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ORIGINAL ARTICLE

Comparison of the characteristics of gold nanoparticles synthesized using aqueous plant extracts and natural plant essential oils of *Eucalyptus globulus* and *Rosmarinus officinalis*

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KEYWORDS

Gold nanostructures;
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Green synthesis;
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Abstract In this work we successfully utilized 1% (m/v) aqueous leaf extracts and 1% (v/v) natural essential oils originating from *Eucalyptus globulus* and *Rosmarinus officinalis* as bioreducing and capping agents for gold nanoparticles (AuNPs) synthesis. UV/Vis absorption spectra revealed that AuNPs were well-dispersed and spherical when synthesized with *E. globulus* aqueous leaf extract, but also with *R. officinalis* aqueous leaf extract and its essential oil. Only AuNPs fabricated by utilizing *E. globulus* essential oil exhibited various shapes and a partial aggregation. TEM analysis showed that the average sizes of AuNPs produced with the aid of *E. globulus* aqueous leaf extract and its essential oil were 12.8 ± 6.3 nm and 42.2 ± 42.0 nm, while in the case of *R. officinalis*, resultant AuNPs reached 8.66 ± 2.03 nm and 60.7 ± 60.6 nm in diameter, respectively. By EDS, Au, O, and C were detected in all tested nanofluids. Functional groups of organic compounds occurring in the investigated aqueous plant extracts and essential oils were identified by ATR-FTIR, and they

Abbreviations: AuNPs, gold nanoparticles; APP, atmospheric pressure plasma; dc-μAPGD, direct-current atmospheric pressure glow microdischarge; HIFU, high-intensity focused ultrasound; ATR-FTIR, attenuated total reflection-Fourrier transformation infrared spectroscopy; GC-MS, gas chromatography-mass spectrometry; UV/Vis, ultraviolet-visible absorption spectrophotometry; TEM, transmission electron microscopy; EDX, X-ray energy dispersive spectroscopy; LSPR, localized surface plasmon resonance

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were established as quite similar among the analyzed plant extracts, but also among the essential oils. Finally, GC-MS analysis were implemented to determine the key constituents of the *E. globulus* and *R. officinalis* aqueous extracts and their essential oils.

1. Introduction

There are several methods of AuNPs production, and these mainly involve chemical (Das et al., 2012; Qin et al., 2010), physical (Dzimitrowicz et al., 2015a,b, 2016a; Kabashin and Meunier, 2003), and sonochemical (Yusof and Ashokkumar, 2015; Chen et al., 2001) processes. In chemical methods, appropriate reduction agents in addition to compounds that prevent aggregation and sedimentation of the final products have to be used. Another approach to AuNPs production is the use of physical methods based on low-temperature atmospheric pressure plasmas (APPs), i.e. direct-current atmospheric pressure glow microdischarge (dc-μAPGD) generated in contact with a flowing liquid solution, where the Au(III) ions are reduced by reactive species from the plasma-liquid interface of dc-μAPGD (Dzimitrowicz et al., 2015a,b, 2016a). APPs efficiently facilitate the synthesis of AuNPs and enable the production of large amounts of them in a relatively short time. However, they need well-equipped specialized laboratories with devices not routinely used in the industrial facilities.

A sustainable alternative to conventional reduction methods lies in green chemistry, which requires natural substances acting as both the reducing and capping agents (Vankar and Bajpai, 2010; Huang et al., 2007, 2010) for the reduction of Au(III) ions. It appears that such biomediated green synthesis constitutes a highly ecological and cost-effective form of synthesizing nanostructures with a high production rate and that is why it provides many significant advantages over the chemical and physical methods (Yasmin et al., 2014). Plant extracts have repeatedly been described as a rich source of active biomolecules that enable the production of stable AuNPs that are free of toxic additives (Huang et al., 2007; Dzimitrowicz et al., 2016b; Valencia et al., 2014). Different plant extracts or essential oils (Table 1) have been used to synthesize Au nanofluids of well-defined morphology, which is of huge interest to the field of applied research (Dwivedi and Gopal, 2010; Huang et al., 2007, 2010; Kuppusamy et al., 2016; Lallawmawma et al., 2015; Mishra et al., 2016).

High demand for effective methods of obtaining AuNPs has resulted in a necessity for developing alternate green synthesis using concentrated natural compounds. It needs to be taken into account that the reducing agents present in crude plant extracts are relatively diluted, and that many of the remaining components are unlikely to contribute to the process of AuNPs synthesis. So, the use of concentrated plant-derived extracts or essential oils as the reducing agents allows high-throughput reduction of Au ions. The ability to obtain high purity AuNPs with the use of concentrated essential oils has been reported by Muniyappan and Nagarajan (2014) and their further industrial and medical applications were suggested. Biosynthesis of AuNPs was conducted using *Curcuma pseudomontana* essential oil and the resulting nanostructures exhibited cytotoxic, antibacterial, anti-inflammatory and antioxidant activities against T47D ductal human breast carcinoma cells (Muniyappan and Nagarajan (2014)). Sheny et al. (2012) examined hexagonal AuNPs that were produced using essential oil from *Anacardium occidentale* for catalytic

Table 1 The size of AuNPs biosynthesized with the use of various plant extracts or essential oils.

