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Original Article

Environmentally biopreparation of selenium and zinc nanoparticles using *Ginkgo biloba* extract in preservation of edible oils

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Keywords

Ginkgo biloba, oil preservation, antioxidant, selenium, zinc nanoparticles

A B S T R A C T

This research was conducted to study the antioxidant activity of *Ginkgo biloba* extract and the green synthesis of selenium and zinc nanoparticles with the biocompatible extract of *Ginkgo biloba*. The structural and optical properties of nanoparticles showed that a spherical shape of zinc with particle size ranged from 70.63 to 82.57 nm, and 52.89 and 66.47 nm for selenium. The HPLC technique was used to identify the phenolic components of *Ginkgo biloba* extract, it contained 15 polyphenol compounds. *Ginkgo biloba* extract and synthetic nanoparticles of selenium and zinc were added to corn and soybean oils at concentrations of 200, 400 and 800 ppm as natural antioxidants in comparison with TBHQ as synthetic. Rancimat time at 110°C indicated that the induction period of the control oils varied from 10.70 and 5.53 hours, respectively, for corn oil and soybean oil. Corn and soybean oils treated with selenium nanoparticles prepared with *Ginkgo biloba* extract at a concentration of 800 ppm showed the highest stability times which were 12.5 and 23.9, respectively. Zinc nanoparticles of *Ginkgo biloba* extract can involve with the bio-reduction reaction at a concentration of 800 ppm to prevent oxidation and rancidity of oils as indicated for 7.07 and 6.02 hours for oils corn and soybeans, respectively. Thus, the addition of selenium and zinc nanoparticles of *Ginkgo biloba* extract to corn and soybean oils has shown a positive effect on the oxidative and thermal stability of these raw materials and could be recommended as an alternative antioxidant in oils.

Introduction

Ginkgo biloba L. is the sole surviving species of the Ginkgoaceae family and Ginkgoales order. Recently, extracts of G. biloba leaves have been used in commercial medical products and food supplements in China and many other countries. Terpenetrilactones and flavonoid glycosides are the main bioactive constituents in ginkgo leaves and extracts, which are prescribed to improve the circulation and treat dementia (Shan *et al*., 2018). Lipid oxidation is a major cause for food quality deterioration and generation of off odours and off flavours, decreasing shelf life, altering texture and color and decreasing the nutritional value of food. Numerous methods have been developed to control the rate and extent of lipid oxidation in foods, but addition of antioxidants is most effective. Antioxidants have become an indispensible group of food additives mainly because of their unique properties of extending the shelf-life of food products without any adverse effect on their sensory or nutritional qualities (Shahidi and Ambigaipalan, 2015).

There is a growing interest in the use of renewable resources in the development of preserving oils from deterioration. The oxidative deterioration of fats and oils in foods is responsible for rancid odors and flavors, with a consequent decrease in nutritional quality and safety caused by the formation of secondary, potentially toxic, compounds. The addition of antioxidants is required to preserve flavor, color and to avoid vitamin destruction. For instance, one useful strategy to reduce food deterioration is based on the utilization of synthetic antioxidants. Among the synthetic types are the most frequently used to preserve food namely, butylated hydroxyl anisole (BHA), butylated hydroxyl toluene (BHT), propyl gallate (PG) and tertiary butylhydroquinone (TBHQ), but their use is restricted due to possible toxicity and carcinogenesis effects (Babbar *et al*., 2011). Natural antioxidants are more ideal as food additives, not only for their free radical

scavenging properties, but also on the belief that natural products are healthier and safer than synthetic ones. Thus, they are more readily acceptable to the modern consumers (El-Gammal, 2016). Corn oil is considered nutritious due to its high content of polyunsaturated fatty acids (PUFA), mainly linoleic acid (18:2). However, due to its high PUFA content, it is even more susceptible to oxidative degradation leading to rancidity, off-flavors, and discoloration (Baştürk *et al*., 2018). Soybean oil is the most common vegetable oil source in America, and it takes around 57% of all vegetable oil resources. Additionally, the US is the major producer about 33% of the total production around the world. Mechanical process and solvent extraction are two conventional approaches used in industry. Organic solvent extraction is the most common and efficient method for oil production, including ethanol, heptane and butane and hexane is the most used in the vegetable oil production due to its low cost and high efficiency (Cheng and Rosentrater, 2017).

Nanotechnology is the manufacture and use of materials and structures at the nanometer scale (a nanometer is one millionth of a millimeter). It offers a wide range of opportunities for the development of innovative products and applications in food system (El-Gammal, 2016). Preparation of stable nanoparticles using natural sources to prevent metal ions from agglomeration by bio-reduction to metal nanoparticles instead of any artificial or chemical stabilizers such as polyvinyl alcohol (PVA), tripolyphosphate (TPP), polyacrilic acid (PAA), mercaptosuccinic acid (MSA), 3-mercaptopropionic acid (MPA), etc. Zero Valente of metals aggregated around bioactive compounds to form nanoparticles (El-Refai *et al*., 2018).

