**Green synthesis and characterization of Nb2O5 nanoparticles from *Carya illinoinensis* nutshell extract.**

Luis Fernando Wentz Brum1, Maurício Dalla Costa Rodrigues da Silva1, Cristiane dos Santos1, Giovani Pavoski2,, Denise Crocce Romano Espinosa2, William Leonardo da Silva1 *a 1*Applied Nanomaterials Research Group (GPNAp), Franciscan University (UFN), Santa Maria - RS, Brazil

2Polytechnical School of Chemical Engineering, University of the Sao Paulo (USP), São Paulo, SP, Brazil

**Abstract**

Niobium is a metal that has been attracting great interest to produce high technology materials, in which niobium oxide nanoparticles (Nb2O5-NPs) are inserted. The objective of this work was to develop and characterize structurally and morphologically the Nb2O5-NPs using niobium chloride as a precursor in a solution of extract of agroindustrial residue of pecan nutshell (*C. illinoinensis*). The Nb2O5-NPs were characterized using the techniques of X-ray diffraction (XRD), zeta potential (ZP) and zero charge point (pHPCZ). Thus, it was possible to observe average crystallite diameter (dc) for Nb2O5-NPs calculated using the Debye-Scherer equation was 26.0 ± 13.8 nm., the zero charge point (pHPCZ) obtained experimentally was 6.37 and, when pH < 6.37 the surface of Nb2O5-NPs is protonated and when pH> 6.37 it is deprotonated, making it possible to develop Nb2O5-NPs using agroindustrial residue of pecan nutshell.

*Keywords:* Niobium oxide / Green synthesis / Nanoparticles.

**1. Introduction**

Niobium is a metal that has a silvery appearance, with a body-centered cubic (CCC) structure, which is soft and ductility in its pure state [1]. Brazil holds 98% of known commercially viable reserves of niobium. Furthermore, the growing interest in niobium is related to its multiple uses to produce high-technology materials. Niobium is one of the strongest Lewis acids known, allowing its use in nanomaterials for catalysis in the form of niobium oxide [2].

The growing interest in niobium is related to its multiple uses to produce high-technology materials. Niobium is one of the strongest Lewis acids known, allowing its use in nanomaterials for catalysis in the form of niobium oxide [3]. The number of studies on the properties of niobium (V) oxide nanoparticles (Nb2O5-NPs) in biological environments is increasing, due to the different physical and chemical characteristics of their micrometric compounds [4,5]. Nanotechnology, in turn, is a field of research in growing development and relates concepts from physics, chemistry, biology and technological objects on a reduced scale, with interdisciplinary application, such as metallic nanoparticles, which have been increasingly studied due to their unique properties, including antioxidant activity [6].

According to [7], there are around 3.4 thousand hectares dedicated to the production of pecan nuts (*Carya illinoinensis*) in Rio Grande do Sul - Brazil, with the use of the fruit being around 40 - 60%, making it necessary to find alternatives for using the agro-industrial residue. The pecan nutshells present bioactive molecules that can act as reducers and stabilizers for application in the synthesis of nanoparticles.

Green synthesis is a method that uses bioactive compounds naturally present in roots, stems, leaves and nutshells as reducing, stabilizing and nucleation agents for the synthesis of nanoparticles. Thus, the green synthesis is an eco-friendly method to synthesized nanoparticles without the use of hazardous and toxic substances [8].

In the literature there are research using the green synthesis to produce a variety of metallic oxide nanoparticles (TiO2, CuO, ZnO, etc) for application in heterogenous photocatalysis [9]. Additionally, there studies reporting the potential of the *C. illinoinensis* nutshell extract in the green synthesis of Pd-nano catalysts [10]. However, there is a lack of studies showing the feasibility of synthesis of Nb2O5-NPs using green synthesis. Therefore, the present work aims to synthesize and characterize Nb2O5-NPs by the green synthesis method using an extract from the agro-industrial residue of pecan nutshell (*C. illinoinensis*).

**2. Methodology**

The synthesis of niobium V oxide nanoparticles (Nb2O5-NPs) was conducted using the green synthesis method [11]. Thus, a solution of 0.1 mol Nb2O5. L-1 was used as a metal precursor. The reduction of the metal precursor was carried out using an aqueous extract of pecan nut shell (*C. illionensis).*

The extract was prepared by infusing 10 g of pecan shell in 500 mL of distilled water at 90°C for 10 min under magnetic stirring (300 rpm). At the end of the time, the extract was cooled until it reached room temperature and filtered using qualitative filter paper. The solution was subsequently stored in an amber bottle at room temperature until use.

