Algae-Mediated Synthesis and Structural Characterization of Iron Nanoparticles using *Galaxaura rugosa* Seaweed

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ABSTRACT: A simple reduction method has been used for successfully synthesizing *Galaxaura rugosa*-mediated iron nanoparticles (FeNPs). The FeNPs were characterized using UV-visible spectroscopy, X-ray diffraction analysis (XRD), Transmission electron microscopy (TEM), Selected area electron diffraction (SAED), Scanning electron microscopy (SEM), Energy dispersive analysis of X-rays (EDAX), Zeta potential, and Fourier transform infrared spectroscopy (FTIR). The early formation of FeNPs is supported by rapid color change from yellow to dark brown and UV-visible absorption peaks at 327 nm. The XRD pattern and SAED analyses show a crystalline nature of FeNPs. Biogenic FeNPs were found to be spherical with mean diameter sizes varying from 14.4 to 17.2 nm by TEM image. The high abundance of FeNPs produced is visible in SEM, and the particles are in aggregates. The biosynthesized FeNPs had a negative surface charge with zeta potential values of -38.4 mV. According to FTIR analysis, functional groups play a significant role in the bioreduction of iron ions and the stability of FeNPs. This method is straightforward in application and could be performed in eco-friendly projects.

Keywords: *Galaxaura rugosa,* iron nanoparticles, biosynthesis, characterization, seaweed

INTRODUCTION

Nanoparticles (NPs) due to their small size, high surface area, crystal form, unique network order, and high reactivity are considered a novel technology (He et al., 2023). Metallic NPs have unique characteristics such as surface Plasmon resonance, extremely small size, and large surface-to-volume ratio (Sharma et al., 2016). They also exhibit magnetic and optical polarizability, as well as electrical and thermal conductivity (Yaqoob et al., 2020). These properties have driven significant advancements in both scientific research and industrial applications. Among all metal NPs, iron nanoparticles (FeNPs) are of much interest to the scientific community because of their high magnetic nature, high surface area, and electrical and thermal conductivity (Fahmy et al., 2018). FeNPs are also characterized by their low toxicity and simple separation methodology (Ali and El-Shehawy, 2023). Several methods exist for the fabrication of NPs including physical, chemical, and biological methods. Biological ones are generally cost-effective, nontoxic, scalable, and eco-friendly (El Shehawy et al., 2023b). Among the biological materials, algae are called 'bionanofactories' because both the live and dead dried biomasses were used for the synthesis of metallic NPs (Davis et al., 1998). The key merits of FeNPs green synthesis using algae seaweeds including the algae culturing is relatively convenient and easy to handle, synthesis at low temperatures with greater energy efficiency, less toxicity, high-yielding, low-cost technology, and safety to the environment (Rajeshkumar et al., 2017; El Shehawy et al., 2023a). Among seaweeds, the red seaweed *Galaxaura rugosa* is found in tropical to subtropical marine environments where its presence is indicative of the ecosystem's overall health (El-Tabakh et al., 2023). *G. rugosa* extract contains bioactive substances including; polysaccharides, peptides, and pigments that are efficient in reducing metals to form nanometals (Arguelles, 2022; Mondal et al., 2023). Therefore, the primary objective of this research is to synthesize iron nanoparticles utilizing *Galaxaura rugosa* marine algal extract and subsequently conduct a comprehensive characterization of the produced nanoparticles.

MATERIALS AND METHODS

Algal sampling and preparation of algal extract

The seaweed samples were selected and picked from Zaafarana Beach located at the Gulf of Suez, the Red Sea coast of Egypt; 82 km south of Al-Ain EL-Sokhna (29.06" N and 32.43" E) in June 2021. It was identified according to Aleem (1993). The algal extract was prepared by soaking 5 g of dry algal powder in 100 ml of deionized water for 24 hours with frequent shaking then filtered through Whatman Filter paper No.1.The supernatant was used to prepare FeNPs.

FeNPs phyco-synthesis

The established protocol reported by Mahdavi et al. (2013b) was applied to synthesize FeNPs by mixing the algal extract with 0.1 M $FeCl_3$ solution in a volume ratio 1:1, stirring for one hour, and left at room

temperature for another 30 min. The synthesized FeNPs were collected by centrifugation, washed with ethanol, and then washed several times with deionized water for characterization.

