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Amal F Kamil
Open Educational College, Wasit Center, Iraq

Corresponding Author:
Amal F Kamil
Open Educational College, Wasit Center, Iraq

Green synthesis and eco- friendly methods to preparation of zinc oxide nanoparticles by extract of plants

Amal F Kamil

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Abstract
Nanomaterials rely primarily on the size and the crystalline form (large surface area) in determining the effectiveness of nanoparticles, besides the type of synthesized method and their importance in various applications. Extracting the nanoparticles (Zno Nps) from plants and studying their structural and light. Zno Nps is extracted from plants using the green extraction method. A comparative study was done in the latest literature on green synthesis of zinc nanoparticles using environmentally friendly methods by plant extracts. The result was found that everything mentioned by all researchers agreed that the size of nanoparticle depends primarily on several factors (pH, concentration, temperature and time), as all of these factors play a major role in the size of the zinc oxide nanoparticle. Zno Nps can be extracted from plants using the green extraction method. The extracted particles were of good structural and optical properties, making them suitable for different applications in areas such as medicine, industry and agriculture.

Keywords: Nanoparticles oxide particles, vegetative extraction, structural properties, light properties, Green synthesis, nanomaterial

1. Introduction

Numerous intriguing and unique properties of nanoparticles have led to their widespread synthesis and encourage their application in a wide range of industries, including photocatalytic luminescence and photodiode reaction on the one hand, and nano-diagnosis, nanomedicine, and antimicrobial products on the other (Wu, Y., Liu, et al 2018) [43]. In particular Zinc oxide nanoparticles (ZnO NPs) are environmentally friendly and easy to manufacture, non-toxic, safe, and biocompatible, making them suitable for biological uses. Zinc oxide's semiconduction, antibacterial action, vulcanization activator, and UV absorption are its main properties. With the advent of nanotechnology, these properties can be enhanced as the material's surface area increases with particle size decreases, and nanomaterials are manipulated. Researchers have therefore developed methods to increase the development of nanoparticles with greener technologies, using metal and metal oxide (H Mirzaei, et al 2017; A Sirelkhatim, et al 2015) [22, 39]. Green Chemistry includes the use and accessibility of eco-friendly products for pharmaceutical and biomedical applications, where the synthesis process does not contain toxic chemicals (H Mirzaei, et al 2017) [22]. The biological method involving different types of microorganisms was used to synthesize various metallic NPs, which has advantages over other chemicals, as they are greener, save energy, and cost-effective (Kuppusamy, et al 2016) [19]. Bio-inspired NPs have a very fascinating biocompatibility in biomedicine and related fields (Shrestha, et al 2017) [34]. Through the use of plant extract to synthesize the ZnO oxide NP, functional molecules that reduce the amount of metal ion have a significant advantage. Phenols, terpenoids, ketones, aldehydes, and amides are primarily responsible for these synthesis Phytochemicals (Yousaf, et al 2018) [30]. The use of plant extracts, such as Hibiscus sabdariffa, Cafea Arabica, Rheum palmatum, Nigella arvensis, and Azadirachta indica was a biosynthesis for nanoparticles from ZnO (Ogunyemi, et al 2019). Because biological and plant extracts are so complex, the process behind the nanoparticles created by green synthesis is still unclear and poorly understood, despite the fact that a lot of research has been published in this field (Saleh, N., et al. 2018) [30]. This study provides an overview of the most recent advancements in the green synthesis of ZnONPs, emphasizing the differences between the different approaches used and the investment made in the green synthesis formulation process employing different plant extracts (Della Pepa, et al 2017) [9]. In this study, the latest published researches are listed in the green synthesis of zinc oxide nanoparticle using plants and comparison between them.

