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Green synthesis of TiO₂ for furfural production by photohydrolysis of tortilla manufacturing waste

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Corn nixtamalization generates a waste byproduct that requires diverse environmental preservation measures depending on the country. Such measures could include catalytic and advanced oxidation processes. This study aims to exploit the hemicellulose within the nejayote (32.5%) to create added value chemicals such as furfural using photocatalytic hydrolysis. In the present work, titania (TiO₂) nanoparticles (NPs) were greenly synthesized using *Ricinus Communis* (RC), *Moringa Oleifera* (MO) or *Bougainvillea Spectabilis* (BS) plant extracts. Obtained nanoparticles were characterized using XRD, SEM, EDS, BET, XPS and UV–vis techniques. Furthermore, the photocatalytic performance of the obtained samples was evaluated in the furfural production from nejayote. Furfural yield reached 44% in 30 min using the BS synthesized material, which is 1.6 × the yield obtained by the material synthesized with MO extract (26.4% at 45 min) and 6 × the yield obtained by the material obtained with RC (7.2% at 90 min). Such results have not been reported before in the literature and could be the groundwork for novel waste treatments in the tortilla-making industry.

Consumption of processed food has increased dramatically in recent years growing agro-industrial waste generation, which is considered an environmental, social and economic problem worldwide. Tortilla making industry is a wide spread business with huge success in México, Central America, United States of America, Asia and Europe. The tortilla-making involves a pretreatment step for the corn called nixtamalization^{1,2}. Nixtamalization generates large amounts of alkaline liquid waste, known as nejayote, which are usually disposed of in the urban sewer system. Nejayote contains significant amounts of organic matter (carbohydrates, proteins, phenolic compounds, among others) and inorganic compounds (calcium and magnesium from the lime used in the process)^{2,3}. Nejayote is considered to be an environmental pollutant that requires processing. One of the processing technologies that have been proposed is the work reported by Castro-Muñoz et al. that use nejayote to obtain carbohydrates, calcium and phenolic compounds by means of a filtering membrane⁴. Ramírez-Romero et al. and López-Pacheco et al. use nejayote as a culture medium to obtain by-products of interest, such as: probiotics and bacteriocins^{5,6}. However, it could also be considered as a source of biocomposites and could be converted to value-added chemicals, as has been reported with other wastes that are rich in polysaccharides (cellulose and hemicellulose)^{7,8}.

Processes for the transformation of liquid wastes containing polysaccharides, such as nejayote⁶, to compounds with high added value can utilize hydrolysis or photocatalysis reactions. Dumesic's team has used hydrolysis for the conversion of corn waste, using high temperature and high pressure conditions to obtain furfural or hydroxymethyl furfural⁹. The photocatalysis reaction has not been extensively studied for this purpose; however, there is a large amount of literature for the processing of wastewater with high organic loads^{10–14}. Photocatalysis is a process that requires the presence of UV–Vis radiation, environmental conditions (in some studies), and a photocatalytic medium achieving partial oxidation (obtaining value-added chemicals) or total oxidation (water and CO₂). Some materials that have been used in photocatalysis are based on TiO₂ using several morphologies and formulations: TiO₂ nanoparticles in their anatase crystalline phase^{10,11,14}, Ag/TiNPs¹⁵, O₂/Ag^{16,17}, among others. The efficiency of TiO₂ is attributed to its optoelectronic and physicochemical properties^{16,17}, which depend directly on the conditions and methods of synthesis used. TiO₂ NPs are synthesized through various methodologies^{18–20}. Among

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the most recognized are sol–gel^{11,21}, hydrothermal^{22,23}, combustion²⁴, vapor phase^{25,26}, controlled precipitation, polymer precursor²⁷, etc. However, the application of such methodologies requires the use of solvents, reducing agents and stabilizing materials, which can generate various toxic or harmful compounds; moreover, it increases the production costs of TiO₂ NPs. Green synthesis may be considered as an alternative way to reduce health risks and the environmental impact during the synthesis of nanomaterials²⁸. This methodology explores the potential of certain plant extracts known as S-Met (terpenes, essential oils, flavonoids, phenols, etc.), to reduce metal ions and to generate stable nanoparticles with unique morphologies¹³. Until now, green synthesis has been mainly applied to produce noble metals (Ag, Au, Pt and Pd, Cu) and metal oxides (Zn and Ti) NPs^{29,30}. The source of S-Met can be associated with the demand for specific compounds (polyphenols, flavonoids, acids, etc.) required for the synthesis of NPs and their final application, as well as the geographical conditions and variety of available plants. For example, plants of historical relevance for disease treatment (Indian rosewood, gooseberry, tea leaves, etc.) are widely studied for the synthesis of metal NPs with antimicrobial applications³⁰. Some researchers reported the use of S-Met, extracted from BS, MO and RC, for the synthesis of silver NPs with various applications^{31,32}. Recently, anatase TiO₂ NPs have been synthesized using alcohol extracts from *B. spectabilis*, obtaining materials with crystal sizes of about 6 nm; other TiO₂ NPs synthesized from *R. communis* extracts have drawn some attention since the extracts contain catechins, flavonols, hydroxycoumarins, and scopoletin all of which contain OH groups that result in more photoactive materials³³.

The present work aims to establish the basis for photocatalytic processes capable of transforming the organic content of nejayote (polyacharides) into furfural using greenly synthesized materials. The TiO₂ NPs obtained through the green synthesis using S-Met extracts from RC, MO and BS plants from the marshland region of Chapala, México are analyzed. The physicochemical and electronic properties of the greenly synthesized TiO₂ NPs are discussed, as well as their potential use for furfural production by photohydrolysis of the unexplored nejayote. Commercial TiO₂ (comm TiO₂) was also analyzed parallelly and presented as reference material.

Materials and methods

Materials. Sulfuric acid (H₂SO₄ Sigma Aldrich), sodium bicarbonate (NaHCO₃, Sigma Aldrich), hydrochloric acid (HCl Sigma Aldrich), magnesium (Mg, Golden Bell), titanium isopropoxide (Ti[OCH(CH₃)₂]₄, Sigma Aldrich) and comm TiO₂ (TiO₂, Fermont) were used as reagents for the analysis of S-Met and TiO₂ NPs synthesis. The furfural (C₄H₃OCHO, Sigma Aldrich) was used as the standard for the calibration curve. The RM, MO and BS plants were collected nearest Chapala Lake, in Jalisco, México. For the photohydrolysis reaction, the nejayote sample was obtained from a local industry in Sahuayo, Michoacán, México. Nejayote is considered fresh and useful up to 3 days before its collection.

Metabolites extraction. Different sections of each plant were used for the S-Met extraction, flowers and bracts from BS, and leaves from RC and MO. The methodology commonly applied to extract the S-Met is reported³¹. In the present work, the extraction conditions were modified to increase the efficiency of the process. In brief, each plant extract was obtained by mixing 20 g of the plant with 100 mL of water. Then, the mixture was heated up to 90 °C and kept for 10 min. Finally, the aqueous extract was separated by vacuum filtration and kept refrigerated until use³⁴. All methods were performed in accordance with the relevant guidelines and regulations.