Accordingly, this study was conducted to investigate the antioxidant activity of nanoparticles of Ginkgo biloba extract using selenium and zinc oxide nanoparticles as natural antioxidant compared with TBHQ. Also, oxidation stability and thermal stability of Corn oil and mixed soybean oil treated with nanoparticles of Ginkgo biloba extracts were studied.

Materials and Methods

Materials

Leaves of *Ginkgo biloba* were purchased from local market, Mansoura city, Egypt. Raw materials were conveyed directly to the laboratory of Food Industries Department, Faculty of Agriculture, Mansoura University, Mansoura, Egypt and dried away from sunlight to final moisture content of the sample which was set to 9.5±0.3% and crushed to fine powder using Braun GmbH Grinding (Model, KSM2; Type, 4041, Germany). Grinded plant powder was separated to be fine enough to pass through sieve size (75–100µm).

Folin-Ciocalteu's phenol reagent (Fluka, Biochemica, Germany), gallic acid (MB, Biomedical Inc., USA), Quercetin (Sigma Chemical Co., Germany), DPPH (Aldrich Chemistry, Germany), ABTS (Sigma Chemical Co., Germany), Aluminium chloride anhydrous LR (sd fine-Chem limited, India), potassium acetate and sodium carbonate (El-Nasr Pharmaceutical Chemicals Company, Egypt), selenium dioxide (SeO_2, Merck Schuchardt OHG, Germany), zinc sulphate ($ZnSO_4$, BDH Chemical Co., England) were purchased from El-Nasr Pharmaceutical Chemicals Company, Mansoura, Egypt.

Refined, bleached and deodorized (RBD) Corn and mixed soybean oils and Tertiary Butylhydroxy Quinone (TBHQ) were kindly gift form Arma Company for Oils at 10th of Ramadan City, Egypt.

Methods

Chemical Composition of *Ginkgo biloba* leaves

Moisture, ash, crude protein, crude lipids, crude fiber and total carbohydrate contents of Ginkgo biloba were determined according to the method described by (AOAC, 2016).

Minerals Content

Magnesium, calcium, potassium, aluminum, bismuth, boron and iron were detected using plasma instrumental technique ICAP 7000 Plus Series, Thermo Fisher Scientific Inc, (Bremen) GmbH, Germany, at Laboratory of Soil Fertility Tests and Fertilizers Quality Control, Central Laboratory, Faculty of Agriculture, Mansoura University, Mansoura, Egypt.

Sodium, phosphorus, cadmium, cobalt, chromium, copper, manganese, nickel, lead, and zinc were determined in digested samples using the Atomic Absorption Spectrometer Buck Scientific 214 Accusystem Series air/acetylene flames. The concentration of elements in plant samples was considered ppm according to Allen *et al.,* (1997). Previous determinations have been obtained in the Applied and Multi-Purpose Experimental Integrated Unit for Biotechnology and Genetic Engineering, Mansoura University, Mansoura, Egypt.

Fractionation and identification of phenolic compounds

Phenolic compounds were identified using high performance liquid chromatography (HPLC) Technique at Food Safety and Quality Control (FSQC) Laboratory, Faculty of Agriculture, Cairo University, Egypt, according to Yang *et al*., (2014). Retention time and peak area were used to calculate the concentrations of phenolic compounds content by analyzing the data of Hewllet packed software.

Extraction of Active Ingredients

To choose the suitable solvent for the extraction, a known weight of *Ginkgo biloba* sample (2g) was extracted in soxhlet apparatus using several solvents with different polarities such as, methanol, ethanol, ethanol (30%), diethyl ether, acetone, n-hexane, ethyl acetate and water, separately, as a solvent for 24 hours. Then, the extracts were subjected to rotary evaporator at 40ºC under reduced pressure for removing the solvents and the percentages of the yield extracts were calculated according to Iqbal *et al*., (2008).

Ginkgo biloba extract was prepared at Agricultural Chemistry Department, Faculty of Agriculture, Mansoura University, Mansoura, Egypt, according to the method described by Dent *et al*., (2013). Accurately 100g of algae powder was extracted using 1L of ethanol (30%) performed at 60°C for 30 minutes on a horizontal water bath shaker (Memmert WB14, Germany). The extract was then filtered through Whatman no. 1 filter paper (Whatman International Ltd., Kent, UK) using a Büchner funnel and the filtrate was adjusted to 100mL in volumetric flasks with appropriate deionized water. The extract was stored at -18°C till use.

Total Polyphenols and Total Flavonoids Content

The total phenolic content was determined using Folin-Ciocalteu reagent method and the colorimetric method of aluminum chloride was used to estimate the total flavonoids content of *Ginkgo biloba* extract according to Yadav *et al.,* (2011).

