4 mL of *Allium sativum* (Garlic) extract, the corrosion rates dropped to 0.0285 mpy with 16% inhibition efficiency (IE), 0.0202 mpy with 40% IE, 0.0145 mpy with 57% IE, and 0.0101 mpy with 70% IE, respectively, indicating a more noticeable improvement. The inhibition efficiency increased gradually with *Allium sativum* concentration, attaining 92% inhibition at 5 mL, while the corrosion rate (CR) was significantly lowered to 0.0028 mpy.

Table 5. Tafel extrapolation for various concentrations of *Allium sativum* (Garlic) extract.

Volume of <i>Allium sativum</i> Extract (mL)	Rate of Corrosion (mpy)	Inhibition Efficiency (%)
100 mL NaCl (Control)	0.0339	0
99 mL NaCl + 1 mL Garlic	0.0285	16
98 mL NaCl + 2 mL Garlic	0.0202	40
97 mL NaCl + 3 mL Garlic	0.0145	57
96 mL NaCl + 4 mL Garlic	0.0101	70
95 mL NaCl + 5 mL Garlic	0.0028	92

This sharp decline in corrosion rate is attributed to the protective adsorbed film included in organosulfur mixtures, phenolics and flavonoids present in the extraction of *Allium sativum*. These molecules block active corrosion sites on the surfaces of metals, decreasing anodic and/or cathodic reactions [33]. The Tafel plots exhibited a shift, representing that the garlic extract acts like a mixed-type inhibitor including stronger anodic suppression. High inhibition efficiency at 5 mL is consistent with surface passivation behavior, which is also supported by the OCPT results [31].

Electrochemical Impedance Spectroscopy (EIS)

Measurements of EIS were made in the OCPT with a 10 mV AC fluctuation, spanning a range of frequencies from 100 kHz to 10 mHz following a 30-minute stabilizing period. Figure 15 shows Nyquist plots for various concentrations of the extraction of *Allium sativum*. One depressed semicircle can be seen in all spectra, which is indicative of a charge-transfer-controlled corrosion process. The equivalent circuit $R_s + [R_{ct} || CPE]$ was used to fit the experimental data. R_s , R_{ct} represent the resistances of solution and charge transfer, respectively. The CPE (constant phase element) is the capacitive behavior. In certain instances, a Warburg element (W) was added to enhance the fit when diffusion effects manifested at low frequencies. Table 6 provides a summary of the fitted parameters (R_s , R_{ct} , CPE-T, CPE-n, and χ^2 values). The Nyquist semicircle diameter gradually increased when the concentration of *Allium sativum* extract rose from 1 mL to 5 mL per 100 mL NaCl, suggesting a higher polarization resistance and thus acting as better corrosion protection. The development of a semi-permeable organic film from garlic phytochemicals, which adsorbs its active surface sites and prevents electron transfer at the metal–electrolyte interface, is confirmed by the increase in the R_{ct} values.

These findings are in line with earlier research on green corrosion inhibitors [27,31,33], which shows that the organosulfur and flavonoid chemicals in *Allium sativum* (garlic) provide a barrier of protection on the composite surface and increase corrosion resistance in a concentration-dependent manner.

