Green titanium nanoparticles obtained using Lima orange peel

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Abstract

The nanostructures obtained by the green synthesis method are formed from the bioreduction of metal ions and salts. Its structure, morphology, capping and physical-chemical characteristics are directly related to the bioactive compounds present in the organic material used and the metal chosen. Due to their size, these small particles can perform internal actions in cells and organisms, covering their use in different areas, with their use in waste treatment processes being one of the most studied. The characterization of the Lima orange peel extract was carried out using antioxidant activity techniques using the DPPH, ABTS and FRAP methods, total flavonoids e phenolics and nuclear magnetic resonance (NMR), with favorable values for the green synthesis process. The characterization of the nanoparticles was carried out using Scanning Electron Microscopy (SEM) techniques coupled with Energy Dispersive Detector (EDS), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), Surface Area Determination (BET) obtaining area around 11.04 m2 g-1, Spectroscopy in the Infrared Region with Fourier Transform (FTIR), Raman Spectroscopy (ER), and the Point of Zero Charge (PCZ) which obtained a value of 7.5. The results obtained are like those found in the literature for other types of nanoparticles and validate the obtaining of these titanium dioxide nanostructures using Lima orange peel extract.

Keywords: Green synthesis; Titanium nanoparticles; *orange peel*

1. Introduction

Unlike other methods of obtaining metallic nanoparticles (NPS), in the green synthesis method there is no use of toxic and recalcitrant solvents [1]. The organic compounds used can come from plants, leaves, fruits, as well as their residues, which influences the diversity of materials that can be used, reducing the cost of the process, and increasing the multiplurality of the characteristics of the nanoparticles produced, since most of its characteristics come from organic compounds [2].

The objective of this work was to obtain and characterize, from green synthesis, titanium dioxide nanoparticles using Lima orange peel extract, to have nanostructures capable of carrying out actions in the treatment of contaminated water.

2. Materials and Methods

2.1 Materials

All chemicals used have analytical purity (AP). Distilled water, titanium dioxide (TiO_2) and sodium hydroxide (NaOH) were used in the green synthesis method. The Lima orange was purchased in a local supermarket located in the city of Curitiba in the state of Paraná (PR).

2.2 Green synthesis

Orange peel extract was obtained by adding 100ml of distilled water to 20g of orange peels (immersed). The composition was subjected to Dubnoff bath equipment for a period of 1 hour at 60°C [3].

The synthesis was carried out by coprecipitation method adding 40 ml of Lima orange peel extract, 3g of titanium oxide and addition of sodium hydroxide (1M NaOH) until reaching pH 8.0 where the formation of precipitates is visible. The precipitates were separated from the liquid portion using the Whatman filter and then dried in a forced

convection oven (Solab, model SL-102) for 6h and 30 minutes at 70°C [4].

2.3 Characterization of Lima orange peel extract

The antioxidant capacity of the extracts was expressed by the antiradical activity necessary to eliminate the DPPH radical by 50% [5]. The ABTS was based on the generation of radicals with cations (ABTS-+) [6]. The plasma ferric reducing capacity (FRAP) was expressed in mg of Trolox, which is equivalent to 100g of the sample [7]. Total flavonoids were expressed as mg of catechin per g of the calibration curve [8]. The identification of compounds present in Lima orange was analyzed by NMR in the Avance III 400 NMR spectrum operating at 9.4 Tesla. and observing the hydrogen nucleus at 400 MHz. and the carbon-13 nucleus at 100 MHz. The NMR analysis was carried out at the Nuclear Magnetic Resonance Multiuser Laboratory located in the Chemistry Department of the Federal University of Paraná in Curitiba.

2.4 Characterization of NPS

SEM/EDS (HV: 15.0 kV, VEGA 3 TESCAN) and TEM (JOEL, JEM 1200 EX-II) analyzes were carried out at the Electron Microscopy Center of the Federal University of Paraná in Curitiba to determine the shape, size and surface characteristics of NPS.

The determination of the surface area was obtained from the nitrogen sorption isotherm in the adsorption and desorption of Nps at a temperature of 77K (St 2 in NOVA 600, serial number 1050030634).

