UNIVERSIDAD SAN FRANCISCO DE QUITO USFQ

Colegio de Ciencias e Ingeniería

Synthesis and Characterization of Gold nanoparticles and microparticles using citrus sinesis and solanum quitoense fruit extract

Amanda Eugenia García Faller

Física

Trabajo de titulación presentado como requisito

para la obtención del titulo de

Licenciado en Física

Quito, 18 de agosto de 2023

UNIVERSIDAD SAN FRANCISCO DE QUITO USFQ

Colegio de Ciencias e Ingeniería

HOJA DE CALIFICACIÓN DE TRABAJO DE FIN DE CARRERA

Amanda Eugenia García Faller

Nombre del profesor, Titulo académico: Pedro Ducos, PhD

August 18, 2023

© Derechos de Autor

Nombres y apellidos:	Amanda Eugenia García Faller
Código:	00206661
Cédula de Identidad:	1725835365
Lugar y fecha:	August 18, 2023

ACLARACIÓN PARA LA PUBLICACIÓN

UNPUBLISHED DOCUMENT

Acknowledgement

I am profoundly grateful to all the individuals who have supported and guided me throughout the journey of creating this project. Their unwavering encouragement, assistance, and inspiration have been fundamental in bringing this work to fruition.

First and foremost, I would like to express my heartfelt gratitude to my family. Their constant love, understanding, and patience have been my pillars of strength, motivating me to persevere through the challenges of this academic endeavor. Their unwavering belief in my abilities has been my driving force.

I extend my heartfelt thanks to my friends for their support. Their enthusiastic discussions, insightful feedback, and willingness to lend an ear during moments of doubt have been invaluable to me.

I am indebted to my academic advisors and mentors for their expert guidance and invaluable insights that shaped the direction of this thesis. Their dedication to teaching and commitment to excellence have greatly enriched my academic experience.

I would also like to express my appreciation to all the individuals who participated in my research, provided valuable input, or offered assistance in any form. Your contributions have significantly enhanced the quality of this work.

Lastly, I would like to thank the countless others whose names might not appear here but have played a role, no matter how small, in shaping my academic journey. Your collective support and encouragement have not gone unnoticed.

In conclusion, this thesis stands as a testament to the collaborative efforts of many. Without the unwavering support of my family, the encouragement of my friends, and the guidance of my mentors, this endeavor would not have been possible.

Thank you all for being a crucial part of my journey.

Sincerely,

Amanda

Resumen

Los extractos de Citrus sinensis (naranja) y Solanum quitoense (naranjilla) se utilizan en esta investigación para estudiar la síntesis y caracterización de nanopartículas de oro. El objetivo de la investigación fue determinar cómo las diversas proporciones de extracto afectaban las características morfológicas de las nanopartículas sintetizadas. Las nanopartículas de Citrus sinensis tenían una forma triangular única, mientras que las de Solanum quitoense tenían una morfología cúbica. Las nanopartículas sintetizadas se analizaron utilizando métodos como la microscopía electrónica de barrido (SEM) y la difracción de rayos X (XRD).

La investigación demostró una tendencia significativa en la variación del tamaño de las partículas. Un aumento en la cantidad de extracto de fruta resultó en una reducción constante en el tamaño de las partículas, independientemente del extracto de fruta utilizado. Este resultado destaca la importancia de la cantidad de extracto como factor clave que afecta las dimensiones finales de las partículas.

Palabras clave: *nanopartículas de oro, Citrus sinensis, Solanum quitoense, microscopía electrónica de barrido, difracción de rayos X*

Abstract

In this work, the synthesis and characterisation of gold nanoparticles utilizing extracts from Solanum quitoense (naranjilla) and Citrus sinensis (orange) are explored. The goal of the study was to determine how varied extract proportions affected the morphological properties of the produced nanoparticles. Citrus sinensis extract-produced nanoparticles had a recognizable triangular shape, but Solanum quitoense-produced nanoparticles had a cubic morphology. The produced nanoparticles were examined using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

The study discovered an interesting pattern in particle size variation. Increases in fruit extract concentration consistently resulted in smaller particle sizes, regardless of the type of fruit extract utilized. This result emphasizes how important the extract amount is as a factor affecting the final particle dimensions.