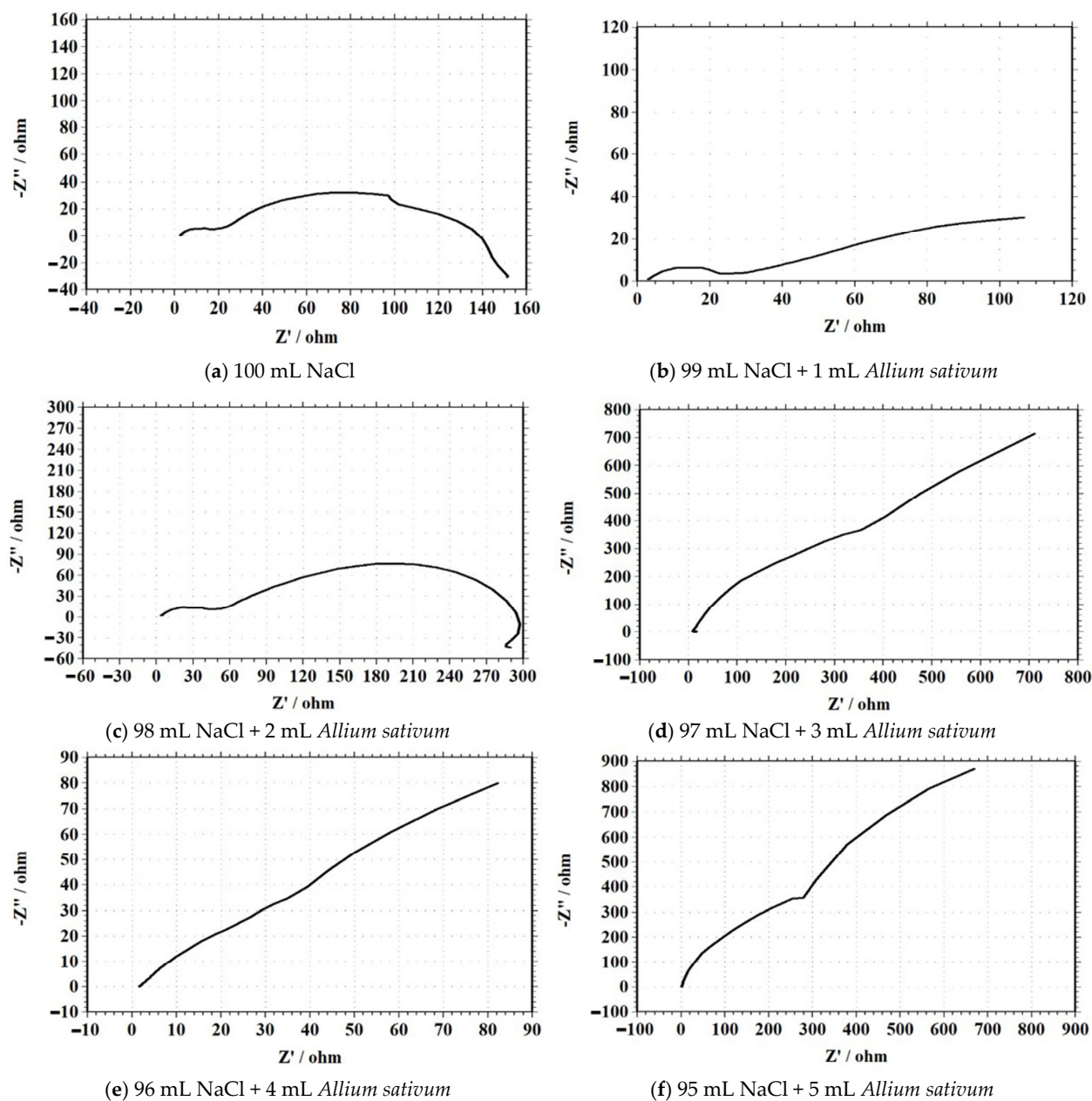


Figure 15. EIS plots for various concentrations of *Allium sativum* (garlic) extract.

Table 6. Electrochemical impedance spectroscopy for various concentrations of *Allium sativum* (garlic) extract.

S.No	<i>Allium sativum</i> (mL)	NaCl (mL)	Total Volume (mL)	Inhibition Zone (mm)	% Activity vs. Max (15 mm)
1.	0	100	100	0	0%
2.	1	99	100	9	46.7%
3.	2	98	100	11	60%
4.	3	97	100	13	73.3%
5.	4	96	100	14	86.7%
6.	5	95	100	15	100%

Linear Sweep Voltammetry (LSV)

The electrochemical behavior of Cu–seashell composites in a NaCl solution, depending on the different amounts of *Allium sativum* extract, was evaluated using the LSV

technique. The current response gradually dropped as the extract volume increased, as seen in Figure 16 and shown in Table 7, suggesting improved surface passivation. In the blank NaCl solution, the system exhibited a peak anodic current of 0.028 A at approximately 0.20 V, indicating typical active dissolution of the copper surface. Upon the addition of 1 mL garlic extract, the peak current increased slightly to 0.036 A with a shift to 0.25 V. This initial increase suggests a mild surface interaction, which is possibly due to the partial adsorption of organic molecules. Interestingly, with 2 mL extract, a decrease in peak current to 0.030 A and a shift to a lower potential (~ 0.15 V) was observed, implying an early formation of a protective surface layer. As the garlic concentration increased further (3 to 5 mL), the current consistently dropped with the lowest observed value of 0.016 A at 5 mL extract, which was accompanied by a peak potential around 0.05 V.