1.1. Nanoparticle synthesis methods

For nanoparticle synthesis, two approaches have been suggested: Bottom-up and top-down (Mahesh, et al 2014) [20]. The friction or depletion of large macroscopic particles is part of a top-down approach (Chen, et al 2013; Ashik, et al 2018) [8, 3]. This calls for creating large-scale prototypes first, then using plastic deformation to reduce them to nanoscale (Casimir, et al 2016) [7]. This is an inefficient and slow process that cannot be used to manufacture large-scale nanoparticles (Dong, et al 2012) [10]. The most popular technique used in the field of nanomaterial synthesis is an Interferometric Lithographic (1L) (Zohar, et al 2014) [45]. This technique involves the synthesis by self-assembly of nanoparticles from miniature atomic components, it's fairly inexpensive (Anandharamakrishnan, C., 2014) [2]. It is based on the approach of kinetic and thermodynamic equilibrium. MBE (molecular beam epitaxy) is part of the kinetic method (Boubiche, et al 2019) [6]. The hydrophobicity of the capping agents used is primarily responsible (Atta, A.M., et al 2020) [4].

2. Eco-friendly method to synthesis ZnO Nps

In the last decade, interest in synthesizing nanoparticles with zinc oxide using biological processes has increased significantly. The primary cause of the production and the great interest in the unique technology is the lack of dangerous chemicals or a high energy level required for biological synthesis, which makes the process more economical and environmentally friendly (Saratale et al., 2018) [31]. Scientists support that biological nanoparticle applications for metal and metal oxide production represent a greener process compared to conventional chemical or physical methods (Saratale, R.G., et al 2018) [31]. Such biological approaches have gained their own designation as "green synthesis" according to Ahmed S. and fellow researchers (2016). The term became associated with this agreement since it pledges support for the twelve principles of green chemistry as shown in Fig.1. (Bandeira, M., et al 2020) [5].

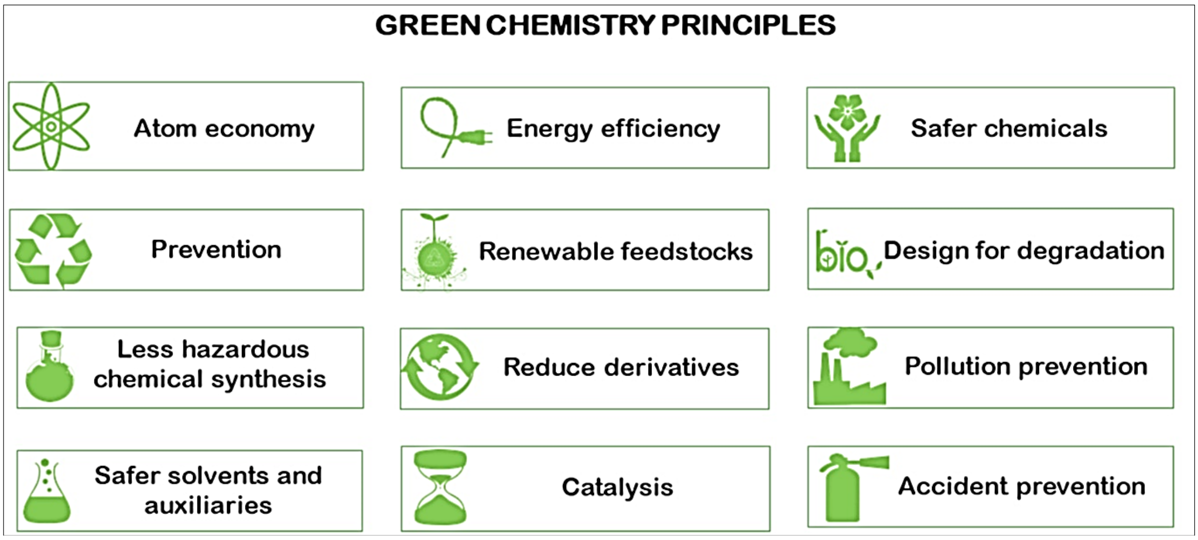

Fig 1: Green chemistry principles (Bandeira, M., et al 2020) [5]