Keywords: *gold nanoparticles, Citrus sinensis, Solanum quitoense, scanning electron microscopy, X-ray diffraction*

Contents

List of Figures

Chapter 1

Introduction

Due to their small size and substantial surface area, nanoparticles are distinctive nanoscale materials with exceptional features, such as biocompatibility, catalytic activity and enhanced optical properties. The gold atoms that make up gold nanoparticles can be arranged in a variety of shapes, such as spheres, rods, stars, cages, and even triangles. Based on size, spherical gold nanoparticles are renowned for their stability and different colors based on shape. Nanoparticles with a rod shape have tunable optical characteristics and are used in imaging [1]. The branched structure of star-shaped nanoparticles make them perfect for spectroscopy [2]. With their distinctive geometries, cage-shaped and triangular gold nanoparticles are intriguing and provide fascinating potential for a variety of applications, for example, photo-thermal therapy[3] since they strongly absorb light in the near infra-red region which has high light transmission in tissue. The distinctive characteristics of both gold nanoparticles and microparticles continue to be explored, offering promising prospects for cutting-edge advancements across various disciplines. Metal nanoparticles such as gold (Au) and silver (Ag) have recognized importance in chemistry, physics, and biology because of their unique optical, electrical, and photothermal properties [4, 5].

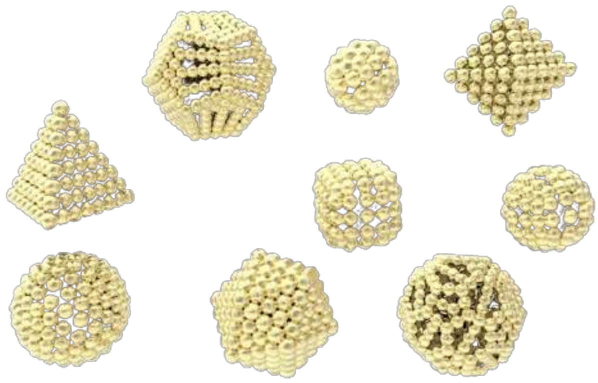


Figure 1.1: Gold Nanoparticle structure diagram

Gold nanoparticles, typically with sizes ranging from 1 to 100 nanometers, exhibit unique physicochemical properties due to their small size and high surface area-to-volume ratio. These properties make them highly attractive for applications in biomedicine [3], catalysis, electronics, and environmental remediation. On the other hand, gold microparticles, which are larger with sizes ranging from 100 to 1000 micrometers, possess different properties and are used in diverse applications, including as catalyst supports, additives in composites, and in the fabrication of electronic devices.

Toxic chemicals and energy-intensive processes are frequently used in conventional synthesis methods, which adds to environmental problems. In response, the idea of "green synthesis"—which emphasizes the use of environmentally friendly and sustainable methods to generate nanomaterials—has evolved [6]. If noble metal nanoparticles are to be manufactured on a large scale, then considering green chemistry principles will be important for their widespread industrial adoption [7]. During the past years as an approach for a greener method of synthesizing gold nanoparticles, various plant extracts, such as *Hibiscus rosa sinensis* extract [8] and one that came from the combination of several different plants [9], have been studied, as well as other fruits [10, 11].

The goal of this project is to investigate the environmentally friendly synthesis and characterisation of gold nanoparticles and microparticles utilizing orange (citrus sinesis) and naranjilla (solanum quitoense) juice as a natural reducing agent. A reducing agent is a substance that donates electrons or hydrogen atoms to another chemical species during a chemical reaction. This transfer of electrons or hydrogen atoms results in the reduction of the other species, while the reducing agent itself gets oxidized. As a commonly available fruit extract rich in citric acid, ascorbic acid (vitamin C), and other antioxidants, the juice from these fruits can be used as an innovative and ecologically friendly substitute for conventional reducing agents. By using environmentally friendly reducing agents, green synthesis approaches its goal to minimize the environmental impact and promote sustainability in nanoparticle production.

In nanoparticle synthesis, citric acid as well as ascorbic acid, both present in considerable quantities in the fruits used, has been used as a reducing agent for the preparation of various metal nanoparticles, including silver, gold, and iron nanoparticles[12, 6]. It can effectively reduce metal ions to their corresponding metal nanoparticles when combined with the appropriate reaction conditions. Citric acid also acts as a stabilizing agent in some cases, preventing the agglomeration of nanoparticles and providing colloidal stability. On the other side ascorbic acid gets its reducing properties from the presence of two adjacent hydroxyl groups and a carbonyl group in its chemical structure.

For chemical synthesis of gold nanoparticles the gold ion precursor - in this case tetrachloroauric acid trihydrate $HAuCl_4$- is generally mixed with sodium citrate ($Na_3C_6H_5O_7$), which is an ion of citric acid with either one, two or three sodium Na atoms. Upon addition, sodium citrate, with its functional groups, acts as a reducing agent. It donates electrons to the gold ions ($Au_3{}^+$) in $HAuCl_4$. As a result, the gold ions go through reduction, leading to the formation of neutral gold atoms (Au_0). The reduction of gold ions results in the nucleation of gold atoms. Nucleation refers to the formation of small clusters or seeds of gold atoms, which serve as the building blocks for the growth of gold nanoparticles. The reduced gold atoms continue to aggregate and grow, forming gold nanoparticles. The rate of growth is influenced by the concentration of the gold precursor and the reducing agent. The growth process can be controlled by adjusting these concentrations and the reaction conditions. This synthesis method is known as Turkevich method [13].

