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Green Synthesis of Titanium Oxide Nanoparticles Using Natural Extracts

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Abstract

Green synthesis is an alternative method for obtaining nanoparticles for environmentally friendly purposes. The present work describes the synthesis and characterization of titanium oxide nanoparticles, starting from three natural sources: orange peel, hibiscus *rosa sinensis* and *Aloe vera*. Titanium (IV) tetrabutoxide in ethanol solution was used as precursor. The methodology used was based on the sol-gel technique, through which TiO_2 nanoparticles were obtained in the anatase phase. The characterization of the nanoparticles was carried out by means of x-ray diffraction (XRD), scanning electron microscopy (SEM) and infrared spectrophotometry (FTIR), which allowed the identification of a good degree of purity and crystallinity of the samples obtained.

Keywords

TiO_2, Nanoparticles, Green Synthesis, Sol-Gel Methodology, Natural Sources

1. Introduction

An important area of nanotechnology is related to the synthesis and characterization of nanomaterials [1], in addition to identifying and developing potential applications. The synthesis of nanomaterials has gained momentum in recent years, due to the fact that numerous uses and advantages have been identified, related to their structure and properties [2] [3], that make them ideal in applications diverse in fields such as medicine, electronics, chemical catalysis, the food industry, contaminant control, among others.

Within this area, the synthesis and characterization of nanoparticles of various materials is becoming a relevant research niche, due to the need to improve and adapt the synthesis methodologies used, and the search for better conditions for the reactions involved, which also includes minimizing the amount of possible waste, or the release of potentially hazardous substances into the environment.

In recent years, this last aspect has become more relevant, in what tends to be called the green synthesis of chemical substances or reagents, defined as that which takes into account aspects such as the use of harmless chemical or biological precursors, or the reduction or total absence of chemical residues that can be released into the surrounding environment. The green synthesis of nanoparticles, (NPs) has four main characteristics: simple procedures, non-toxic, economical, and ecologically friendly. Furthermore, green synthesis processes, do not formally require high temperatures or high pressures, as well as expensive equipment or reagents.

The uses of various natural sources to provide stabilizing agent and cover (coverage) to prevent agglomeration in the synthesis process, and thus contribute to achieving the desired shape and size of the TiO_2 particles, have been reported in the literature [4]. Within such natural sources, the literature indicates the leaves of aloe (*Aloe sp.*), the leaves of guava (*Psidium guajava*), leaves of trees or shrubs such as *Syzigium cumini*, *Moringa oleifera* or *Jatropha curca* [1] [3]. Other investigations [5] [6] have used extracts from flower petals, such as hibiscus (hibiscus sp.) or citrus peel.

The most used methodologies for the synthesis of metallic nanoparticles in general, have been those of the sol-gel type. In this type of procedure, the principle is based on two main phases or stages. In the first stage, the reagents, solvents or additives to be used are homogenized, normally at room temperature and using constant agitation to avoid the formation of granules or lumps. This type of procedures allows the gradual formation of the desired crystals through a process of nucleation, growth and subsequent precipitation.

In a second phase, the precipitate is separated from the liquid phase by filtration, accelerated with a vacuum pump. Subsequently, the solid obtained is washed with distilled water, to finally be dried and calcined. Some of the characteristics that affect the formation of nano-particulate crystals are the following: the type of solvent or additive used, and the effectiveness in initiating the formation and nucleation process.

In principle, sol-gel processes involve the transition from a liquid-state system (sol, which is a colloidal suspension of nanometric-sized solid particles), to a solid phase called "gel" [7], where this solid in turn is made of two phases: a liquid phase trapped and immobilized in a solid phase. The reactions involved in the formation are of two types: a hydrolysis followed by a condensation.

Normally, an inorganic titanium salt is used as a precursor, which undergoes a process of hydrolization and polycondensation of the colloidal suspension. The subsequent transformation to "gel" allows obtaining the nano-particulate material, which after a drying and calcination process, allows it to be obtained in the form of ceramic powder.

The importance of titanium oxide (TiO_2) nanoparticles lies in some of its properties, such as being thermally stable, poor soluble (it is hydrophobic), and it is not classified as a harmful or dangerous substance (according to the classification system and UN GHS chemical labeling [3]), one of its three crystalline phases, that of anatase, is characterized by having appropriate physical and chemical properties for various environmental remediation processes.

