Green synthesis and characterization of magnesium nanoparticles using pumpkin peel extract (*Tetsukabuto*)

Síntese verde e caracterização de nanopartículas de magnésio usando extrato de casca de abóbora (*Tetsukabuto*)

Síntesis verde y caracterización de nanopartículas de magnesio utilizando extracto de cáscara de calabaza (*Tetsukabuto*)

DOI: 10.55905/oelv22n7-120

Receipt of originals: 06/08/2024
Acceptance for publication: 06/28/2024

Rúbia Martins Bernardes Ramos  
Master in Food Engineering  
Institution: Universidade Federal do Paraná  
Address: Curitiba, Paraná, Brazil  
E-mail: rubia.martins@ufpr.br

Pablo Inocêncio Monteiro  
PhD in Food Engineering  
Institution: Universidade Federal do Paraná  
Address: Curitiba, Paraná, Brazil  
E-mail: pabloinocencio@ufpr.br

Ana Paula Biz  
PhD in Food Engineering  
Institution: Universidade Federal do Paraná  
Address: Curitiba, Paraná, Brazil  
E-mail: anapbiz@gmail.com

Luana Cristina Paludo  
PhD in Food Engineering  
Institution: Universidade Federal do Paraná  
Address: Curitiba, Paraná, Brazil  
E-mail: luanacristinapaludo@gmail.com

Ivisson de Souza Tasso  
Master in Food Technology  
Federal Technological University of Parana  
Londrina, PR, Brazil  
E-mail: ivisjs@gmail.com
ABSTRACT
Pumpkin (Tetsukabuto) peel extract was utilized to synthesize nanoparticles of magnesium. The nanoparticles were characterized using scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS), X-ray diffraction (XRD), selected area electron diffraction (SAED), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), raman spectroscopy (RS) as well as Brunauer-Emmett-Teller (BET) analysis. The results showed that the synthesis of magnesium nanoparticles is possible by use of pumpkin peel extract. The characterization analyses indicated the presence of functional groups on the surface of the nanoparticles, which aided in the bioreduction of the metals to oxides. The nanoparticles can be applied in studies involving microbial agents due to their spherical shape, which allows for easy penetration into the cell wall of microorganisms. This work provides relevant information for the field of nanoparticles and the area of green synthesis.

Keywords: Bioreduction of Metals, Green Route, Nanostructures, Nanotechnology.

RESUMO
O extrato de casca de abóbora (Tetsukabuto) foi utilizado para sintetizar nanopartículas de magnésio. As nanopartículas foram caracterizadas usando microscopia eletrônica de varredura/espectrometria de raios X por dispersão de energia (SEM/EDS), difração de raios X (XRD), difração de elétrons de área selecionada (SAED), microscopia eletrônica de transmissão (TEM), espectroscopia de infravermelho por transformada de Fourier (FT-IR), análise termogravimétrica (TGA), espectroscopia Raman (RS), bem como análise de Brunauer-Emmett-Teller (BET). Os resultados mostraram que a síntese de nanopartículas
de magnésio é possível através do uso do extrato de casca de abóbora. As análises de caracterização indicaram a presença de grupos funcionais na superfície das nanopartículas, que auxiliaram na biorredução dos metais a óxidos. As nanopartículas podem ser aplicadas em estudos envolvendo agentes microbianos devido à sua forma esférica, que permite fácil penetração na parede celular dos microrganismos. Este trabalho fornece informações relevantes para o campo das nanopartículas e a área de síntese verde.

**Palavras-chave:** Biorredução de Metais, Rota Verde, Nanoestruturas, Nanotecnologia.

**RESUMEN**

El extracto de cáscara de calabaza (Tetsukabuto) se utilizó para sintetizar nanopartículas de magnesio. Las nanopartículas se caracterizaron utilizando microscopía electrónica de barrido/espectrometría de rayos X por dispersión de energía (SEM/EDS), difracción de rayos X (XRD), difracción de electrones de área seleccionada (SAED), microscopía electrónica de transmisión (TEM), espectroscopía de infrarrojo por transformada de Fourier (FT-IR), análisis termogravimétrico (TGA), espectroscopía Raman (RS), así como análisis de Brunauer-Emmet-Teller (BET). Los resultados mostraron que la síntesis de nanopartículas de magnesio es posible mediante el uso del extracto de cáscara de calabaza. Los análisis de caracterización indicaron la presencia de grupos funcionales en la superficie de las nanopartículas, que ayudaron en la bioreducción de los metales a óxidos. Las nanopartículas pueden ser aplicadas en estudios que involucren agentes microbianos debido a su forma esférica, que permite una fácil penetración en la pared celular de los microorganismos. Este trabajo proporciona información relevante para el campo de las nanopartículas y el área de síntesis verde.