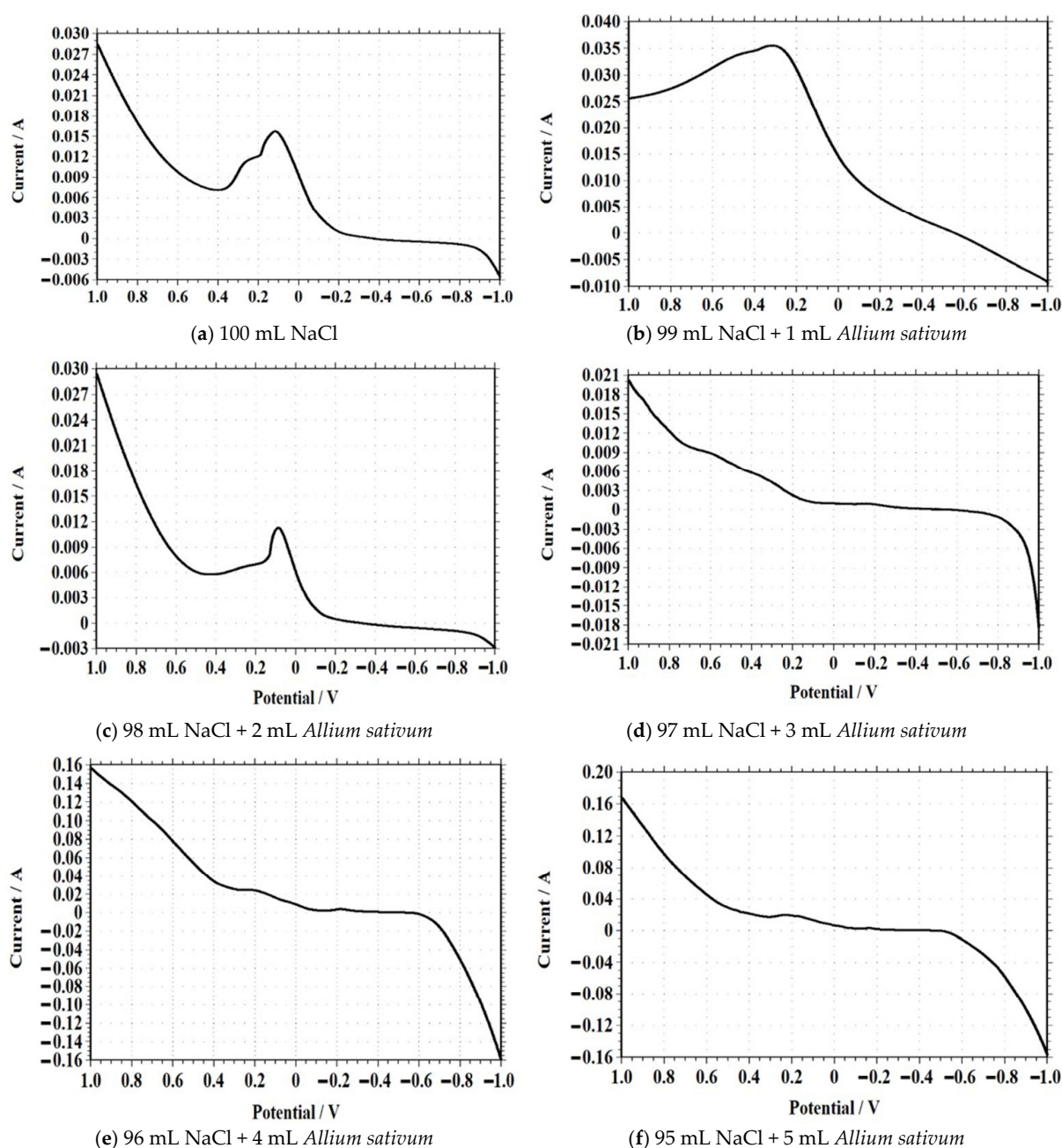


Figure 16. Linear sweep voltammetry plots for various concentrations of *Allium sativum* (Garlic) extract.

Table 7. Linear sweep voltammetry for various concentrations of *Allium sativum* (Garlic) extract.

Solution Composition (NaCl + <i>Allium sativum</i>)	Peak Current (A)	Peak Potential (V)	Observation
100 mL NaCl (Blank)	0.028	~0.20	Baseline oxidation peaks
99 mL NaCl + 1 mL Extract	0.036	~0.25	Mild increase in current
98 mL NaCl + 2 mL Extract	0.030	~0.15	Suppressed current, early peak
97 mL NaCl + 3 mL Extract	0.021	~0.10	Lower current, stable profile
96 mL NaCl + 4 mL Extract	0.16	~0.05	Steady inhibition pattern
95 mL NaCl + 5 mL Extract	0.16	~0.05	Most effective inhibition observed

This significant reduction in anodic current confirms the inhibiting effect of the garlic extract. The occurrence of bio-active compounds promote adsorption onto the surface of the composite, impeding electrochemical oxidation. The consistent potential shift toward more cathodic values also supports passivation behavior. The outcomes are consistent with other studies that highlighted the value of LSV in examining inhibitor effectiveness and reactions toward kinetics in chloride environments [34–38].

