UDK 67.017:621.791.725:669.715
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 54(6)755(2020)

IMPROVEMENT OF TITANIUM DIOXIDE NANOPARTICLE SYNTHESIS WITH GREEN CHEMISTRY METHODS USING LEMONGRASS (*CYMBOPOGON CITRATUS*) EXTRACT

IZBOLJŠANA, OKOLJU PRIJAZNA KEMIJSKA SINTEZA NANODELCEV TITANOVEGA OKSIDA Z UPORABO IZVLEČKA LIMONSKE TRAVE

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Prejem rokopisa – received: 2019-08-21; sprejem za objavo – accepted for publication: 2020-07-15

doi:10.17222/mit.2019.200

In this research, titanium dioxide (TiO_2) nanoparticles were synthesized through green chemistry using a plant extract, obtained from lemongrass (*Cymbopogon citratus*) leaves. Two different methods for the leaf extraction were used, allowing the formation of smaller nanoparticles as well as obtaining a greater amount of the product via synthesis. The first method was the synthesis with ultrasound-assisted green chemistry, which used a precursor solution of titanium tetra-isopropoxide, obtaining nanoparticles of 20.01 nm in size and a production of 0.05 g of TiO_2 nanoparticles via synthesis; the second method was based on the modification of the synthesis method using ultrasound-assisted green chemistry through the application of the pure precursor (titanium tetra-isopropoxide), obtaining nanoparticles with an average size of 18.67 nm and a production of 1.00 g of TiO_2 nanoparticles via synthesis. According to the results, the best synthesis method used the pure precursor, obtaining nanoparticles of a smaller size and a production 20 times greater than the one obtained with the method using the precursor solution. As a result, future studies will benefit by optimizing the production process, reducing the environmental impact by using less reagents, maximizing the extraction of terpenes and flavonoids from lemongrass leaves and obtaining nanoparticles with sizes similar to those available commercially.

Keywords: titanium dioxide, nanoparticles, lemongrass, improvement

Avtorji v članku opisujejo raziskavo izdelave nanodelcev titanovega oksida, ki so jih sintetizirali s pomočjo okolju prijaznega kemijskega postopka pri katerem so uporabili izvleček iz listov limonske trave (*Cymbopogon citratus*). Pri tem so uporabili dve različni metodologiji ekstrakcije listov, ki omogočata tvorbo večje količine manjših nanodelcev. Pri prvi metodi (metodologiji) so uporabili z ultrazvokom podprto okolju prijazno sintezo, pri kateri so kot prekurzor (izhodno surovino) uporabili titanov tetra-izopropoksid. S to metodo so dobili 0,05 gramov TiO_2 nanodelcev velikosti 20,01v nm. Druga metoda temelji na modifikaciji prve z uporabo čistega prekurzorja. S to metodo so izdelali 1 gram nanodelcev TiO_2 s povprečno velikostjo 18,67 nm. Rezultati so tako pokazali, da je ta metodologija s katero so uspeli izdelati 20-krat večjo količino manjših delcev primernejša kot prva pri kateri so uporabili prekurzor v raztopini. Z nadaljnjimi študijami bodo poizkušali še optimizirati proces izdelave in zmanjšati vpliv na okolje z zmanjšanjem količine reagentov, povečanjem ekstrakcije terpenov in flavonoidov iz listov limonske trave in tako dobiti nanodelce, ki so po velikosti podobni komercialno dosegljivim.

Ključne besede: titanov dioksid, nanodelci, limonska trava, izboljšava

1 INTRODUCTION

Nanotechnology (NT) has strengthened during the last decades due to extraordinary properties that a particle may exhibit at a nanometer level. Most of the applications that have been made, have been chemically synthesized using NPs, commercially obtained at a certain size and having a high environmental impact due to the process and the amount of reagents in the synthesis.[1] A variety of physical and chemical procedures have been developed to synthesize nanoparticles of different compositions, sizes and shapes.[2] However, the physicochemical techniques of the nanoparticle production such as the photochemical reduction, laser ablation, electrochemistry, aerosol technologies, ultrasound fields, UV, lithography or high irradiation energy are highly expensive and use highly toxic substances.[3]

This paper presents an affordable, environmentally friendly and straightforward synthesis alternative to obtain TiO_2 nanoparticles using phytocomponents from vegetables as the reducing agents[4] whose procedure does not require neither strong and toxic chemical agents nor organic solvents. Several investigators, among others,[5–8] have reported using natural resources such as inactivated biomass and plants to produce silver or gold nanoparticles.

