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Production of Biodiesel from *Zygnema carinthiacum* Using Eggshell as a Catalyst and Impregnation with Green Produced Silver Nanoparticles

SUDAD ASAAD ALKINANI*, AFRODET A. SALEH[1] AND A. M. ATHBI[2]

Department of Ecology, College of Science, University of Basrah , Basra, Iraq
**(e-mail: sudad.mutashar@uobasrah.edu.iq; Mobile: 00960 79013 15232)*

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ABSTRACT

Biodiesel is a promising renewable fuel that can be used as an alternative to fossil fuels. In this study, biodiesel was produced from *Zygnema carinthiacum* green algae by extracting oil and then converting the oil in two steps (esterification and transesterification) using two types of catalysts: calcium oxide (CaO) produced from eggshells and calcium oxide impregnated with silver nanoparticles (CaOAgNPs) produced from the same algae *Z. carinthiacum*. The properties of algal oil and biodiesel produced were investigated using Gas Chromatography-Mass Spectrometry (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR). The AgNPs were synthesized and characterized using a UV-visible Spectrophotometer, (FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM), which confirmed the synthesis of mostly spherical nanoparticles with sizes ranging from 19.92-52.38 nm. Fuel properties, including density, kinematic viscosity, cloud point, pour point, and acid value were determined and their values were 0.877 g/cm^3, 4.71 mm^2/s, 3°C,-4°C, 0. 34 mg KOH/g, respectively, for biodiesel produced by used CaO catalyst, as for the biodiesel produced using CaOAgNPs catalyst their values were 0.867 g/cm^3, 4.12 mm^2/s, -2°C, -7°C, 0.46 mg KOH/g., respectively. The results also revealed that a biodiesel yield of approximately 78% was obtained using CaO and nearly 80% using CaOAgNPs. In conclusion, the production of biodiesel from *Z. carinthiacum* oil as an alternative feedstock using an AgNPs-impregnated CaO catalyst made from eggshell waste was discovered to be an environmentally-friendly and promising technique.

Key words: Biodiesel, transesterification, eggshells catalyst, *Zygnema,* calcination, AgNPs green synthesis

INTRODUCTION

It is well known that fossil fuels pollute the air, and that global energy consumption is constantly increasing, which has resulted in dwindling fuel resources, leading to an increase in studies aimed at producing alternative fuels and renewable energy sources around the world (Deshmukh *et al.,* 2021). Biofuel produced from biomass, the most important of which include biodiesel, bioethanol, biohydrogen, biomethane and biogasoline, is currently one of the most important sources of sustainable and renewable energy (Sharma *et al.,* 2020). Biofuels are separated into three generations. The first generation is produced from food crops rich in sugars, starches and oils, such as corn, wheat, sugarcane, barley, sorghum and sunflower; the second generation is produced from cellulosic materials derived from plant residues such as wheat straw, grass and others (Leong *et al.*, 2018), while the third generation is produced from algae (Leong *et al.*, 2018).

Biodiesel is one of the most important types of biofuels, chemically is monoalkyl esters of long chain fatty acids derived from renewable feed stock such as vegetable oils (Shaah *et al.,* 2021), fish oils (Kadhim *et al.,* 2020), animal fats (Hasan and Ratnam, 2022), fungal oils (Alrubayae and Kadhim, 2020), as well as algal oils (Alwan and Al, 2021). It is produced by transesterification in which the oil or fat reacts with alcohol in the presence of a catalyst to give the corresponding monoalkyl esters (Mishra and Goswami, 2018).