At the microscopic level, TiO_2 nanoparticles have high volume/radious ratio, in addition to a wide bandwidth that absorbs electromagnetic radiation in the UV region [7], characteristics that are related to their photo-sensitivity and photocatalytic reactions [6]. In this work, the synthesis of titanium oxide nanoparticles was carried out because this compound has various applications, among them, the removal of pollutants in water or the photo-degradation of atmospheric pollutants such as nitrogen oxides (NO_x), to mention a few [4].

2. Experimental Methodology

2.1. Preparation of Plant Extracts

In the case of *Aloe vera*, the leaf was selected and subsequently cut and washed with tap water followed by distilled water to remove dust particles and other contaminants, 50 g. of the leaves were weighed using and electronic balance and transferred to a 250 mL beaker containing 100 ml of distilled water. The content was heated for 2 hours at 90˚C. The extract was filtered using filter paper.

It was the sored in a place away from dust and sunlight to later be used in the synthesis of nanoparticles (**Figure 1**).

For the case of orange peel, 20 g of small pieces of fresh orange peel were taken in a beaker with 100 mL of deionized water and boiled for two hours. The extract was recovered by filtration (**Figure 2**).

Finally, for the extraction by means of *hibiscus rosa-sinensis* flowers, the flowers were collected in the town of Doxey, Hgo. The petals were obtained and dried in the shade (**Figure 3**). 5 g of dried petals were taken and placed in the beaker together 100 mL of water to be heated at 90˚C for 2 hours. The extract was filtered to remove impurities.

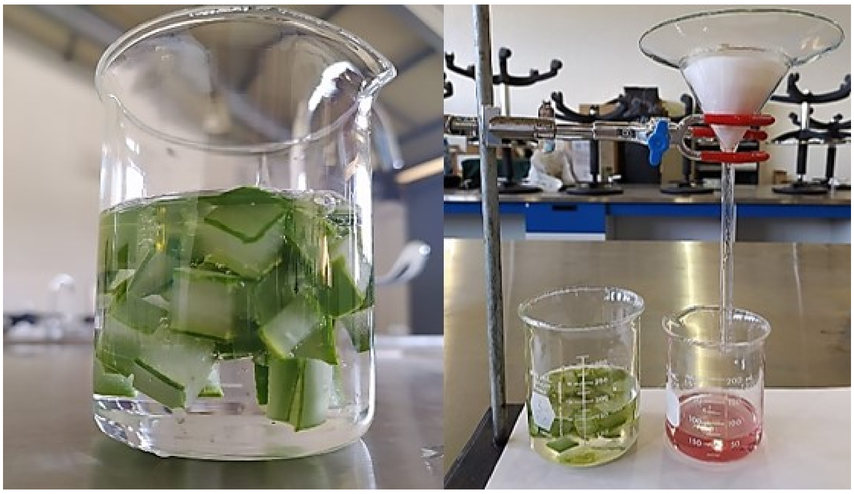

Figure 1. *Aloe vera* extraction process.

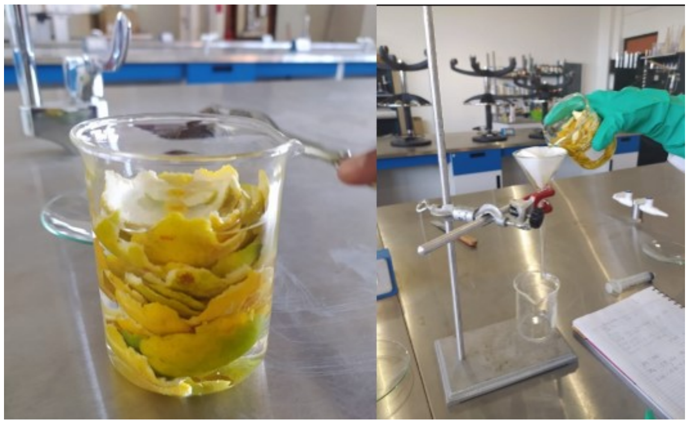

Figure 2. Orange peel extraction process.