Antioxidant Activity

DPPH Radical Scavenging Assay

The (DPPH, 2,2-diphenyl-1-picrylhydrazyl) and (ABTS, 2,2'-azino*bis* 3-ethylbenzothiazoline-6-sulfonic acid) Scav-

enging capacity of *Ginkgo biloba* extract were determined according to the method of Li *et al.,* (2015) and Christodouleas *et al.,* (2015) calculated according to the following equation:

$$\mathbf{RSA(\%)} = \frac{A_o - A}{A_o} \times 100$$

where **Ao**is the absorbance of control and **A** is the absorbance of sample.

Synthesis of Metal Nanoparticles

The metals of selenium and zinc nanoparticles were synthesized at Agricultural Chemistry Department, Faculty of Agriculture, Mansoura University, Mansoura, Egypt, according to the method described by Devasenan *et al.,* (2016). An aqueous solution of metal salts (1 mmoL), such selenium and zinc sulfate (20 mL) was prepared using deionized water and added to 20 mL of prepared extract. The reaction mixture was kept under stirring for 2 hours at room temperature. The resulting nanoparticles were synthesized in an equimolar ratio of (1:1) for both selenium and zinc nanoparticles.

Instrumental Analysis for Metal Nanoparticles

The reduction of pure selenium and zinc ions and capping of the resulting selenium and zinc nanoparticles were monitored according to Devasenan *et al.,* (2016) using ATI Unicom UV–Vis Spectrophotometer vision software V 3.20, by detecting the UV–Vis spectra of the reaction mixture at different wavelengths at Faculty of Science, Mansoura University, Mansoura, Egypt.

Transmission Electron Microscope (TEM) Measurements

The size, shape, surface, crystal structure and morphological data of the obtained nanoparticles were characterized according to Otunola *et al.,* (2017) using transmission electron microscopy, TEM (JEOL TEM-2100) at Electron Microscope Unit, Central Laboratory, Faculty of Agriculture, Mansoura University, Mansoura, Egypt.

Nanoparticles Characteristic via Zeta potential

Zeta potential analysis is a technique for determining the surface charge of nanoparticles in suspensions using Malvern Instruments Ltd Zeta Potential Ver. 2.3 according to Bhattacharjee, (2016) at Electron Microscope Unit, Central Laboratory, Faculty of Agriculture, Mansoura University, Mansoura, Egypt.

Physical properties of corn and soybean oils

Color, Specific gravity and Refractive index were determined in corn and soybean oils according to the method described by AOAC, (2016).

Chemical properties of corn oil and soybean oils

Acid value, Free fatty acids, Peroxide value, Iodine value and Saponification value were assessed according to AOAC, (2016).

Determination of fatty acids content of corn oil and soybean oils

Fatty acids methyl esters were prepared from total lipid by using rapid method according to the method of ISO12966-2 (2011) using gas liquid chromatography technique (GC-MS) at Food Technology Research Institute (FTRI), Agricultural Research Center (ARC), Egypt.

Oxidative Stability by Rancimat Measurements

The oxidative stability of oil samples was determined by rancimat method using Metrohm 892 and induction period (IP) was conducted with rancimat at 110˚C for both oil samples using three concentrations of 200, 400, 800ppm compared with TBHQ in recommended manufacturing concentration of 200ppm. For simplicity, all treatments were distributed to four treatments namely: T1: Oil treated with *Ginkgo biloba* extract, T2: Oil treated with Ginkgo biloba+ SeNPs, T3: Oil treated with *Ginkgo biloba*+ ZnNPs and T4: Oil treated with TBHQ. The oxidative stability of oil samples was determined according to AOAC (1997) at Food Technology Research Institute (FTRI), Agricultural Research Center (ARC), Egypt. All the samples were studied at the same temperatures of 110˚C under a constant air flow (20 L/h). The induction periods [h] were printed automatically by the apparatus software with the accuracy of 0.005. During the rancimat test, oil samples were taken and content of primary oxidation products (PV) generated during heating and aeration was tested.

Results and Discussions

Table 1. Chemical composition of *Ginkgo biloba* on dried weight basis.

Sample	Moisture %	Ash %	Crude Protein (CP) %	Ether Extract (EE) %	Crude Fiber (CF) %	Total carbohydrate %
Ginkgo biloba	9.15	7.38	14.71	2.5	22.54	77.46

% Protein = % Nitrogen × 6.25

Total carbohydrate = 100 – (Ash+CP+EE+CF)

Data in Table (1) showed that moisture, ash, crude protein, Ether Extract, Crude Fiber and total carbohydrate contents were identified in *Ginkgo biloba*. All results were calculated as (g/100g dry weight). It was clear that the *Ginkgo biloba* contain 9.15, 7.38, 14.71, 2.5, 22.54 and 77.46% for Moisture, Ash Crude Protein, Ether Extract, Crude Fiber, and Total carbohydrate, respectively. Our data were in agreement with Pereira *et al.,* (2013) who studied the Chemical composition of *Ginkgo biloba* on dried weight basis and they found Carbohydrates, (72.98 g/100 g dw). proteins and ash were 12.27 and 10.01 g/100 g dw, respectively.