These ideas are currently considered the cornerstones to promote sustainable growth, and they contain instructions for introducing new chemical products, new syntheses, and new processes (Khan, S.H., et al 2020) [16]. In summary, the principles of green chemistry are based on atom economy, Improved reaction effectiveness, energy efficiency, avoiding energy-intensive procedures, More secure chemicals, Minimizing the toxic effects of methods and products, prevention, Minimizing consumption at each step of the procedure, utilizing energy-efficient feedstocks, via compounds that come from sources that are sustainable, design for breakdown, designing recyclable and environmentally friendly products, less harmful synthetic chemicals, reducing derivatives, avoiding the use of derivatives products like stabilizing agents or protectors, lowering pollution levels, preventing the release of harmful chemicals, secure solvents and auxiliaries, using a minimum quantity of dangerous solvent or chemical, usage catalysis to enhance procedures such as energy usage or efficiency and accident avoidance in order to reduce the likelihood of accidents (Kidwai, M.et al 2005; García-Serna, et al 2007; Bandeira, M., et al 2020) [18, 12, 5]. For example, using renewable resources and cleaner solvents and auxiliaries while creating safer compounds are the primary benefits of biological synthesis (Bandeira, M., et al 2020) [5]. Green synthesis has only been used at the laboratory scale, and Generating nanoparticles on a large scale is challenging (Saldanha et al., 2017) [29]. However, since no heavy machinery is required and much progress has been made in comprehending the composition of biological isolates and their interaction with metallic ions., its industrial application is probably going to happen soon. In essence, biological substrates like plants are used in green synthesis (Bandeira, M., et al 2020) [5]. The environmentally friendly green synthesis can be illustrated in Figure 2 in the preparation of ZnO nanoparticles.

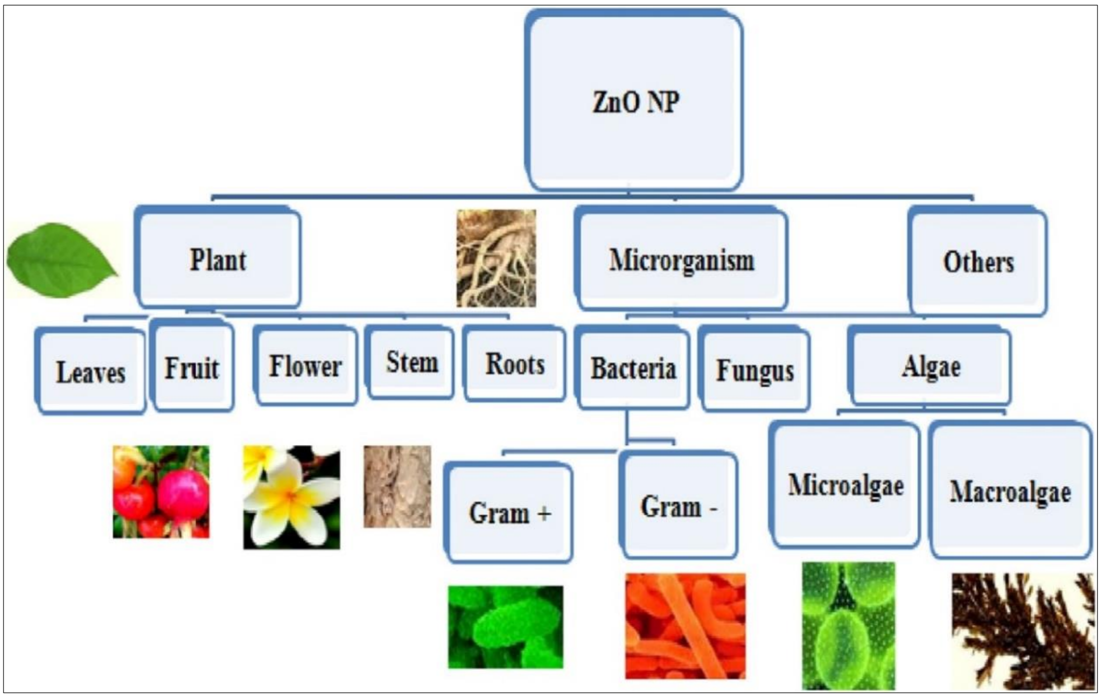

Fig 2: ZnO NPs synthesis from different sources (Bandeira, M., et al 2020) [5].