It is a renewable and biodegradable fuel that is environmentally safe for use and provides energy needs, so it represents a practical solution to the crisis of depletion of fossil fuels on the one hand and the crisis of environmental degradation on the other (Bhatt *et al.*, 2018). It has been identified as a potential alternative fuel for diesel engines

[1]Department of Pathological Analyses, College of Science, University of Basrah, Basra, Iraq.
[2]Department of Biology, College of Education for Pure Sciences, University of Basrah, Basra, Iraq.

because it is renewable in nature and reduces fossil fuel consumption and does not cause pollution when burned compared to conventional fuels and leads to lower greenhouse gases because it does not contain sulfur compounds and contains low levels of carbon monoxide and hydrocarbons (Gopal *et al.*, 2014). The ability to use various nanomaterials with different sizes ranging from (1-100) nanometres has fueled interest in nanotechnology over the last few decades (Ghimire *et al.,* 2015). Due to their physical, chemical and mechanical properties, nanoparticles can play a crucial role in the development of biofuel production processes. As a result, nanoparticles are utilized in a variety of applications, including biofuel production processes. Numerous studies have demonstrated that the use of nanoparticles in processes, such as nanofibres, nanotubes and metal nanoparticles, has a positive effect on boosting and enhancing biofuel production (Sekoai *et al.*, 2019). So, the primary goal of this study is to biosynthesis silver nanoparticles AgNPs from *Z. carinthiacum* extract and use them to increase the production of biodiesel produced from the same algae.

MATERIALS AND METHODS

Z. carinthiacum was isolated and characterized in accordance with AlKinani *et al.* (2023). Extract of *Z. carinthiacum* was prepared by dissolving 200 mg of powdered algae in 100 ml of sterile distillated water. The extract was heated at 60°C for 20 min, the mixture was centrifuged at 8000 rpm, and the filtrate was used to produce silver nanoparticles. A volume of 5 ml of algae aqueous extract was added to 95 ml of silver nitrate $AgNO_3$ solution at a concentration of 1 mM. The mixture was shaken well and heated in water bath at 60°C for 15 min in the dark to prevent oxidation of silver nitrate. The acidity of the mixture was adjusted to 11, and the mixture was left for two days at 25°C before the nanoparticles were deposited using centrifugation for 30 min at 6000 rpm. The AgNPs nanoparticles were then washed three times with distilled water and dried in an oven for 24 h at 40°C before being stored in sterile containers until use.

AgNPs was characterized using UV-visible spectrophotometer (Aquarius- ce-7200/ England) at 350-900 nm, XRD (Philips-pw1730/ USA) to determine the size and composition of nanoparticles, FTIR (Jasco-4200/Germany), and SEM (Quantum450-FEI/Germany) to determine the morphology and diameter of the nanoparticles.

Lipid extraction from algae was carried out using the Soxhlet apparatus. A 20 g dry weight of *Z. carinthiacum* was placed in a thimble and carried to a specific cylinder in the Soxhlet. A 250 ml mixture of solvent (chloroform: methanol) as (1:3) was added to the flask, and the extraction process was continued for 24 h before the solvent was separated from the extract using a rotary evaporator at 40°C. The extract was kept in clean and sterile containers until analysis, and samples were analyzed using GC-MS and FTIR. To contrast the oil extraction product of pretreatment with AgNPs to destroy algal cells with direct extraction. The Razack *et al.* (2016) method was used. A dry algal biomass was mixed with water (in a 3:1 water-to-biomass ratio) and placed in a 250 ml conical flask. 150 µg of AgNPs were added per 1 g of dried algal mass (AgNPs were exposed to ultraviolet sonication for 20 min before being added) and mixed with sterile distilled water, then the mixture was incubated for 40 min in a shaking incubator at 100 rpm, and the samples were oven-dried for 8 h at 60°C. Following that, the oil was extracted with a 3:1 mixture of chloroform and methanol.

The percentage of lipid productivity in algal species was estimated by calculating the weight of the algae powder and the weight of the resulting lipid (Subramanian *et al.,* 2015) as:

$$\% \text{ Lipid yield} = \frac{W1}{W2} \times 100 \qquad \ldots(1)$$

Where, W_1 – Weight of lipid extracted (g) and W_2 – Weight of the dried algae sample (g)

GC-MS analysis was carried out at the Basra Oil Company Laboratory, by using an Agilent Technologies, 7890B GC system coupled to an Agilent Technologies 5977A MSD with EI Signal detector, using HP-5ms 5% phenyl, 95% methyl siloxane (30 m × 250 µm × 0.25), the oven temperature was set at 40°C hold for 4 min then raised to 10°C min to 300°C for 20 min , Helium carrier gas flow rate was 1 ml/ min and purge flow of 3 ml/min. The injection

mode was split, the injection temperature was 290°C, and the injection sample volume was 1 micro litter. The mass spectrometer used an Ion source temperature of 230°C, a mass range of 44-650 m/z, and data were run through the NIST 2014, data base as an additional tool to confirm compound identity.