Table 2. Minerals contents of *Ginkgo biloba*.

Element	*Ginkgo biloba* (ppm)
Calcium	33465.380
Potassium	11992.430
Magnesium	6722.456
Aluminum	-
Bismuth	-
Boron	-
Iron	2330.250
Sodium	5.430
Phosphorus	3337.040
Cadmium	3.247
Cobalt	3.103
Chromium	1.348
Copper	1.490
Manganese	2.528
Zinc	11.355

From Table (2), it could be seen that Calcium and Potassium were 33465.380 and 11992.430 ppm, respectively, followed by Magnesium, Phosphorus and Iron in concentrations of 6722.456, 3337.040 and 2330.250 ppm, separately. Furthermore, the rest of elements were ranged from 11.355 ppm for zinc to 1.348 ppm for chromium. On the other hand, Aluminum, bismuth and boron were absent in *Ginkgo biloba*.

Our data were in agreement with RM *et al.*, (2018) who studied the content of trace element in *Ginkgo biloba* leaves and found that manganese, copper and zinc ranged from 1.8 to 15.2 ppm, and selenium and lead (0.40 and 0.79 ppm), cadmium arsenic and cobalt (0.007 – 0.07ppm) and Yu *et al.*, (1992) who studied the content of trace element in *Ginkgo biloba* leaves and found 0.1 – 2.17 ppm of selenium, 2.8-6.9 ppm of copper, 6.1-17.1 ppm of zinc and 15.73 ppm of manganese.

Table 3. Fractionation and identification of phenolic compounds of *Ginkgo biloba* HPLC technique.

Compound	*Ginkgo biloba*	
	Plant Concentration [ppm]	Extract Concentration [ppm]
Pyrogallol	8.582	2.057
Quinol	12.913	-
Gallic acid	55.145	12.051
Catechol	-	-
p- Hydroxy benzoic acid	20.639	-
Caffeine	57.241	-
Chlorogenic acid	3.941	6.362
Vanillic acid	81.390	-
Caffeic acid	71.845	13.146
Syringic acid	99.812	2.060
Vanillin	3.406	1.251
p- Coumaric acid	15.475	3.847
Ferulic acid	33.542	6.238
Benzoic acid	384.583	53.946
Rutin	-	-
Ellagic acid	5232.827	113.553
o- Coumaric acid	13.555	-
Salicylic acid	47.387	16.747
Myricetin	1174.165	55.404
Cinnamic acid	1.698	-
Quercitin	685.205	92.129
Rosemarinic acid	272.517	-
Neringein	190.590	111.050
Kaempferol	78.572	13.604

High performance liquid chromatography (HPLC) procedure was used for qualitative analysis of polyphenol compounds in *Ginkgo biloba* plants and *Ginkgo biloba* extracts. Twenty-four polyphenol compounds were detected in *Ginkgo biloba* extracts. They were available at authentic samples namely: Pyrogallol, Quinol, gallic acid, Catechol, p- Hydroxy benzoic acid, Caffeine, Chlorogenic, Vanillic acid, Caffeic acid, Syringic acid, Vanillin, p- Coumaric acid, Ferulic acid, Benzoic acid, Rutin, Ellagic, o- Coumaric acid, Salicylic acid, Myricetin, Cinnamic acid, Quercitin, Rosemarinic, Neringein and Kaempferol.

Table (3) shows the 24 compounds by using HPLC they found 22 compounds in the plant of *Ginkgo biloba*. The highest concentration is Ellagic acid and Myricetin 5232.827, 1174.165 ppm, respectively. Followed by Quercitin 685.205, Benzoic acid 384.583, Rosemarinic acid 272.517 and Neringein 190.590 ppm, respectively. while Pyrogallol 8.582, Chlorogenic acid 3.941, Vanillin 3.406 and Cinnamic acid 1.698 ppm were the lowest concentrations. On the other hand, Catechol and Rutin were disappear in *Ginkgo biloba* plants.

In addition, Ginkgo biloba extract contains 15 polyphenol compounds. The highest concentration is Ellagic acid 113.553 and Neringein 111.050 ppm, respectively. Followed by Quercitin 92.129, Myricetin 55.404 and Benzoic acid 53.946 ppm, respectively. While Pyrogallol 2.057, Syringic acid 2.060 and Vanillin 1.251 were the lowest concentrations. On the other hand, Quinol, Catechol, p- Hydroxy benzoic acid, Caffeine, Vanillic acid, Rutin, O- Coumaric acid, Cinnamic acid and rosemarinic acid were absent in Ginkgo biloba extract.

Our data for phenolic compounds fractionation were in agreement with Ma *et al.*, (2016) who separate twelve flavonol glycosides, three aglycones and two isolavones in *Ginkgo biloba* leaves. And the main polyphenols were quercetin, genistein, rutin, kaempferol and isorahmentein. Also, Kobus *et al.*, (2009) separated morin, quercetin, myristin, kaempferol and isorahmentein.