2.1 Comparison of the literature in the green synthesis of ZnO NPs and the mechanics of plant extraction

In the review article (Happy) the researchers pointed outdated to Green synthesis of ZnO NPs using plant extract, it can be for multiple parts of the plant including the root, stem, leaves, fruit, and seeds in the synthesis of nanoscale zinc oxide due to the special phytochemicals that called reducing agents. Using plant extract to prepare NPS is an environmentally friendly and entirely low-cost method that does not use any fundamental intermediate group. It does not take a long time in that way and involves the use of inexpensive materials and components while giving a highly pure product that is free of impurities, these reasons are referred to through most researchers and confirmed by the researchers into the articles (Saratale, R.G., et al 2018; Irfan, M., et al 2020) [31, 13]. Through the essential reduction of metal oxide and metal ions to obtain nanoscale materials with the aid of chemicals like polysaccharides, polyphenolic compounds, vitamins, amino acids, alkaloids, and terpenoids secreted from the plant, the researchers also stated that the reason for using plants in the preparation of nanoparticles is that their products are stable and diverse in size, shape, and extensive range. I also find that the researcher (Vishnukumar, P., et al 2018; Nasrollahzadeh, M., et l 2019; Marina Bandeira a,b, et al.2020) [40, 24, 5] describes the green synthesis in obtaining the nanoparticles with the same aforementioned description But the compounds found in the plant are called antioxidants that are responsible for the green synthesis, that play an important role in converting zinc salts into nanoscale zinc oxide in sizes, shapes, and high efficacy represented by the following materials like (phenolic acids, saponins,methylxanthines and flavonoids,) (Mohammadinejad, et al 2019) [23]. The researcher mentioned in the experimental part that the plant parts (leaves and flowers) contain reduced materials that are needed to preparing the nanomaterials. Mechanism of formation.is as follows;

The part of the plant was washed by distilled water, then drying at room temperature and Crushed by mortar and pestle. The powder of plant (Known weight) was mixed with known volume according to the required concentration. The mixture was boiling under magnetic stirrer, then filtered. A clear solution of the extract plant was formed. A certain volume of the plant extract was added to 0.5 mm of zinc salts. The mixture was heated at the temperature and time required Happy. The yellow color change in the mixture is an indication of the formation of zinc oxide nanoparticles. To be sure, we measure the UV spectrum to confirm the nanoparticle synthesis. Many of devices used to diagnose of nanoparticles such as Atomic force microscopy (AFM), Energy-dispersive analysis of x-rays (EDAX), Field emission Scanning electron microscopy(FE- SEM), Fourier Transform infrared (FTIR), Photoluminescence (PL), Scanning electron microscopy (SEM), Thermogravimetry-differential thermal analysis (TG-DTA), Transmission electron microscopy (TEMX-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman Spectroscopy, Attenuated total reflectance(ATR), Dynamic light scattering (DLS),) and Ultraviolet - Diffuse reflection spectroscopy (UV-DRS).When applying the previous steps in preparing the zinc oxide nanoparticles using Vitex Negundo leaves and flowers and after comparing the results by diagnostic devices And calculates the volume in the Debye-Scherrer equation Nanoparticles are equal to 38.17 nm there are Some of the information gathered by the researcher in this article about some types of plants that gave nanoparticles products, but with clusters or large sizes, explain this due to the plant content (plant components) of alcohol, alkane, amide, carbonate, and carboxylic acid, as is the case in plant leaves Azadirashta Indika family of Melia. So that can be seen in Table No. (1), Listed some studies on the topic of green synthesis which the researcher put in the article, which includes a set of studies by other researchers for different parts of plant).

Table 1: Synthesis of ZnO NP mediated by plants.