$$6\,HAuCl_4 + Na_3C_6H_5O_7 + 5\,H_2O \longrightarrow 6\,Au + 6\,CO_2 + 21\,HCl + 3\,NaCl$$

By utilizing the reducing power of orange and naranjilla juice and adjusting reaction conditions to control particle size and form, we aim to develop a green synthesis technique for producing gold nanoparticles and microparticles. In addition we mean to thoroughly describe the synthesized nanomaterials by examining

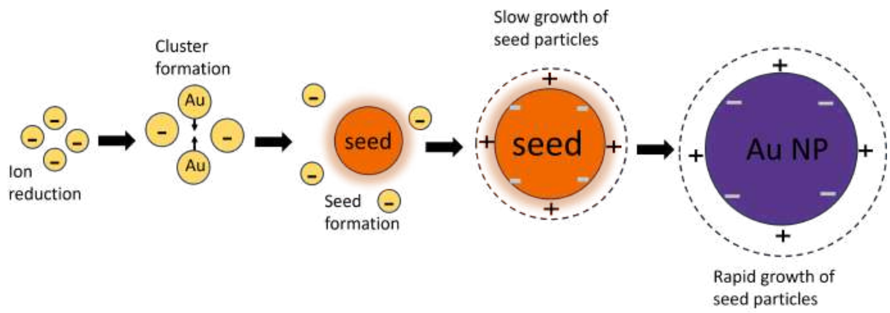


Figure 1.2: General growth mechanism of the Turkevich synthesis

their morphological, and structural characteristics using X-ray diffraction (XRD) and Scanning Electron Microscope (SEM).

Chapter 2

Methods

2.1 Preparation of the fruit extract

2.1.1 Citrus Sinesis

For the production of the extract used in the samples examined we used twenty oranges to normalize the amount of reducing agents present in each individual fruit. The oranges were washed, to prevent contaminants such as dirt or pesticides, that can be present in the skin of the oranges, to sip into the extract. Afterwards the same fruits were squeezed to obtain pure juice. The juice was filtered through paper coffee filters, which were changed every half an hour to optimize the time it took to filter. From that, the extract was centrifuged at 4000 rpm for 10 minutes to remove solids.

2.1.2 Solanum Quitoense

When making the extract from naranjilla, the natural frozen pulp was utilized. This pulp is the result of blending multiple naranjillas and was frozen for preservation. This gives a good normalized sample. The pulp was defrosted and then filtered through a reusable cloth coffee filter. The extract obtained was centrifuged at 4000rpm for 12 minutes to remove the solids.

2.2 Synthesis

The same synthesis process was used for all the samples analized from both fruits. A solution of $HAuCl_4$ at 1mM was prepared, and heated at 50°C for an hour, in a magnetic hot plate. For each sample 25ml of the gold ion precursor $HAuCl_4$ was heated in the same hot plate, until it reached 90°C. At that temperature the reducing agent was added. The mixture was stirred by a magnetic stirrer and kept at 90° for an hour, before removing from the heat and left to cool. For the naranjilla samples, the amount of extract added to the $HAuCl_4$ solution was (in mililiters): 3, 6, 10, 13, 17, 20, 23, 26, 30, and 33. For the Orange samples it was: 5, 10, 15, 20, 25, 30, 35, 40, 45 and, 50 mililiters.

2.3 X-ray Diffraction

The XRD peak broadening is inversely proportional to the crystallite size. A crystallite is a small, distinct, and crystallographically coherent region within a larger crystalline material. By analyzing the peak broadening in the XRD pattern, researchers can estimate the average size of the gold nanoparticles. Also, XRD helps in identifying the presence of any impurities or other phases that might be present in the synthesized gold nanoparticles.

To properly analyze the samples in the diffractometer, 20 drops of each one were put in a silicon plate and left to dry in a chamber with a drying agent for at least 48 hours. The instrument used was a Bruker D8 Advance Eco, with a copper tube. Once the samples were no longer liquid, they were placed as smoothly as possible in the Si low background sample holder. The gold nanoparticles were measured in the rotary stage, starting 2θ at 35 up to 70 degrees, range broad enough to see the characteristic diffraction pattern for gold. 0.025 degree increments and 2s per step. The X-ray generator was set at 40kV an 15mA.

Determining the size of gold nanoparticles from the X-ray diffraction (XRD) pattern involves analyzing the peak broadening observed in the XRD data. The Scherrer equation is commonly used to estimate the average crystallite size of the nanoparticles from the XRD data.