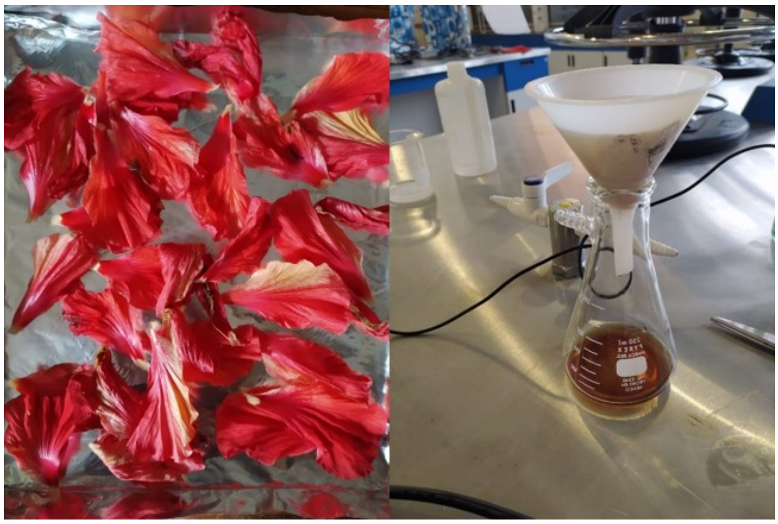

Figure 3. *Hibiscus rosa-sinensis* extraction process.

2.2. Preparation of Nanoparticles

In the case of the *Aloe vera* sample, for the synthesis of nanoparticles, a 1.0 M solution was prepared by dissolving Titanium Butoxide in Ethanol. The extract was added dropwise under constant stirring to brings its pH to 7. The mixture was kept stirring for 4 continuous hours. In this process, a white precipitate was formed that was subsequently separated using filter paper and the washed with distilled water to remove impurities. It was then subjected to heating in a drying oven at 100˚C for 24 hours and finally heat treatment at 500˚C for 4 hours (**Figure 4**).

For the orange peel samples, the NPs were prepared by dissolving 1.0 M of titanium butoxide in 100 mL of ethyl alcohol, then 10 ml of prepared extract was added slowly with magnetic stirring for 3 hours and the pH was maintained at 7. After the stirring process, the nanoparticles were deposited in the beaker and collected through Whatman No. 40 filter paper. The prepared NPs were washed several times with deionized water to remove impurities, dried at 100˚C for 10 hours and calcined at 500˚C for 4 hours (**Figure 5**).

Figure 4. Preparation of nanoparticles from *Aloe vera* extract.

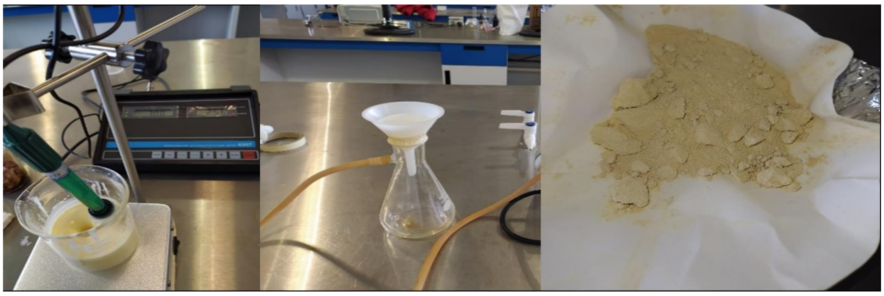

Figure 5. Preparation of nanoparticles using orange peel extract.

On the other hand, for the *Hibiscus rosa-sinensis* samples, a 1.0 N solution was prepared by dissolving 8.59 ml of titanium butoxide in 91.41 mL of ethyl alcohol. The flower extract was added dropwise with constant stirring to bring pH of the solution to a value of 7, subjecting the mixture to constant stirring for 3 hours. In this process the nanoparticles were formed, then they are separated by vacuum filtration. Finally, the nanoparticles were dried at 100˚C overnight and calcined at 500˚C for 4 hours (Figure 6).

3. Results and Discussions

The chemical method used, and the green synthesis using a polymeric precursor and controlled precipitation, allowed to obtain ceramic powders with anatase structure and nanostructured size. The synthesized ceramic powder presented a certain agglomeration as can be seen in the images of Figure 7, which when crushed, a fine powder was obtained (Figure 8).