3.2.8. Chronocoulometry (CC)

The charge transfer behavior of Cu–*Crassostrea madrasensis* composites in a NaCl solution (3.5 wt.%) with various amounts of *Allium sativum* extraction was assessed by chronocoulometry. The chronocoulometric plots of various concentrations of *Allium sativum* (Garlic) extract are shown in Figure 17. In the absence of *Allium sativum* (Garlic) extract (blank), a baseline charge of 1.1 C was recorded, indicating the typical charge flow associated with active corrosion and metal ion dissolution. Upon the addition of 1 mL garlic extract, the charge slightly decreased to 0.48 C (~56% efficiency), while 2 mL further reduced it to 0.88 C (~20% efficiency). The lowest charge transfer 0.22 C (~80% efficiency) was observed at 3 mL extract, signifying the maximum suppression of electrochemical activity. However, at higher concentrations (4 and 5 mL), the charge values increased to 4.7 C and 7.5 C (−327% and −582%), respectively. Interestingly, at higher concentrations (4 and 5 mL), the charge transfer increased, suggesting a potential saturation or desorption effect that reduced inhibition efficiency. This non-linear behavior indicates that the optimum inhibitory effect was observed at 3 mL of garlic extract, where the lowest total charge transfer was recorded [35–37].

Table 8 shows charge values obtained from chronocoulometry for different concentrations of *Allium sativum* (garlic) extract. *Allium sativum* (Mixed type inhibitor) reduces charge accumulation over time with predominant cathodic control [38,39].

The electrochemical performance of copper matrix composites (CMCs) in a NaCl solution (3.5 wt.%) with various concentrations of *Allium sativum* extract was systematically evaluated using OCPT, Tafel polarization, EIS, LSV, and chronocoulometry. OCPT analysis revealed a consistent positive shift in open-circuit potential with increasing garlic concentration, which confirms the enhancement of thermodynamic stability. Tafel plots demonstrated a considerable reduction in the corrosion rate (CR) from 0.0339 toward 0.0028 mpy by using inhibition efficiency reaching up to 92% at 5 mL garlic extract. Electrochemical impedance spectroscopy additionally supported these findings and showed a proportional increase in the inhibition zone up to 15 mm, which was indicative of effective surface coverage and increased charge transfer resistance. LSV data showed a significant suppression of anodic current and a cathodic shift in peak potential, reflecting the strong inhibition of electrochemical activity. Chronocoulometry revealed the lowest total charge transfer (0.22 C) at 3 mL garlic concentration, indicating the most efficient dosage for surface passivation. Interestingly, higher concentrations (4–5 mL) resulted in increased charge, suggesting pos-

sible over-adsorption effects. The *Allium sativum* extract demonstrated excellent corrosion inhibition properties for copper composites in saline environments with a synergistic effect observed across all electrochemical techniques. The optimal performance was observed between 3 and 5 mL, depending on the technique used, highlighting the potential of natural, plant-based inhibitors in green corrosion protection strategies.