The Scherrer equation is given by:

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{2.1}$$

Where D is the average crystallite size, or particle size of the nanoparticles. K is the Scherrer constant, which is typically around 0.9. The value of K depends on the shape of the crystalline domains and is often used as an approximation. λ is the wavelength of the X-ray used for the measurement β is the full width at half maximum (FWHM) of the dominant diffraction peak in radians. θ is the angle at which the diffraction peak occurs in radians, also known as Bragg angle.

To find the FWHM the measurements were processed in OriginLab. The base line of each one was removed, and they were normalized. From there a Lorentz fit was utilized to find the width, which was plotted for the porcentual concentration.

2.4 Scanning Electron Microscope

To study the morphology and size of the gold nanoparticles a Scanning Electron Microscope (SEM) was used. This is an advanced microscopy technique that uses a focused beam of electrons to image the surface of a sample at high resolution.

For the bigger nanoparticles, and microparticles, the sample was scanned using SED (Secondary Electron Detector). This scan mode involves detecting secondary electrons released from the sample's surface after it has been hit with a concentrated electron beam. SED imaging provides high-resolution images with a three-dimensional appearance which offer precise information on the sample's surface topography and shape.

As the particle size became smaller, the technique changed to Backscattered

Electrons (BSE). It works since other primary electrons undergo scattering upon interacting with the atoms in the sample. Some of these backscattered electrons have higher energies than secondary electrons and are collected and detected.

The images collected from the SEM scans are then examined with ImageJ software that can process images and calculate the area of the particles. The data collected from this software was transferred to OriginPro to analyze and create an histogram for the particle diameter with each concentration of reducing agent. Also, the average diameter vs the porcentual concentration was plotted.

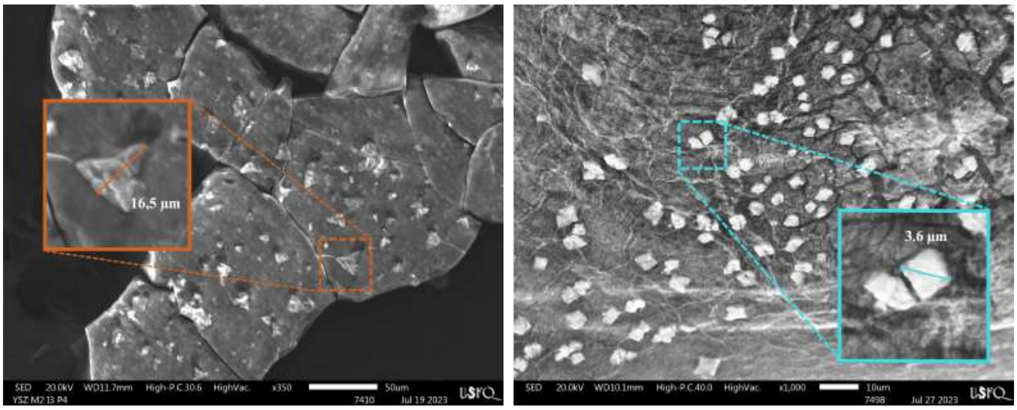
Chapter 3

Results

3.1 SEM results

From the synthesis method we were able to obtain gold microparticles and nanoparticles which vary in shape depending on which fruit extract was used, as shown in 3.1

The previous example crearly shows how the addition of Citrus Sinesis extract (in this case 10%) results in particles with a triangular shape. In the case of Solanum Quitoense (10%) the predominant shape of the microparticles is cubic. Given the reaction conditions were the same for every sample the change in shape may be due to the change in concentration of the different reducing and stabilizing agents present in each fruit, for example, the amount of citric acid is different in solanum quitoense and citrus sinesis. Different reducing agents may interact with