Plant species	Reducing agent	Size [nm]	Method of measurement	References
Aloe vera	Leaves extract	50–350	TEM	Chandran et al. (2006)
Anacardium occidentale	Essential oil	av. 36	TEM	Sheny et al. (2012)
Cassia fistula	Bark extract	55.2–98.4	SEM	Daisy and Saipriya (2012)
Centella asiatica	Leaf extract	9.3–10.9	TEM	Das et al. (2010)
Cinnamomum camphora	Leaf extract	10–40	TEM	Huang et al. (2007)
Cinnamomum verum	Powder or pure active compounds	32 ± 2	TEM, DCS	Chanda et al. (2011)
Citrus lemon	Juice extract	av. 32.2	DLS	Sujitha and Kannan (2013)
Citrus reticulata	Juice extract	av. 43.4	DLS	Sujitha and Kannan (2013)
Citrus sinensis	Juice extract	av. 56.7	DLS	Sujitha and Kannan (2013)
Emblica officinalis	Fruit extract	15–25	TEM	Ankamwar et al. (2005)
Eucalyptus globules	Leaf extract	12.8 ± 6.3	TEM	This study
Eucalyptus globules	Essential oil	42.2 ± 42.0	TEM	This study
Hibiscus rosa sinensis	Leaf extract	~14	TEM	Philip (2010)
Magnolia kobus	Leaf extract	10–40	TEM	Song et al. (2009a)
Memecylon edule	Leaf extract	20–50	TEM	Elavazhagan and Arunachalam (2011)
Murraya koenigii	Leaf extract	~20	TEM	Philip et al. (2011)
Nyctanthes arbortristis	Flower extract	19.8 ± 5.0	TEM	Das et al. (2011)
Rosa hybrida	Petal extract	~10	Particle Metrix PMX-200CS	Noruzi et al. (2011)
Rosa rugosa	Leaf extract	av. 11	TEM	Dubey et al. (2010b)
Rosmarinus officinalis	Leaf extract	8.66 ± 2.03	TEM	This study
Rosmarinus officinalis	Essential oil	60.7 ± 60.6	TEM	This study
Tanacetum vulgare	Fruit extract	10–40	TEM	Dubey et al. (2010a)
Terminalia catappa	Leaf extract	10–35	TEM	Ankamwar (2010)
Trigonella foenum-graecum	Seed extract	15–25	TEM	Aromal and Philip (2012)

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Table 2 Localization (nm) of the maximum of the LSPR absorption band for obtained AuNPs.

Plant species	Aqueous leaf extract	Natural essential oil
Eucalyptus globulus	534.6	544.2
Rosmarinus officinalis	532.8	528.9

The absorption spectra were recorded using 50 mg L^{-1} solutions of Au(III).

hydrogenation of *p*-nitrophenol to *p*-aminophenol. A growing rate of various applications for Au nanofluids is forcing researchers to further develop biological methods of their synthesis.

We focused our scientific interest on *Eucalyptus globulus* and *Rosmarinus officinalis* as the sources of reductive and capping agents in AuNPs synthesis. Djenane et al. (2011) determined γ-terpinene, 1,8-cineole, α-terpenyl acetate, terpinen-4-ol, and p-cymene as the five main constituents of *E. globulus* essential oil with the following percentage values: 94.5%, 3.2%, 0.1%, 0.1% and 0.1%. Concerning *R. officinalis*, its essential oil constitutes 1% of the plant total mass and contains 50% of mono-terpenes, approx. 7% of alcohols and 10% of ketones (Tuberose et al., 1998); however, the chemical composition varies strongly depending on the country of plant origin with high divergence in the ratios between certain monoterpenes i.e. 1,8-cineole, α-pinene and camphor (Pintore et al., 2002).

Hence, the present work was aimed at comparing the optical properties and morphology of AuNPs obtained using aqueous leaf extracts and essential oils from *E. globulus* and *R. officinalis*, in addition to determining which is the most suitable for further studies and subsequent applications. To our best knowledge, characteristics of AuNPs obtained with the aid of aqueous leaf extracts and essential oils originating from *E. globulus* and *R. officinalis* have not been previously reported. The purity of AuNPs obtained with aqueous leaf extracts and essential oils of both plants was also examined. Finally, ATR-FTIR and GC-MS analyses of aqueous leaf extracts and essential oils were performed, providing an insight into the composition of the compounds that might have been involved in reduction of Au(III) ions and stabilization of the resultant AuNPs.