Characterization of FeNPs

Characterization of the phyco-synthesized FeNPs was carried out by several processes. The UV-visible absorption spectra in the 200-600 nm wavelength range using UV-visible absorption spectroscopy (Uni cam UV-VIS. Spectrometer UV2, U.S.A) (Basavaraja et al., 2011). FT-IR of the studied seaweed and FeNPs were measured over the range of 400-4000 cm^{-1} on a Bruker, Tensor 37 FT-IR spectrophotometer (Wen et al., 1996). The size and shape of FeNPs were visualized by TEM (JEOLJEM-2100, U.S.A). The crystalline structure was described through the crystallographic experimental technique performed inside the TEM by SAED (Ruud et al., 1976). Also, the FEI-TITAN 80-300 kV SEM was used to study the morphological structure of the FeNPs. The elements presented in FeNPs were determined by EDX integrated into the SEM. XRD analysis was obtained by a DX-1000 X-ray powder diffractometer range at 40 kV and 30 mA, in the 2θ range of 10°-90° (Sharma et al., 2012).

RESULTS AND DISCUSSION

Collection and taxonomic description of seaweed sample

Figure 1(a) shows the study area where the algal samples were selected and picked. Algae are identified as red algae (Rhodophyta) namely; *Galaxaura rugosa* (J.Ellis & Solander) (Figure 1b) (Aleem, 1993).

Biosynthesis and UV-visible analysis of FeNPs

UV-visible absorption spectra were used to confirm the phyco-synthesis of FeNPs. The maximum absorption peak of FeNPs was observed at 327 nm (Figure 2a), while the algal extract shows a major absorbance peak in the UV region at 230 nm (Figure 2b). This result is similar to what was reported in earlier studies by Saranya et al. (2017) that exhibited a characteristic absorption peak of iron nanoparticles between 250-350 nm. The inset photo shows the preliminary indication for the formation of FeNPs where the color of the algal extract changes from pale yellow to yellowish brown. The color change is due to the excitation of the surface plasmon resonance in the metal nanoparticles (Mahdavi et al. 2013a).

FT-IR analysis of FeNPs

FT-IR analysis is known as a fundamental applying technique of functional group detection and it has been used in this study to support the determination of the reduction or formation of the functional groups during the bio-reduction, capping, and stabilization processes of the phyco-synthesized FeNPs (Rehman and Bonfield, 1997; Malik et al., 2021). FTIR of the aqueous extracts of *G. rugosa* (Figure 3) exhibit a distinctive peak at 3421 cm^{-1}, attributed to the O-H stretching vibrations within polyphenols and OH groups of sugar rings (Balaraman et al., 2020). As shown in Figure 3, the presence and shifting peaks in the FeNPs indicate interaction among the functional groups of the extract and the iron salt precursor (Rasheed et al., 2018). The absorption peaks that appeared at 1598 cm^{-1} may be due to the vibrations in the C=O bond stretching within the aromatic rings of different phenolic compounds, including polyphenols and flavonoids that are present in the extract (Venkateswarlu et al., 2019). The FTIR spectra of the FeNPs showed a minor shift with slight changes, indicating that the main biomolecules present in extracts were capped to the FeNPs surface El-Kassas and El Komi (2014).

TEM Analysis and SAED pattern of FeNPs

To further study the microstructure, morphology, and distribution of the phyco-synthesized FeNPs, TEM was used (Kouhbanani et al., 2019). The TEM image of the phyco-synthesized FeNPs presented in spherical shapes with approximately poly-dispersed particles with a size range smaller than 50 nm in size (Figure 4a). This coincides well with previous results (Sathishkumar et al., 2018). Compared to previous similar studies, the nanoparticles in this study exhibited a smaller size compared to those reported in previous research. While other iron nanoparticles typically range from 50 to 100 nm (Ting and Chin, 2020). This can be related to pH, temperature, incubation time, type, and concentration of precursors that are influencing the biosynthesis of nanoparticles at varying levels (Patra and Baek, 2014). Analysis of the SAED pattern (Figure 4b) confirms the characteristics of polycrystalline material rings that are attributed to crystalline FeNPs (Łukowiec and Radoń, 2020).

