

Fig. 3. Color evolution during the synthesis of CuFe_2O_4 NPs using *Chlorella vulgaris* extract: Initial orange solution of metal precursors (left) gradually darkens to a brownish color after 1 h of reaction (center) and further deepens into a darker shade after 4 h of reaction (right), indicating nanoparticle formation.

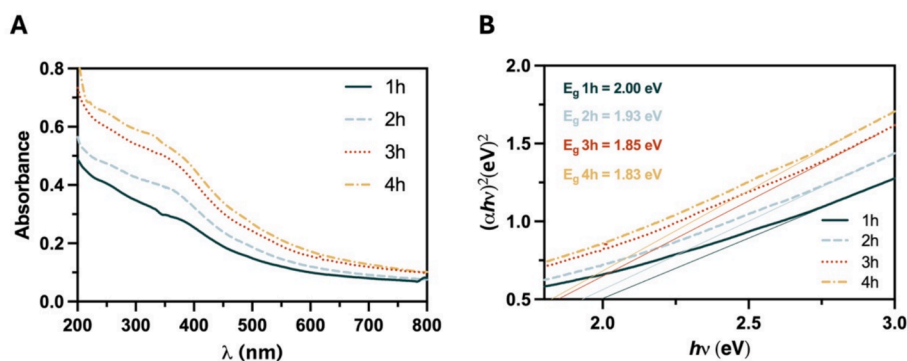


Fig. 4. (A) UV-Vis absorption spectra and (B) band gap energy of CuFe_2O_4 NPs during the synthesis reaction times of 1 h, 2 h, 3 h, and 4 h.

stabilized during this time. The slight difference observed between 3 h and 4 h could be attributed to the final stages of the reaction, where the formation rate slows down as the reaction approaches completion.

The band gaps of the CuFe_2O_4 NPs were calculated at various synthesis reaction times, as summarized in Fig. 4B, and showed a decreasing trend with increasing reaction time. At 1 h, the band gap was larger, suggesting smaller NPs due to the stronger quantum confinement effect, which is known to increase band gap energy [37,38]. As the reaction progressed, the growth of CuFe_2O_4 NPs reduced the quantum confinement effect, resulting in a gradual decrease in the band gap from 2 eV to 1.83 eV. In addition to particle size, surface defects, and non-stoichiometric compositions in the early stages of synthesis contribute to states within the band gap, leading to higher band gap values [39,40]. With longer synthesis times, these defects are minimized, improving the crystallinity and yielding a band gap closer to the intrinsic bulk value. This trend aligns with the observed blue shift in absorption spectra, as reduced surface defects and improved stoichiometric control may offset the effect of increasing particle size, resulting in a shift toward higher energy wavelengths.

3.2. Scanning electron microscopy and energy dispersive spectroscopy analysis of copper ferrite nanoparticles

The morphology and structural properties of CuFe_2O_4 NPs were characterized through SEM and size distribution analysis (Fig. 5). SEM images revealed dense agglomerates of NPs with relatively uniform morphology. The particle size distribution, derived from SEM images analysis using ImageJ software, exhibited a Gaussian profile with an average size of 130.1 ± 26.0 nm. These sizes are similar to those obtained by Sravanthi et al. [41], who synthesized CuO NPs using *Antigonon leptopus* leaf extract, reporting clustered particles with sizes ranging from 110 to 280 nm. However, other studies have demonstrated significantly smaller NPs sizes, underscoring the influence of synthesis conditions and the composition of plant extracts. For instance, Khatami et al. [42] synthesized CuO NPs with sizes between 17 and 41 nm using *Capparis spinosa* fruit extract, while Alhalili [43] reported particle sizes of approximately 88 nm using plant-derived capping agents.