A JASCO FTIR-4200/Germany device was used to obtain spectra from oil samples, biodiesel samples, algal extract and nanoparticles produced from algae were diagnosed at the Polymer Research Centre of University of Basra using Fourier Transform Infrared Spectroscopy to determine the bonds between chemical compounds.

By transesterification, *Z. carinthiacum* crude oil was converted into biodiesel. Due to the extremely high free fatty acid (FFA) content of the crude algal oil, a two-step esterification process was carried out: acid esterification followed by base transesterification (Karmakar *et al.*, 2018). Before beginning this type of esterification, the algal oil was heated at 75°C for 5 min to remove water, then it was mixed with methanol in a 1:7 (v: w) ratio, and 1.5% concentrated sulfuric acid H_2SO_4 was added as a catalyst. The mixture was placed in a three-necked flask and vibrated hot plate at 60°C for 90 min. The mixture was stirred at 250 rpm, and the system was equipped with a condenser to prevent solvent evaporation after the period expired. After it cooled, it was transferred to a separation funnel for 3 h, and the mixture was washed with warm water to get rid of the catalyst. Then the bottom layer containing water and excess methanol was removed. The esterification product was transferred to complete the base transesterification process.

The catalyst was prepared following Rizkianto *et al.* (2020) by washing the eggshell using distilled water to remove the impurities then dried in an oven at 105°C for 24 h, then they were crushed and turned into a fine powder using the electric mill and the powder was calcined in a muffle furnace at 800°C for 3 h to convert the calcium carbonate $CaCO_3$ present in the eggshell into calcium oxide CaO to be used as a catalyst. In this procedure, esterified algal oil was mixed with methanol in a 1:6 (v: w) ratio. The heterogeneous catalyst CaO was then added at a concentration of 3%. The mixture was placed in a three-necked flask and connected to a condenser to prevent solvent evaporation. Then the flask was fastened on a vibrating hot plate at 60°C, the mixture was stirred at 500 rpm for 75 min. The mixture was left to cool and transferred to the separating funnel to get rid of the glycerin layer and to obtain the biodiesel layer (the upper layer), washing the biodiesel with hot distilled water at 55°C (30% v: v), the solvent was evaporated and the biodiesel was heated at 100°C for 15 min to remove water and other solvent residues.

This procedure was performed on the esterified algal oil of *Z. carinthiacum* using a CaO catalyst supported by AgNPs. In order to prepare this catalyst, the method of Rizkianto *et al.* (2020) was followed by impregnating fine eggshell powder with AgNPs prior to the calcination process; 2 g of eggshell powder was added to 5 ml of AgNPs solution, and the mixture was stirred thoroughly for 2 h at 25°C in a vibrating incubator. Then it was centrifuged at 3000 rpm for 10 min, the liquid was removed, and the solid was dried at 100 °C for 2 h. Following this, the base transesterification process was carried out.

The percentage yield of biodiesel was determined (Abdala *et al.*, 2020) as:

$$\text{Biodiesel yield (\%)} = \frac{\text{Weight of biodiesel produced}}{\text{Weight of algal oil}} \times 100 \quad \ldots(2)$$

The chemical characterization of the synthesized biodiesel was carried out using FTIR spectroscopy (Jasco-4200/Germany) and GC-MS (Agilent 5977 A MSD/USA) techniques. FTIR analysis was used to confirm the conversion of fatty acid into fatty acid methylesters using an FTIR spectrophotometer. Spectra were collected for a scanning range of 400-4000/cm. Major fatty acid methyl esters (FAME) were detected by GC-MS. Fuel properties: density (ASTM D1480), kinematic viscosity (ASTM D445), cloud point (ASTM D2500), pour point (ASTM D97), acid values (D664) of FAMEs were determined by performing standard ASTM tests.