Determination of *Ginkgo biloba* extract yield in different solvents system.

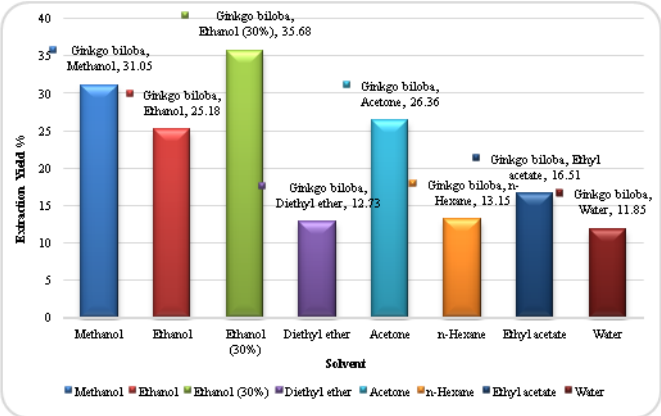

Fig 1. Determination of *Ginkgo biloba* extract yield in different solvents system.

Fig (1) shows the percentage yield of Ginkgo biloba extracts in different extraction media. Extracts yield ranged 11.85 – 35.68 % among different solvent systems. The highest yield was observed for Ethanol (30%) followed by Methanol, acetone, Ethanol, ethyl acetate, n-Hexane, Diethyl ether and water.

Our data were in agreement with Dent *et al.*, (2013) who stated that The effect of extraction solvents (30, 50 and 70 % aqueous solutions of ethanol and acetone, and 100% distilled water), extraction temperature (60 and 90°C) and extraction time (30, 60 and 90 min) on the composition and mass fraction of polyphenolic compounds in Dalmatian wild sage (*Salvia officinalis* L.) extracts has been investigated. The aqueous solutions of ethanol or acetone (30%), extraction temperature of 60°C and extraction time of 30 min were the most efficient for the extraction of polyphenols from dry sage leaves. In addition, Iqbal *et al.*, (2008) shows the percentage yield and antioxidant activity of poly phenols extracts in different extraction media. Extracts yield ranged 13.96–29.16% among different solvent systems. The highest yield was observed for methanol followed by ethanol, acetone, chloroform, ethyl acetate and water, respectively.

Total polyphenols, flavonoids, antioxidant of *Ginkgo biloba*

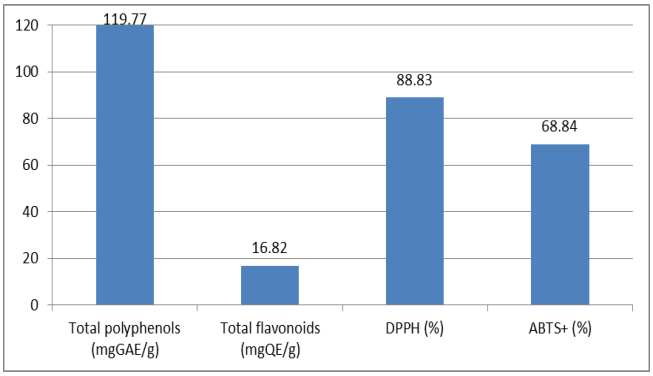

Fig 2. Total polyphenols (mgGAE/g), total flavonoids (mgQE/g), antioxidant activities (DPPH) and (ABTS+) cation radical contents of *Ginkgo biloba.*

The antioxidant activity of the extracted *Ginkgo biloba* eco-friendly synthesized nanoparticles was evaluated using free radical scavenging $ABTS^{+}$ and DPPH assays.

Phenolic compounds can play an important role as antioxidants and in preserving various foods from damaged by inhibiting or killing harmful microorganisms. Fig (2) showed that the polyphenols determined for investigated plant samples. It was noticed the content of total polyphenols was (119.77mg/100g sample) and higher antioxidant agent with inhibition (88.83%). In addition, the Total flavonoids (16.82mg/100g) and antioxidant activity (68.84%) of *Ginkgo biloba* plants extract.

Our data were in agreement with Kobus *et al.*, (2009) who studied the Contents of total polyphenols and flavonols aglycones in extracts of Ginkgo (*Ginkgo biloba* L.) leaves and they found The scavenging effect of the DPPH radical by extracts of Ginkgo (*Ginkgo biloba* L.) leaves prepared using different solvents Total flavonols [513 mg/g dm] and Total polyphenols [204.4 mg/g dm] DPPH 1.02 mM Trolox/g dm.

Nanoparticles characteristic *via* UV-Vis spectroscopy and Zeta potential.