XRD analyzes (Rigaku Ultima IV, 40 kV, 20 mA, using Cu target, at room temperature, in the range of $2\theta = 2$–50 °C, 0.05 °C s^{-1}) were performed to verify the crystallinity of the Nps. To verify the approximate value of the crystallites of the Nps particles, it was applied the Scherrer Equation [9].

FTIR analyses were performed to identify functional groups on the surface of nanoparticles. This analysis was carried out in a PerkinElmer spectrophotometer Frontier FT-IR/FIR (Spectrum version 10.4.2) com 60 consecutive scans and 4 cm^{-1} resolution within the range of 500 – 4,000 cm^{-1}.

Raman spectroscopy (WITEC, ALPHA 300 R at 21 °C, pressure atmosphere and 532 nm green laser) was performed to verify the compounds present in NPS.

PCZ analyzed the acid/base behavior of the nanoparticle in an aqueous medium [10].

3. Results and discussion

3.1 Characterization of the extract

TABLE 1 shows the values obtained from the characterization of the orange peel extract. The results showed that the antioxidants, flavonoid and phenolic content have satisfactory concentrations and are like those found in the literature and in Lima orange juice [11].

Table 1. Antioxidant activity extract.

METHODS	PEEL EXTRACT
DPPH	10,07 ± 0,17 μmol ET/ g sample
ABTS	19,20 ± 0,39 μmol ET/ g sample
FRAP	561,50 ± 0,02 μmol ET/ g sample
FLAVONOIDS	1, 97 ± 0,23 mg CE/ g sample
PHENOLICS	0,58 ± 0,17 GAE g sample

The identification of the compounds was carried out qualitatively through existing studies in the segment [12] and the main compounds found were inserted in Table 2. Having identified the compounds, we can observe that the spectrum is divided into 3 main regions. The first region comprises the chemical shift between 0.5 and 3.0 ppm with a predominance of the aliphatic group (amino acids, alcohols and acidic organic compounds) present at low levels. The second region ranges from 3.0 to 5.5 ppm and contains sugars (sucrose, fructose, glucose) predominant in greater quantities. The third and final region (5.5 – 10 ppm) comprises aromatics (phenylalanine, chlorine, tyrosine).

Fig. 1. Spectrum of extract

Table 2. Compounds present in the extract

Components	Chemical Displacement (ppm)	Multiplicity
Proline	2,10; 2,35	m
Citric acid	2,95	d
Malic acid	2,89; 4,54	d; d
Dimethylproline	3,09; 3,24	s
Ascorbic Acid	4,93	d
Fructose	4,09; 4,11	m
Sucrose	3,7; 3,9; 4,20; 5,40	t; t; d; d
Fumaric acid	6,74	s
Phenylalanine	7,45	m
Tyrosine	7,20	m
Phylline	6,15; 6,21	m

s-simplet, d-doublet, dd-doublet, t-triplet; q-quartet, m-multiplet.

3.2 Characterization of NPS

The alkalinization of the solution that occurred in the process of obtaining the nanoparticles is the first visually proven indication of the formation of nanoparticles. Figure 2.a shows titanium oxide nanoparticles produced from Lima orange peel extract. The white color obtained is similar and characteristic of the metal used.

Figure 2 presents the TEM (b) and SEM (c) analyzes of the NPS, which we can see spherical structures with smooth surfaces having small rough cracks and sizes between 13 - 130 nm resulting from good capping of the nanoparticles. In the figures it is also possible to see the formation of small agglomerates generated by the nucleation of smaller to larger particles. The EDS analysis (d) indicates that titanium and oxygen have the highest composition in the material.
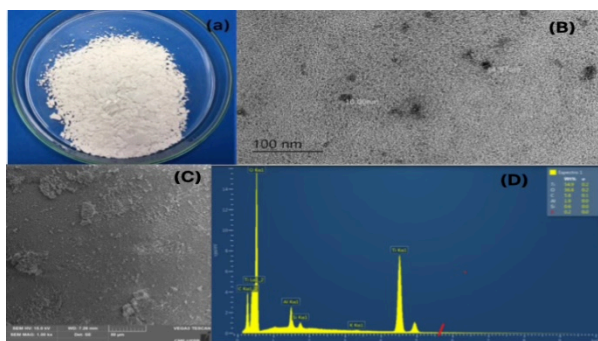
Fig. 2. Nps (a) and Analysis of TEM (b), SEM (c) and EDS (d)

The nitrogen sorption isotherm for BET was classified as type V with the presence of hysteresis. According to the literature, this type of isotherm may indicate a material with low porosity, however, in this case, according to the other results presented in Table 3, it is classified as mesoporous [13].