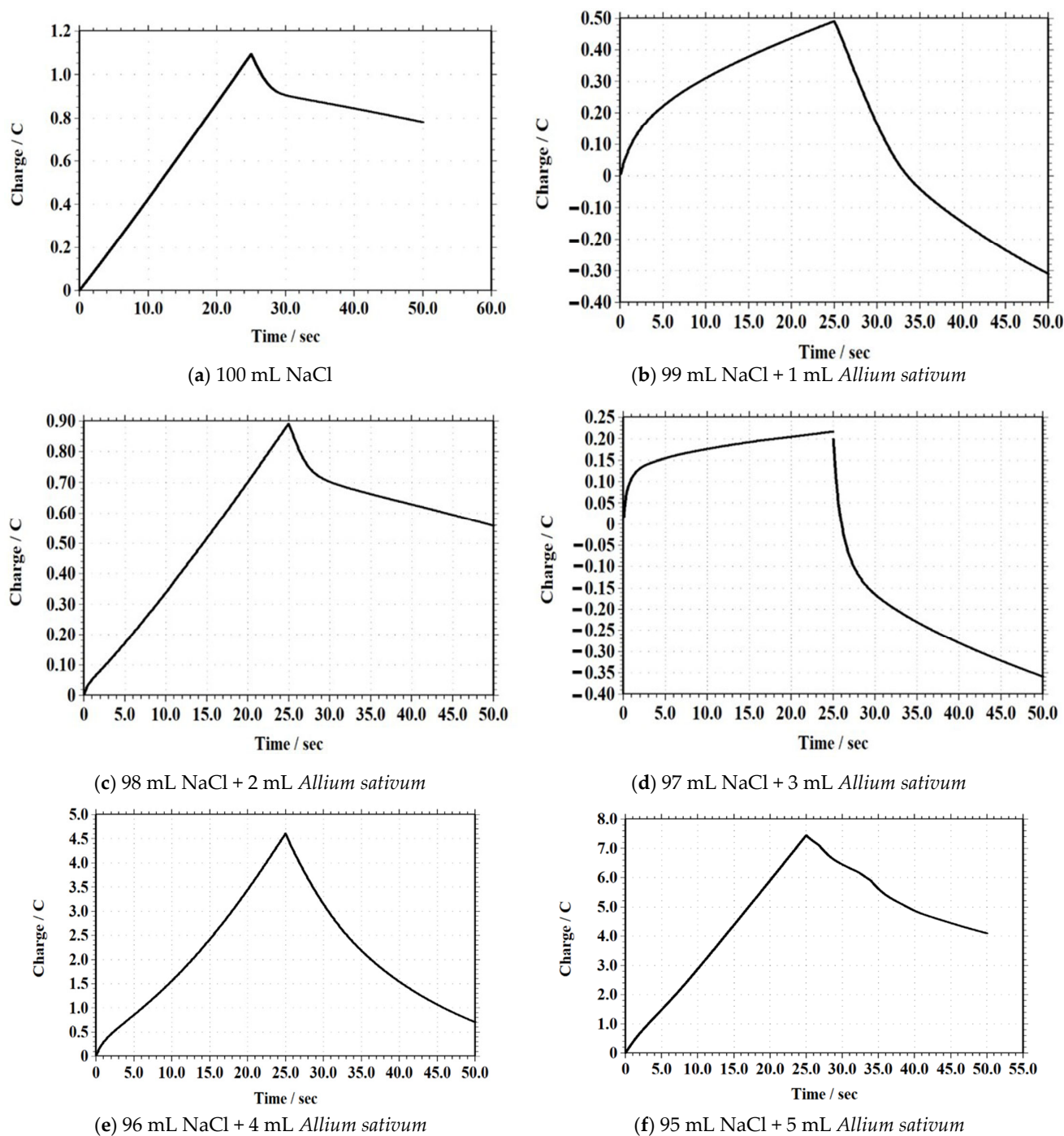


Figure 17. Chronocoulometric plots for various concentrations of *Allium sativum* (Garlic) extract.

Table 8. Chronocoulometric for various concentrations of *Allium sativum* (garlic) extract.

Sample Composition	Maximum Charge (C)
100 mL NaCl (Blank)	1.1
99 mL NaCl + 1 mL <i>Allium sativum</i>	0.48
98 mL NaCl + 2 mL <i>Allium sativum</i>	0.88
97 mL NaCl + 3 mL <i>Allium sativum</i>	0.22
96 mL NaCl + 4 mL <i>Allium sativum</i>	4.7
95 mL NaCl + 5 mL <i>Allium sativum</i>	7.5

4. Conclusions

A copper matrix composite reinforced with 12 wt.% *Crassostrea madrasensis* seashell powder was effectively developed via powder metallurgy. XRD analysis verified the presence of crystalline calcite and metallic copper phases, indicating copper mixing without altering the shell's crystal structure. The FTIR spectra showed maintained carbonate bands, while minor new peaks suggested interactions between copper ions and organic/inorganic components. TGA/DSC analysis showed a three-step decomposition pattern with copper addition enhancing thermal stability and decomposition sharpness. FESEM images revealed angular, fine particles with a high surface area, promoting better mechanical bonding in the composite. EDX analysis confirmed the presence of Ca, C, O, and Cu, validating successful copper doping while preserving the calcium carbonate framework and confirming its purity and effectiveness as a natural reinforcement for Cu-based composites. Microstructural examination showed a uniform dispersion of shell particles, refined grain structure, and strong matrix–reinforcement bonding. Hardness increased from 54 HV to 56 HV, reflecting a 3.7% improvement due to the *Crassostrea madrasensis* seashell reinforcement. Compression tests demonstrated high mechanical strength with an ultimate tensile strength of 686 MPa and yield strength of 270 MPa.

The experimental results confirm that *Allium sativum* extract exhibits significant corrosion inhibition properties for copper matrix composites in a 3.5 wt.% NaCl environment. According to Tafel polarization, the maximal inhibitor concentration of 92% was reached at 5 mL. Complementary analyses using OCPT, EIS, LSV, and chronocoulometry supported these results through observable shifts in potential, reduced anodic current, and decreased total charge transfer.