The results were analyzed using the IBM SPSS Statistics 20 statistical analysis programme, and the averages were tested using the L. S. D. method.

RESULTS AND DISCUSSION

UV-visible spectroscopy was used to examine the nanoparticles in aqueous suspensions based on their size and shape. The colour changes and absorption were measured, and the highest absorption peak was at 421 nm (Fig. 1).

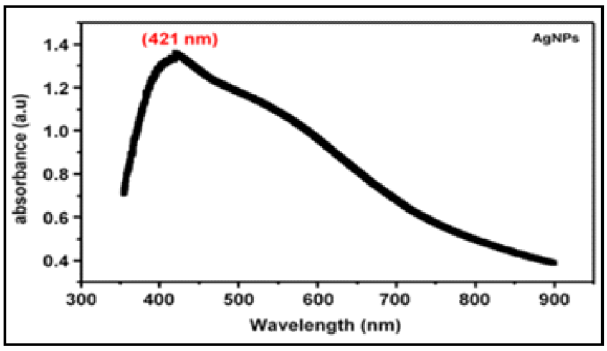

Fig. 1. The UV results of silver nanoparticles from *Z. carinthiacum*.

The physical structure and crystal size of silver nanoparticles were analyzed using X-ray diffraction pattern, the XRD patterns of synthesized AgNPs was characterized at 2θ equal by four distinct diffraction peaks at 24.60°, 45.26°, 61.56° and 76.08° corresponding to 111, 200, 220 and 311, respectively (Fig. 2).

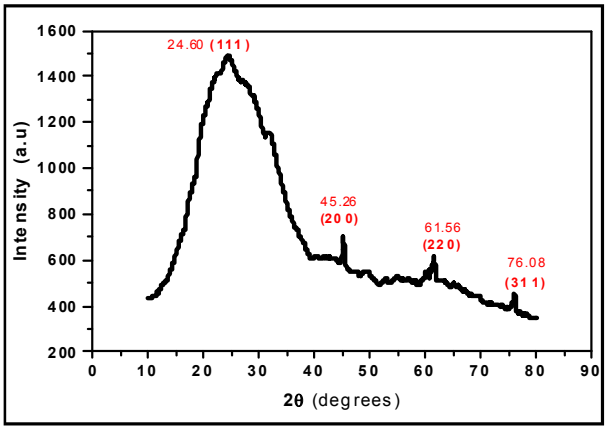

Fig. 2. XRD of silver nanoparticles produced from *Z. carinthiacum*.

FTIR measurements were performed on *Z. carinthiacum* aqueous extract to confirm the presence of functional groups that act as reducing agents in the production of nanoparticles. The results revealed the presence of various functional groups. The band at 3343/cm was due to the presence of the N-H amino bond (Liu *et al.*, 2015), the band appeared at 2929/cm was due to the presence of the CH_2 asymmetric stretching (Ashokkumar and Ramaswamy, 2014), the band appeared at 1657/cm indicating the presence of the C = O bond as a result of the presence of active alkene compounds, the band appeared at 1423/cm indicating the presence of the aromatic C=C bond (Deepika, 2018), and the band appeared at 1041/cm evidenced the presence of the C-N stretch due to the presence of aliphatic amines, and also at 873/cm evidence of the presence of the C-H bond (Panhwar *et al.*, 2019). The FTIR analysis was also carried out to verify the silver nanoparticles. The results showed the presence of band at 3491/cm indicating the presence of the amino bond N-H, the strong band at 2924/cm due to the presence of the asymmetric C-H stretch (Abdel-Raouf *et al.*, 2018), as well as the presence of the C=C bond indicating the presence of nitrogenous compounds at the 2360/cm (Singh *et al.*, 2022). $CaCO_3$ is converted to CaO and CO_2 during calcinations (Figs. 3 and 4), so the sharp expansion at about 711/cm indicated the presence of a Ca-O bond, indicating the presence of CaO.