For the synthesis of Nb2O5-NPs, 50 mL of aqueous extract of pecan nut shells were mixed with 50 mL of Nb2O5 and ammonium hydroxide solution until reaching a pH in the range of 10-11. The process was carried out at room temperature with magnetic stirring (300 rpm) for 60 min. Then, a drying step (80°C for 12 h) and calcination (500 °C at 10 °C.min-1 for 2 h) was carried out to stabilize and activate the Nb2O5-NPs.

*2.1 Characterization*

The crystalline phases were determined by X-ray diffraction (XRD) using the Bruker diffractometer (D2 Advance, λCu-α = 0.15418 nm) ranging from 10° to 90°. To determine the crystalline diameter (dc) the Debye-Scherer equation was used according to Eqs. (1).

|  |  |
| --- | --- |
| $d\_{c}= $$\frac{}{β\*cos (θ)}$ | (1) |

Where: β is the Width at Half Height (FWHM), λ is the characteristic wavelength (0.1531 nm), and θ (º) is the Bragg diffraction angle.

For the zeta potential (ZP) it was used to determine the surface charge on the Malvern-Zetasizer® equipment (ZEN3600, UK). The zero charge point (pHPCZ) was determined using an 11-point test with a pH in the range of 2 to 12, according to the literature [12].

**3. Results and discussion**

Figure 1 shows the X-ray diffractogram of Nb2O5-NPs. The results shown in Figure ° (102) (JCPDS] no. 28-0317). The average crystallite diameter (dc) for Nb2O5-NPs calculated using the Debye-Scherer equation was 26.0 ± 13.8 nm. In this way, the nanometric size of the particles synthesized through green synthesis is proven. Furthermore, the zero charge point (pHPCZ) obtained experimentally was 6.37 as shown in Figure 2. Therefore, when pH < 6.37 the surface of Nb2O5-NPs is protonated and when pH> 6.37 it is deprotonated [13].

Figures may be placed next to each other to save space.



Fig. 1. X-ray diffraction diagram of Nb2O5-NPs.



Fig. 1. Zero charge point of Nb2O5-NPs.

**3. Conclusion**

Nb2O5-NPs were produced by green synthesis using *C. Illinoiensis* nutshells extract. XRD diffractogram showed that the Nb2O5-NPs were crystalline with the presence of pseudohexagonal phase and an average crystallite size of 26.0 ± 13.8 nm. The green Nb2O5-NPs, when pH < 6.37 the surface is protonated and when pH> 6.37 it is deprotonated the zero charge point was 6.37, and the band gap energy was 3.25 eV.

**Acknowledgements**

This study was financed by the Conselho Nacional de Desenvolvimento Científico e Tecnológico - Brazil (CNPq/MCTI/FNDCT nº 23/2022) - InovaNióbio (nº408422/2022-0).

**References**

[1] Lopes OF, Paris EC, Ribeiro C. Appl. Catal. B: Environ. 2014; 144:800-808.

[2] Su K, Liu H, Gao Z, Fornasiero P, Wang F. Adv. Sci. 2021; 8:2003156 – 2003181.

[3] Cordeiro PFO, Geology Reviews, 2011; 41:112.

[4] Bayot D, Devillers M. C. Chem. Rev. 2006; 250:2610-2626.

[5] Malyshev D, Bósca F, Crites COL, Hallet-Tapley GL, Netto-Ferreira JC, Alarcon EI, Scaiano JC. Dalton Trans. 2013; 42:14049–14052.

[6] Zan RA, Zan ASHS, Braz. Journal of Devel. 2022; 8:38637-38658.

[7] Georgin J, Marques BS, Piccilli DGA, Dotto GL. Engevista 2017; 19:1449-1465.

[8] Ying S, Guan Z, Ofoegbu PC, Clubb P, Rico C, He F, Hong J. Environ. Technol. Innov 2022; 26:102336-102346.

[9] Radulescu DM, Surdu VA, Ficai A, Ficai D, Grumezescu AM, Andronescu E. Int. J. Mol. Sci. 2023; 24:15397 – 15436.

[10] Hidalgo AIC, Aguirre MR, Valenzuela E, Gomez JYV, Dávila AC, Varma RS, Sánchez VHR. Int. J. Hydrogen Energy 2016; 41:23329-23335.

[11] Kocakaya Z, Dokan FK, Karatoprak GS. Green synthesis of bioactive nanocomposites using Diploschistes scruposus lichen and investigation of cytotoxic effects on cancer cells. Materials chemistry 2024; 317:129141-129141.

[11] Prauchner MJ, Rodríguez-Reinoso F. Microporous Mesoporous Mater 2012;152:163–71.

[12] Jang M-H, Rodríguez-Reinoso F. Chemosphere 2022; 299:134388-134388.

[13] Vouters, RD. Surfaces and interfaces 2024; 48:104282-104282.