**Palabras clave:** Biorreducción de Metales, Ruta Verde, Nanoestructuras, Nanotecnología.

**1 INTRODUCTION**

In the field of nanoparticles, green synthesis has gained emphsly, partly due to the use of materials that are naturally present in the environment, such as fungi, bacteria, agricultural by-products, and even extracts from plants, seeds, or peels (Sharma; Yngard; Lin, 2009; Thakkar; Mhatre; Parikh, 2010; Faramarzi; Sadighi, 2013; Mittal; Chisti; Banerjee, 2013)

Pumpkin peels contain bioactive compounds, such as phenolic, flavonoids, and carotenoids, as well as minerals (Hussain et al., 2022) and sugars, such as glucose,
sucrose, and fructose (Dhenge et al., 2022). The presence of these compounds makes the pumpkin peels viable for the bioreduction of metals to their oxides by green synthesis, leading to the production of high-quality metallic nanoparticles. These materials have superior properties to those synthesized by conventional methods, such as greater stability and less agglomeration and toxicity (Bolade; Williams; Benson, 2020).

Nanoparticles are applicable in several areas, such as health and environmental remediation. They can serve as antimicrobial agents in the healthcare sector, aiding medication management, and as photocatalysts and adsorbent agents in the environmental sector (Schröfel et al., 2014; Shubhashree et al., 2022). However, the functionality of nanoparticles depends on their final characteristics. The final properties of nanoparticles are influenced by several factors, including the type of metal used in synthesis (such as iron, zinc, titanium, gold, silver, magnesium, copper, etc.) and the choice of green solvent. Each metal interacts differently with the bioactive compounds in green synthesis precursors and results in nanoparticles with unique properties. Although there are several studies on the characterization of iron nanoparticles (Mohammadpour et al., 2023; Yaghoobi; Asjadi; Sanikhani, 2023; Yildirim; Ozkaya, 2023), and titanium (Shekhar et al., 2023; Saravanakumar et al., 2023; Inamdar et al., 2023), there is a lack of research on other metals, such as magnesium.

In this work, we report the green synthesis and characterization of magnesium (MgNp) nanoparticles produced from Tetsukabuto pumpkin peel extract. Magnesium was selected for this study due to its natural abundance, and the Tetsukabuto pumpkin was chosen because it is known worldwide.

2 MATERIALS AND METHODS

2.1 MATERIALS

Analytical grade reagents, such as sodium hydroxide (NaOH) and magnesium sulfate heptahydrate (MgSO₄·7H₂O), were used as received, without any additional
purification. The *Tetsukabuto* pumpkin was sourced from a local supermarket. Distilled/deionized water was employed in the synthesis process.

2.2 SYNTHESIS OF MgNp

The *Tetsukabuto* pumpkin peels were cut and washed three times with distilled/deionized water to remove impurities. Subsequently, 20 grams of the peels were placed in 100 mL of distilled water and heated in a Dubnoff apparatus at 60°C for 60 minutes. After heating, the peels were separated from the extract solution by filtration, and the extract was then used for green synthesis. For this purpose, 3 g of MgSO₄·7H₂O was added to 40 mL of the previously prepared aqueous extract solution, with the pH adjusted to 8 using 1.0 mol L⁻¹ NaOH. The resulting sample was a precipitated material that was filtered and dried in an oven with forced air circulation (Solab, SL-102, Brazil) at 70°C for 390 minutes (Ramos et al., 2023).

2.3 SURFACE AREA

The equipment used to determine the surface area of the nanoparticles was the Quantachrome Touchwin (St 2 on Nova touch 2LX). The surface area was obtained using nitrogen sorption isotherms (77.35 K).

2.4 MORPHOLOGICAL ANALYSIS AND ELEMENTAL COMPOSITION

The morphology of the material, including its shape and size, was analyzed using transmission electron microscopy (TEM, Jeol, JEM 1200 EX-II), Scanning electron microscopy with SEM HV: 15.0 kV, WD: 7.03 mm, SEM MAG: 1.00 kx (SEM, Tescan, VEGA3 LMU), and energy-dispersive X-ray spectroscopy (EDS, Oxford, X-Max 80).
2.5 THERMAL ANALYSIS

Thermal analysis was conducted to assess the stability of the nanomaterials over a temperature range of 30 to 700 °C at a heating rate of 10 °C per minute. The instrument used for this purpose was the TGA Q500 V20.10 Build 36.