The synthesis of the nanoparticles has been elucidated by scanning the UV–Vis spectra. As shown in Fig. (3), the maximum absorption peak that recorded at 280 nm is due to the characteristic surface plasmon resonance of the produced metal nanoparticles. The prepared selenium and zinc nanoparticles were found to be very stable due to possible presence of polyphenolic compounds present in the *Ginkgo biloba* extract that prevent accumulation. polyphenols are an antioxidant agent with specific chemical structure have an essential role in the reduction process for synthesis of metal nanoparticles. The properties of synthesized nanoparticles were examined as a function of UV irradiation. The use of UV–Vis spectroscopic analysis is an effective method for demonstrating the presence of metal nano-structures Sun *et al.*, (2002) and Darroudi *et al.*, (2011). The UV irradiation role was confirmed to describe the progress of selenium and zinc reduction in the presence of algae extract at ambient temperature.

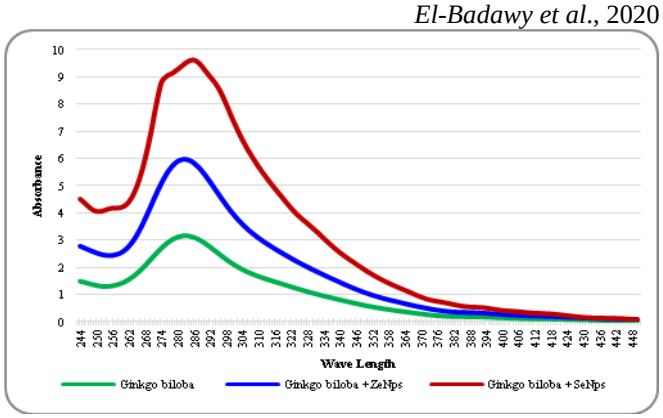

Fig 3. UV-Vis spectroscopic measurements of *Ginkgo biloba* and its nanoparticles.

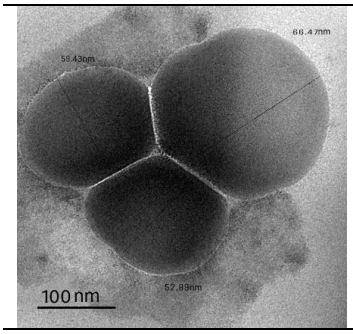

Fig (4). TEM micrographs and size distributions for selenium nanoparticles synthesized by *Ginkgo biloba* extract at 100nm magnification value.

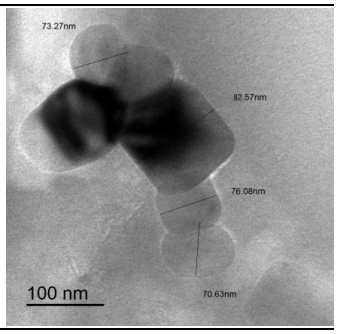

Fig (5). TEM micrographs and size distributions for zinc nanoparticles synthesized by *Ginkgo biloba* extract at 100nm magnification value.

Data in (Fig 4 and 5) showed that TEM images of selenium and zinc nanoparticles indicated clearly the size and the shape which have a spherical, smooth and granular shape from zinc was observed and particle size ranged between 70.63 to 82.57 nm, and selenium was observed and particle size ranged between 52.89 to 66.47 nm, this is considered as Nano-particle size were presented this resulted were in accordance with El-Khateeb *et al.*, (2019) which prepared Nanoparticles by using algae extract were characterized by TEM measurements to evaluate the SeNPs and ZnNPs presence.

An estimation of the synthesized nanoparticles particles size, shape, and aggregation were done. They showed the conducted TEM at 100 nm magnification value for the synthesized nanoparticles. The particles size was ranged from 22.31 to 95.16 nm for both selenium and zinc nanoparticles.

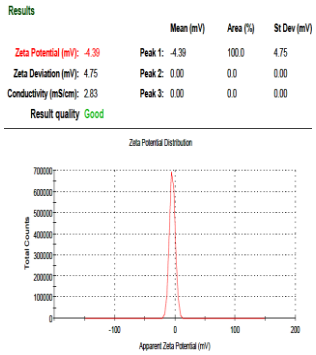

Fig (6). Zeta potential distribution for selenium nanoparticles synthesized by *Ginkgo biloba* extract.

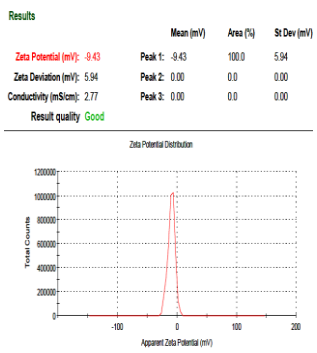

Fig (7). Zeta potential distribution for zinc nanoparticles synthesized by *Ginkgo biloba* extract.

Nanoparticles Characteristic *via* Zeta potential.

Zeta Potential is an important tool for understanding the state of the nanoparticle surface and predicting the long-term stability of the nanoparticle. Nanoparticles have a surface charge that attracts a thin layer of ions of opposite charge to the nanoparticle surface, Zeta Potential technique was used to determine the nanoparticles surface charge. Nanoparticles have double layer of ions travels as it diffuses throughout the solution, the electric potential at the boundary of the double layer is known as the Zeta potential of the particles and has values that typically ranged from +100 mV to -100 mV. Figs (6 and 7) showed that synthesized selenium and zinc nanoparticles using *Ginkgo biloba* extract has Zeta Potential value of -4.39 and -9.43 mV which were high stability because nanoparticles with Zeta potential values lesser than +25 mV or greater than -25 mV typically have high degrees of stability as stated by Soheyla and Zahir (2013).