2. Material and methods

2.1. Preparation of aqueous plant extracts

The aqueous leaf extracts of *R. officinalis* and *E. globulus* were prepared as has been described in the previous studies (Dzimitrowicz et al., 2016b; Valencia et al., 2014). Briefly, dried leaves of *R. officinalis* (PRYMAT®, Jastrzebie-Zdroj, Poland) and *E. globulus* (NAT, Mirkow, Poland) were washed with re-distilled water and finally dried in the dark. A fine powder of each plant was obtained by grounding the dried leaves with a pestle in a marble mortar. 2.0 g of each fine powder was mixed with 200 mL of re-distilled water to get a final concentration of 1% (m/v) (Valencia et al., 2014), heated up to boil and kept boiling for 10 min. Next, the resulting aqueous leaf extracts were filtered using qualitative filter paper discs (Munktell, grade 388). After filtration, the final leaf extracts were collected in glass vials and kept for further studies.

2.2. Preparation of natural essential oil solutions

To provide optimal conditions for AuNPs synthesis using natural essential oils, a 100 μL aliquot of commercial essential oil of *E. globulus* (SEMIFARM, Gdansk, Poland) or *R. officinalis* (SEMIFARM, Gdansk, Poland) was mixed with a re-distilled water:ethanol (Avantor Performance Materials, Gliwice, Poland) solution in a 4:1 ratio, as was described by Muniyappan and Nagarajan (2014) for silver nanoparticles production. The final concentration of such natural essential oils were 1% (v/v).

2.3. Green synthesis of AuNPs by using aqueous leaf extracts

For AuNPs synthesis, 10.0 mL of filtered 1% (m/v) aqueous leaf extract of *E. globulus* or *R. officinalis* was mixed with $HAuCl_4 \times 4H_2O$ (Avantor Performance Materials, Gliwice, Poland) solution, to get a final 50.0 mg L^{-1} concentration of Au in the reaction mixtures (Dzimitrowicz et al., 2016b; Valencia et al., 2014).

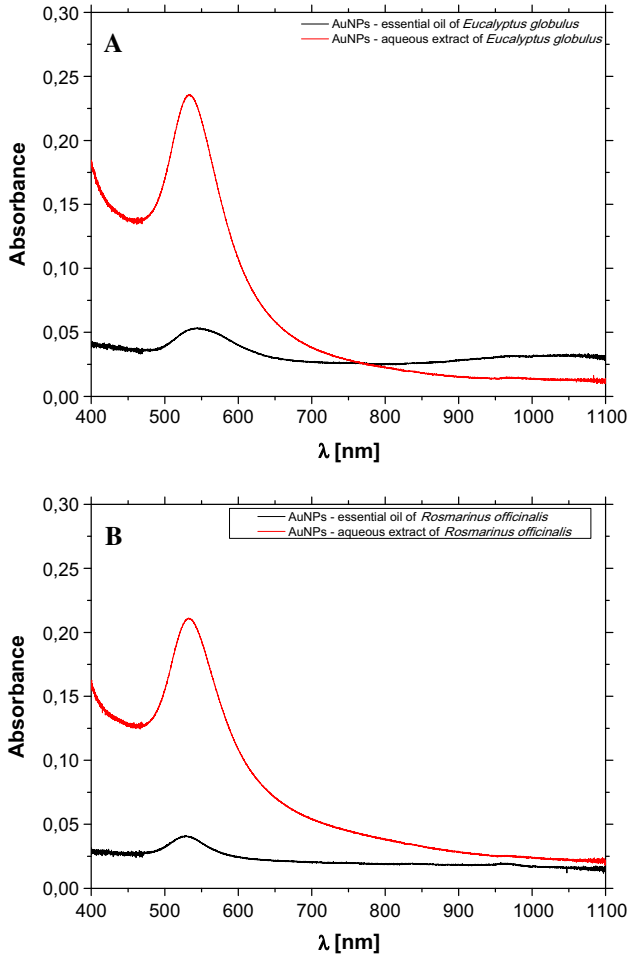

Figure 1 UV/Vis spectra of AuNPs. AuNPs were synthesized from 50 mg L^{-1} of Au in the presence of aqueous plant leaf extracts and natural plant essential oils of (A) *E. globulus* or (B) *R. officinalis*. Samples were diluted 20-fold prior to analysis.

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2.4. Biosynthesis of AuNPs by utilizing natural essential oils

When using natural essential oils of *E. globulus* or *R. officinalis* to produce AuNPs, it was necessary to perform the synthesis at 95 °C, as was previously suggested by Shukla et al. (2008). A heated 1% water-ethanol solution of natural essential oil was mixed with $HAuCl_4 \times 4H_2O$ (Avantor Performance Materials, Gliwice, Poland) to get 50.0 mg L^{-1} final concentration of Au in the reaction mixtures.