S. No	A plant (family) And Common Name	Functional group	The part of the extract	Size & Shape	References
1	*Coptidis Rhizoma* (Ranunculaceae Coptis Rhizome	Alcohol (OH), carboxylic acid(COOH), alkyl halides, alkynes, types of amines	Dried Rhizome	2.9-25.2 nm (TEM) Rod shaped, spherical	P.C. Nagajyothi, et al. (2014)
2	*Parthenium hysterophorus L.* (Asteraceae) Santa maria feverfew, carrot grass, congress weed	A phosphorus group, secondary sulphonamide, alkyne, amine salt, vinyl cis-tri substituted, NH stretching mode	Leaf	22-35 (XRD, TEM) (50% plant extract), 75-90 (25% plant extract) Round, hexagonal	P. Rajiv, et al. (2013)
3	*Ocimum basilicum L. var. purpurascens* (Lamiaceae) Red Rubin basil	/	Leaf	14.28 nm (XRD) 50 nm (TEM, EDS), Hexagonal	H. Abdul, et al. (2014)
4	*Nephelium lappaceum L.* (Sapindaceae) Rambutan	HOH bending and OH stretching	Fruit peels	50.95 nm (XRD) Agglomerate-forming needle-shaped	R. Yuvakkumar, et al. (2014)
5	*Aloe vera* (Liliaceae) Aloe vera	/	Dry leaves	25-65nm (TEM) Hexagonal, spherical	Y. Qian, et al. (2015)
6	*Pongamia pinnata* (Legumes) Indian beech	OH stretching, COH bending mode, and CO stretching of carboxylic acids or their ester.	Fresh leaves	26nm (XRD), 100 nm (SEM, TEM) agglomeration Cylindrical, hexagonal	M. Sundrarajan, et al. (2015)
7	*Anisochilus carnosus* (Lamiaceae) Kapur	Alcohol(OH), phenol(C_6H_6O), and water Alkane's, carboxylic acid's, and the nitro group's NO_3	Leaf	56.14nm (30 mL of extract), 49.55 nm (40 mL), 38.59nm (50 mL) [XRD], 20-40 nm (FE-SEM), and 30-40nm (TEM)]. A quasispherical hexagonal wurtzite	M. Anbuvannan, et al. (2015)
8	*Agathosma betulina* (Rutaceae) Buchu	Stretching band ZnO, OH	Dry leaves	15.8nm (TEM), 12-26 nm (HRTEM) Agglomerates that are almost spherical	F.T. Thema, et al. (2015)
9	*Azadirachta indica* (Meliaceae) Neem	Alcohol(OH), ketone(C=O), carboxylic acid(COOH), and amine(NH_2)	Fresh leaves	18 nm (XRD) Spherical	K. Elumalai, et al. (2015)
10	*E. crassipes* (Pontederiaceae) Water hyacinth	/	Leaf	32nm (XRD) Spherical without aggregation, 32-36nm (SEM)	P. Vanathi, et al. (2014)
11	*Phyllanthus niruri* (Phyllanthaceae) Bhuiamla, stone breaker	stretching of OH, CH, CO, and aromatic aldehyde(H-C=O).	Leaf	25.61 nm (SEM & XRD) Quasispherical, hexagonal wurtzite	M. Anbuvannan, et al. (2015)
12	*Solanum nigrum* (Solanaceae) Black nightshade	Protein amide III bands, carboxyl side groups(C=O), amine NH_2, and aldehydic CH	Leaf	20-30 nm (XRD and SEM), 29.79nm (TEM) Wurtzite quasi-spherical, hexagonal	M. Ramesh, et al. (2015)