This paper seeks to present a green-chemistry synthesis method, with which it is possible to obtain small nanoparticles with high stability from plant extracts. In

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this case, the synthesis of titanium oxide nanoparticles from lemongrass (*Cymbopogon citratus*) leaf extracts was performed at room temperature. In the present paper, two nanoparticle-synthesis methods will be described; with the first one, a stock solution of titanium tetra-isopropoxide obtained with ultrasound-assisted green chemistry was used; the second one was based on the application of the pure precursor (titanium tetra-isopropoxide) with modifications to the previous method.

2 EXPERIMENTAL PART

2.1 Methods of TiO_2 nanoparticle synthesis

A comparison between the two methods of synthesis was conducted to evaluate the production performance according to the precursor used:

Synthesis of nanoparticles from the precursor solution.

Synthesis of nanoparticles from the pure precursor.

2.2 Methodology for the nanoparticle synthesis from the precursor solution

2.2.1 Extraction of terpenes and flavonoids from lemongrass leaves

To obtain the leaf extract, 100 g of leaves were dried for six hours in a hot-air circulation oven at 60 °C and mashed to get fine solids. The leaf extract was obtained, using the Soxhlet method, from 50 g of biomass crushed for 6 h in 250 mL of ethanol (solvent) 10 % v/v. At the end of the extraction, the extract was stored at 4 °C until its final disposition.

2.2.2 Preparation of the TiO_2 precursor solution

The precursor solution (stock solution) of titanium tetraisopropoxide was prepared by mixing 1.26 mL of this reagent with 850 mL of distilled water. This mixture was subjected to ultrasound-assisted agitation for 30 min. The result was a white solution with a 5 mM concentration.

2.2.3 Synthesis of the nanoparticles from the precursor solution

The synthesis of nanoparticles was carried out in 5 mL of titanium tetraisopropoxide. For this purpose, 20 mL of the lemongrass aqueous extract was added at a rate of 1 mL/s. The reaction was carried out with magnetic stirring for 40 min. To complete this process, the nanoparticles were subjected to three washes including ethanol-water-ethanol 70 % v/v, using separation by centrifugation at 6000 min^{-1} for 15 min. Afterwards, the nanoparticles were dried in a laboratory oven for 2 h at 80 °C. Finally, the product was calcinated in a muffle furnace at 550 °C for 5 h.

2.3 Methodology for the nanoparticle synthesis from a direct precursor

The extraction of terpenes and flavonoids from the lemongrass leaves was done with the previously mentioned Soxhlet method. With this method, a difference arose from the preparation of the TiO_2 solution.

2.3.1 Synthesis of the nanoparticles from the TiO_2 direct precursor

The synthesis of nanoparticles was performed by mixing 5 mL of pure titanium isopropoxide (to optimize the time and number of nanoparticles) and 20 mL of lemongrass aqueous extract. The reaction took place over 30 min of an ultrasound exposure. The obtained extract was washed twice with ethanol and distilled water at 70 % v/v, while separation by centrifugation was performed for 15 min at 6000 min^{-1}. The nanoparticles of titanium dioxide were subjected to a calcination at 550 °C for 2 h to promote their crystalline anatase phase.[9,10]

2.4 Characterization of the titanium oxide nanoparticles

A scanning-electron-microscopy (SEM) analysis of the titanium oxide nanoparticle solution was carried out with a Quanta FEG 650 environmental scanning electron microscope (ESEM) in the mode of high vacuum operation, using a secondary electrons detector, Everhart Thornley detector (ETD), and a backscatter electron detector (BSED). Elemental analyses were made on this instrument, which is coupled to an EDAX Apollo X detector with a 126.1 eV (in MN K_α) resolution to perform EDS (energy dispersive spectroscopy) analyses, providing qualitative and semi-quantitative information about the chemical elements present in the synthesis of TiO_2 nanoparticles. In addition, an XRD (X-ray diffraction) analysis was performed on a BRUKER D8 ADVANCE powder diffractometer with DaVinci geometry, and transmission electron microscopy (TEM) was carried out at a maximum 1 million × magnification with a resolution of 0.1 nm.

3 RESULTS AND DISCUSSION

The nanoparticles synthesized from lemongrass-leaf extracts were analysed using of SEM, EDS, DRX, TEM and the size distribution. **Figure 1** shows the micrographs of the nanoparticles synthesized with the TiO_2 green chemistry, obtained with SEM for the two methods of synthesis: the precursor solution and direct precursor. In **Figures 1a** and **1b**, agglomerates of the titanium dioxide nanoparticles obtained with the synthesis methods are observed, with an average NP size of 20.01 nm for the precursor solution and average size of 18.67 nm for the pure precursor.