Characterization of Nanoparticles

Figure 9 shows the diffractogram obtained from the hibiscus nanoparticle sample as well as the identified crystalline phase, which is anatase (TiO_2). The results were good according to card 84 - 11,285. The 2θ diffraction peaks were 25˚, 36˚, 37˚, 38˚, 47˚, 53˚, 54˚, 62˚, 68˚, 70˚, 74˚, 75˚, y 76˚ corresponding to the values of Miller indices (101), (103), (004), (112), (200), (105), (211), (204), (116), (204),

Figure 6. Preparation of nanoparticles using hibiscus rosa-sinensis extract.

Figure 7. Ceramic powder obtained for (a) *hibiscus* (b) *Aloe vera* (c) *orange peel* (from left to right).

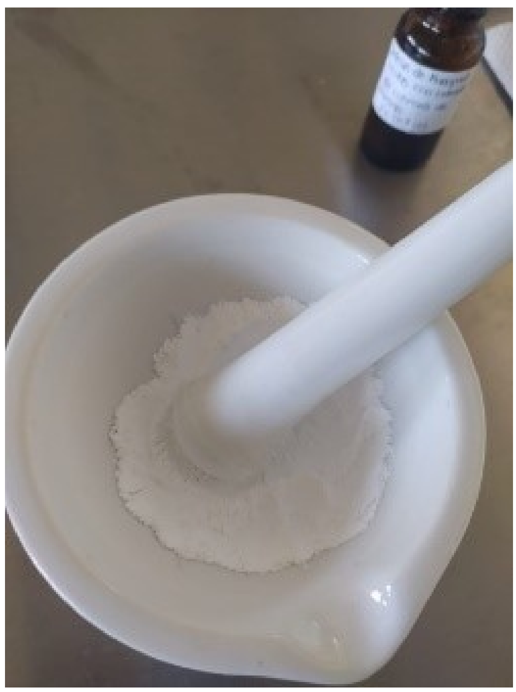

Figure 8. Fine powder of TiO_2 nanoparticles.

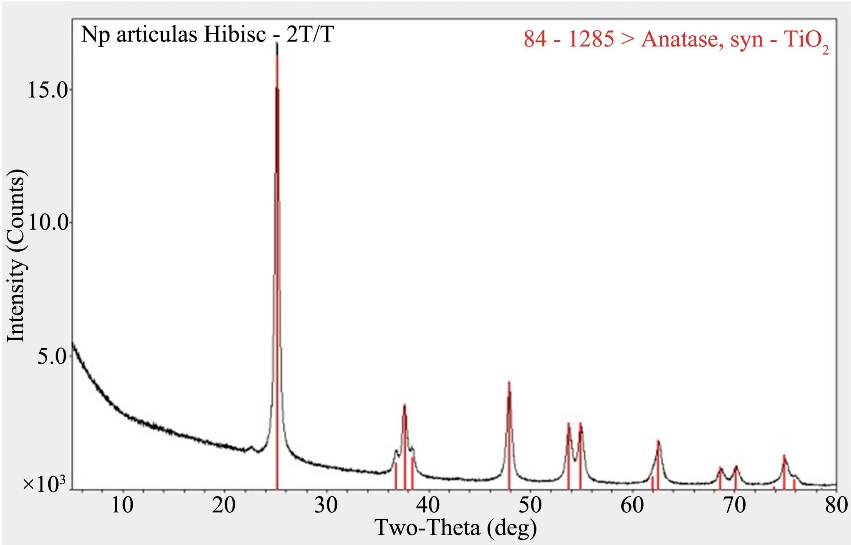

Figure 9. Diffractogram corresponding to the sample of nanoparticles obtained by hibiscus extract.

(215), and (301) respectively. It is observed that as the width of the peak increases, the size of the nanoparticle decreases, resembling the present material in the nano range.

The following figure shows the diffractogram obtained from the sample using orange peel extract (**Figure 10**), where the crystal structure corresponding to the anatase phase is observed. The diffraction peaks in 2θ are detected around 25˚, 36˚, 37˚, 38˚, 47˚, 53˚, 54˚, 62˚, 68˚, 70˚, 74˚ and 75˚ corresponding to the planes of Miller indices (101), (103), (004), (112), (200), (105), (211), (213), (204), (216), (220), (215) and (301) which correspond to card 84 - 1285 of the anatase phase structure.