This investigation focused on the microstructure, mechanical properties, and corrosion behavior of Cu–seashell composites fabricated via powder metallurgy. Future research will examine further reinforcement levels (0–16 wt.%) to determine the full composition–property link. The current work shows that 12 wt.% reinforcement offers a balanced improvement. In addition to mechanical and electrochemical performance, other functional properties such as thermal and electrical conductivity and tribological behavior will be evaluated to determine application-specific suitability. The practicality of powder metallurgy in terms of cost and energy consumption demands further optimization despite its effectiveness in composite fabrication. To completely evaluate long-term durability in actual maritime and industrial settings, other elements including temperature variations, chloride cycling, and microbial attack must be taken into account.

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References

1. Sridhar, M.M.J.; Ravichandran, M.; Meignanamoorthy, M. Effect of Silicon Carbide on Microstructural, Mechanical and Corrosion Behavior of Electrolytic Copper Matrix Composite Produced by the Powder Metallurgy Route. *Silicon* **2022**, *14*, 5877–5886. [\[CrossRef\]](#)
2. Simić, M.; Ružić, J.; Božić, D.; Stašić, J. The Effect of Ball-Powder Ratio on The Mechanical and Structural Properties of CuZrB Composite Materials Fabricated by Powder Metallurgy. *Adv. Funct. Mater.* **2023**, *1*, 19–24. [\[CrossRef\]](#)
3. Kalidas, N.; Gopal, P.M.; Kavimani, V. Development and Characterization of Silicon Nitride and Synthesized Graphene Oxide Reinforced Cu/GO/ x Si₃N₄ Composites. *Silicon* **2025**, *17*, 141–153. [\[CrossRef\]](#)
4. Ankur; Bharti, A.; Prasad, D.; Kumar, N.; Kuldeep, K.S. A Re-investigation: Effect of various parameters on mechanical properties of copper matrix composite fabricated by powder metallurgy. *Mater. Today Proc.* **2021**, *45*, 4595–4600. [\[CrossRef\]](#)
5. Taha, M.A.; El-zaidia, M.M.; Zaki, M.Z.; Abomostafa, H.M. Influence of Nano-Hybrid Reinforcements on the Improvement Strength, Thermal Expansion and Wear Properties of Cu–SiC–Fly Ash Nanocomposites Prepared by Powder Metallurgy. *ECS J. Solid State Sci. Technol.* **2023**, *12*, 33011. [\[CrossRef\]](#)
6. Vijay Ponraj, N.; Azhagurajan, A.; Vettivel, S.C.; Shajan, X.S.; Nabhiraj, P.Y.; Sivapragash, M. Graphene nanosheet as reinforcement agent in copper matrix composite by using powder metallurgy method. *Surf. Interfaces* **2017**, *6*, 190–196. [\[CrossRef\]](#)
7. Yan, Y.M.; Kou, S.; Yang, H.; Shu, S.; Qiu, F.; Jiang, Q.; Zhang, L. Ceramic particles reinforced copper matrix composites manufactured by advanced powder metallurgy: Preparation, performance, and mechanisms. *Int. J. Extrem. Manuf.* **2023**, *5*, 32006. [\[CrossRef\]](#)
8. Kumar, N.; Bharti, A.; Dixit, M.; Nigam, A. Effect of Powder Metallurgy Process and its Parameters on the Mechanical and Electrical Properties of Copper-Based Materials: Literature Review. *Compos. Mater.* **2023**, *59*, 401–410. [\[CrossRef\]](#)
9. Dixit, M.; Srivastava, R.K. Effect of compaction pressure on microstructure, density and hardness of Copper prepared by Powder Metallurgy route. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *377*, 12209. [\[CrossRef\]](#)
10. Venkatesh, V.S.S.; Rao, R.N.; Patnaik, L. Effect of Spark Plasma Sintering Temperature on Phase Evaluation and Mechanical Behaviour of Cu–4 Wt% SiC Composite. *Silicon* **2023**, *15*, 6439–6449. [\[CrossRef\]](#)
11. Silva, T.H.; Mesquita-Guimarães, J.; Henriques, B.; Silva, F.S.; Fredel, M.C. The Potential Use of Oyster Shell Waste in New Value-Added By-Product. *Resources* **2019**, *8*, 13. [\[CrossRef\]](#)
12. Magnabosco, G.; Giuri, D.; Di Bisceglie, A.P.; Scarpino, F.; Fermari, S.; Tomasini, C.; Falini, G. New Material Perspective for Waste Seashells by Covalent Functionalization. *ACS Sustain. Chem. Eng.* **2021**, *9*, 6203–6208. [\[CrossRef\]](#)
13. Zhu, Y.; Chen, D.; Yu, X.; Liu, R.; Liao, Y. Properties of Cementitious Materials Utilizing Seashells as Aggregate or Cement: Prospects and Challenges. *Materials* **2024**, *17*, 1222. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Bamigboye, G.O.; Nworgu, A.T.; Odetoyan, A.O.; Kareem, M.; Enabulele, D.O.; Bassey, D.E. Sustainable use of seashells as binder in concrete production: Prospect and challenges. *J. Build. Eng.* **2021**, *34*, 101864. [\[CrossRef\]](#)
15. Sankar, M.; Devaneyan, S.P.; Pushpanathan, D.P.; Myszk, D. Microstructural Characterization and Mechanical Behavior of Copper Matrix Composites Reinforced by B₄C and Sea Shell Powder. *J. Cast. Mater. Eng.* **2018**, *2*, 24. [\[CrossRef\]](#)
16. Srirama, D.; Jayanthi, P.N.V. Experimental investigation of lime produced from oyster shell waste as a potential soil stabilizing material: A sustainable approach for lime replacement. *Prog. Eng. Sci.* **2025**, *2*, 100111. [\[CrossRef\]](#)
17. Pruncu, C.I.; Vladescu, A.; Hynes, N.R.J.; Sankaranarayanan, R. Surface Investigation of Physella Acuta Snail Shell Particle Reinforced Aluminium Matrix Composites. *Coatings* **2022**, *12*, 794. [\[CrossRef\]](#)
18. Lu, J.; Cong, X.; Li, Y.; Hao, Y.; Wang, C. Scalable recycling of oyster shells into high purity calcite powders by the mechanochemical and hydrothermal treatments. *J. Clean. Prod.* **2018**, *172*, 1978–1985. [\[CrossRef\]](#)
19. Gbadeyan, O.J.; Adali, S.; Bright, G.; Sithole, B.; Onwubu, S. Optimization of Milling Procedures for Synthesizing Nano-CaCO₃ from *Achatina fulica* Shell through Mechanochemical Techniques. *J. Nanomater.* **2020**, *2020*, 4370172. [\[CrossRef\]](#)