Qualitative phytochemical analysis of extracts. Each plant extract underwent a phytochemical screening to know the phytoconstituents of the obtained S-Met. The presence of flavonoids, tannins, phenols, quinones and saponins was evaluated following well-known methodologies such as Shinoda, Foam tests, FeCl₃ test and others, described^{35–37}.

Nanoparticles green synthesis. Titanium isopropoxide (12 mL) was mixed with 78 mL of distilled water and 10 mL of the S-Met plant extract obtained from each selected plant. The formed suspension was kept at 50 °C for 4 h under magnetic stirring. Subsequently, the obtained product was washed with distilled water and dried at 60 °C overnight. Finally, the samples were calcined at 500 °C for 3 h. The powdered sample was collected and saved for later testing and characterization.

Physicochemical characterization. The morphology and elemental composition of the greenly synthesized TiO₂ NPs were studied by scanning electron micrographs and X-Ray energy dispersion spectra, respectively, obtained with a JSM-6610-LV microscope, JEOL. Structural analysis of samples was performed using X-ray diffraction patterns collected in a D8 Avance A25 Bruker X-Ray diffractometer equipped with CuKα radiation. Textural properties of titania samples were determined by the N₂ thermal adsorption measurements using TriStar II-3020 equipment, Micromeritics. Before the analysis, the samples were dried under vacuum (10^{−3} torr) at 300 °C for 3 h using a VacPrep 061-Sample degas system, Micromeritics. Obtained isotherms were analyzed via the Brunauer-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) models for the surface area and porosity determination, respectively. The optical characterization of the powder samples was determined by UV–Vis spectroscopy in diffuse reflectance mode using an UV-3600 Plus UV–VIS–NIR spectrophotometer, Shimadzu, equipped with an integrating sphere. The samples were placed in a quartz cell with 2 mm in the light path for the measurement. The electronic state of prepared samples was studied by the XPS technique with a PHOIBOS spectrometer, SPECS, with 150 WAL hemispherical energy analyzer and a monochromatic source (AlKα Xray, 1486.6 eV).

Photocatalytic evaluation. *Nejayote characterization.* Fresh nejayote (100 mL) was treated with 4%w of H₂SO₄ at 200 °C for 2 h, using an autoclave. Then, the obtained solution/suspension was analyzed by means of liquid chromatography using an Ultimate 300 High-Pressure Liquid Chromatographer, Thermo Scientific, equipment to determine the presence of sugars. Additionally, 100 mL of fresh nejayote was diluted in 100 mL of water and then centrifuged. The supernatant was separated while the precipitated solids were calcined at 500 °C for 5 h. Calcined samples were analyzed by EDS to determine the inorganic matter.

Nejayote photohydrolysis. The photocatalytic performance of the obtained TiO₂ NPs was evaluated at the photohydrolysis of nejayote to produce furfural. Reactions were carried out in a cylindrical quartz batch reactor of 1 L with a constant oxygen flow rate of 2 ml per minute. The reactor had a continuous stirring speed of 400 rpm at room temperature. Typically, 1 g of catalyst was dispersed in 800 mL of nejayote (fresh sample without any variations in the nixtamalization process). Before the light irradiation, the reaction mixture was stirred for 30 min to reach adsorption equilibrium. Then, the UV-light lamp with a wavelength of 365 nm was turned on and the reaction progress was monitored by analyzing the products at 5, 15, 30, 45, 60, and 90 min. The reaction mixture samples were centrifuged for 5 min at 700 rpm and the catalyst was separated and stored. The furfural concentration was quantified using Perkin Elmer Clarus 680 gas chromatograph with a mass spectrometer (GC–MS), and the column employed was a 30 m capillary column Elite 1 PerkinElmer (inner diameter of 0.32 mm and film thickness of 0.25 µm) with a flow of 1.5 ml/s of Helium as carrier gas. All reactions were performed in triplicate.

For the catalyst recycle evaluation, the recovered catalyst from BS extract was calcined at 500 °C for 2 h with a heating rate of 10 °C per min. The calcined material was characterized using XRD, SEM–EDS, and UV–Vis.

Results and discussion

Metabolites characterization. It is well-known that S-Met assists the biosynthesis of metal NPs by acting as a reducing and/or stabilizing agent³⁸. The qualitative information on phytochemical constituents of obtained S-Met used in the green synthesis of TiO₂ NPs is shown in Table 1. The presence of flavonoids, saponins, tannins and phenols characterized the S-Met extracts from the three plants. The absence of essential oils and fatty substances was observed for all analyzed plants; meanwhile, flavones were only found in RS and MO extracts. The slight variations in the constituents found for each plant may be attributed to using different plant parts for the extraction: leaves from RC and MO where used, while flowers and branches from BS were used³⁸. Flavonoids and phenols are considered potential reducers of metallic precursors³⁹. Indeed, Bharathi³¹ showed that flavonoids and phenols obtained from BS are the principal for forming silver nanoparticles by reducing silver nitrate. On the other hand, Mintiwb and Jeyaramraja reported that flavonoids, tannins, saponins, alkaloids, triterpenes and steroids extracted from RC leaves allow for the reduction and stabilization of silver nanoparticles³⁹. Moodley reported that flavones, terpenoids and polysaccharides obtained from MO leaves are primarily responsible for the reduction and stabilization of silver³² and TiO₂ NPs⁴⁰. It is expected that found constituents (flavonoids, saponins, tannins and phenols) can reduce the titanium precursor salt to titanium ion intermediates for their further conversion into TiO₂ NPs.

Nanoparticles characterization. The elemental analysis of TiO₂ samples confirmed the presence of titanium and oxygen mostly (Table S1). However, some traces of potassium were found in the samples obtained with S-Met plants extract. The latter may be assigned to the chemical composition of plants, where inorganic matter, such as potassium, indicates that the extracellular inorganic moieties are absorbed in the TiO₂ NPs surface^{40,41}. Nevertheless, its contribution was insignificant to interfere with the sample properties, such as the morphology or composition.