2.5. Determination of the optical properties and morphology of AuNPs

All solutions were analyzed to confirm the formation of nanostructures and to define the optical traits and morphology of the generated AuNPs. UV/Vis absorption spectrophotometry was used for evaluating optical properties of AuNPs. The measurements were carried out with a double-beam UV/Vis Specord 210 Plus (Analytik Jena AG, Jena, Germany). Other details are given in the Supplementary Material.

Transmission electron microscopy (TEM) and X-ray energy dispersive spectroscopy (EDX) were applied to determine the morphology of AuNPs and to define the elemental composition of the nanocolloidal fluids. The FEI Tecnai G220 X-TWIN instrument (FEI, Hillsboro, OR, USA) equipped with the EDAX X-ray microanalyzer (FEI) was utilized. Other details are given in the Supplementary Material.

2.6. Qualitative analyses of the chemical composition of aqueous plant extracts and essential oils

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and gas chromatography-mass spectrometry (GC-MS) were applied to determine the chemical composition of the aqueous leaf extracts and essential oils from both *E. globulus* and *R. officinalis*. The ATR-FTIR spectra of 1% (m/v) aqueous leaf extracts and non-diluted essential oils were recorded using a Vertex 70v instrument (Bruker, Bremen, Germany) equipped with a diamond ATR accessory. Other details are given in the Supplementary Material. Identification of chemical compounds present in the investigated aqueous leaf extracts and essential oils was achieved within the mass scanning range of 40–500 Da by comparing the obtained mass spectra to the available spectra libraries including SciFinder (Chemical Abstracts Service) and literature data (Hameed et al., 2015; Song et al., 2009b). TurboMass ver-5.1 software was used.

3. Results

3.1. Optical properties of synthesized AuNPs

It was previously found that colloidal dispersion of AuNPs lead to a change in the color of nanofluids from yellow to ruby red or bluish due to absorption or scattering of the light that

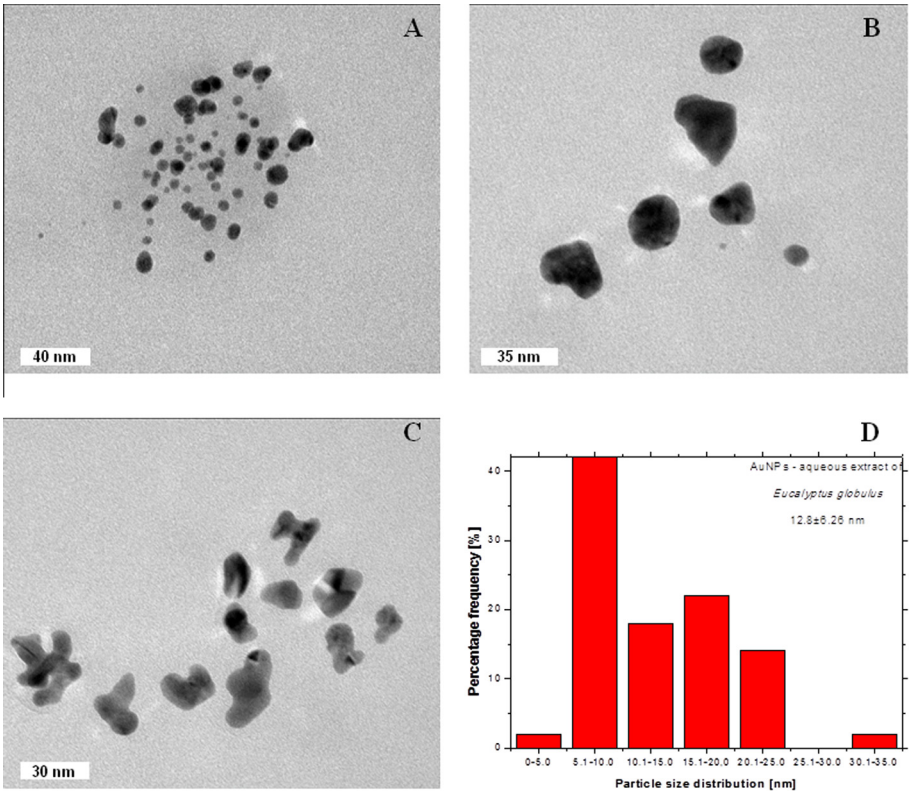

Figure 2 Morphology of AuNPs synthesized from *E. globulus* aqueous leaf extract. (A–C) Representative TEM micrographs of AuNPs obtained using 50 mg L^{-1} of Au and *E. globulus* aqueous leaf extract. (D) Size distribution of AuNPs was determined on the basis of TEM micrographs.

passes through them (Cademartiri and Ozin, 2009). Therefore, the first evidence for AuNPs production is a visible color change of the reaction mixtures. For this reason, visual observations were performed to examine capability of fresh aqueous leaf extracts and natural essential oils to reduce Au(III) ions to the respective Au nanofluids after the addition of 50 mg L^{-1} of Au.