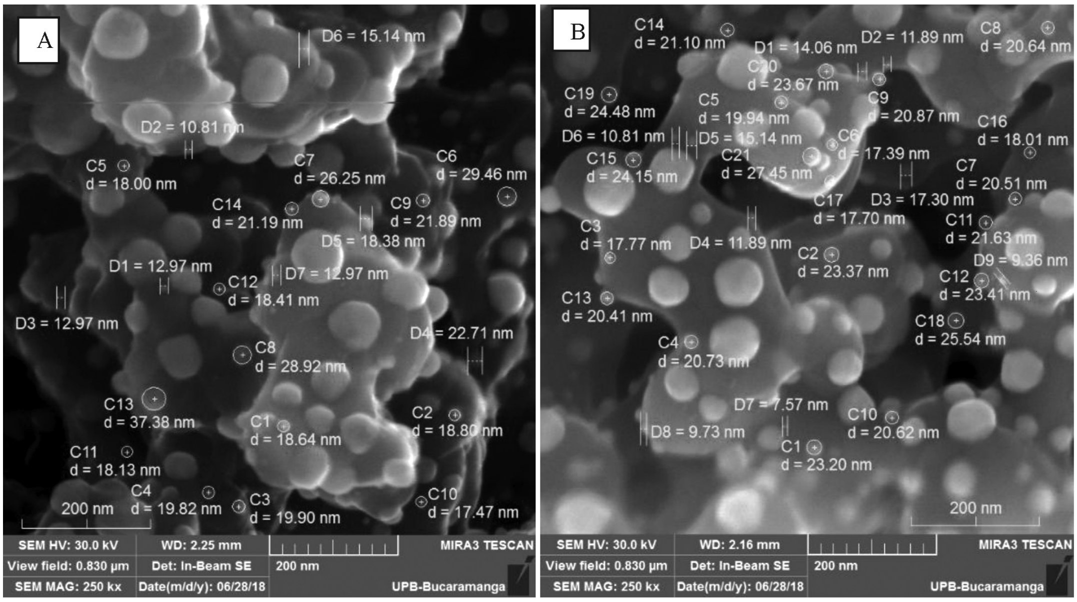

Figure 1: Nanoparticles synthesized from the extracts of lemongrass leaves: a) with precursor solution; b) from direct precursor

The elemental composition obtained with EDS shows that the TiO_2 nanoparticles synthesized with the precursor solution include titanium (47.81 %), oxygen (49.25 %), carbon (1.95 %) and calcium (0.97 %). The elemental composition of the TiO_2 nanoparticles synthesized with the direct-precursor method was found to include titanium (41.55 %), oxygen (42.81 %), carbon (1.70 %) and calcium (0.86 %), demonstrating that the compositions for both methods are very similar and confirming that the composition includes some elements from the leaf extract.

From the size distribution shown on **Figure 2**, it can be observed how the synthesis method using the pure precursor exhibits smaller nanoparticles with an average size of 18.67 nm and a composition of titanium and oxygen. The comparison of the two methods shows that a higher quantity of nanoparticles was produced with the synthesis method that uses pure precursor, i.e., 1.00 g per synthesis, while the method using the precursor solution exhibits nanoparticles with an average size of 20.01 nm and a quantity of 0.05 g per synthesis.

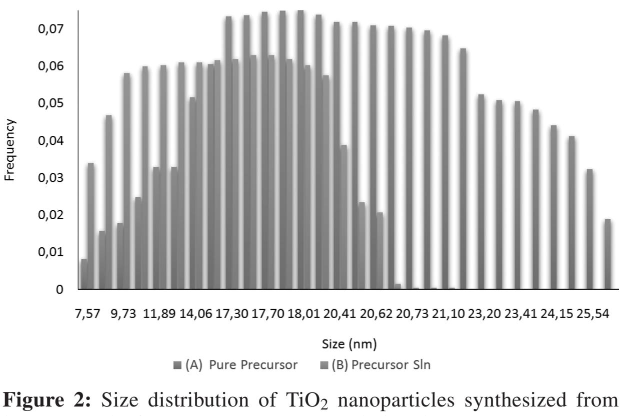

Figure 2: Size distribution of TiO_2 nanoparticles synthesized from lemongrass-leaf extracts: a) precursor solution, b) pure precursor

According to the results, both methods help us obtain TiO_2 nanoparticles with similar physicochemical characteristics. This result was achieved by controlling the preparation processes of the two performed methods.

The performance of the production of nanoparticles through synthesis (gram/synthesis) is better with the method using the direct precursor since a production of 1 gram is achieved. When using the method with the precursor solution, the synthesis would have to be performed twenty times to match the production of the nanoparticles obtained with the first method. The direct-precursor synthesis method facilitates a greater production of TiO_2 nanoparticles, maintaining the required properties of the size and shape through the control of the preparation process.