Table 1. Antioxidant activity extract.

PROPERTIES	NPS
Surface area BET, m^2/g	11,0444
Total pore volume, cm^3/g	0,0290
Mean pore radius, nm	10,7283

Figure 3.a shows the main diffraction planes found in 2 (θ), (110), (101), (111), (210), (211), (220), (310), (301), (112) and (222) corresponding to reflections at 27.88°, 36.26°, 41.01°, 43.98°, 54.60°, 56.7 °, 64°, 79.16°, 79.97° and 87.33°. The peaks for all Nps were similar. The values found are characteristic of the mixture of TiO2 in the rutile and anatase phase, with greater peak intensity for the rutile phase. JCPDS (Joint Committee on Powder Diffraction. 5Standards) cards no. 71–750, 71–441 and 77-442.

Figure 3.b shows the infrared spectrum (FTIR) with a peak recorded by the equipment around 3335 cm^{-1}, characteristic of the stretching of the OH bonds. The peaks around 2966 cm^{-1} and 2915 cm^{-1} refer to stretching and the C-H band. At 1645 cm^{-1}, it presented a peak characteristic of the Ti-OH bond. The carbonyl group (C=O) was identified around 1640 cm^{-1}. The vibration around 1047 cm^{-1} is characteristic of the stretching of the C-O bond responsible for promoting greater interaction of the material with water. Finally, around 680 cm^{-1} (Ti-O) and 517 cm^{-1} (Ti-O-Ti) it was possible to verify the presence of peaks characteristic of the stretching of the bond between titanium and oxygen [14], confirming the impregnation of the metal in organic matter.

The Raman spectrum presented in Figure 3.c identified the vibrational peaks remained at 123.44 cm^{-1} and 213.72; 274.97 cm^{-1} in Raman displacement presenting characteristics of titanium oxide in the rutile and anatase phases in vibrational modes A1g, B1g, B2g and Eg [15], corroborating the XRD analyses.

Figure 3.d shows the graph of the initial pH versus the final pH of the samples submitted to the experiment. The average data constancy to obtain the PCZ for the nanoparticles produced from the

bark extract was 7.50. This means that when NPS are present in solutions with a pH below their PCZ value, they will present a positively charged surface and will be more susceptible to adsorbing anionic compounds and when subjected to a solution with a pH higher than their PCZ, their surface will be negatively charged. more easily attracting cationic compounds [10].
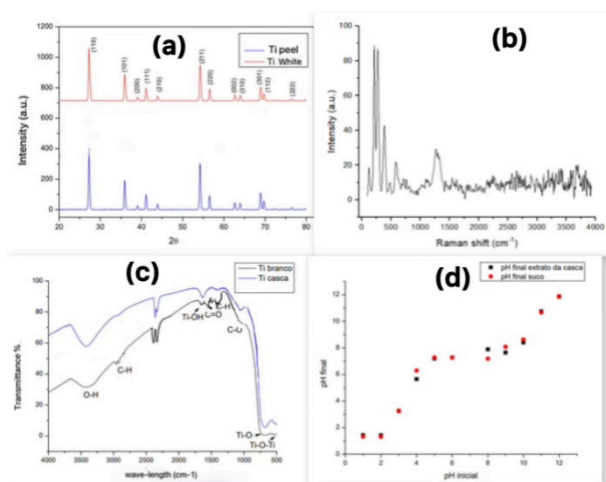

Fig. 3. XRD (a), FTIR (b), Raman (c) and PCZ (d).

4. Conclusion

Obtaining titanium dioxide nanoparticles synthesized through green synthesis using Lima orange peel extract obtained satisfactory results, like those found in the literature. These results allowed us to better understand the characteristics of this material, as well as its behavior, and will help future research on the production of titanium nanoparticles using the green route.

Acknowledgements

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