13	*Azadirachta indica* (Meliaceae) Neem	amide II stretching band,, and types of amine C-NH_2 stretching band, alcohol(OH), phenol(C_6H_6O), amino acid, alkane and aromatics, alkynes, and carbonyl group	Leaf	9.6-25.5 nm TEM Spherical	T. Bhuyan, et al. (2015)
14	*Sphathodea campanulate* (Bignoniaceae) African tulip tree	Polyphenols' OH stretching, nitrile group, and carbonyl group	Leaf	30 to 50 nm (TEM) Round	P.E. Ochieng, et al. (2015)
15	*Gossypium* (Malvaceae) Cotton	Types of carbon oxygen bonds [C=O, C-O, C-O-C] and OH	Cellulosic fiber	13 nm (XRD) Spherical, nanorod, wurtzite	R. Aladpoosh, et al. (2015)
16	*Moringa oleifera* (Moringaceae) Drumstick tree	Alkane's OH, CH, alcohol's CO, and carboxylic acid (COOH)	Leaf	FE-SEM 16-20nm and XRD 24 nm Nanoscale granular & spherical form with a collection of aggregates	K. Elumalai, et al. (2015)
17	*Plectranthus amboinicus* (Lamiaceae) Mexican mint	Phosphorus compound, ZnO and CO-SO_3	Leaf	Rod-shaped nanoparticles with agglomerates, 50-180nm (SEM)	L. Fu, Z. Fu (2015)
18	*Vitex negundo* (Lamiaceae) Nochi	CH, OH, and C=C stretch band.	Leaf	75-80 nm (SEM & EDX) ,38.17nm (XRD), Spherical	S. Ambika, et al. (2015)
19	*Vitex negundo* (Lamiaceae) Nochi	/	Flowers	SEM / EDX 75-80 nm, XRD 38.17nm, Spherical	M. Sundrarajan, et al. (2015)
20	*S. album* (Santalaceae) Sandalwood	Alcohol(OH), (carboxylate and carbonyl groups), NH stretching of amide II	Leaves	100nm (SEM) 70-140 nm (TEM), nanorods	K. Kavithaa, et al. (2016)
21	*Aloe Vera* (Liliaceae) Aloe Vera	Alkanes, the amide of proteins and enzymes, the OH of phenol, amines, and alcohol (OH)	Leaf	8-20nm (XRD) Hexagonal, oval, and spherical	K. Ali, et al. (2016)
22	*Trifolium Pratense* (Legumes) Red clover	Stretching modes include hydroxyl, carbonyl group, and alkanes	Flower	60-70nm XRD Spherical	R. Dobrucka, et al. (2016)
23	*Calatropis Gigantea* (Apocynaceae) Crown flower	/	Fresh leaves	(30-35) nm SEM analysis reveals spherical agglomerates.	C. Vidya, et al. (2013)
24	*Rosa canina* (Rosaceae) Dog rose	Stretching of CO and C = O of esters, hydroxyl (OH) and Stretching of CH.	The Fruit	[11.3 nm (MI) and 13.3nm (CH)] (XRD), [CH 25-204nm, MI 21-243nm] (DLS), Round	S. Jafarirad, et al. (2016)
25	*Azadirachta indica* (Meliaceae) Neem	OH between carbonate moieties, HOH and O=C=O	Fresh leaves	10-30nm (TEM) 9-40nm (XRD), Nanobuds and a hexagonal disk	H.R. Madan, et al. (2016)
26	*Cocus nucifera* (Arecaceae) Coconut	Carbonyl group of ketones, amine aromatic, amines aliphatic, alcohol and carboxylic acid	Coconut water	XRD 21.2 nm, TEM 20-80nmMostly hexagonal and spherical, with no aggregation	A.N.D. Krupa, et al. (2016)