Figure S1 presents the typical SEM micrographs of the TiO₂ NPs samples prepared from different plant extracts, with comm TiO₂ as reference. The green synthesis approach resulted in a quasispherical shape of TiO₂ NPs with a size below 100 nm. In comparison, comm TiO₂ was characterized with larger aggregates (up to 300 nm) (Fig. S1). According to the micrographs analysis, the diameters of the formed TiO₂ NPs were 49, 41 and 55 nm when BS, MO and RC were used, respectively. Despite the slight differences in the qualitative

Method	Phytochemical constituent	<i>Bougainvillea spectabilis</i>	<i>Moringa oleifera</i>	<i>Ricinus communis</i>
Shinoda test	Flavonoids	+	+	+
Shinoda test with heat	Flavonoids	+	+	+
H ₂ SO ₄ test	Flavone	–	+	+
	Quinones	+	–	–
Foam test (5 min)	Saponins	+	+	+
Foam test (30 min)	Saponins	+	+	+
NaHCO ₃ test	Saponins	+	+	+
HCl test	Tannins and phenols	+	+	+
FeCl ₃ test	Tannins and phenols	+	+	+
Essential oils and fatty substances	Essential oils and fatty substances	–	–	–

Table 1. Qualitative information on phytochemical constituents of secondary metabolites. – Absent, + Present.

characterization of the S-Met extract (see Table 1), it seems that both the S-Met dispersion and solubility in the reaction media are responsible for the morphology inhomogeneity of the obtained TiO_2 NPs, as was discussed for the Ag nanoparticles synthesis from BS and MO extracts^{31,32}. Indeed, some studies related to the green synthesis of TiO_2 NPs, using the same Ti precursor ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$), resulted in the formation of heterogeneous morphology accompanied by the contribution of NPs with different sizes (even up to micrometers)⁴², unless a tensoactive is used⁴³.

Figure 1 shows the X-ray diffraction patterns for the green synthesized samples compared to that for the reference comm TiO_2 powder. All samples were characterized with well-distinguishable reflections between 20° and 90° of 2θ . However, the reflections for TiO_2 prepared by green synthesis were less intensive and broader than those of the commercial sample. XRD analysis revealed the preferential formation of the TiO_2 anatase phase. The most intensive peaks were located at 25° and 48° of 2θ , corresponding to [101] and [200] crystallographic planes of the TiO_2 anatase phase, according to the PDF 00-064-0863 card. The low intensity and high broadness of the peaks for nanostructured TiO_2 may be attributed to the presence of TiO_2 crystals with the nanodomain size, the formation of which was promoted by the active species from the metabolites used, as reported by Logeswari et al., during the green syntheses of silver nanoparticles from organic aqueous extracts of different plants as well as *Solanum tricornatum*, *Syzygium cumini*, *Centella asiatica* and *Citrus sinensis*⁴⁴. The crystal formation processes are based on the titania primary species nucleation principles, so their ordered growth in one direction is limited by the components presented in the metabolites. The crystal size of TiO_2 was estimated by Scherrer's equation (see Table 2). The results confirmed that all green synthesized TiO_2 NPs were composed of relatively small crystals around 20 nm, while the reference TiO_2 sample was characterized with a bigger crystal size (41 nm). These results correlate well with the SEM data.

Figure 2 presents the adsorption–desorption isotherms for all samples. The isotherms for the green synthesized samples were characterized by a Type 4. At the same time, the comm TiO_2 obtained isotherm was a Type III, commonly assigned to mesoporous and nonporous materials, according to the IUPAC classification. In addition, the hysteresis loop shape (H1) revealed the presence of cylindrical-like pore channels³¹. Therefore, thermal physisorption of N_2 for prepared TiO_2 NPs presented significant differences in the amount of gas adsorbed in comparison with the reference commercial sample (see Fig. 2). The latter coincided well with the

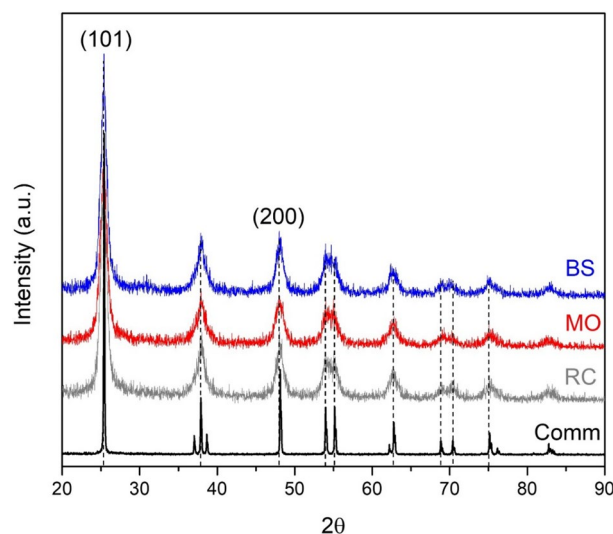


Figure 1. X-ray diffraction patterns of TiO_2 samples prepared under a green synthesis from different plant extracts: *Ricinus communis* (RC), *Moringa oleifera* (MO) and *Bougainvillea spectabilis* (BS). A diffractogram from commercial TiO_2 (Comm) is presented as a reference. Bragg index corresponds to the PDF 00-064-0863 chart.

TiO_2 source	Crystallite size*, nm	Gap energy values**, eV	Specific surface area, m^2/g	Pore volume, cm^3/g
<i>Bougainvillea spectabilis</i>	20	3.20	113	0.21
<i>Moringa oleifera</i>	25	3.22	124	0.21
<i>Ricinus communis</i>	18	3.25	115	0.19
Commercial	41	3.29	7	0.007

Table 2. Summary of physicochemical properties of TiO_2 nanoparticles prepared via green synthesis using different plant extracts. *Calculated using the Scherrer's equation on the peak at $2\theta = 25^\circ$. **Estimated by the Tauc plot method.

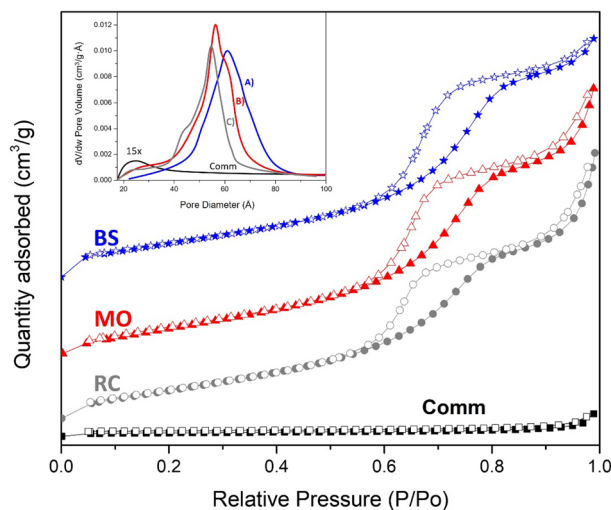


Figure 2. Isotherms of N₂ adsorption for the green synthesized TiO₂ samples using plant extracts of (A) RC, (B) MO and (C) BS and TiO₂ (Comm) as a reference sample. The solid symbols indicate adsorption, while the open ones represent the desorption step. The inset presents the corresponding pore size distribution.

remarkable improvement of the specific surface area values for green synthesized TiO₂ NPs (see Table 2). The TiO₂ NPs prepared by green synthesis were characterized with similar values of surface area (~ 120 m²/g) and pore volume (~ 0.21 m³/g); meanwhile, for the comm TiO₂ sample, these values were lower (7 m²/g and 0.007 m³/g, respectively). Furthermore, applying the BJH model for the physisorption data displayed an average porous size of around 5.5 nm for all synthesized samples (Table 2). Note that the TiO₂ samples prepared using RC and MO demonstrated two types of pores (4.2 and 6.3 nm, respectively). Thus, the applied green synthesis allowed the formation of relatively small TiO₂ nanocrystals to form TiO₂ NPs in the anatase phase with a remarkable enhancement of the surface area. Furthermore, the mesoporous nature of the green synthesized TiO₂ NPs was revealed. Therefore, it may conclude that the green synthesis affects the textural properties of the prepared TiO₂ NPs, which makes them functional for the proposed photocatalytic reaction because no mass transport limitations are expectable.