The observed differences in NPs size and morphology across these studies can be attributed to variations in reaction parameters such as temperature, pH, precursor concentration, and the type and concentration of bioactive compounds in plant extracts [44]. Capping agents present in the extracts, such as flavonoids, phenols, and polysaccharides, play a crucial role in stabilizing nanoparticles, inhibiting overgrowth,

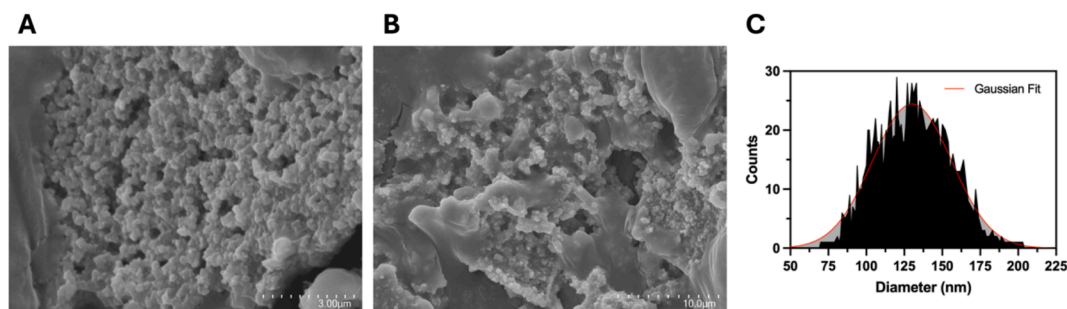


Fig. 5. (A) and (B) SEM images of CuFe₂O₄ NPs synthesized using *Chlorella vulgaris* extract taken at 3 μm and 10 μm, respectively; (C) Nanoparticle size distribution analysis, including particle count and Gaussian curve fitting, derived from SEM image analysis using ImageJ software.

and preventing aggregation in colloidal solutions [35]. In this study, the size of CuFe₂O₄ NPs may be attributed to the specific bioactive profile of the *Chlorella vulgaris* extract, which influences both the nucleation and growth processes during synthesis.

The elemental composition of the synthesized CuFe₂O₄ NPs was confirmed by EDS, as shown in Fig. 6. The spectrum exhibits distinct peaks for copper (Cu), iron (Fe), and oxygen (O), validating the successful formation of CuFe₂O₄. The Cu peaks at ~ 8.1 keV (Kα) and ~ 9.0 keV (Kβ), along with Fe peaks at ~ 6.3 keV (Kα) and ~ 7.1 keV (Kβ), confirm the incorporation of these elements. The O Kα peak (~0.5 keV) indicates oxygen’s presence in the ferrite structure. A carbon (C Kα) peak (~0.3 keV) is also observed, likely originating from *Chlorella vulgaris* residues in the green synthesis or from carbon coating used during SEM-EDS. Additionally, minor traces of bromine (Br), chlorine (Cl), and sulfur (S) are detected, which may stem from organic residues or precursor materials. However, their low intensity suggests minimal impact on the final product’s purity. Literature on CuFe₂O₄ NPs synthesized reports similar elemental compositions, reinforcing the reliability of this green synthesis method [45–47]. The strong Cu, Fe, and O signals confirm the expected stoichiometric composition of CuFe₂O₄ without significant impurity phases.

3.3. Wettability of copper ferrite nanofluids

Wettability is a key parameter used to characterize the chemical and physical properties of a surface and is typically determined by measuring the contact angle of a liquid droplet on the surface [48]. The interaction between a solid surface and a fluid is influenced by factors such as surface energy, surface texture, and chemical composition [49].

Additionally, the fluid’s properties, such as surface tension, can also impact wettability measurements.

In this study, the contact angles of CuFe₂O₄-based nanofluids at concentrations of 0.1 wt%, 0.5 wt%, and 1 wt% were measured on two types of substrates: (i) Aluminum, a widely used material in heat exchangers due to its high thermal conductivity, lightweight nature, oxidation resistance, and cost-effectiveness compared to copper; (ii) PDMS, as the heat exchanger later used to evaluate the heat transfer capacity of the nanofluids is made from this material. To assess the significance of variations in contact angle under different conditions relative to the control group (water-based fluid without NPs), a Dunnett multiple comparison test was conducted (for detailed information, see Table S1 in supplementary material).