The diffraction pattern of the nanoparticles synthesized by means of the *Aloe vera* extract is shown in **Figure 11**, where it is shown that the phase obtained corresponds to the structure in the anatase phase, because the 2θ diffraction peaks are at 25˚, 36˚, 37˚, 38˚, 47˚, 53˚, 54˚, 62˚, 68˚, 70˚, 74˚ and 75˚ corresponding to the Miller indices (101), (103), (004), (112), (200), (105), (211), (213), (204), (216), (220), (215) and (301), which match card 84 - 1285 of TiO_2 in anatase phase.

To determine the presence of functional groups, characterization was performed by Fourier Transform Infrared Spectroscopy (FTIR). **Figure 12** shows the spectra corresponding to the samples synthesized using three natural extracts, which are orange peel, Hibiscus rosa-sinensis and *Aloe vera*. In these spectra it can be seen that the structure was obtained in the anatase phase with the minimum of impurities, since they do not present other bands that indicate the presence of components other than Ti-O bonds.

In **Figure 12**, the spectra of the samples synthesized by green synthesis using the sol-gel methodology at 500˚C are reported. The region of the spectrum observed is between 4000 and 400 cm^{-1} where the characteristic TiO_2 bonds of

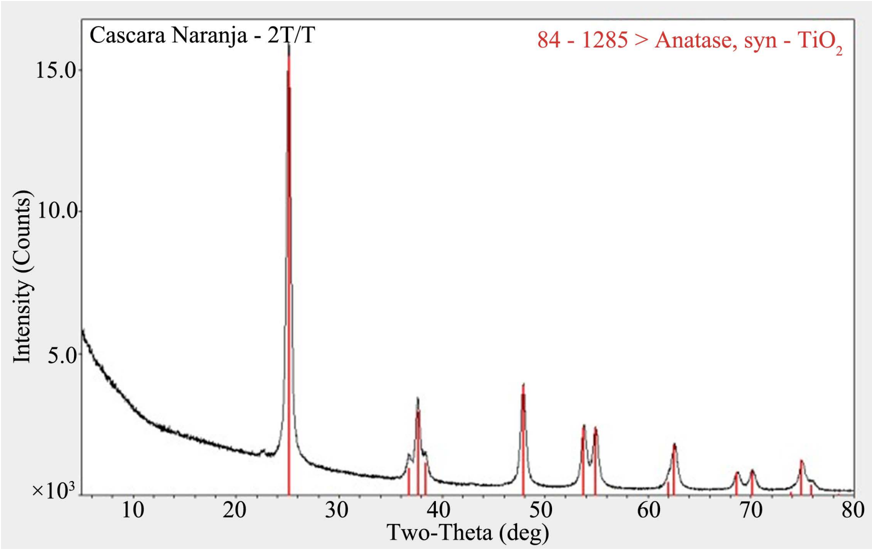

Figure 10. Diffractogram corresponding to NPs synthesized using *orange peel* extract.

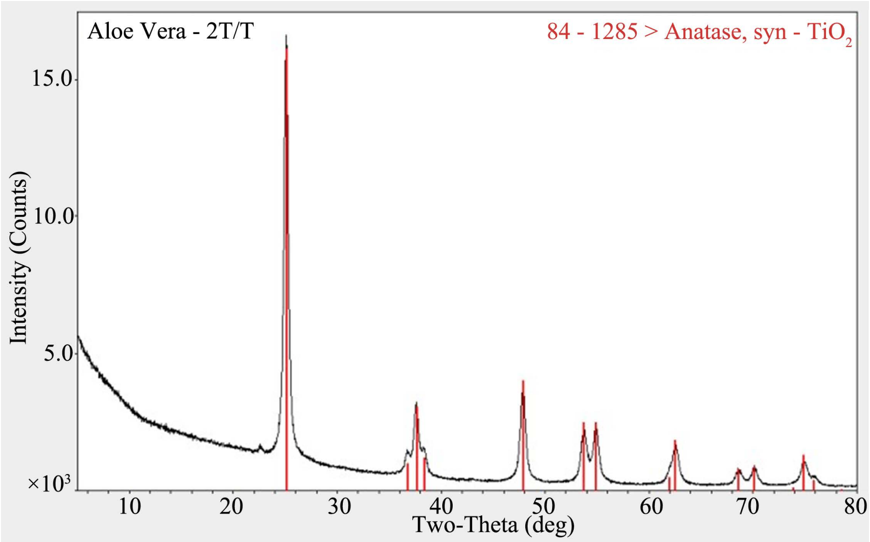

Figure 11. Diffractogram corresponding to TiO_2 NPs synthesized by *Aloe vera* extract.