The high-resolution XP spectra of comm TiO₂ (D) and prepared samples BC (A), MO(B) and RC (C) for the Ti2p region are presented in Fig. 3. For the TiO₂ sample, the Ti2p spectrum is characterized by two spin-orbit components, Ti2p_{3/2} and Ti2p_{1/2}, that are separated by 5.7 eV⁴⁵, this signals exhibited several doublets attributed to different Ti oxidation states such as Ti³⁺ or Ti⁴⁺⁴⁶. For all samples, the obtained Ti2p core level spectra presented two symmetric bands centered at binding energies of c.a. 458.5 and 464 eV assigned to Ti2p_{3/2} and Ti2p_{1/2}, respectively, for the Ti⁴⁺ chemical state. Similar results are cited in the literature for TiO₂ prepared via green methods^{46–48}. Furthermore, a Ti³⁺ oxidation state is reported when surface defects are formed⁴⁶ or dopants are incorporated into the TiO₂ green synthesis procedure. In contrast, the Ti⁴⁺ oxidation state is found when only plant extracts are used^{49,50}. Thus, it was confirmed that the maximum oxidation state of Ti for the green synthesized TiO₂ NPs was reached. However, the plant extract did not affect the Ti chemical state achieved under green synthesis.

The UV–Vis absorption spectra of the synthesized samples were similar to those of the comm TiO₂ (see Fig. 4A), characterized by an absorption edge in the near UV region due to the charge transfer between Ti and O. It is well-known that the band gap energy values are associated with the photocatalytic performance of titanium. The band gap energy for these materials was estimated from the UV–Vis absorption edge wavelength of the interband transition according to the Tauc plot method described in Ref.⁵¹ (see Fig. 4B). The band gap energy value for comm TiO₂ was 3.29 eV, which is in good agreement with the literature data for the TiO₂ oxide in the anatase phase (~ 3.30 eV)⁵². Meanwhile, the values obtained for the green synthesized TiO₂ samples were 3.20, 3.22 and 3.25 eV, which were samples obtained from BS, MO and RC, respectively (see Table 2). These results agree with those reported for TiO₂ NPs prepared via a green approach¹³. The decreased optical band gap for green synthesized TiO₂ NPs makes it possible to propose that e⁻ and h⁺ pairs can be generated, promoting photocatalysis. Usually, synthesized TiO₂ NPs are characterized by a decrease in band gap energy value because the structure formation is hardly influenced by the ordered aggregation of fine crystals, as was previously discussed. Instead, these fine crystals promoted the presence of surface defects that decreased the band gap energy value⁵¹. Therefore, the estimated band gap energy values were influenced by forming domains with several sizes promoted by the phytochemical components presented in the extract plant. The latter was previously confirmed by the crystal size calculations (see Table 2).

Photocatalytic evaluation. *Nejayote characterization.* The composition analysis of nejayote revealed 32.5% of pentoses (ribose, arabinose, and xylose) and 47% of hexoses (glucose). Another 20.5% was attributed to other compounds such as lignin, inorganic matter (Ca, mainly), proteins, etc.

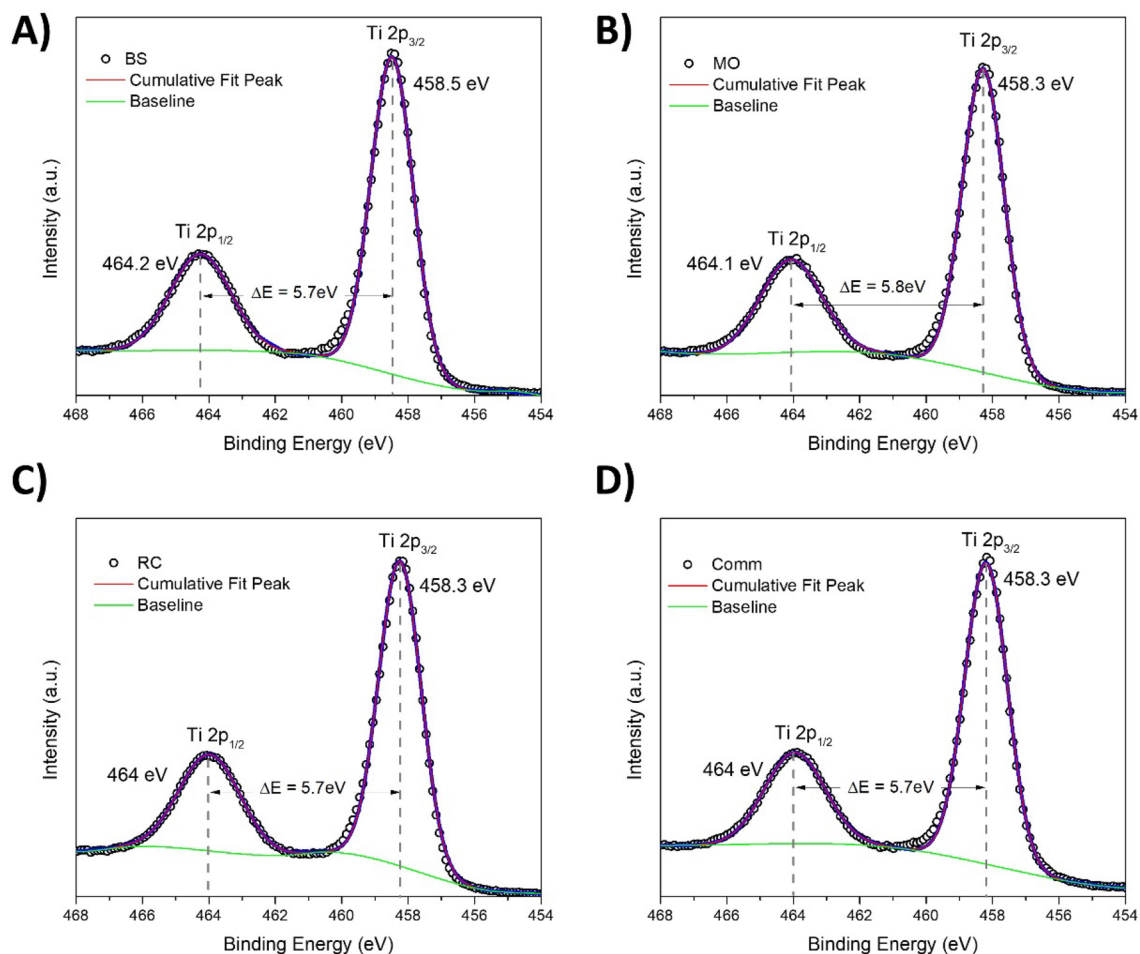


Figure 3. Ti2p XPS spectra for the TiO₂ samples prepared with the plant extract BS (A), MO (B) and RC (D) and the reference comm TiO₂ (D). The circles represent the experimental data; the blue curves represent the Gaussian fits of the experimental data.