The contact angles of CuFe₂O₄-based nanofluids at concentrations of 0.1 wt%, 0.5 wt%, and 1 wt% on both substrates are shown in Fig. 7. On the aluminum substrate, a significant increase in the contact angle was observed at the lowest concentration (0.1 wt%) compared to the control (water). However, no significant changes were noted at higher concentrations. This behavior may indicate better dispersion of CuFe₂O₄ NPs at lower concentrations, which optimally covers the surface and alters the surface energy of the aluminum substrate, resulting in a higher contact angle. At higher NP concentrations, increased particle interactions and aggregation reduce their effective interaction with the substrate, diminishing their influence on surface energy and contact angle. These findings suggest that at higher concentrations, the wettability behavior of the nanofluid becomes similar to that of water.

For the PDMS substrate, a generalized increase in contact angles compared to aluminum was observed. This result is expected, as PDMS is a silicone-based polymer with inherently low surface energy, making it

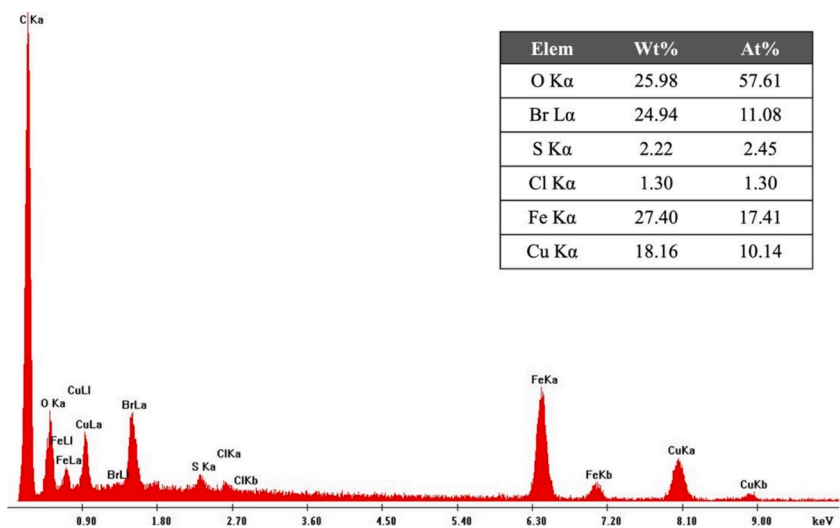


Fig. 6. EDS spectrum of the green synthesized CuFe₂O₄ NPs using *Chlorella vulgaris* aqueous extract.

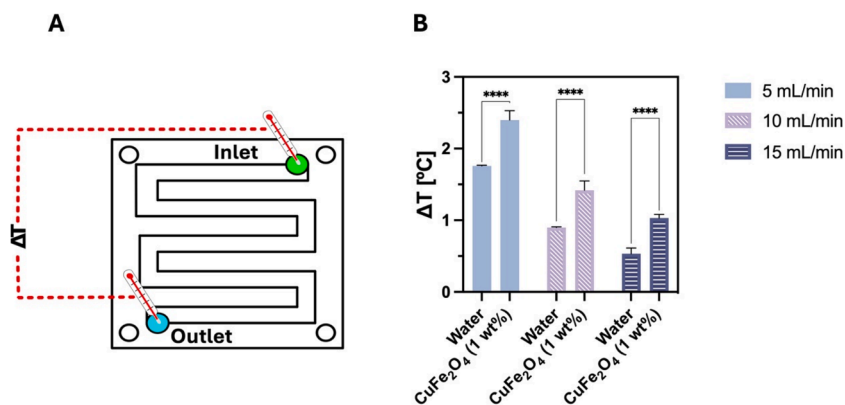


Fig. 10. (A) Schematic representation of the temperature variation measurement between the inlet and outlet, and (B) experimental temperature variation between the inlet and outlet of the serpentine channel for water and CuFe₂O₄ 1 wt% nanofluid at 5 mL/min, 10 mL/min and 15 mL/min flow rates. Data represent the mean \pm standard deviation of three independent experiments. Error bars indicate the standard deviation of three measurements. Multiple comparisons with using Šídák's test. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; **** $p < 0.0001$, ns: not significant; by ANOVA followed by Šídák's post-test.