EDX and SEM Analysis of FeNPs

The elemental composition of FeNPs was ascertained through EDX analysis. EDX spectral analysis of FeNPs (Figure 5) shows strong peaks observed at 0.5, 6.0,

and 6.6 keV confirming the presence of FeNPs (Salem et al., 2019). SEM analyses (inset in Figure 5) strongly confirm the spherically shaped, highly distributed, and polydisperse of the phyco-synthesized FeNPs, this

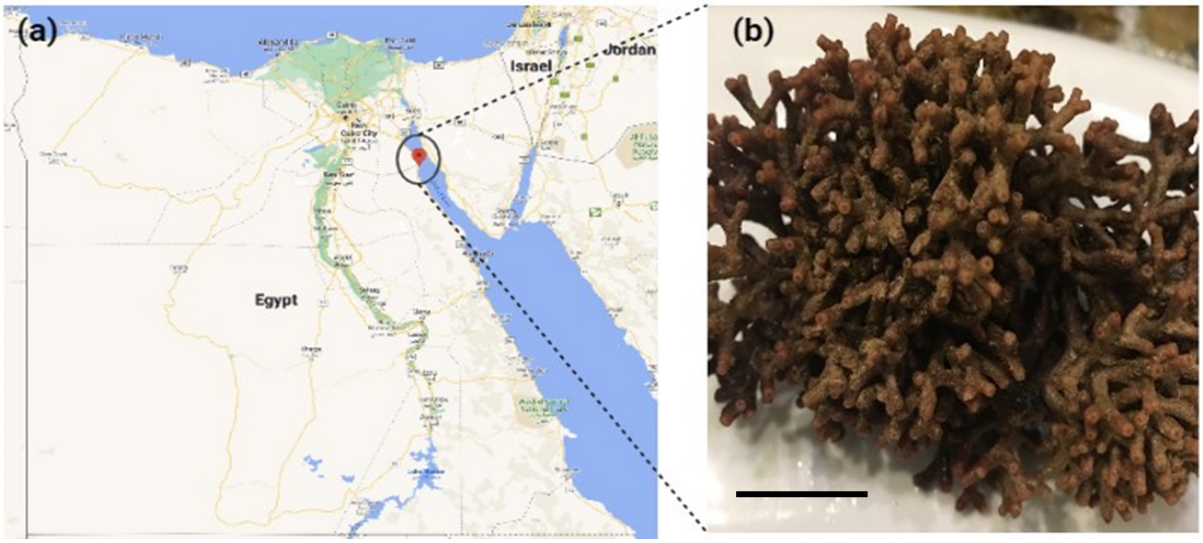

Figure 1. (a) Map showing the collection site at Zaafrana beach, Red Sea, Egypt, and (b) the collected wet seaweed *Galaxaura rugosa* (scale bar = 2cm).

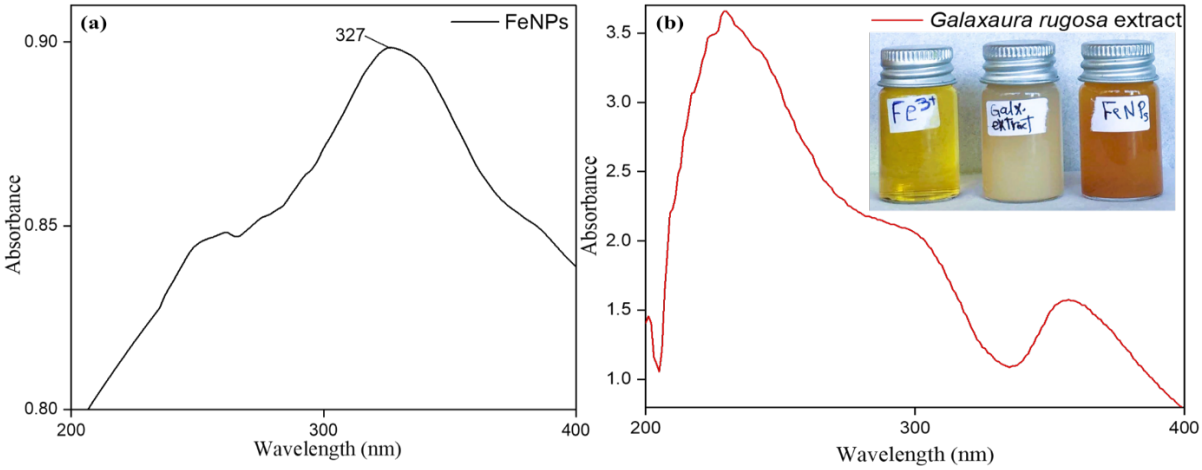

Figure 2. UV–vis spectra of (a) the phyco-synthesized FeNPs and (b) *Galaxaura rugosa* marine algal extract, inset shows extract before and after exposure to Fe solution.

is well in line with previous observations (Salem et al., 2019).