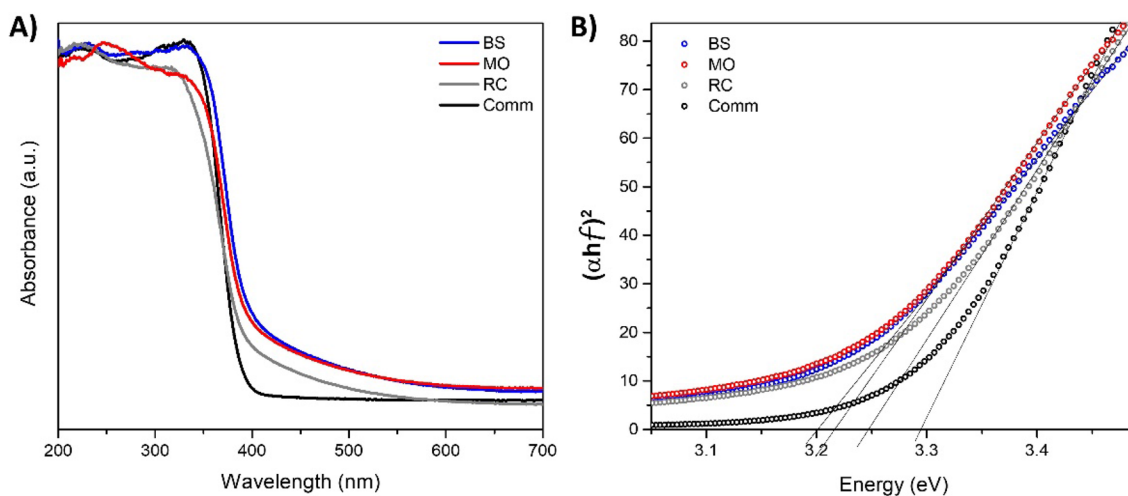


Figure 4. (A) UV-Vis absorption spectra of TiO₂ samples prepared via green synthesis using extracts of BS, MO and RC. The UV-Vis spectrum of commercial TiO₂ (Comm) is presented as a reference. (B) Estimation of band gap energies based on the Tauc plot method.

Table 3 shows the determination of elements in the solid sample of nejayote and ash (product of heat treatment of the nejayote solid sample). The results showed a high contribution of calcium and oxygen that's characteristic of "calcium oxide", which is used for the "nixtamalization" process and the generation of nejayote (wastewater). In addition, it was observed that there was no carbon in the ash sample, which proves the absence of organic matter (polysaccharides and/or sugars).

Furfural production. Figure 5 displays the furfural yields obtained from the nejayote photohydrolysis using the greenly synthesized TiO_2 NPs and comm TiO_2 as catalysts. All samples displayed some degree of furfural production during the 90 min of reaction monitoring. Figure S2 shows the proposed reaction pathway that lead to furfural production. The first step is the polysaccharide decomposition to form the xylose (pentose) that reacts further to form furfural; the newly formed furfural can react even further going through resinification, condensation or degradation. This furfural reactions lead to furfural loss⁵³ that competes with the furfural production, causing instability that could explain the variations observed. Furfural concentration can be affected by:

- 1) The rate of polysaccharide decomposition to form xylose.
- 2) The rate of dehydration reaction of xylose to form furfural.
- 3) Furfural decomposition to form organic acids⁵⁴.
- 4) The rate at which the furfural reacts with other molecules in the molecules in the reaction mixture; condensation reaction rate.
- 5) The rate at which the furfural reacts with other furfural molecules; resinification rate.

All reactions represented in Fig. S2 are affected by the reaction conditions and the photocatalytic properties of the catalyst.

Within the first 30 min the materials catalytic activity can be ordered as $\text{BS} > \text{MO} \approx \text{comm TiO}_2 > \text{RC}$. TiO_2 NPs obtained using S-Met from BS displayed a 44% furfural yield. Since the feedstock employed was nejayote, instead of high-purity xylose, this result was unprecedented. Indeed, the furfural yield reached by the BS sample was 0.6 and 0.5 times that of the yield presented by Alonso et al.⁹ and Gallo et al.⁵⁵, respectively, when xylose was used. Additionally, the reaction conditions in the present work were environmentally beneficial because (1) no extra water or energy to raise the temperature of the reactor was required^{9,55}; and (2) no additional solvents such as GVL, toluene, THF, etc.^{9–56} were used.

The furfural production was very low for the RC sample, with a yield below 6% during the reaction. On the contrary, the MO and comm TiO_2 samples demonstrated similar behavior for the furfural production with relatively constant product formation for MO the maximum yield (~25%) was detected at 45 min. From the data obtained, it can be inferred that the MO and comm TiO_2 have a slower xylose hydration stage than that of

Sample	%C	%Ca	%Cl	%K	%O
Nejayote (solids)	36.61	48.95	0.46	1.46	12.54
Nejayote (ash)		35.24	1.21	7.93	53.44

Table 3. Elemental evaluation of organic and inorganic matter in the nejayote.

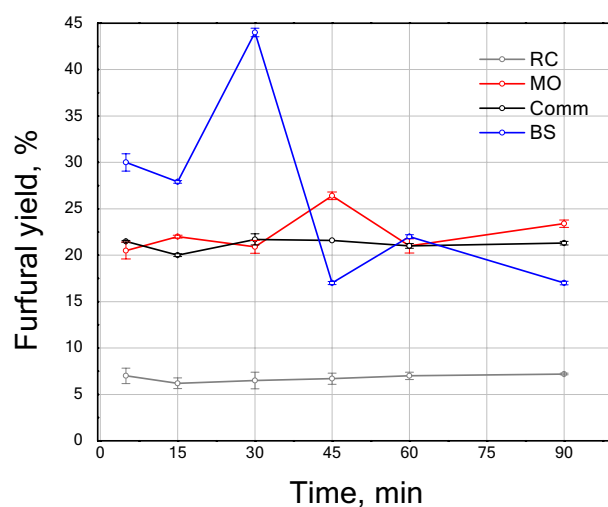


Figure 5. Furfural yield versus time from nejayote conversion using TiO_2 comm and TiO_2 sample prepared via green synthesis using extracts of BS, MO and RC at room temperature.

the BS sample. As the BS sample reached the highest furfural concentration in a very early stage, this accelerated the undesired furfural reactions and prompted the depletion of xylose towards the end of the reaction time here studied²⁴.