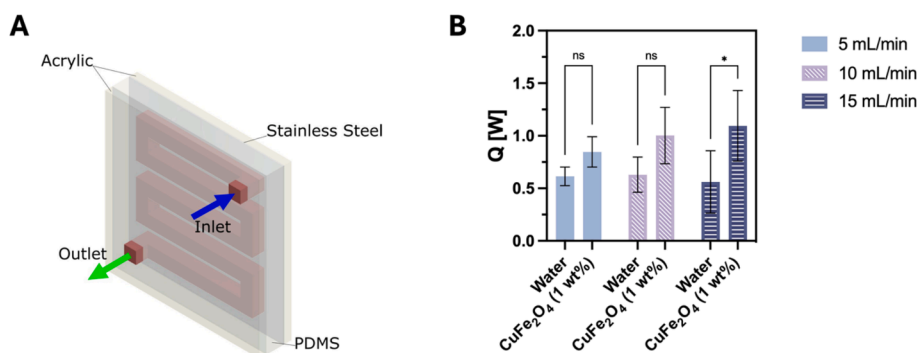


Fig. 11. (A) Schematic representation of the PDMS-based heat exchanger (serpentine) and (B) heat storage rate as a function of the volumetric flow rate of water and CuFe₂O₄ (1 wt%) nanofluid with the respective standard deviation. Data represent the mean \pm standard deviation of three independent experiments. Error bars indicate the standard deviation of three measurements. Multiple comparisons with using Šídák's test. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; **** $p < 0.0001$, ns: not significant; by ANOVA followed by Šídák's post-test.

%, 0.5 wt%, and 1 wt% to create nanofluids, and their properties were comprehensively characterized. Wettability results highlighted substrate-specific behavior. On aluminum, a significant increase in contact angle at 0.1 wt% (compared to water) suggested optimal NPs dispersion, while at higher concentrations, NPs aggregation reduced their surface interaction. On the more hydrophobic PDMS substrate, only the 1 wt% nanofluid significantly altered the contact angle, underscoring the concentration-dependent interaction of nanoparticles with surfaces. These variations, however, are unlikely to impact heat transfer performance in single-phase systems but may influence two-phase systems.

Viscosity measurements revealed a slight increase across all nanofluids compared to water, with the 0.1 wt% concentration showing the highest viscosity (~ 1.1 mPa·s). This behavior suggests that lower concentrations may exhibit better dispersion, while higher concentrations lead to aggregation, limiting further viscosity changes. Importantly, the viscosities remained within manageable limits, ensuring minimal impact on pumping power requirements and practical applicability.

Thermal conductivity testing showed that the nanofluids improved thermal performance, with the 1 wt% nanofluid achieving a 4.8 % enhancement compared to water. This improvement translated into substantial heat transfer efficiency gains during experiments using a serpentine heat exchanger. The 1 wt% nanofluid demonstrated remarkable heat absorption increases, ranging from 38 % to 95 %, depending on the volumetric flow rate (5–15 mL/min). These results highlight the nanofluid's capacity to outperform water, particularly under higher flow rates, where its enhanced thermal properties

significantly improve heat removal.

In summary, the CuFe₂O₄-based nanofluids synthesized via a green synthesis demonstrated substantial improvements in heat transfer properties while maintaining practical wettability and viscosity features. These findings emphasize the potential of green-synthesized nanofluids as sustainable, high-performance alternatives for thermal management applications in both monophasic and biphasic systems. The results also encourage further exploration of bio-synthesized nanoparticles for a wide range of industrial and energy applications.

CRediT authorship contribution statement

Beatriz Cardoso: Writing – original draft, Supervision, Software, Methodology, Formal analysis, Conceptualization. **Glauco Nobrega:** Supervision, Methodology, Investigation. **Mariana Machado:** Writing – original draft, Investigation, Formal analysis, Data curation. **Rui A. Lima:** Writing – review & editing, Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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