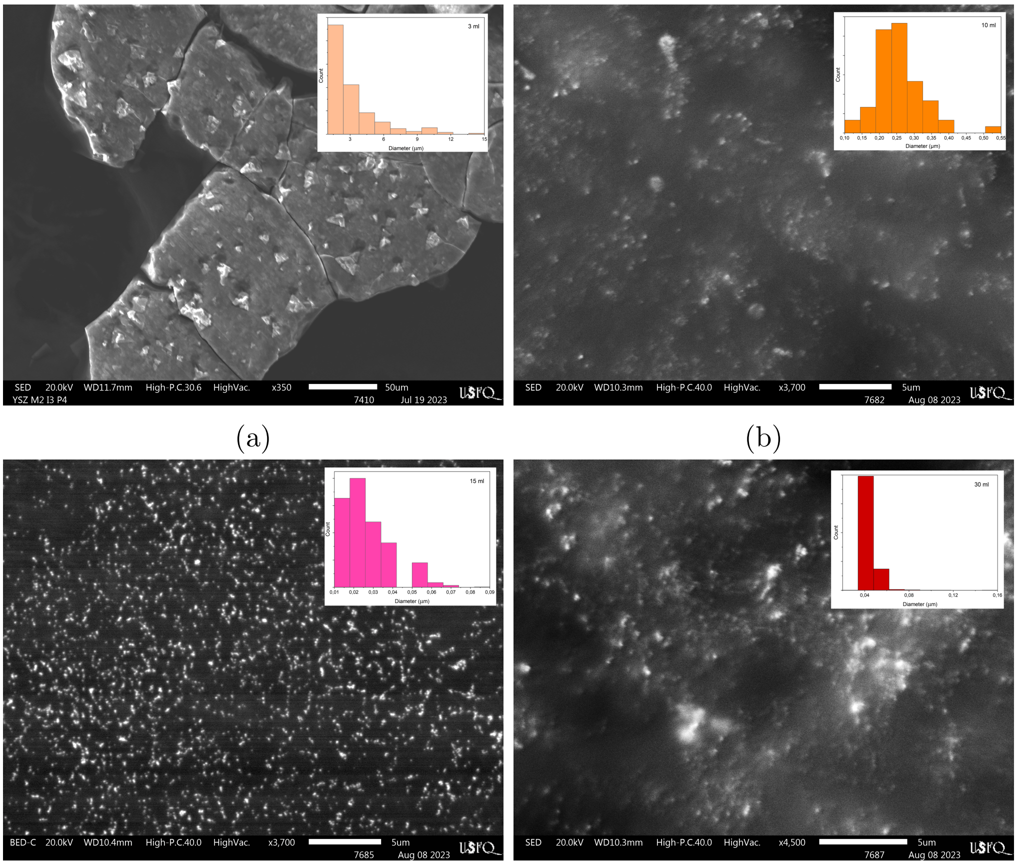
(a) (b)

Figure 3.1: Gold microparticles shapes (a)Citrus sinesis 10% (b) Solanum quitoense 10%

the gold ions and surface atoms in a way that favors the growth of certain facets over other leading to preferential growth along specific directions.

Utilizing the ImageJ software, a robust and widely recognized tool in the realm of image analysis, we engaged in a quantitative assessment of the geometric attributes of the gold microparticles and nanoparticles. This entailed the meticulous determination of particle area, which subsequently facilitated the derivation of diameter distributions across varying concentrations, as visually depicted in Figure 3.2 and Figure 3.1a.

It is notable that these figures collectively capture the intricate relationship between concentration and diameter within our experimental samples. The distributions portray the spectrum of particle sizes and their respective prevalence, thereby facilitating an objective comprehension of the heterogeneous sizes of the investigated particles at different concentration levels. We examined 4 different concentrations for each fruit. For the citrus sinesis samples 10%, 28%, 37% and



(a) (b)

(c) (d)

Figure 3.2: SEM Image and diameter distribution for gold nanoparticles made with citrus sinesis (a) 10% orange extract (b) 28% orange extract (c) 37% orange extract (d) 55% orange extract

55% extract, and 10%, 28%, 40% and 48%. It is notable in the change of range in the diameter for each image that the particle size seems to be decreasing.

The average diameter decreases in size exponentially as the percentage of fruit extract is increased. This happens for both fruits. As explained before, the reducing agent lends electrons to the gold ion $(Au)_3{}^+$ to form neutral atoms $(Au)_0$ which undergo nucleation, increasing the concentration of the reducing agent means there are more electrons available which affects the reduction rate therefore the nucle-