XRD Pattern and Zeta Potential Analysis of FeNPs

As shown in Figure 6a, the XRD pattern of the FeNPs gives strong and sharp diffraction peaks indicating that the sample was well crystallized. Their associated lattice planes were compared to JCPDS files No. 33-0664, and No. 65-3107, respectively. The major diffraction peaks were observed at 29.41°, 31.61°, 36.01°,39.49°, 40.47°, 43.19°, 50.17°, and 57.41° and were assigned to the crystalline planes (220), (104), (110), (311), (113), (400), (042) and (018), respectively. The diffraction peaks can be readily indexed to a mixture of α-Fe_2O_3 and Fe_3O_4 as reported earlier (Li et al., 2021). The stability of the FeNPs gives good stability as indicated by its -42.2-mV zeta potential value (Figure 6b). The high value of zeta potential increases the repulsive force and the solution becomes resistant to aggregation (Singh et al., 2020).

CONCLUSIONS

In the current research work, a green synthesis approach was used to synthesize FeNPs that were cost-effective and environmentally friendly. The

aqueous extract of *Galaxaura rugosa* encompasses sufficient biomolecules, which serve as both an anti-agglomeration and reducing agent. UV-Vis, FT-IR, TEM, SAED, EDX, SEM, XRD, and Zeta potential

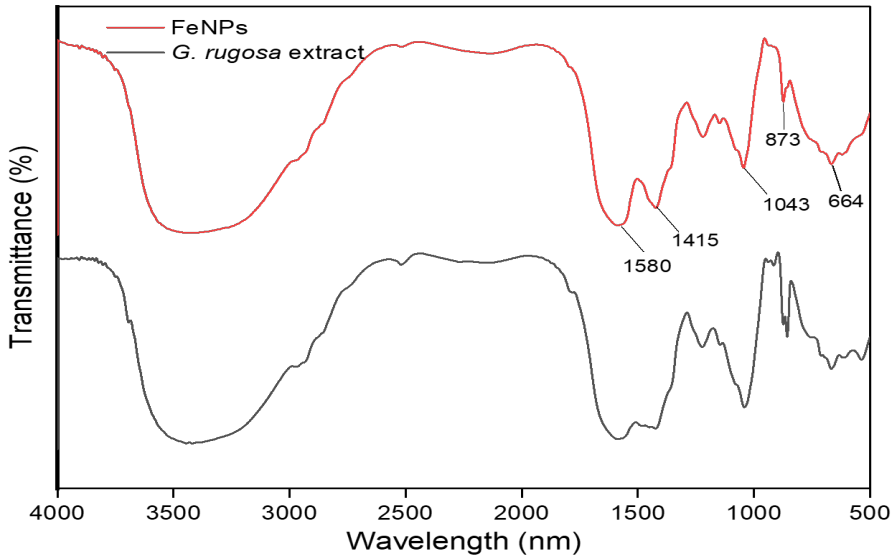

Figure 3. FTIR of the phyco-synthesized FeNPs and *Galaxaura rugosa* marine algal extract.

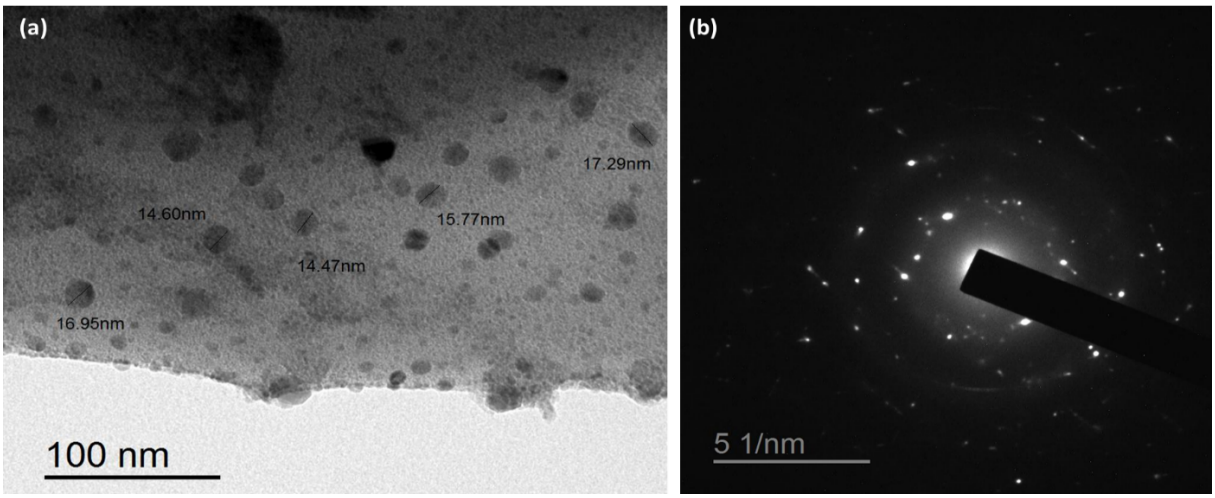

Figure 4. (a) TEM and (b) SAED of the biosynthesized FeNPs capped by *Galaxaura rugosa* marine algal extract.