Also, it was found that, with respect to volume (mL), the performance of producing nanoparticles from a precursor was better with the method using a precursor solution; this is possibly due to the amount of the plant extract used in the synthesis, since that is the limiting reagent in the synthesis of TiO_2 nanoparticles. This can be maximized by increasing the amount of the plant extract to achieve a performance similar to the con-

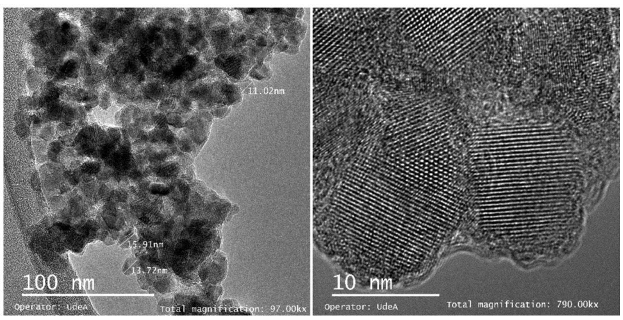

Figure 3: TEM micrographs of TiO_2 nanoparticles synthesized with green chemistry using pure precursor

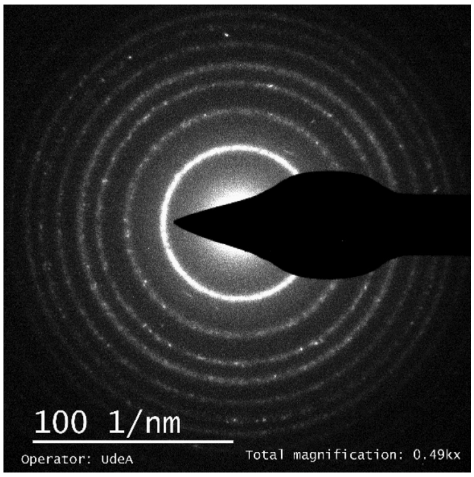

Figure 4: Electron-diffraction pattern of TiO_2 nanoparticles obtained with TEM

sumption of the precursor. Once the method with a better performance was identified, characterization tests of the TiO_2 nanoparticles obtained with the pure precursor were performed. These analyses included TEM (transmission electron microscopy) and XRD (X-ray diffraction) to confirm the shape, size and formation of the desired crystalline phase, in this case, anatase. **Figure 3** shows the micrograph obtained with TEM for the TiO_2 NPs synthesized with green chemistry.

In **Figure 3**, nanoparticles with a hemispherical shape are shown, having sizes between 11 and 16 nm and an elemental composition of titanium, having a large percentage of 65.93 % and 34.06 % of oxygen, carbon and nitrogen in low proportions. Additionally, an X-ray diffraction analysis was performed to confirm the desired anatase crystalline phase, where the qualitative analysis confirmed the presence of this phase in the titanium dioxide nanoparticles, in addition to the halos obtained with the electron diffraction of the TEM presented in **Figure 4**, where the circular shape of the halos confirms the presence of the anatase phase.[11,12]

The nanoparticles of the size obtained with the above methods can be used in different areas. In medicine, the implementation of nanoparticles synthesized with plant extracts is being investigated for the transport of medicines and complementary treatments.[13,14] In addition, NPs are implemented in crops, with the purpose of improving the properties of the soil and the growth of different plantations, having very positive results.[15,16]

4 CONCLUSIONS

In the present work, green-chemistry methods were evaluated to obtain TiO_2 nanoparticles with average sizes of 20.01 nm and 18.67 nm. The nanoparticles were obtained from lemongrass-leaf (*Cymbopogon citratus*) extracts and two methods of the precursor application were used. Also, the nanoparticles were characterized with SEM and EDX. With a direct implementation of the precursor, the preparation method allowed the highest production of nanoparticles, representing an attractive option for their production on a larger scale. The anatase crystalline phase of these TiO_2 nanoparticles was confirmed with X-ray diffraction and TEM. The implementation of this method will allow a process with shorter production times, lower costs and environmental impacts, the use of renewable sources such as lemongrass leaves, as well as a lower level of chemical-reagent consumption. These nanoparticles with sizes between 18.61 nm and 20.01 nm can be applied in the same way as the NPs synthesized with chemical methods because this size allows the nanoparticles to cover a larger surface area. They can be used as fungicides for crops and asphalt modifiers; they can also be used in the transport of crude oil, food preservation, waste-water treatment and in many other areas.

Acknowledgment

The authors thank Universidad Pontificia Bolivariana, Bucaramanga Headquarters and ECOPETROL – Instituto Colombiano del Petróleo I.C.P. for the support and financing of the research, carried out under the convention "Marco de Cooperación de Ciencia y Tecnología" No. 5226851 and "Acuerdo de Cooperación" (Cooperation Agreement) No. 09. Moreover, authors are grateful to Universidad de Cartagena for the technical support with the green synthesis of TiO_2 nanoparticles.

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