The low output of the furfural for the RC sample may be attributed to differences in the polysaccharides rupture (glycosidic bond) pathways^{56,57}, which can produce a different ratio of xylose, arabinose, and ribose⁵⁶. The latter may impact the product distribution in their subsequent hydrolysis. Furfural production is favored at high ratios of xylose, which has been described as a molecule with an isomerization process that leads to faster furfural production through xylulose and lyxose⁵⁸. Additionally, nejayote contains relatively big molecules, such as polymers and proteins, that can affect the depolymerization and dehydration processes involved in furfural synthesis. From this perspective, the pore size and morphology of greenly synthesized TiO₂ NPs may affect the diffusion of the molecules due to the nature of the feedstock.

Note that the performance of the MO sample is comparable with that presented for the comm TiO₂. The comm TiO₂, characterized by low surface area, mainly contributes to the external surface area. The latter may explain the lack of diffusional limitations of byproducts or impurities. In contrast, all greenly synthesized TiO₂ NPs displayed a smaller particle size and higher surface area promoting the diffusion of the reactive species. However, the MO samples present the largest crystal size compared to the green synthesized BS and RC. The big crystal size accompanied by the small particle size could promote the formation of external active sites, favoring the photocatalytic activity of the material particles' external surfaces, leading to a similar behavior to that of the comm TiO₂.

It was determined that the recovered catalyst for the recycling test absorbed organic and inorganic components from the nejayote. These components were identified by EDS and XRD after calcination; EDS revealed that Ca has deposited in the recovered material, ~ 5% Ca after reaction (Table S2). The XRD of the calcined sample also showed some carbon structure peaks that were not present in the fresh catalyst. The UV-Vis analysis of the recycled samples also showed a shift in the bandgap (from 3.2 to 3.06 eV) (Fig. S3). This is strong evidence of catalyst modification that could promote hemicellulose reactions that are detrimental for furfural production. Furfural yield reached 7.8% in 30 min using reused BS, which is 5.6 × the maximum yield obtained by BS in the first reaction (44%).

Conclusions

The present work reports the effect of the plants' S-Met on the physicochemical properties and photocatalytic performance of the greenly synthesized TiO₂ NPs. The S-Met extract from the BS plant to synthesize TiO₂ NPs is used for the first time, the BS metabolites differ greatly RC and MO metabolites. When BS is used the crystal size and gap energy values decreased; meanwhile, the surface area increased up to 17 times in the greenly synthesized TiO₂ NPs when compared to the comm TiO₂. In this study we reported for the very first time the furfural production via the photohydrolysis of the nejayote, which is an unexplored residual biomass. The maximum furfural yield achieves 44% on the BS catalysts. The furfural yield reached by the greenly synthesized TiO₂ NPs is comparable and 2 times superior to the reference comm TiO₂, following the BS > MO ≈ comm TiO₂ > RC trend. The intrinsic nejayote composition and the catalysts' surface both interfere with the polysaccharide fragmentation through the glucoside bond breakage to form pentoses and their subsequent transformation into furfural. The nejayote photohydrolysis reaction on the greenly synthesized TiO₂ NPs presents a comparable furfural yield to those reported when a high-purity xylose reagent is used.

The Chapala, México marshland region provides beneficial S-Met extracts to promote the synthesis of active, sustainable, and environmentally friendly catalysts. Furthermore, this work shows the potential to exploit a complex feedstock, promoting the lignocellulosic residual biomass valorization, to produce highly valuable compounds, such as furfural.

Data availability

The datasets generated and/or analysed during the current study are not publicly available due, but could be available from the corresponding author on reasonable request.

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References

- Valderrama-Bravo, C. *et al.* Physico-mechanic treatment of nixtamalization by-product (nejayote). *CyTA-J. Food* **11**(sup1), 75–83. <https://doi.org/10.1080/19476337.2013.781680> (2013).
- Meraz, K. A. S. *et al.* Eco-friendly innovation for nejayote coagulation–flocculation process using chitosan: Evaluation through zeta potential measurements. *Chem. Eng. J.* **284**, 536–542. <https://doi.org/10.1016/j.cej.2015.09.026> (2016).
- García-Zamora, J. L. *et al.* Enzymatic treatment of wastewater from the corn tortilla industry using chitosan as an adsorbent reduces the chemical oxygen demand and ferulic acid content. *Process Biochem.* **50**, 125–133. <https://doi.org/10.1016/j.procbio.2014.10.012> (2015).
- Castro-Muñoz, R., Cerón-Montes, G. I., Barragán-Huerta, B. E. & Yañez-Fernández, J. Recovery of carbohydrates from nixtamalization wastewaters (nejayote) by ultrafiltration. *Rev. Mex. Ing. Quím.* **14**(3), 735–744 (2015).
- Ramírez-Romero, G., Reyes-Velázquez, M. & Cruz-Guerrero, A. Estudio del nejayote como medio de crecimiento de probióticos y producción de bacteriocinas. *Rev. Mex. Ing. Quím.* **12**(3), 463–471 (2013).
- López-Pacheco, I. Y. *et al.* Combination of nejayote and swine wastewater as a medium for *Arthrospira maxima* and *Chlorella vulgaris* production and wastewater treatment. *Sci. Total Environ.* **676**, 356–367 (2019).
- Gilcher, E. B., Chang, H., Huber, G. W. & Dumesic, J. A. Controlled hydrogenation of a biomass-derived platform chemical formed by aldol-condensation of 5-hydroxymethyl furfural (HMF) and acetone over Ru, Pd, and Cu catalysts. *Green Chem.* **24**(5), 2146–2159. <https://doi.org/10.1039/D1GC04650K> (2022).