20. Chen, J.; Bao, S.; Li, J.; Yu, B.; Li, K.; Yang, X.; Zuo, K.; Gao, T.; Xie, G. Powder metallurgy process enables production of high-strength conductive Cu-based composites reinforced by Cu₅₀Zr₄₃Al₇ metallic glass. *Intermetallics* **2023**, *163*, 108062. [\[CrossRef\]](#)
21. Sundar, G.; Hynes, N.R.J. Corrosion issues in metal matrix composites & Bi-metals. *AIP Conf. Proc.* **2019**, *2142*, 70007. [\[CrossRef\]](#)
22. Guo, Y.; Yu, K.; Niu, J.; Sun, M.; Dai, G.; Sun, Z.; Chang, H. Effect of reinforcement content on microstructures and mechanical properties of graphene nanoflakes-reinforced titanium alloy matrix composites. *J. Mater. Res. Technol.* **2021**, *15*, 6871–6882. [\[CrossRef\]](#)
23. Vidyuk, T.M.; Ukhina, A.V.; Gavrilov, A.I.; Shikalov, V.S.; Anisimov, A.G.; Lomovsky, O.I.; Dudina, D.V. Synthesis of Tungsten Carbides in a Copper Matrix by Spark Plasma Sintering: Microstructure Formation Mechanisms and Properties of the Consolidated Materials. *Materials* **2023**, *16*, 5385. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Usca, Ü.A.; Şap, S.; Uzun, M.; Giasin, K.; Pimenov, D.Y. Evaluation of Mechanical and Tribological Aspect of Self-Lubricating Cu-6Gr Composites Reinforced with SiC–WC Hybrid Particles. *Nanomaterials* **2022**, *12*, 2154. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Samad, A.; Ansari, S.; Arif, S.; Muaz, M.; Khan, A.U.; Muhammad, Z.; Bashiri, A.H.; Zakri, W. Tribological performance of Cu-silica sand hybrid composite reinforced with graphene nanoparticles by electric resistance sintering: Experimental studies and modeling. *Eng. Sci. Technol. Int. J.* **2024**, *54*, 101713. [\[CrossRef\]](#)
26. Hynes, N.R.J.; Vignesh, N.J.; Barile, C.; Velu, P.S.; Baskaran, T.; Jappes, J.T.W.; Al-Khashman, O.A.; Brykov, M.; Ene, A. Green Corrosion Inhibition on Carbon-Fibre-Reinforced Aluminium Laminate in NaCl Using Aerva Lanata Flower Extract. *Polymers* **2022**, *14*, 1700. [\[CrossRef\]](#)
27. Hynes, N.R.J.; Selvaraj, R.M.; Mohamed, T.; Mukesh, A.M.; Olfa, K.; Nikolova, M.P. Aerva lanata flowers extract as green corrosion inhibitor of low-carbon steel in HCl solution: An in vitro study. *Chem. Pap.* **2021**, *75*, 1165–1174. [\[CrossRef\]](#)
28. Darweesh, M.A.; Emam, S.M.; Wahba, A.M.; Ayad, M.I.; El-Nahass, M.N.; Abd-Elhamied, A.S.; Hammad, W.A. Onion Peel Extract/Copper Oxide Nanoparticles as Corrosion Inhibitors for Carbon Steel in Hydrochloric Acid: Extraction, Characterization, Electrochemical Study, and Theoretical Explorations. *Results Chem.* **2024**, *9*, 101626. [\[CrossRef\]](#)
29. Devikala, S.; Kamaraj, P.; Arthanareeswari, M.; Patel, M.B. Green corrosion inhibition of mild steel by aqueous Allium sativum extract in 3.5% NaCl. *Mater. Today Proc.* **2019**, *14*, 580–589. [\[CrossRef\]](#)