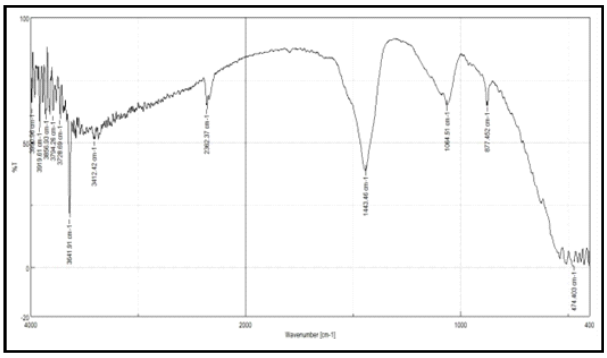

Fig. 3. FTIR analysis of the calcium oxide CaO catalyst.

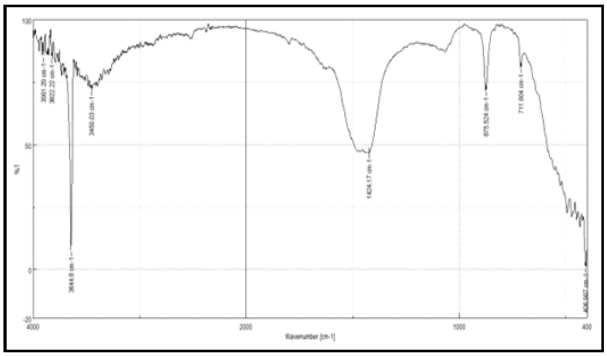

Fig. 4. FTIR analysis of the CaO AgNPs catalyst.

The thickness of the algal cell walls, the small size of the cell and the complexity of the cell

membrane all had a negative impact on the release of lipids within the cells; therefore, solvent extraction and mechanical pressure produced less oils. To improve oil extraction from algae, a pretreatment method was used to disrupt the cell wall and release more oils. In present study, AgNPs was used instead of direct extraction to disrupt algal cell walls. The method of using AgNPs yielded the highest rate of oil extraction, which was 27%. The highest percentage of extracted oil was 27 using silver nanoparticles (AgNPs), with a significant difference from the direct extraction method. The method of using AgNPs is one of the best pretreatment methods for increasing the efficiency of oil extraction from algal cells, as shown in Table 1. This is in consistent with the findings of Razack *et al.* (2016), who demonstrated in their study that silver nanoparticles were capable of destroying the algal cell wall and could be used to increase extraction efficiency as a green and cost-effective method to conventional methods.

Table 1. Products of direct extraction and extraction using AgNPs

Extraction with AgNPs		Direct extraction		Average (%)
g/g	%	g/g	%	22.75
0.27	27	0.185	18.5	

L.S.D. = 8.406.

The fatty acid profile of *Z. carinthiacum* oil was determined using GC-MS based on the (Agilent 5977 A MSD/USA) GC-MS spectrum. Three fatty acids were identified and quantified. It was discovered that there was one polyunsaturated fatty acid α-Linolenic acid (C18:3) and two saturated fatty acids Palmitic acid (C16:0) and Myristic acid (C14:0) in the algal oil and it mainly contributed to the production of biodiesel, oil with polyunsaturated fatty acids with more than three double bonds with less oxidized and more thermal stability (Dutta *et al.,* 2014). As a result, the oil used in this study was excellent (Table 2 and Fig. 5).