Table 4. Physical properties of investigated oils.

Oils	Colour Lovibond scale		Specific gravity g.cm^{-3} at 32ºC	Refractive index at 32ºC
	Red	Yellow		
Corn	4	35	0.924	1.472
Soybean	2	20	0.917	1.469

Physical properties of corn and soybean oils were determined; results are found in table (4). Colour, specific gravity and refractive index were measured at 32ºC in corn oil, colour on the lovibond scale were 4 and 35 for red and yellow colour respectively. Specific gravity was found to be 0.924 g.cm-3 and the refractive index was 1.472. Colour, specific gravity and refractive index were measured at 32ºC in soybean oil, colour on the lovibond scale were 2 and 20 for red and yellow colour respectively. Specific gravity was found to be 0.917 g.cm^{-3} and the refractive index was 1.469.

Table 5. Chemical properties of investigated oils.

Oils	Acid value	Free fatty acids (%)	Peroxide value	Iodine value	Saponification value
Corn	0.52	0.26	3.01	127	191
Soybean	0.44	0.25	2.99	125	189

Table (5) shows the chemical properties of corn oil and soybean oil such as acid value, free fatty acids, peroxide value, iodine value and saponification value. From the same table, it could be shown that acid value, free fatty acids (% as oleic acid), peroxide value, iodine value and saponification value were as follow in corn oil: 0.52, 0.26, 3.01, 127 and 191 respectively. On the other hand, acid value, free fatty acids (% as oleic acid), peroxide value, iodine value and saponification value were as follow in soybean oil: 0.44, 0.25, 2.99, 125 and 189 respectively. This resulted were in agreement with Hammond *et al.*, (2005), they studied the physical and chemical properties in soybean oil. They found Triacylglycerol 94.4%, Phospholipids 3.7%, Free fatty acids 0.3–0.7% and Iodine Value 132.7%. Abdulkadir and Abubakar (2011) studied the physical and chemical properties in refined corn oil and they found specific gravity 0.92, refractive index1.470, peroxide value 0.25meq/ kg, saponification value 195.30 mgK0H/g and iodine value 119.92 g Iodine/100g.

Table 6. Fatty acids identification of investigated oils using GC-MS.

Fatty acids		Corn Oil	Soybean Oil
Myristic acid	C14:0	0.03	0.10
Palmitic acid	C16:0	10.60	7.48
Palmitoleic acid	C16:1	0.13	0.15
Margric acid	C17:0	0.17	0.08
Hemptadecenoic acid	C17:1	0.13	0.03
Stearic acid	C18:0	1.92	3.57
Oleic acid	C18:1	24.81	23.46
Linolenic acid	C18:2T	N.D	0.54
Linoleic acid	C18:2	56.41	62.87
Linolenic acid	C18:3	1.10	0.54
Arachidic acid	C20:0	0.41	0.23
Eicosapentaenoic acid	C20:1	0.31	0.15
Behenic acid	C22:0	0.19	0.58
Lignoceric acid	C24:0	0.16	0.19
Total		**96.37**	**99.97**

Gas liquid chromatography technique (GC-MS) was used for qualitative analysis of fatty acids in corn and soybean oils. Fourteen fatty acids were detected in corn and soybean oils. They were available at authentic samples namely: myristic acid, palmitic acid, palmitoleic acid, margric acid, heptadecenoic acid, stearic acid, oleic acid, linolenic acid, linoleic acid, linoleic acid, arachidic acid, eicosapentaenoic acid, behenic acid, ligoceric acid.

Table (6) shows the total of fatty acids in corn and soybean 96.37 and 99.97 respectively the highest concentration is Linoleic acid in the both of oils 56.41,62.87 respectively followed by oleic acid 24.81 and 23.46 in corn and soybean oils respectively. While the concentration of palmitoleic acid was 10.60 and 7.48 in corn and soybean respectively. While the remaining ratios of fatty acids range from 3.57 to 0.03 in corn and soybean oils. Trans of Linolenic acid was disappeared in corn oil while it appeared with concentration o.54 in soybean oil this resulted were in accordance with Zeb and Murkovic (2013). Gas chromatographic results show that the corn oil has a high percentage of oleic acid (26.69 mg/100 g) and linoleic acid (52.61 mg/100 g). Also, Jokić *et al.*, (2013) studied the Fatty Acid Composition of Oil Obtained from Soybeans and Their results indicate that the soybean oil is rich in polyunsaturated fatty acids (PUFA). The most abundant unsaturated fatty acid in soybean oil was linoleic acid, in amounts higher than 50% in all the fractions analyzed. Oleic acid, belonging to monounsaturated fatty acids (MUFA), was the second most abundant unsaturated fatty acid in soybean oil, amounting from around 21% to around 25%. According to the data obtained, the third unsaturated fatty acid, and that is very important, was polyunsaturated linolenic acid, in amounts from around 5% to around 6%. The most dominant saturated fatty acid was palmitic acid

Oxidative stability of corn and soybean oils by rancimat method.