8. Wettstein, S. G., Alonso, D. M., Chong, Y. & Dumesic, J. A. Production of levulinic acid and gamma-valerolactone (GVL) from cellulose using GVL as a solvent in biphasic systems. *Energy Environ. Sci.* **5**(8), 8199–8203. <https://doi.org/10.1039/C2EE22111J> (2012).
9. Alonso, D. M., Wettstein, S. G., Mellmer, M. A., Gurbuz, E. I. & Dumesic, J. A. Integrated conversion of hemicellulose and cellulose from lignocellulosic biomass. *Energy Environ. Sci.* **6**(1), 76–80. <https://doi.org/10.1039/C2EE23617F> (2013).
10. Ahmad, W., Singh, A., Jaiswal, K. K. & Gupta, P. Green synthesis of photocatalytic TiO₂ nanoparticles for potential application in photochemical degradation of ornidazole. *J. Inorg. Organomet. Polym. Mater.* **31**(2), 614–623. <https://doi.org/10.1007/s10904-020-01703-6> (2021).
11. Rangel, R., Mercado, G. J., Bartolo-Pérez, P. & García, R. Nanostructured-[CeO₂, La₂O₃, C]/TiO₂ catalysts for lignin photodegradation. *Sci. Adv. Mater.* **4**(5–6), 573–578. <https://doi.org/10.1166/sam.2012.1321> (2012).
12. Bhattacharyya, A., Kawi, S. & Ray, M. B. Photocatalytic degradation of orange II by TiO₂ catalysts supported on adsorbents. *Catal. Today* **98**(3), 431–439. <https://doi.org/10.1016/j.cattod.2004.08.010> (2004).
13. Goutam, S. P. *et al.* Green synthesis of TiO₂ nanoparticles using leaf extract of *Jatropha curcas* L. for photocatalytic degradation of tannery wastewater. *Chem. Eng. J.* **336**, 386–396. <https://doi.org/10.1016/j.cej.2017.12.029> (2018).
14. Voisin, H., Falourd, X., Rivard, C. & Capron, I. Versatile nanocellulose-anatase TiO₂ hybrid nanoparticles in Pickering emulsions for the photocatalytic degradation of organic and aqueous dyes. *JCIS Open* **3**, 100014. <https://doi.org/10.1016/j.jciso.2021.100014> (2021).
15. Muraro, P. C. L. *et al.* Ag/TiNPS nanocatalyst: Biosynthesis, characterization and photocatalytic activity. *J. Photochem. Photobiol. A* **439**, 114598. <https://doi.org/10.1016/j.jphotochem.2023.114598> (2023).
16. Cozzoli, P. D. *et al.* Role of metal nanoparticles in TiO₂/Ag nanocomposite-based microheterogeneous photocatalysis. *J. Phys. Chem. B* **108**(28), 9623–9630. <https://doi.org/10.1021/jp0379751> (2004).
17. Viana, M. M., Soares, V. F. & Mohallem, N. D. S. Synthesis and characterization of TiO₂ nanoparticles. *Ceram. Int.* **36**(7), 2047–2053. <https://doi.org/10.1016/j.ceramint.2010.04.006> (2010).
18. Malekshahi Byranvand, M., Nemati Kharat, A., Fatholahi, L. & Malekshahi Beiranvand, Z. A review on synthesis of nano-TiO₂ via different methods. *J. Nanostruct.* **3**(1), 1–9. <https://doi.org/10.7508/JNS.2013.01.001> (2013).
19. Gupta, S. & Tripathi, M. A review on the synthesis of TiO₂ nanoparticles by solution route. *Open Chem.* **10**(2), 279–294. <https://doi.org/10.2478/s11532-011-0155-y> (2012).
20. Nyamukamba, P., Okoh, O., Mungondori, H., Taziwa, R. & Zinya, S. Synthetic methods for titanium dioxide nanoparticles: A review. In *Titanium Dioxide—Material for a Sustainable Environment* (ed. Yang, D.) 151–175 (Intech, 2018). <https://doi.org/10.5772/intechopen.75425>.
21. Pecchi, G., Reyes, P., Sanhueza, P. & Villasenor, J. Photocatalytic degradation of pentachlorophenol on TiO₂ sol–gel catalysts. *Chemosphere* **43**(2), 141–146. [https://doi.org/10.1016/S0045-6535\(00\)00265-4](https://doi.org/10.1016/S0045-6535(00)00265-4) (2001).
22. Chen, M., Ma, C. Y., Mahmud, T., Lin, T. & Wang, X. Z. Population balance modelling and experimental validation for synthesis of TiO₂ nanoparticles using continuous hydrothermal process. *Adv. Mater. Res.* **508**, 175–179. <https://doi.org/10.4028/www.scientific.net/AMR.508.175> (2012).
23. Ahn, K. H. *et al.* Effects of surface area of titanium dioxide precursors on the hydrothermal synthesis of barium titanate by dissolution–precipitation. *Ind. Eng. Chem. Res.* **52**(37), 13370–13376. <https://doi.org/10.1021/ie401161x> (2013).
24. Wu, J. *et al.* Photocatalytic oxidation of gas-phase Hg₀ by CuO/TiO₂. *Appl. Catal. B Environ.* **176**, 559–569. <https://doi.org/10.1016/j.apcatb.2015.04.044> (2015).
25. Avril, L. *et al.* Thermal stability of Au–TiO₂ nanocomposite films prepared by direct liquid injection CVD. *Vacuum* **122**, 314–320. <https://doi.org/10.1016/j.vacuum.2015.06.018> (2015).
26. Lee, H., Song, M. Y., Jurng, J. & Park, Y. K. The synthesis and coating process of TiO₂ nanoparticles using CVD process. *Powder Technol.* **214**(1), 64–68. <https://doi.org/10.1016/j.powtec.2011.07.036> (2011).
27. Malagutti, A. R., Mourao, H. A., Garbin, J. R. & Ribeiro, C. Deposition of TiO₂ and Ag: TiO₂ thin films by the polymeric precursor method and their application in the photodegradation of textile dyes. *Appl. Catal. B* **90**(1–2), 205–212. <https://doi.org/10.1016/j.apcatb.2009.03.014> (2009).
28. Zamri, M. S. F. A. & Sapawe, N. Kinetic study on photocatalytic degradation of phenol using green electrosynthesized TiO₂ nanoparticles. *Mater. Today Proc.* **19**, 1261–1266. <https://doi.org/10.1016/j.matpr.2019.11.131> (2019).
29. Jadoun, S., Arif, R., Jangid, N. K. & Meena, R. K. Green synthesis of nanoparticles using plant extracts: A review. *Environ. Chem. Lett.* **19**(1), 355–374. <https://doi.org/10.1007/s10311-020-01074-x> (2021).
30. Shanker, U., Jassal, V., Rani, M. & Kaith, B. S. Towards green synthesis of nanoparticles: from bio-assisted sources to benign solvents. A review. *Int. J. Environ. Anal. Chem.* **96**(9), 801–835. <https://doi.org/10.1080/03067319.2016.1209663> (2016).
31. Bharathi, D., Kalaichelvan, P. T., Atmaram, V. & Anbu, S. Biogenic synthesis of silver nanoparticles from aqueous flower extract of *Bougainvillea spectabilis* and their antibacterial activity. *J. Med. Plants* **4**(5), 248–252 (2016).
32. Moodley, J. S., Krishna, S. B. N., Pillay, K. & Govender, P. Green synthesis of silver nanoparticles from *Moringa oleifera* leaf extracts and its antimicrobial potential. *Adv. Natl. Sci. Nanosci. Nanotechnol.* **9**(1), 015011. <https://doi.org/10.1088/2043-6254/aaabb2> (2018).
33. Vera-García, P. F., Saenz-Galindo, A., de León, R. E. D. & Castañeda-Facio, A. O. Síntesis de nanopartículas de TiO₂ utilizando el extracto de *Ricinus communis* L. *Afinidad* **79**(597), 509–516. <https://doi.org/10.55815/411478> (2022).
34. Nabi, G. *et al.* Green synthesis of TiO₂ nanoparticles using lemon peel extract: Their optical and photocatalytic properties. *Int. J. Environ. Anal. Chem.* **102**(2), 434–442. <https://doi.org/10.1080/03067319.2020.1722816> (2022).
35. Vimalkumar, C. S. *et al.* Comparative preliminary phytochemical analysis of ethanolic extracts of leaves of *Olea dioica* Roxb., infected with the rust fungus *Zaghouania oleae* (EJ Butler) Cummins and non-infected plants. *J. Pharmacogn. Phytochem.* **3**(4), 69–72 (2014).
36. Mahesh, A. R., Ranganath, M. K. & Harish Kumar, D. R. Enrichment of flavonoids from the methanolic extract of boerhaavia diffusa roots by partitioning technique. *Res. J. Chem. Sci.* **3**, 43–47 (2013).
37. Tamilselvan, A., Srividhya, P., Karuthapandian, S. & Mehalingam, P. Plant—Driven to synthesis of silver nanoparticles using *Craeteva religiosa* hook & frost and its utility in detecting antimicrobial and antioxidant assay. *Int. J. Green Herbal Chem.* **5**, 390–402 (2016).
38. Aslam, M., Abdullah, A. Z. & Rafatullah, M. Recent development in the green synthesis of titanium dioxide nanoparticles using plant-based biomolecules for environmental and antimicrobial applications. *J. Ind. Eng. Chem.* **98**, 1–16. <https://doi.org/10.1016/j.jiec.2021.04.010> (2021).
39. Mintiwab, A. & Jeyaramraja, P. R. Evaluation of phytochemical components, antioxidant and antibacterial activities of silver nanoparticles synthesized using *Ricinus communis* leaf extracts. *Vegetos* **34**(3), 606–618. <https://doi.org/10.1007/s42535-021-00244-8> (2021).
40. Pushpamallini, T., Keerthana, M., Sangavi, R., Nagaraj, A. & Kamaraj, P. Comparative analysis of green synthesis of TiO₂ nanoparticles using four different leaf extract. *Mater. Today Proc.* **40**, S180–S184. <https://doi.org/10.1016/j.matpr.2020.08.438> (2021).
41. Sundararajan, M. & Gowri, S. Green synthesis of titanium dioxide nanoparticles by *Nyctanthus arbor-tristis* leaves extract. *Chalcogenide Lett.* **8**(8), 447–451 (2011).
42. Shimi, A. K. *et al.* Synthesis and applications of green synthesized TiO₂ nanoparticles for photocatalytic dye degradation and antibacterial activity. *J. Nanomater.* <https://doi.org/10.1155/2022/7060388> (2022).