Immediately after the addition of the solution containing Au(III) ions to the fresh aqueous leaf extracts or natural essential oils, a color change from yellow to ruby red was observed. Based on the above-stated phenomenon of absorption and scattering of the light by AuNPs, the color change of the reaction mixtures was consistent with occurrence of the maximum (λ_{max}) of the localized surface plasmon resonance (LSPR) absorption band, which for Au nanofluids typically occurs in the range of 520–570 nm (Pal and Kryschi, 2015). To find the position of the λ_{max} of the LSPR absorption band, UV/Vis absorption spectrophotometry was applied. The λ_{max} positions of the LSPR absorption band for Au nanofluids synthesized using aqueous plant extracts and essential oils are summarized in Table 2. The area and localization of the λ_{max} of the LSPR depend on the size and shape of AuNPs, the concentration of the AuNPs precursor, the type of solvent, and the reaction temperature (Lee et al., 2016). Representative absorption spectra for AuNPs obtained using the examined aqueous plant extracts and essential oils are presented in Fig. 1. As can be observed, the absorption spectrum of AuNPs synthesized using aqueous leaf extract of *E. globulus* is symmetrical, indicating the production of predominantly spherical nanostructures. In contrast, the absorption spectrum of AuNPs produced using *E. globulus* essential oil included two peaks.

The first LSPR band is characteristic of spherical nanostructures and is associated with a single plasmon resonance frequency. The second one, indicative of two plasmon resonance frequencies, is connected with AuNPs aggregation or formation of nanostructures of different shapes. In contrast, only one LSPR absorption band was observed for AuNPs generated by using aqueous leaf extract or essential oil of *R. officinalis* indicating the production of well-dispersed and spherical AuNPs.