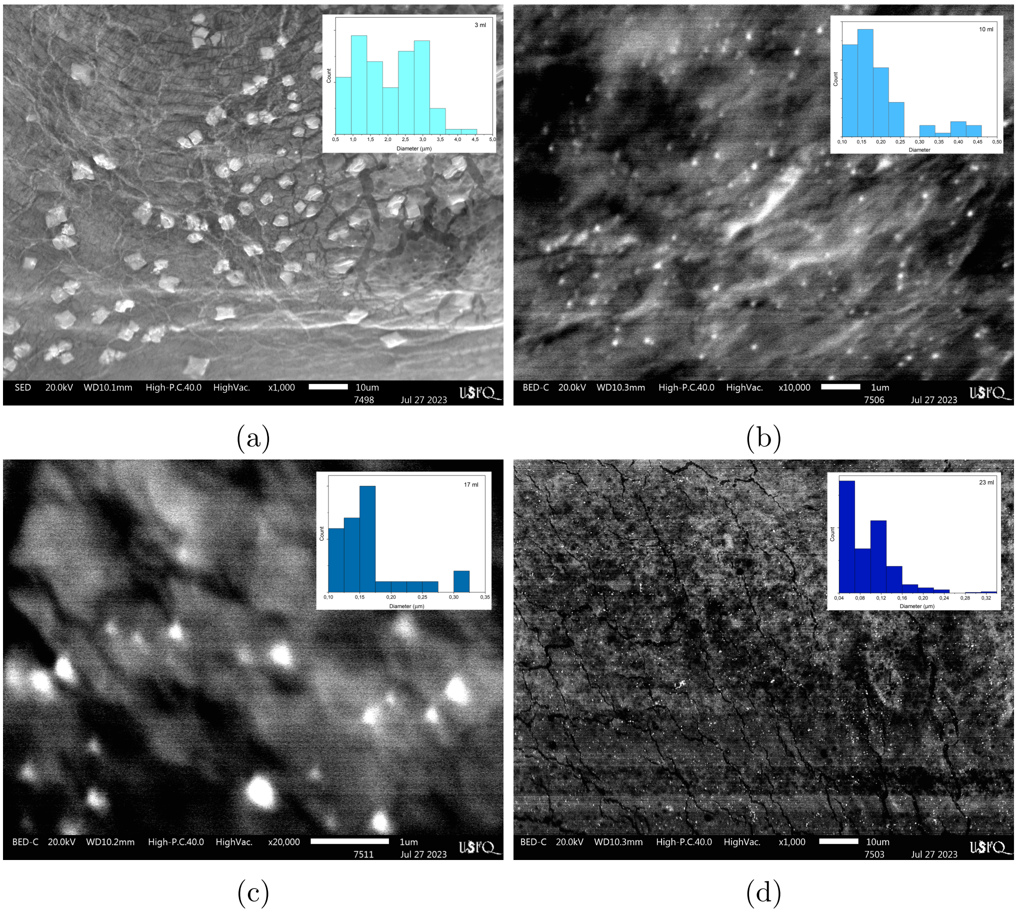
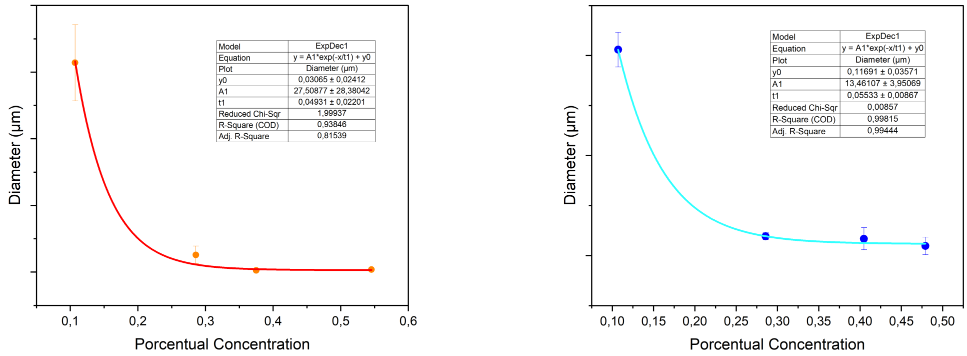


Figure 3.3: SEM Image and diameter distribution for gold nanoparticles made with solanum quitoense (a) 10% naranjilla extract (b) 28% naranjilla extract (c) 40% naranjilla extract (d) 48% naranjilla extract

ation process. The high concentration of gold atoms in the solution can promote the nucleation of new gold atoms and the growth of additional nanoparticles. So, if the reduction reaction is extremely rapid due to excessive reducing agent, it can lead to rapid nucleation and smaller-sized nanoparticles. The results shown in 3.4 are consistent with the Kumar model [14], which explains this process. The error bars for this figures have been enlarged to ensure their visibility, however, the standard deviation from which each has been selected is quite small, this information was obtained from the distibution analysis previously shown in 3.2 and 3.1a.

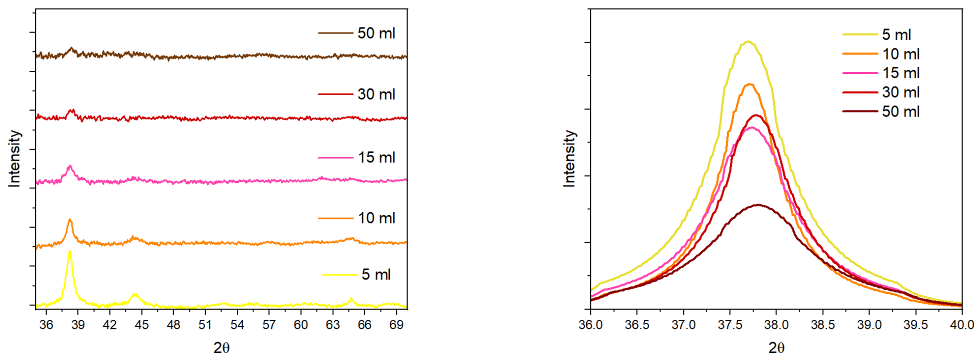


(a) (b)

Figure 3.4: Average diameter for gold nanoparticles vs extract percentual concentration (a) Citrus sinesis (b) Solanum quitoense