30. Hajsafari, N.; Razaghi, Z.; Tabaian, S.H. Electrochemical study and molecular dynamics (MD) simulation of aluminum in the presence of garlic extract as a green inhibitor. *J. Mol. Liq.* **2021**, *336*, 116386. [\[CrossRef\]](#)
31. Bhavyasree, P.G.; Xavier, T.S. Green synthesis of Copper Oxide/Carbon nanocomposites using the leaf extract of Adhatoda vasica Nees, their characterization and antimicrobial activity. *Heliyon* **2020**, *6*, e03323. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Guma, T.N.; Aremo, J.O. A Review of Up-To-Date Research Knowledge on the Corrosion Inhibiting Capability of Garlic (*Allium sativum*) for Steel Materials. *Int. J. Adv. Eng. Manag.* **2025**, *7*, 104–117. [\[CrossRef\]](#)
33. Parthipan, P.; Elumalai, P.; Narenkumar, J.; Machuca, L.L.; Murugan, K.; Karthikeyan, O.P.; Rajasekar, A. *Allium sativum* (garlic extract) as a green corrosion inhibitor with biocidal properties for the control of MIC in carbon steel and stainless steel in oilfield environments. *Int. Biodeterior. Biodegrad.* **2018**, *132*, 66–73. [\[CrossRef\]](#)
34. Cáceres, L.; Frez, Y.; Galleguillos, F.; Soliz, A.; Gómez-Silva, B.; Borquez, J. Aqueous Dried Extract of Skytanthus acutus Meyen as Corrosion Inhibitor of Carbon Steel in Neutral Chloride Solutions. *Metals* **2021**, *11*, 1992. [\[CrossRef\]](#)
35. Pérez, F.A.N. Electrochemical Analysis of Corrosion Resistance of Manganese-Coated Annealed Steel: Chronoamperometric and Voltammetric Study. *AppliedChem* **2024**, *4*, 367–383. [\[CrossRef\]](#)
36. Rossi, R.; Pant, D.; Logan, B.E. Chronoamperometry and linear sweep voltammetry reveals the adverse impact of high carbonate buffer concentrations on anode performance in microbial fuel cells. *J. Power Sources* **2020**, *476*, 228715. [\[CrossRef\]](#)
37. Nan, T.; Yang, J.; Chen, B. Electrochemical mechanism of tin membrane electrodeposition under ultrasonic waves. *Ultrason. Sonochem.* **2018**, *42*, 731–737. [\[CrossRef\]](#)
38. Wang, F.; Cui, Y.O.; Sang, J.; Zhang, H.; Zhu, H. Cross-linked of poly (biphenyl pyridine) and poly(styrene-*b*-(ethylene-co-butylene)-*b*-styrene) grafted with double cations for anion exchange membrane. *Electrochim. Acta* **2022**, *405*, 139770. [\[CrossRef\]](#)
39. Salcı, A.; Yüksel, H.; Solmaz, R. Experimental studies on the corrosion inhibition performance of 2-(2-aminophenyl) benzimidazole for mild steel protection in HCl solution. *J. Taiwan Inst. Chem. Eng.* **2022**, *134*, 104349. [\[CrossRef\]](#)
40. Annaraj, J.P.; Bose, N.; Hynes, N.R.J. A review on mechanical and tribological properties of sintered copper matrix composites. *AIP Conf. Proc.* **2019**, *2142*, 70027. [\[CrossRef\]](#)

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