2.6 RAMAN SPECTROSCOPY

The equipment used for molecular structure analysis was the Alpha300 by WITec with a green laser, operating at 21°C, atmospheric pressure, 531.975 nm, Camera Serial Nr.: 13080, Vertical Shift Speed: [8.25], Horizontal Shift Speed [MHz]: 0.033, Number of Accumulations: 50, and Integration Time [s]: 1.09595.

2.7 CRYSTALLINITY OR AMORPHICITY

X-ray diffraction (XRD) analysis was used to determine whether the material was crystalline or amorphous. The equipment utilized was the Rigaku Ultima IV X-ray diffractometer, operating at 0.05°/s, with 40 kV and 20 mA.

2.8 FUNCTIONAL GROUPS

For the identification of functional groups, a PerkinElmer Spectrum Version 10.4.2, Frontier FT-IR/FIR 98737. The analysis involved 60 consecutive scans and a resolution of 4 cm\(^{-1}\) within the range of 600 - 4000 cm\(^{-1}\).

3 RESULTS AND DISCUSSION

3.1 SURFACE AREA

Figure 3.1 shows the nitrogen sorption isotherm at -195.8°C on MgNp. According to the BET classification (Brunauer; Emmett; Teller, 1938) an isotherm type III with hysteresis is observed. This type of isotherm indicates weak interaction between the
adsorbent and the adsorbate (Do, 1998). As shown in Table 1, MgNp had a surface area of 3.79 m² g⁻¹.

Table 1 - Textural characterization of nanoparticles

<table>
<thead>
<tr>
<th>Properties</th>
<th>MgNp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area BET, m² g⁻¹</td>
<td>3.79</td>
</tr>
<tr>
<td>Total pore volume, cm³ g⁻¹</td>
<td>1.01 x 10⁻²</td>
</tr>
<tr>
<td>Mean pore radius, nm</td>
<td>79.43</td>
</tr>
</tbody>
</table>

Source: Authors

3.2 MORPHOLOGICAL ANALYSIS

Images of MgNp synthesized from Tetsukabuto pumpkin extract obtained from TEM analyzes are shown in Figure 3.2a. It is possible to observed the spherical shape of the nanoparticles whose sizes vary between 28 - 40 nm. The spherical shape observed
for MgNp was similar to that previously reported for copper nanoparticles synthesized using *Red cabbage* (Fernandez; Archana; Revathy, 2020), and MgNp produced by using microorganisms (Ahmed *et al.*, 2021). Spherical-shaped nanoparticles have favorable applications as antimicrobial agents since they easily penetrate the cell walls of microorganisms, such as bacteria (Sharma *et al.*, 2023). Figure 3.2b displays the selected area electron diffraction (SAED) pattern of MgNp. The SAED analysis indicates that the MgNp are amorphous.

SEM micrographs (Figure 3.2c) revealed irregular morphological surfaces for MgNp. Suba *et al.*, (2022) synthesized magnesium nanoparticles doped with rubidium chloride using grape juice and obtained a spherical surface morphology. The difference in shape and size of nanoparticles can be attributed to the fact that different extracts have distinct capping agents, which can interfere with the morphology of the material. Additionally, it is important to emphasize that the formation of nanoparticles depends on various factors, including the type of metal used and the synthesis method. According to Nadeem *et al.* (2021), even the concentration of the salt used can influence the physiological and biological characteristics of the nanoparticles.
Figure 2 - TEM images at magnifications of (a) 100 nm, (b) SAED images, and (c) SEM images of MgNp.

Source: Authors
3.3 THERMAL ANALYSIS

Figure 3.3 displays the TGA (green line) and DGT (blue) curves of MgNp, where a heterogeneous thermal degradation profile was observed: various apparent degradation stages, corroborated by six DTG peaks. The first four thermal events occurred at rates close to 0.3 %, the biggest ones, making them the most relevant. Likely, they are related to the loss of MgNp adsorbed water. Other two thermal degradation events, much flatter in the DGT curves, can be observed around 278 and 696 °C. Beyond this range, a slow but relevant mass loss (approximately 10 %) was observed and could be attributed to the degradation of hydroxyl groups present on the surface of the nanoparticles. Overall, MgNp exhibited a total mass change of 44.28 %. The T75 (temperature at the time when the residual mass corresponded to 75 %) of this sample was estimated at 151.91°C.