anatase phase are found. There is a band around 400 cm^{-1} (Hibiscus at 434.95 cm^{-1}, *Aloe vera* at 432.94 cm^{-1} and orange peel at 450.92 cm^{-1}) that can be mainly assigned to Ti-O vibrational modes.

The analysis of the morphology and size of the samples was carried out in a Nova NanoSEM200 scanning electron microscope (SEM) of the FEI brand, using an acceleration voltage of 15 kV and Helix detector. The results are presented below in the form of micrographs. **Figure 13** shows the micrographs of the nanoparticles synthesized by green chemistry using hibiscus rosa sinensis extract, where agglomerate particles of spherical.

Figure 14 shows the micrographs of the particles synthesized with orange peel extract where agglomerate nanoparticles with better defined and spherical shapes are visualized, reaching nanometric sizes between 100 and 200 nm.

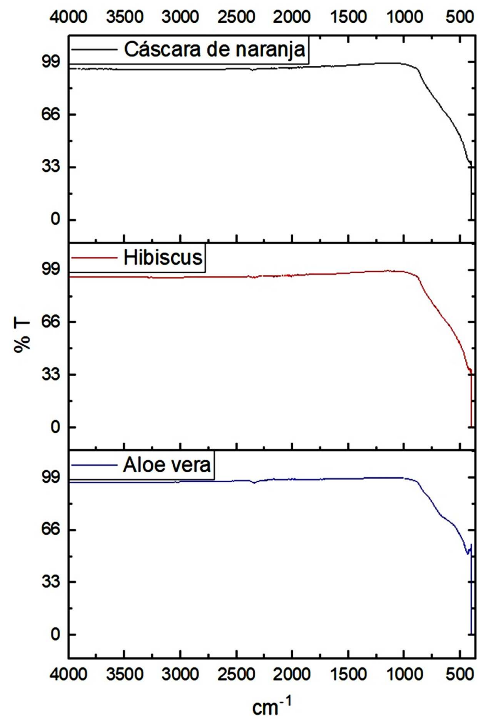

Figure 12. FTIR spectra of *Aloe vera*, *Hibiscus rosa-sinensis* and *orange peel* samples.