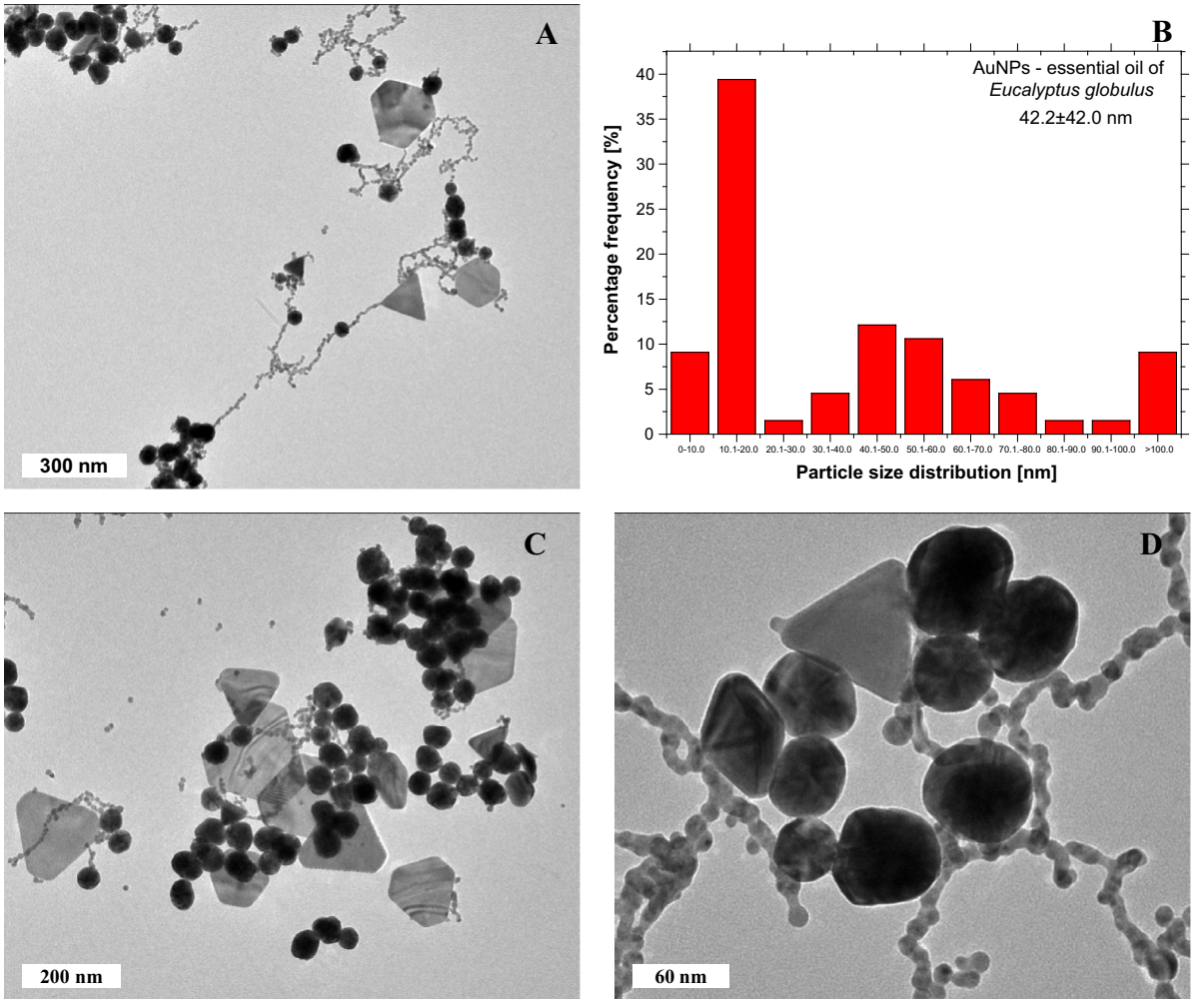

Figure 3 Morphology of AuNPs synthesized from *E. globulus* essential oil. (A, C, D) Representative TEM micrographs of AuNPs obtained using 50 mg L^{-1} of Au and *E. globulus* essential oil. (B) Size distribution of AuNPs was determined on the basis of TEM micrographs.

3.2. Morphology of Au nanofluids

In order to determine the size and shape of the produced AuNPs, TEM analyses were performed. Fig. 2 shows that AuNPs produced using aqueous leaf extract of *E. globulus* have an average size of 12.8 ± 6.3 nm. The generated nanostructures were primarily spherical, but a close-up of the grain sides can also be noticed. A great heterogeneity in shapes of biosynthesized AuNPs was observed when *E. globulus* essential oil was used for AuNPs bioreduction and stabilization (Fig. 3). In this case, the average size of AuNPs was 42.2 ± 42.0 nm. Using the above-mentioned essential oil, a quite high variety of shapes of AuNPs was observed, mostly including spherical (81%), but also triangular (15%), hexagonal (3%), and the rod-shaped (1%). Fig. 4 presents the particle size distribution of AuNPs synthesized using aqueous leaf extract of *R. officinalis*. Concerning the above-described nanofluids, the grain sides are located close to each other. The average size of AuNPs produced by utilizing aqueous leaf extract of *R. officinalis* was 8.7 ± 2.0 nm, while AuNPs produced by using the corresponding essential oil exhibited the average diameter of 60.7 ± 60.6 nm (Fig. 5).

In order to determine the elemental composition of the resulting nanofluids, EDX analyses were performed (Fig. 6). In each of the EDX spectra, strong signals of Au were observed, confirming the successful bioreduction of the AuNPs precursor. Besides Au peaks, signals for O, C, and K (only in the case of aqueous leaf extract of *E. globulus*) were acquired. The presence of above-mentioned elements naturally occurring in aqueous leaf extracts and essential oils can be associated with their binding to the surface of biosynthesized AuNPs. The peak of Cu likely originated from the sample holder, onto which the nanofluids were placed, but it can also be associated with some active centers of plant enzymes, in which Cu ions are fixed, e.g. superoxide dismutase, plastocyanin, tyrosinase (Habtemariam, 2016; Kropat et al., 2015; van Gelder et al., 1997).

3.3. The chemical composition of aqueous plant extracts and the essential oils

ATR-FTIR spectroscopy was used to identify the chemical compounds present in the applied aqueous leaf extracts and essential oils, as well as to search for differences between them that are responsible for significant variation in the morpholog-