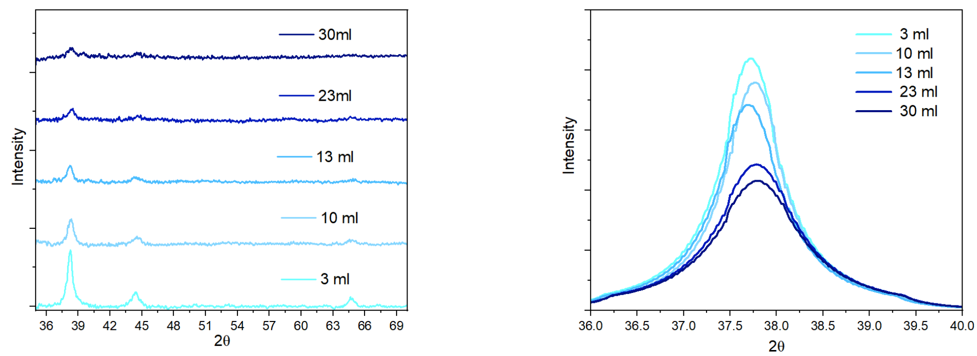
3.2 XRD results

The X-ray diffraction (XRD) analysis was conducted to gain insights into the crystalline structure of the synthesized gold nanoparticles. The results for the X-ray diffraction analysis are presented in Fig 3.5 and 3.6. From the diffraction patterns 3.5a and 3.6a, exhibit distinct diffraction peaks that correspond to different crystallographic planes. Notably, the peaks observed at 2Θ values of 38.2°, 44.4°, and 64.6° are in excellent agreement with the reference values for the (111), (200) and (220) planes of face-centered cubic (FCC) gold, respectively. This pattern confirms the predominance of the FCC crystal structure in the synthesized nanoparticles. In both cases we can see that the peaks were consistent with standard database files (JCPDS card No 04-0784), with no other peaks, indicating their purity.



(a) (b)

Figure 3.5: Citrus sinesis X-Ray Diffraction pattern (a) XRD pattern for gold nanoparticles at 5 different concentrations of orange extract (b) Principal peak, located at a 38° Bragg angle at 5 different concentrations of orange extract



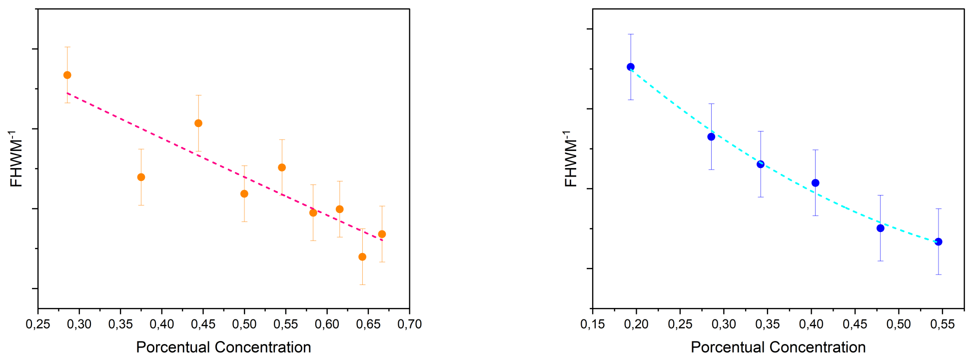
(a) (b)

Figure 3.6: Solaum Quitoense X-Ray Diffraction pattern (a) XRD pattern for gold nanoparticles at 5 different concentrations of naranjilla extract (b) Principal peak, located at a 38° Bragg angle at 5 different concentrations of naranjilla extract

A notable pattern becomes apparent when examining Figures 3.6b and 3.5b. With a progressive increase in the quantity of fruit extract, a distinct trend of broadening and truncation in the dominant peak comes to the forefront. This transformation is accompanied by a notable expansion in the Full Width at Half

Maximum (FWHM) of the peak. This aligns seamlessly with 2.1, which establishes an inverse relationship between the FWHM and the crystallite size. In essence, this correspondence underscores that as the broadening of the peak intensifies, the dimensions of the crystallite concurrently decrease, thereby inducing a proportional reduction in particle size.

Figure 3.7 graphically illustrates the diminishing trend in the reciprocal of the width concerning the percentage concentration. This decline unequivocally indicates a reduction in the crystallite size. Notably, this scaling down of the crystallite size is congruent with the observed reduction in size, as revealed by the SEM results. However, the fitted nonlinear curve shown in the graphics is a polynomial aproximation to the trend of the data.