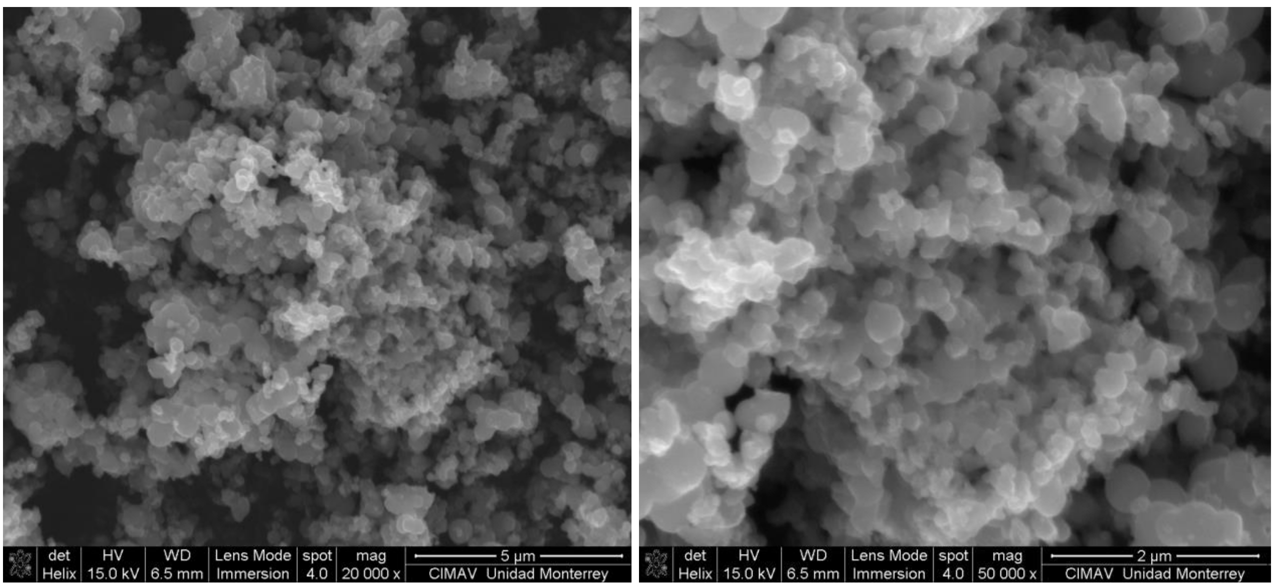

Figure 13. Micrographs of particles obtained by extract of *Hibiscus rosa sinensis*.

Finally, through the synthesis with *Aloe vera* extract, nanoparticles with a lower agglomeration are obtained and spherical particles with an approximate size of 100 nm are observed (**Figure 15**).

In general, the use of various inorganic titanium precursors as a source for obtaining TiO_2 nanoparticulate structures does not have a relevant effect on their physicochemical properties [8], although it is know that the synthesis method if it influences the photocatalytic properties of the product obtained.

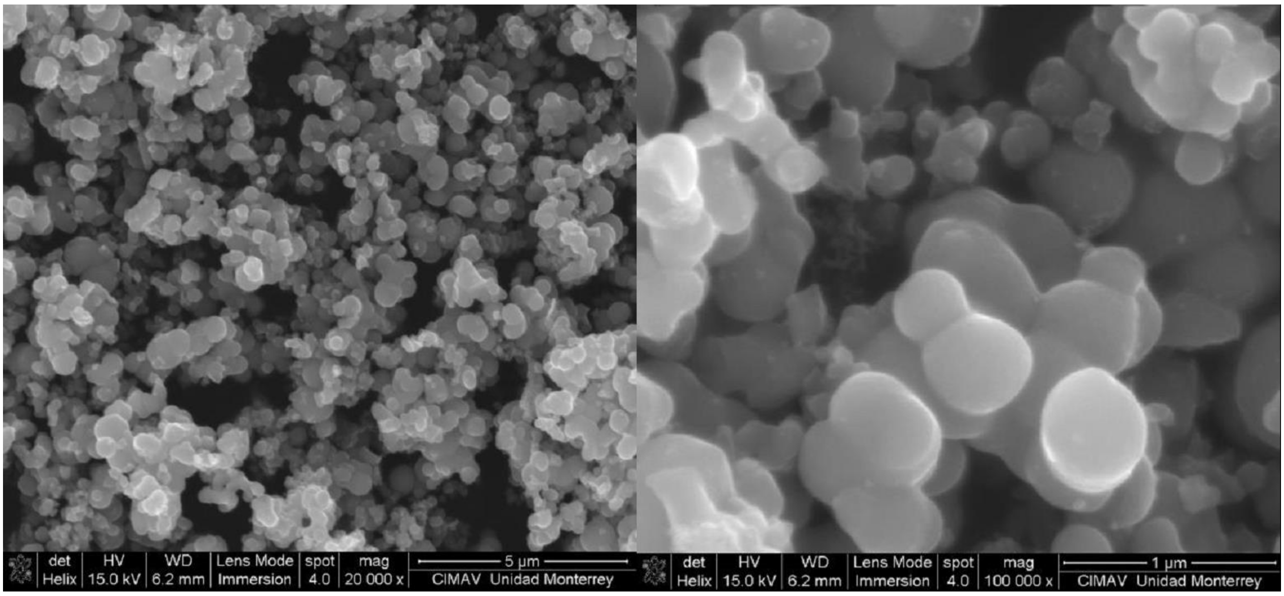

Figure 14. Micrographs of particles obtained by *orange peel* extract.