Table 2. The GC-MS analysis of *Z. carinthiacum* oil

S. No.	Name of fatty acid	Chemical formula	The number of strings	Molar mass (g/mol)	%
1.	α-Linolenic acid	C18H30O2	C18:3	278.43	71.26
2.	Palmitic acid	C16H32O2	C16:0	256.42	18.72
3.	Myristic acid	C14H28O2	C14:0	228.37	0.86
Total					90.84

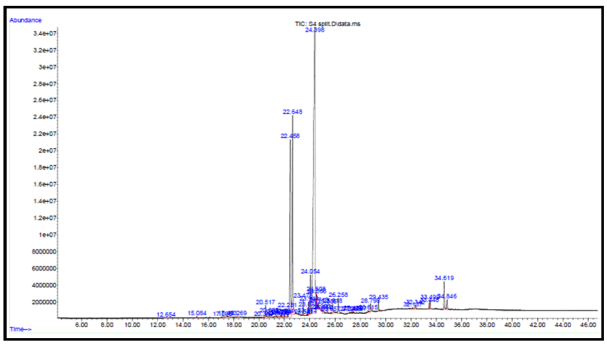

Fig. 5. The GC-MS spectrum for biodiesel produced from alga *Z. carinthiacum*.

The results analysis of *Z. carinthiacum* algal oil showed the appearance of peak at the range 3276/cm, indicating the presence of the O-H stretch, as an evidence of the presence of alcohols or phenols and at 3010-2925/cm, an indication of the presence of the C-H asymmetric stretching bond due to the presence of alkenes and alkanes and this was identical as stated by Errico *et al.* (2019), and at 2360/cm an indication of the presence of the asymmetric O-H stretch as a result of the presence of the OH group, and the prominent presence of ester groups in the extracted algal oil were confirmed by the peaks obtained at 1742, 1625, 1165 and 1064/cm indicating the presence of the carbonyl C-O stretch which revealed that the extracted oil contained sufficient ester groups in it and hence it was suitable for biodiesel production. The extracted oil also contained a peak at 1515/cm, indicating the presence of the asymmetric N-O stretch due to the presence of nitrogenous compounds, and a peak at 1459/cm, indicating the presence of the C-H stretch due to the presence of alkane.

To enable transesterification, acid esterification was used to reduce the FFA in algal oil. This step also assisted in removing impurities that could be present in the oil. The density of the biodiesel produced by used CaOAgNPs was 0.867g/cm^3 which was comparable to 0.865 g/cm^3, the Kinematic viscosity of the biodiesel produced by used CaO

was 4.71 mm^2/s which was comparable to 4.741 mm^2/s of the biodiesel produced from waste fish oil as reported by Kusmiyati and Wulandari (2016), while the Kinematic viscosity of the biodiesel produced by using CaOAgNPs was 4.12 mm^2/s and it was comparable to 4.22 mm^2/s as reported by Ong *et al.* (2020), the cloud point of the biodiesel produced by using CaO and CaO AgNPs was (3, -2) °C, respectively, the pour point of the biodiesel produced by using CaO and CaOAgNPs was (-4 , -7) °C , respectively (Table 3). These results are close to the results obtained by Ong *et al.* (2020), the acid values of the biodiesel were (0.34, 0.46) mg KOH/g. These results are similar to those obtained by Kaewdaeng *et al.* (2017), the yield of biodiesel was 78% when CaO was used as a catalyst, but it was 80% when CaOAgNPs was used as a catalyst in the transesterification process, demonstrating the role of AgNPs. When compared to CaO alone, the results showed a 2% increase in biodiesel yield when using AgNPs impregnated CaO catalyst. These findings are consistent with the findings of Rizkianto *et al.* (2020), who stated that the addition of silver nanoparticles improved the catalytic performance of CaO due to the increased surface area created by nanoparticle impregnation. It was also in line with the results of Bet-Moushoul *et al.* (2016), who reported that using CaO impregnated with gold nanoparticles resulted in a 4% higher biodiesel yield from sunflower oil than using CaO alone.

The statistical analysis of the ANOVA table revealed that there were significant differences in the density of biodiesel produced using different catalysts with the density of biodiesel produced using CaOAgNPs catalyst as 0.867 g/cm^3. Similarly, the statistical analysis of the ANOVA table revealed that there were significant differences in the viscosity of the biodiesel produced using the different catalysts with the viscosity of the biodiesel produced using the CaOAgNPs catalyst as 4.12 mm^2/sec. The statistical analysis of the ANOVA table revealed that the pH value of biodiesel produced using different catalysts differed significantly with the pH value of biodiesel produced using CaOAgNPs catalyst as 0.46 mg KOH/g.