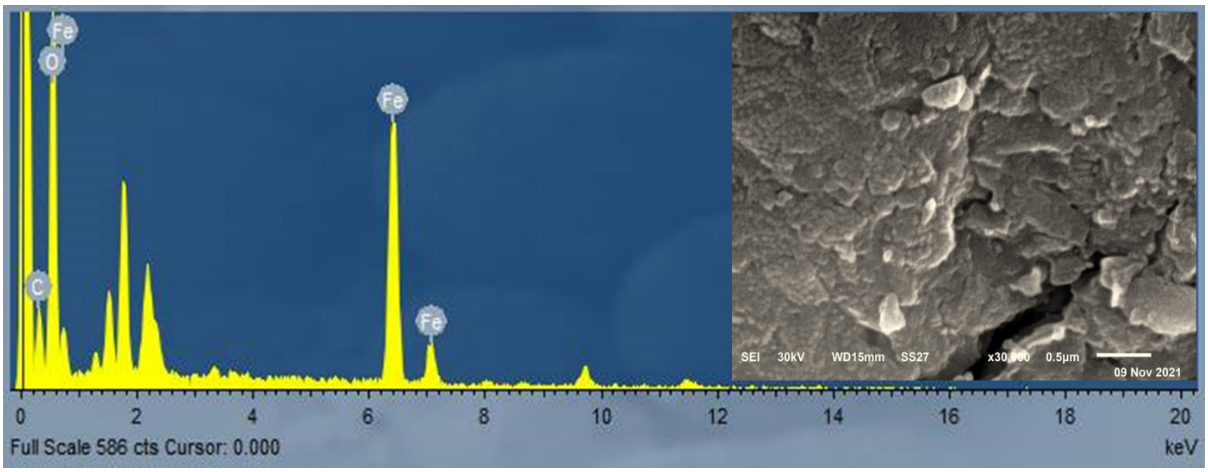

Figure 5. EDX analysis of FeNPs biosynthesized from *Galaxaura rugosa* marine extract; inset: shows SEM image.

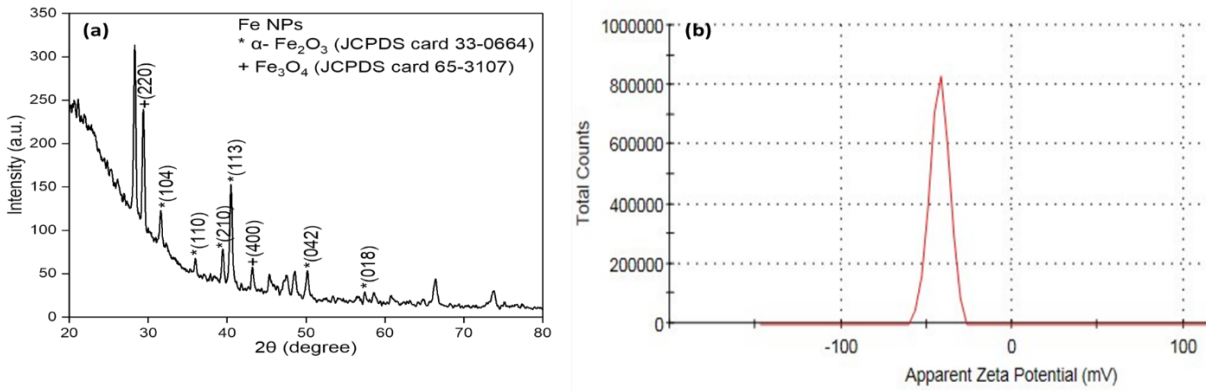

Figure 6. (a) XRD pattern and (b) Zeta potential of FeNPs biosynthesized from *Galaxaura rugosa* marine extract.

analysis confirmed FeNPs biosynthesis. The knowledge of the present study as a green method of synthesizing FeNPs could also be extended to fabricate other, industrially important metal oxides which could serve as an economical source of biosynthesis of nanoparticles.

DATA AVAILABILITY

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest.

ETHICAL APPROVAL

Not applicable.

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