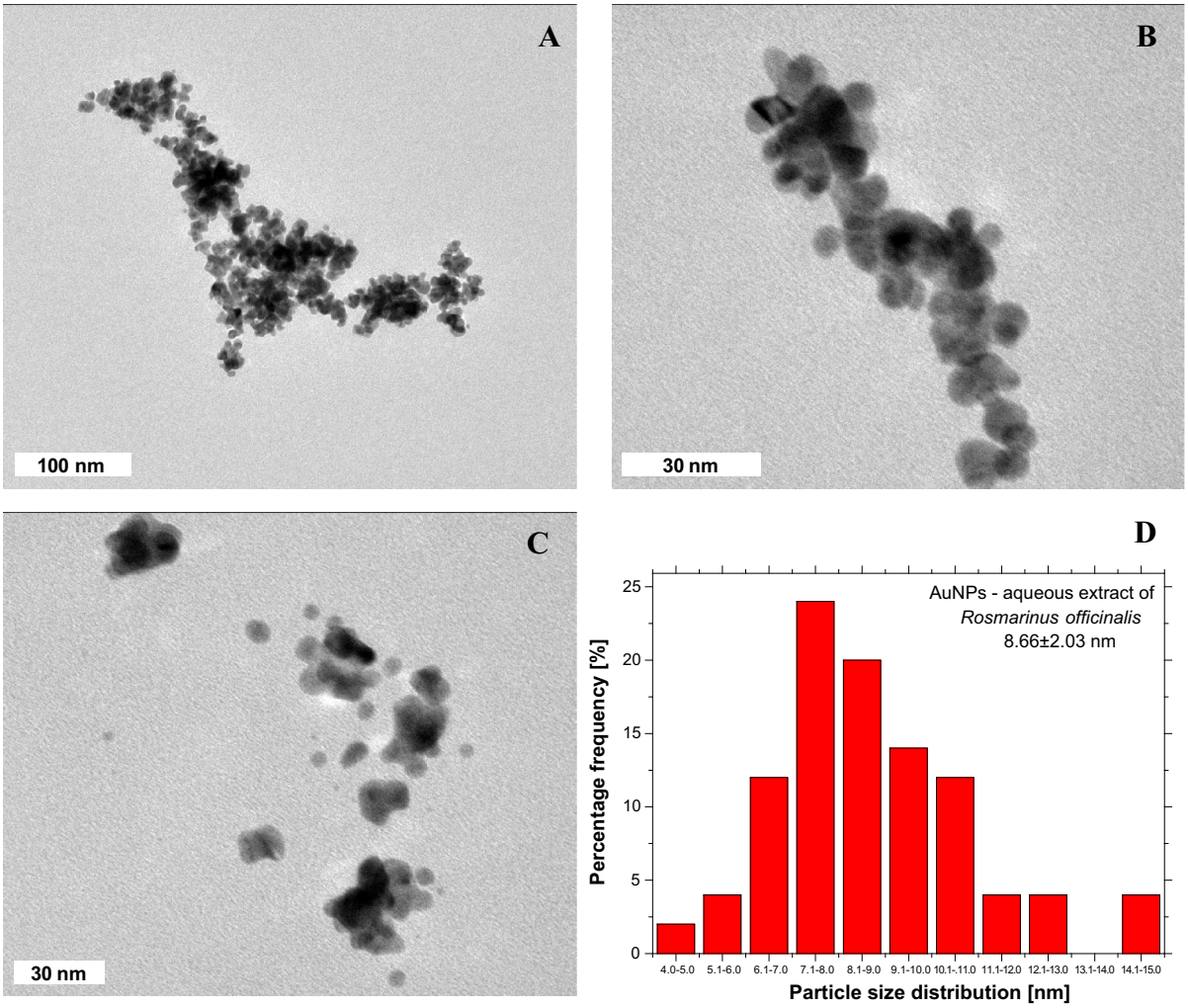

Figure 4 Morphology of AuNPs synthesized from *R. officinalis* aqueous leaf extract. (A–C) Representative TEM micrographs of AuNPs obtained using 50 mg L^{-1} of Au and *R. officinalis* aqueous leaf extract. (D) Size distribution of AuNPs was determined on the basis of TEM micrographs.

ical characteristics of the biosynthesized AuNPs. As can be seen in Fig. 7A and C, there is only one striking difference between the spectra of aqueous leaf extracts of *E. globulus* and *R. officinalis*, i.e. a more intensive band at 1596 cm^{-1} (stretching vibrations ν of the C═O group) in the case of *R. officinalis* as compared to the corresponding band at 1607 cm^{-1} in the case of *E. globulus*. This may stand for a greater abundance of the compounds containing ketone groups in *R. officinalis* aqueous leaf extract. Based on the band at 1698 cm^{-1}, corresponding to stretching vibrations ν of the C═O group from ketones, it is likely that *R. officinalis* aqueous leaf extract contains camphor, while the bands at 1263 and 1070 cm^{-1}, corresponding to stretching vibrations ν of the C—O—C group, may indicate the presence of 1,8-cineole (Schulz et al., 2005; Hameed et al., 2015; Sirvaityte et al., 2011). For *E. globulus* aqueous leaf extract, terpenes such as γ-terpinene and 1,8-cineole were putatively identified according to wagging vibrations ω of the CH_2 group at 919 cm^{-1} as well as stretching vibrations ν of the C—O—C group at 1043 cm^{-1} (Schulz et al., 2005; Hameed et al., 2015; Sirvaityte et al., 2011). In both aqueous leaf extracts, broad bands corresponding to stretching vibrations of the O—H group were also observed.