Table 3. The biodiesel properties

Properties	Biodiesel using CaO	Biodiesel CaOAgNPs	ASTM standards
Density (g/cm^3@15°C)	0.877	0.867	0.86-0.9
Kinematic viscosity mm^2/s (40°C)	4.71	4.12	1.9-6
Cloud point (°C)	3.00	-2.00	-15 to +10
Pour point (°C)	-4.00	-7.00	-3 to 12
Acid value(mg KOH/g)	0.34	0.46	<0.8

L.S.D. density = 0.006, viscosity = 0.084 and acid value = 0.083.

The results of the GC-MS analysis of biodiesel produced from *Z. carinthiacum* by acid-base esterification using an eggshell-derived CaO catalyst revealed the presence of 13 different types of methyl esters of fatty acids (Table 4). The methyl ester of α-linolenic acid accounted for the highest percentage of 33.78, whereas the overall figure was 77.25%.

The results of GC-MS analysis of biodiesel produced from *Z. carinthiacum* by acid-base esterification using the CaOAgNPs nanocatalyst produced by mixing CaO with silver nanoparticles revealed the presence of 20 different types of fatty acid methyl esters,

Table 4. The GC-MS analysis of biodiesel produced using CaO

S. No.	Name of fatty acid methyl ester	Chemical formula	Molar mass (g/mol)	%
1.	?-Linolenic acid methyl ester	C19H32O2	292.46	33.78
2.	Palmitic acid, methyl ester	C17H34O2	270.45	18.3
3.	Linoleic acid, methyl ester	C19H34O2	294.5	12.23
4.	Stearidonic acid, methyl ester	C19H30O2	290.40	4.23
5.	Palmitoleic acid, methyl ester	C17H32O2	268.4	2.64
6.	Stearic acid, methyl ester	C19H38O2	298.5	1.71
7.	Lignoceric acid, methyl ester	C25H50O2	382.7	1.60
8.	?-Linolenic acid, methyl ester	C19H32O2	292.5	1.18
9.	Eicosanoic acid, methyl ester	C21H42O2	326.55	0.58
10.	Docosanoic acid, methyl ester	C23H46O2	354.6	0.44
11.	7,10-Hexadecadienoic acid methyl ester	C17H30O2	266.4	0.41
12.	Pentadecanoic acid, methyl ester	C16H32O2	256.4	0.23
13.	Heptadecanoic acid, methyl ester	C18H36O2	284.5	0.19
				77.25

with a total percentage of 89.26 with 25.28% Palmitic acid methyl ester (Table 5).

The results of the analysis of biodiesel produced from *Z. carinthiacum* by acid-base esterification and using two types of catalysts (CaO and CaOAgNPs) are shown in Table 6. The results of the FTIR analysis of biodiesel produced using the CaO catalyst showed the appearance of peaks at 3420/cm indicating the presence of hydrogen bond O-H stretch for the presence of alcohols or phenols (Mohamed *et al.*, 2020). Peaks at 2925 and 2854/cm showed the presence of the symmetric and asymmetric C-H stretch which indicated the presence of CH_2, CH_3 groups of alkanes. The peak at 1743/cm showed the presence of the C=O stretch, indicating the presence of the ester group. A peak at 1461/cm showed the presence of the C-H stretch corresponding to the asymmetric stretching of CH_3. A peak at 1364/cm showed the presence of the CH_3 symmetric group due to the presence of methyl esters. A peak at 1170/cm showed the presence of the C-O stretch**,** this indicating the presence of an ester group (Asl *et al.,* 2020).

As for the results of the analysis of biodiesel produced from *Z. carinthiacum* using CaOAgNPs catalyst, showed the presence of the characteristic peak at 3010/cm for the presence of the C-H stretch bond indicating the presence of alkane. The characteristic peaks at 2922-2853/cm showed the presence of the symmetrical and asymmetric C-H stretch due to the presence of CH_2, CH_3 groups.