43. Madadi, Z. & Bagheri Lotfabad, T. Aqueous extract of *acanthophyllum laxiusculum* roots as a renewable resource for green synthesis of nano-sized titanium dioxide using sol-gel method. *Adv. Ceram. Progress* **2**(1), 26–31. <https://doi.org/10.30501/ACP.2016.70015> (2016).
44. Logeswari, P., Silambarasan, S. & Abraham, J. Ecofriendly synthesis of silver nanoparticles from commercially available plant powders and their antibacterial properties. *Scientia Iranica* **20**(3), 1049–1054. <https://doi.org/10.1016/j.scient.2013.05.016> (2013).
45. Crist, B. V. Handbook of Monochromatic XPS Spectra Polymers and Polymers Damaged by X-rays.
46. Muniandy, S. S., Kaus, N. H. M., Jiang, Z. T., Altarawneh, M. & Lee, H. L. Green synthesis of mesoporous anatase TiO₂ nanoparticles and their photocatalytic activities. *RSC Adv.* **7**(76), 48083–48094. <https://doi.org/10.1039/C7RA08187A> (2017).
47. Atchudan, R., Edison, T. N. J. I., Perumal, S., Vinodh, R. & Lee, Y. R. In-situ green synthesis of nitrogen-doped carbon dots for bioimaging and TiO₂ nanoparticles@ nitrogen-doped carbon composite for photocatalytic degradation of organic pollutants. *J. Alloys Compd.* **766**, 12–24. <https://doi.org/10.1016/j.jallcom.2018.06.272> (2018).
48. Santhi, K. Synthesis and characterization of TiO₂ nanorods by hydrothermal method with different pH conditions and their photocatalytic activity. *Appl. Surf. Sci.* <https://doi.org/10.1016/j.apsusc.2019.144058> (2020).
49. Ouerghi, O., Geesi, M. H., Riadi, Y. & Ibnouf, E. O. Limon-citrus extract as a capping/reducing agent for the synthesis of titanium dioxide nanoparticles: Characterization and antibacterial activity. *Green Chem. Lett. Rev.* **15**(3), 483–490. <https://doi.org/10.1080/17518253.2022.2094205> (2022).
50. Hariharan, D., Christy, A. J., Mayandi, J. & Nehru, L. C. Visible light active photocatalyst: Hydrothermal green synthesized TiO₂ NPs for degradation of picric acid. *Mater. Lett.* **222**, 45–49. <https://doi.org/10.1016/j.matlet.2018.03.109> (2018).
51. Acosta, B. *et al.* Gold supported on ceria nanoparticles and nanotubes. *Appl. Catal. A* **449**, 96–104. <https://doi.org/10.1016/j.apcata.2012.09.045> (2012).
52. Hafez, H. *et al.* Enhancing the photoelectrical performance of dye-sensitized solar cells using TiO₂: Eu³⁺ nanorods. *Nanotechnology* **21**(41), 415201. <https://doi.org/10.1088/0957-4484/21/41/415201> (2010).
53. Zeitsch, K. J. *The Chemistry and Technology of Furfural and its Many By-Products* (Elsevier, 2000).
54. Luo, Y. *et al.* The production of furfural directly from hemicellulose in lignocellulosic biomass: A review. *Catal. Today* **319**, 14–24 (2019).
55. Gallo, J. M. R. *et al.* Production of furfural from lignocellulosic biomass using beta zeolite and biomass-derived solvent. *Top. Catal.* **56**, 1775–1781. <https://doi.org/10.1007/s11244-013-0113-3> (2013).
56. López-Mercado, J. *et al.* High and low esterification degree pectins decomposition by hydrolysis and modified Maillard reactions for furfural production. *Clean Technol. Environ. Policy* **20**(7), 1413–1422. <https://doi.org/10.1007/s10098-018-1570-y> (2018).
57. Guízar-Amezcu, M. G. *et al.* Evaluation of pectin extractions and their application in the alkaline Maillard reaction. *Sci. Rep.* **12**(1), 1–12. <https://doi.org/10.1038/s41598-022-22002-9> (2022).
58. Mellmer, M. A. *et al.* Solvent effects in acid-catalyzed biomass conversion reactions. *Angew. Chem. Int. Ed.* **53**(44), 11872–11875. <https://doi.org/10.1002/anie.201408359> (2014).

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Author contributions

J.L.-M. and B.A. wrote the main manuscript text. J.L.-M. and A.N. evaluated and analyzed the furfural production. M.-I.G.-D. prepared the secondary metabolites and carried out the reaction of the TiO₂ nanoparticles. F.-J.R.-M. carried out and analyzed the studies of SEM-EDS and DRX of the TiO₂ nanoparticles. B.A. carried out and analyzed the studies of UV-Vis and XPS of the TiO₂ nanoparticles. E.S. evaluated and analyzed the surface area and pore distribution of the TiO₂ nanoparticles. All authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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