(a) (b)

Figure 3.7: $FWHM^{-1}$ vs extract porcentual concentration (a)Citrus sinesis (b)Solanum quitoense

Chapter 4

Conclusions

Using citrus sinesis and solanum quitoense fruit extract as a reducing agent for the synthesis of gold nanoparticles and microparticles proved to be effective. The use of these natural extracts offers a green and eco-friendly method of synthesizing nanoparticles.

The shapes of said particles varies for each fruit, in the first case, the microparticles turned out to have a triangular shape, whereas in the second they were cubic. This demonstrates that the final geometry of the nanoparticles is significantly influenced by the selection of fruit extract.

Scanning Electron Microscopy (SEM) analysis provided detailed insights into the surface morphology and structure of the synthesized nanoparticles. The high-resolution images revealed the characteristic shapes and allowed us to observe the intricate details of the nanoparticles. From the SEM images we were able to prove that the average size of the nanoparticles decreases as the amount of reducing agent increases. This happens for both fruits, and the decay is exponential.

X-ray Diffraction (XRD) analysis further confirmed the crystalline nature of the synthesized nanoparticles. The diffraction patterns matched the expected crystallographic planes for gold, validating the successful formation of gold nanoparticles. The enlargement of the full width at half maximum results in a smaller crystallite, which aligns with the results from the average diameter.

In conclusion, the use of extracts from Citrus sinensis and Solanum quitoense as reducing agents demonstrates their potential as efficient eco-friendly substitutes in the synthesis of nanoparticles. The different forms that each extract produced and the steady trend of particle size reduction offer important information about the processes regulating the synthesis process. This work emphasizes the value of environmentally friendly methods for creating nanomaterials and sets the door for more research in the area of green nanotechnology.

Bibliography

[1] A. Hohenau, J. R. Krenn, G. Schider, H. Ditlbacher, A. Leitner, F. R. Aussenegg, and W. L. Schaich. Optical near-field of multipolar plasmons of rod-shaped gold nanoparticles. *Europhysics Letters*, 69(4):538, jan 2005.

[2] Laura Rodriguez-Lorenzo, Ramon A Alvarez-Puebla, F Javier Garcia de Abajo, and Luis M Liz-Marzán. Surface enhanced raman scattering using star-shaped gold colloidal nanoparticles. *The Journal of Physical Chemistry C*, 114(16):7336–7340, 2010.

[3] Maryam Hajfathalian, Ahmad Amirshaghaghi, Pratap C Naha, Peter Chhour, Jessica C Hsu, Keely Douglas, Yuxi Dong, Chandra M Sehgal, Andrew Tsourkas, Svetlana Neretina, et al. Wulff in a cage gold nanoparticles as contrast agents for computed tomography and photoacoustic imaging. *Nanoscale*, 10(39):18749–18757, 2018.

[4] Soundarapandian Kannan Mohanan V. Sujitha. Green synthesis of gold nanoparticles using citrus fruits (citrus limon, citrus reticulata and citrus sinensis) aqueous extract and its characterization. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, pages 15–23, 2020.

[5] et.al M. Cortez-Valadez. Green synthesis up to geometric gold microparticles. *Journal of Inorganic and Organometallic Polymers and Materials*, page 1079–1085, 2020.

[6] Rostelato Daruich De Souza, Ribeiro Nogueira. Review of the methodologies used in the synthesis gold nanoparticles by chemical reduction. *Journal of Alloys and Compounds*, pages 714–740, 2019.

[7] Terry P. Bigioni Badri Bhattarai, Yeakub Zaker. Green synthesis of gold and silver nanoparticles: Challenges and opportunities. *Current Opinion in Green and Sustainable Chemistry*, 2018.

[8] Daizy Philip. Green synthesis of gold and silver nanoparticles using hibiscus rosa sinensis. *Physica E*, page 1417–1424, 2010.

[9] et.al Paz elia. Green synthesis of gold nanoparticles using plant extracts as reducing agents. *International Journal of Nanomedicine*, page 4007–4021, 2014.

[10] Ch.Murthy R.S.Rimal Isaac, G.Sakthivel. Green synthesis of gold and silver nanoparticles using averrhoa bilimbi fruit extract. *Journal of Nanotechnology*, page 6, 2013.

[11] Anna Timoszyk. A review of the biological synthesis of gold nanoparticles using fruit extracts: scientific potential and application. *Bulletin of Materials Science*, 2018.

[12] et.al Kai Sun. Preparation and characterization of gold nanoparticles using ascorbic acid as reducing agent in reverse micelles. *Journal of Materials Science*, page 754–758, 2008.

[13] et.al Maria Wuithschick. Turkevich in new robes: Key questions answered for the most common gold nanoparticle synthesis. *ACS Nano*, page 7052–7071, 2015.

[14] Sanjeev Kumar, KS Gandhi, and R Kumar. Modeling of formation of gold nanoparticles by citrate method. *Industrial & Engineering Chemistry Research*, 46(10):3128–3136, 2007.