Table 5. The GC-MS analysis of biodiesel produced by using CaOAgNPs

S. No.	Name of fatty acid methyl ester	Chemical formula	Molar mass (g/mol)	%
1.	Palmitic acid, methyl ester	C17H34O2	270.45	25.28
2.	Linoleic acid, methyl ester	C19H34O2	294.5	24.82
3.	Roughanic acid, methyl ester	C17H28O2	264.4	10.08
4.	Stearidonic acid, methyl ester	C19H30O2	290.4	7.17
5.	Eicosapentaenoic acid, methyl ester	C21H32O2	316.5	3.51
6.	Palmitoleic acid, methyl ester	C17H32O2	268.4	2.88
7.	Stearic acid, methyl ester	C19H38O2	298.5	2.85
8.	Myristic acid, methyl ester	C15H30O2	242.4	1.92
9.	Lignoceric acid, methyl ester	C25H50O2	382.7	1.82
10.	?-Linolenic acid, methyl ester	C19H32O2	292.5	1.51
11.	Arachidonic acid, methyl ester	C21H34O2	318.5	1.45
12.	Tricosanoic acid, methyl ester	C24H48O2	368.64	1.18
13.	Docosanoic acid, methyl ester	C23H46O2	354.6	0.82
14.	Eicosanoic acid, methyl ester	C21H42O2	326.55	0.71
15.	7-10, Hexadecadienoic acid, methyl ester	C17H30O2	266.4	0.65
16.	Lauric acid, methyl ester	C13H26O2	214.34	0.40
17.	Heptadecanoic acid, methyl ester	C18H36O2	284.5	0.29
18.	Pentadecanoic acid, methyl ester	C16H32O2	256.4	0.37
19.	Oleic acid, methyl ester	C19H36O2	296.5	0.09
				89.26

Table 6. The FTIR analysis of biodiesel produced using CaO and CaO AgNPs catalysts

FAME	Frequency/cm	Bonds	Functional groups
FAME from	3420 (s,b)	O-H stretch	Alcohols, phenols
Z. carinthiacum by using CaO	2925 (m)	CH_2 asymmetric stretching	Alkanes
	2854 (m)	CH_2 symmetric stretching	Alkenes
	1743 (m)	C=O stretch	Esters
	1461 (m)	C-H stretch	Alkanes
	1364 (m)	CH_3 symmetric	Alkanes
	1170 (s)	C-O stretch	Esters
FAME from	3010 (m)	C-H stretch	Alkanes
Z. carinthiacum by using CaOAgNPs	2922 (m)	CH_2 asymmetric stretching	Alkanes
	2853 (m)	CH_2 symmetric stretching	Alken
	1744 (m)	C=O stretch	Esters
	1710 (m)	C=O stretch	Esters
	1462 (m)	C-H stretch	Alkanes
	1283 (m)	C-O stretch	Esters
	937 (m)	C-O stretch	Esters

The peaks at 1744 and 1710/cm indicated the presence of the C=O stretch due to the presence of ester groups in the biodiesel (Lawer-Yolar *et al.*, 2021). These groups indicated the conversion of triglycerides in oil to methyl esters and the peak at 1462/cm indicated the presence of the C-H stretch due to the presence of the methylene group CH_2 in the alkanes (El-Naggar *et al.*, 2021). The peak at 1283/cm indicated the presence of the C-O stretch, which showed the presence of the ester, and the peak at 937/cm indicated the presence of the ester (Ramadhani and Helmiyati, 2020).

CONCLUSION

Z. carinthiacum was investigated in this study for the synthesis of AgNPs and biodiesel. The results showed that the potential of this alga as a natural source for the synthesis of silver nanoparticles and biodiesel was promising; all properties of the biodiesel produced were within the limits of ASTM standards, and the presence of nanoparticles with a CaO catalyst increased the yield of the produced biodiesel by 2% compared to CaO alone.

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