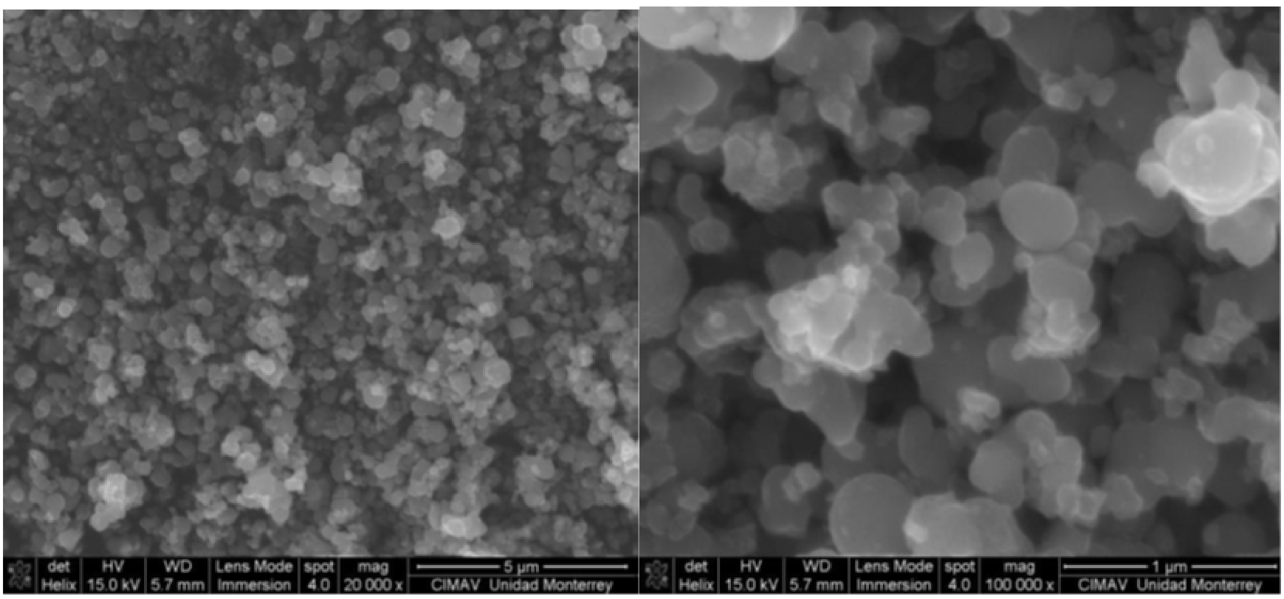

Figure 15. Micrographs of the particles obtained by *Aloe vera* extract.

In short, the results show that unlike other titanium precursors used such as isopropoxide or tetrachloride, in the case of this experimental proposal, some advantages derived from the use of titanium (IV) butoxide as inorganic precursor could be obtained.

In other works [9] it is reported that precursors such as those mentioned in the previous paragraph, in addition to be expensive, have the additional problem of being insoluble in water, due to their rapid hydrolysis when in contact with water or air. To overcome this disadvantage, we used a 1 M solution in ethanol, which allowed it to be kept stable prior to the main reaction.

Furthermore, in our case, the addition of some other chemical agent o reagent was not necessary, as has been the case with glacial acetic acid [10] or ammonium hydroxide or hydrogen peroxide [9] in analogous situations. The natural extracts used naturally contain agents that act for this purpose, as is the case of acemannan sugar found in the *Aloe vera* extract, and identified as a reducing and stabilizing agent. In general, it is reported in the literature that both properties are exhibited by various plant extracts, such as those used in our case.

4. Conclusions

TiO_2 nanoparticles were obtained by means of natural extracts such as orange peel, *Hibiscus rosa-sinensis* and *Aloe vera* extract, with a size of approximately 100 and 200 nm. XRD analysis showed a crystalline phase with anatase structure. It is important to compare the 3 sources used, in the sense that none of them showed greater advantages than another in terms of the degree of purity or crystallinity characteristics of the nanoparticles obtained.

There was also no notable incidence of the natural source used, on the reaction conditions or the use of titanium butoxide as a precursor, which would be reflected in the characteristics of the crystals formed. Due to the above, we consider that the most suitable natural source is only in relation to its availability and cost. It is also important to highlight that in any of the 3 cases, the generation of waste is practically nil, and with this we can confirm that green synthesis through natural extracts turned out to be viable for obtaining nanoparticles, in addition to being an accessible and economical method.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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