Rancimat index is a fast oxidation measurement of the degree of its resistance to oxidation, examine the oxidative stability of edible oils and predict their shelf life of oil which expressed as induction period. The induction period represents the time needed for decomposition of hydroperoxides produced by oil oxidation (Sadoudi *et al.*, 2014).

Data in Table (7) presented the induction periods at 110ºC for control and treated oils with *Ginkgo biloba* extract and biosynthesis selenium and zinc nanoparticles as natural antioxidants in concentrations of 200, 400 and 800 ppm compar-

ing with TBHQ as synthetic antioxidant in manufacture recommended concentration of 200 ppm which indicated that the induction period of control oils were varied from10.70 and 5.53 hours for corn oil and soybean oil, respectively. However, the treated samples with TBHQ exposed 13.30 to 7.03 hours for corn oil and soybean oil, respectively. From the same Table, it was clear that addition of *Ginkgo*. *biloba* extract with different concentrations due to increase the induction periods to 9.98 to 10.7 hours for corn and5.12 to 5.58 for soybean oils, comparing with control oils and treated oils with TBHQ, which related to its bioactive phenolic and flavonoid compounds composition (Liu *et al.*, 2012).

Treated corn and soybean oils with synthesis selenium nanoparticles with Ginkgo biloba extract at the concentration of 800 ppm showed the highest stability times which were 12.5and 23.9hours of storage, respectively, comparing with other treated samples. these results could be due that selenium nanoparticles could bound the essential compounds and functional groups namely phenolic compounds, flavonoid and terpenoids were bound to the surface of selenium nanoparticles, also the effectively of Ginkgo biloba extract enhance the bio-reduction reaction in the biosynthesis of nanoparticles.

Also, from the same Table, it could be detected that synthesis zinc nanoparticles with Ginkgo biloba extract can involve with the bio-reduction reaction in concentration of 800 ppm prevent oils oxidation and rancidity as reported for 7.07 and 6.02hours for corn and soybean oils, respectively.

Obtained results were in accordance with Sagar Raut *et al.*, (2013), who stated the mechanism of zinc nanoparticles stabilization related to the interaction between phenolic acids such as caffeic acid, cinnamic acid and ferrulic acid and zinc ions. And El-Khateeb *et al.*, (2019) who stated the mechanism of using *Sargassum latifolium* algae extract, biosynthetic selenium and zinc nanoparticles as natural antioxidants in concentrations of 200, 400 and 800 ppm, and TBHQ as artificial antioxidant in manufacture recommended concentration of 200 ppm. The induction period of control oils was varied from10.70 and 5.53 hours for corn oil and soybean oil, respectively. However, the treated samples with TBHQ exposed to 13.30 and 7.03 hours for corn oil and soybean oil, respectively. Corn and soybean oils treated with synthetic selenium nanoparticles with *Sargassum latifolium* algae extract at a concentration of 800 ppm showed the highest stability times, which were 31.78 and 12.50 hours of storage, respectively, compared to control and TBHQ-treated samples.

Table 7. Oxidative Stability of corn oil and soyabean oil using *Ginkgo biloba* nanoparticles by Rancimat Measurements.

Samples	Induction Periods (hrs)										
	T1			T2			T3			T4	Control
	200 ppm	400 ppm	800 ppm	200 ppm	400 ppm	800 ppm	200 ppm	400 ppm	800 ppm	200 ppm	-
Corn oil	9.98	10.1	10.7	11.4	11.6	12.5	10.3	10.9	23.9	13.30	10.70
Soybean oil	5.12	5.78	5.58	5.9	6.2	7.07	5.65	5.63	6.02	7.03	5.53

Where: T1: Oil treated with *Ginkgo biloba* extract, T2: Oil treated with *Ginkgo biloba* + SeNPs, T3: Oil treated with *Ginkgo biloba* + ZnNPs and T4: Oil treated with TBHQ.

Conclusion

From the present study, it can be concluded that *Ginkgo biloba* extract and eco-friendly synthesis of selenium and zinc nanoparticles with biocompatible *Ginkgo biloba* extract can stabilize corn and soybean oils very effectively in concentration of 200, 400 and 800 ppm have stabilization efficiency comparable to conventional synthetic antioxidants, i.e. TBHQ at its legal limit. It improves resistance of corn and soybean oils against thermal deteriorative changes. Besides this, polyunsaturated fatty acid content is saved appreciably by creating resistance in oil against oxidative rancidity. Therefore, on behalf of this study, *Ginkgo biloba* extract and synthesis of selenium and zinc nanoparticles can be recommended as a potent source of antioxidants for the stabilization of food systems, especially unsaturated vegetable oils.

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