In table 1 the researcher compared between plants group into a Previous study (2013-2016). And it showed size by diagnostic devices Dynamic light scattering (DLS), Energy-dispersive X-ray spectroscopy (EDX) or (EDS), Field emission Scanning electron microscopy (FE- SEM), High-resolution transmission electron microscopy (HRTEM), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-ray diffraction (XRD) shape and Functional groups reduced agent (antioxidant). And the researcher did not mention the methods (factors and conditions) of the experiment so that we can compare the results that were reached by the researchers, and there is a table No. 2 that can compare the results as shown in the below.

Table 2: Methodologies reported for the environmentally friendly production of ZnONPs

No	Zn source[s]	Plants substrate	Average size (nm) Shape	pH,t(min),temp.(C°)	References
1	Acetate, 5 g / L	*Couroupita guianensis* leaves 50 g /L	Unspecified(NS) Nanoflakes	Unspecifie (NS) 10 min, NS Overnight, 60 °C	Sathishkumar et al. (2018)
2	Acetate 0.2-1.1 g / L	*Eclipta alba* leaves 100 g /L	3-9nm, Spheres	5-75 min, 20-100 °C Not applied	Singh et al. (2018)
3	Nitrate 18.9 g/ L	*Punica granatum leaves Unspecifie (NS)*	10-30nm, Spheres	Unspecifie 3-4 h, 60 °C 3-4 h 400 °C	Singh et al. (2019)
4	Nitrate 20 g / L	*Lycopersicon students* peel 20 g / L	9nm, Polyhedron	Unspecifie (NS) 3 h, Temp. Room 1 h, 60 °C	Nava et al. (2017b) [26]
5	Nitrate Unspecifie (NS)	*Lycopersicon esculentum* fruit Unspecifie, (NS)	40-100nm, Spheres	Unspecifie (NS) 5 min, 80 °C	Sutradhar and Saha (2017)
6	Nitrate 20 g /L	*Citrus paradise* peel 20 g / L	19nm, Polyhedron	Unspecifie (NS) 3 h, Ta, 1 h, 60 °C	Nava et al. (2017b) [26]
7	Nitrate 6-206 g/ L	*Moringa oleifera* leaves 100 g / L	12-30nm, Spheres and rods	5- 18 h, temp. Room (Ta) 1 h, 500 °C	Matinise et al. (2017) [21]
8	Nitrate 50 g/ L	Camelia Sinensis leaves Unspecifie (NS)	8nm, Spheres	NS, NS, 60 °C, 2 h, 400 °C	Nava et al. (2017a) [25]
9	Nitrate 20 g /L	*Citrus sinensis* peel 20 g / L	12nm, Polyhedron	Unspecifie 3 h, Temp. Room, 1 h, 60 °C	
10	Nitrate Unspecifie (NS)	*Peganum harmala* seed, 60 g / L	40nm, Irregular	1 h, NS NS, 50 °C	Fazlzadeh et al. (2017) [11]
11	Acetate 33.4 g/ L	*Oak fruit hull (jaft)* 200 g /L	34 nm, Spheres	Unspecifie NS, 4 h, 60-80 °C 6 h, 80 °C; 4 h, 500 °C	Sorbiun et al. (2018) [40]
12	Acetate 18.3 g/ L	*Stevia* leaves 72.4 g/ L	50nm, Rectangular	Unspecifie NS, 80 °C, 2 h, 600 °C	Khatami et al. (2018a) [17]
13	Nitrate 100 g /L	*Costus woodsonii leaves, 30*-60 g /L	20-25nm, Varied	Unspecifie 60 °C, NS, 2 h, 400 °C	Khan et al. (2019) [15]
14	Nitrate 100 g/ L	*Mentha pulegium* L. leaves 50 g /L	38-49nm, Spheres	Unspecifie (NS), 2 h, 400 °C	Shahriyari Rad et al. (2019)
15	Nitrate 20 g /L	Citrus aurantifolia peel, 20 g/ L	11nm, Polyhedron	Unspecifie, (NS), 3 h, temp. Room (Ta), 1 h, 60 °C	Nava et al. (2017b) [26]

In order to report concentrations using the same unit, they were estimated; NS: Unspecified; Ta: The temperature at room temperature.

Table No. 2 contains a recent study for this topic from (2017-2019) and it is clearer from table no.1 Because it describes all conditions of the experiment from (Thermal treatment, Zinc source pH. the time, and temperature). In Table (2) we notice that spherical shapes and very small nanoscale sizes can be obtained between 3-8 nm and of high efficacy by adopting high temperatures from 100-400 ° C as is the case in vegetarians Camellia sinensis and Eclipta alba leaves (Nava et al. 2017a) [25]. This interpretation does not apply to some types of plants despite the adoption of a long time in preparation and high temperature because they contain other chemical compositions (in addition to anti-oxidants) in large quantities such as alcohols and carbonates As in Stevia leaves, which hinders the process of synthesis and gives a result of the size of nano but may contain clusters or Irregular sizes, as in some types of plants referred to in the above table such as Peganum harmala plant (Fazlzadeh et al, 2017) [11].

3. Conclusion

After the process of comparing the literature in environmentally friendly methods (biocompatible chemicals) in the field of preparing nanoparticles of zinc oxide through plant extract. In this review article, it is important in the field of green synthesis that is friendly to the environment. But what must be pointed out is that the size and final shape of the nanoscale product is one that differs according to studies of other researchers because of the different conditions of temperature, pH, concentrations, time, additives are all factors that greatly affect the final product in terms of size, size, and effectiveness. Although this field (green synthesis) has achieved many results in the treatment of biology and reduced risks to the environment through the decrease of pollutants and effects. Aside from that, the field of preparation must be given more importance shortly by adopting industrial production in greater quantities and higher effectiveness by investing all environmentally friendly biological products.

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