Figure 3 – Thermal degradation process suffered by MgNp: TGA (mass loss) and DTGA (derivative curve) MgNp

Source: Authors
3.4 RAMAN SPECTRUM

Figure 3.4 shows the Raman spectroscopy of MgNp samples, showing vibrational peaks below 500 cm\(^{-1}\) and a vibrational peak near 1000 cm\(^{-1}\). The vibrational peaks below 500 cm\(^{-1}\) may be associated with the flexion vibrations of magnesium oxide bonds. Previous study (Jin et al., 2022) also observed vibrational peaks between 150 and 500 cm\(^{-1}\) when producing magnesium oxides together with vanadium. However, the authors attributed these peaks to the bending vibrations of Oxygen-Vanadium-Oxygen and Oxygen-Magnesium-Oxygen. On the other hand, Sackey et al. (2020) identified a cubic magnesium structure in the Raman spectrum of the MgO formed by green synthesis.

![Raman spectroscopy of MgNP](image-url)
3.5 CRYSTALLINITY OR AMORPHICITY

The DRX analysis of MgNp (Fig. 3.5) nanoparticles also confirms the amorphous nature of the nanoparticles indicated by the SAED analysis (Fig. 3.2 b). Figure 3.5 shows a spectrum without very intense peaks relates to amorphization, due to the crystallographic irregularity of the sample.

3.6 ELEMENTAL COMPOSITION

Figure 3.6 shows spectra obtained from (a) Energy-Dispersive Spectroscopy (EDS) and (b) Sum of Maps Spectrum (SME) analyses of MgNp. The EDS analyses (Fig. 3.6a) reveal that magnesium metals are predominantly present in the nanostructures, along with other elements in lesser quantities. Besides, the SME analysis (Fig. 3.6b)
reveals high contents of magnesium and oxygen, with percentages of 14.6 and 58.6%, respectively, indicating the formation of MgO. Additionally, the SME analysis also shows an optical absorption peak at approximately 1.3 keV, which is consistent with a previous study (Ahmed et al., 2020).

Figure 6 - Energy Dispersive Spectroscopy (EDS) (a) and Sum of Maps Spectrum (SME) (b) results of MgNp.

Source: Authors
3.7 FUNCTIONAL GROUPS

Figure 3.7 shows the FT-IR/ATR spectra of MgNp. The peak at 3203.61 cm\(^{-1}\), which is attributed to the OH group of phenolic compounds. The peak at 1673.41 cm\(^{-1}\) corresponds to the C=O group. These peaks suggest the involvement of compounds from the pumpkin peel extract in the formation of Np’s. Previous work (Nadeem et al., 2021) utilizing \textit{Clematis orientalis} leaf extract has also reported comparable FT-IR/ATR spectra, indicating the existence of functional groups from the extract. The peak at 1058.57 cm\(^{-1}\) indicates the presence of the metal-oxygen (MgO) bond, which is similar with prior findings (Suba; Selvarajan; Devadasan, 2022).

![Figure 7 - FT-IR/ATR of MgNp](source: Authors)
4 CONCLUSIONS

The synthesis of magnesium nanoparticles from *Tetsukabuto* pumpkin peel extract using green synthesis methods was demonstrated. The analyses used for characterization confirmed that the nanoparticles are spherical and irregular in shape, with functional groups that corroborate their formation from bioactive compounds present in the pumpkin peels. The MgNp showed low thermal stability and a surface area of 3.79 m² g⁻¹. It can be concluded that these nanoparticles can be applied as microbial agents due to their spherical shape. Additionally, these nanoparticles can be applied in different areas; however, it is recommended that a complete study be carried out using different techniques to confirm the absence of toxicity before application.

ACKNOWLEDGEMENTS

This work was supported by the Graduation Program of Food Engineering (PPGEAL-UFP) and CAPES - (Coordination Improvement of Higher Education Personnel), a Brazilian Government Agency.
REFERENCES


Mohammadpour, A., Karami, N., Zabihi, R., Fazeliyan, E., Abbasi, A., Karimi, S., ... & Khaneghah, A. M. Green synthesis, characterization, and application of Fe₃O₄ nanoparticles for methylene blue removal: RSM optimization, kinetic, isothermal