When comparing the spectra of essential oils, they looked similar with two exceptions. As can be noticed in Fig. 7B and D, there is a large band at 1658 cm^{-1}, corresponding to stretching vibrations ν of the C═C group, in the spectrum of the *E. globulus* essential oil that is absent in the spectrum of *R. officinalis* essential oil. For the latter essential oil, a large band at 1713 cm^{-1} for stretching vibrations ν of the C═O group was noted. These two bands may indicate the presence of camphor in *R. officinalis* essential oil and α-pinene in *E. globulus* essential oil. In addition, in the spectrum of *R. officinalis* essential oil, there were bands at 1368, 1219, 1087, 995, and 852 cm^{-1}, indicating deforming vibrations δ in the $CH_3(CO)$ group, stretching vibrations ν in the C—O—C group, and wagging vibrations ω in the CH_2 group. All of them likely resulted from the presence of eucalyptol (1,8-cineole), which is consistent with the IR data suggesting the occurrence of this compound in the crude plant extract of *R. officinalis* (Schulz et al., 2005). Finally, a band at 888 cm^{-1} (wagging vibrations ω of the CH_2 group) could sug-

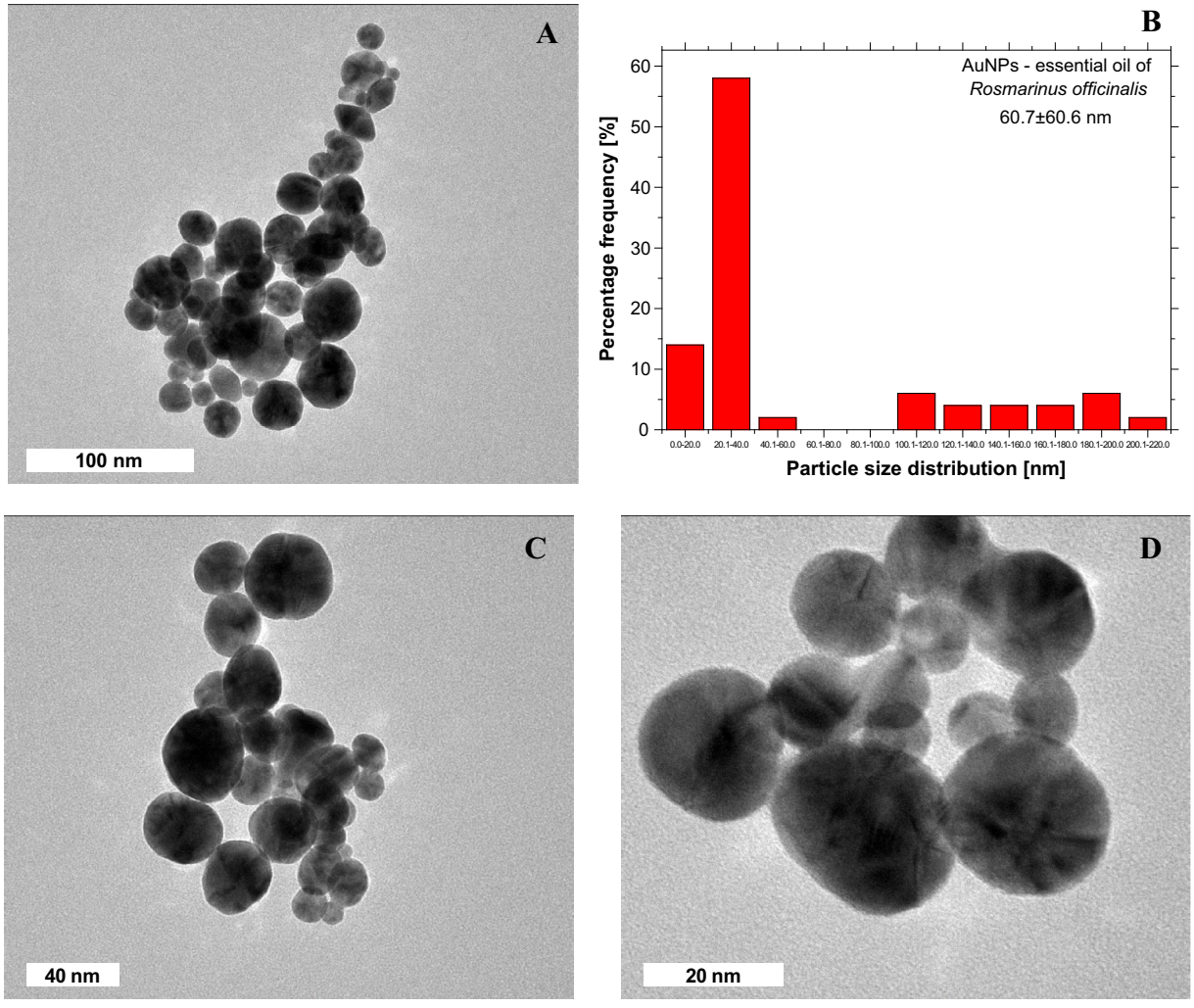

Figure 5 Morphology of AuNPs synthesized from *R. officinalis* essential oil. (A, C, D) Representative TEM micrographs of AuNPs obtained using 50 mg L^{-1} of Au and *R. officinalis* essential oil. (B) Size distribution of AuNPs was determined on the basis of TEM micrographs.

gest the presence of β-caryophyllene. For *E. globulus*, wagging vibrations ω of the CH_2 group at 918 cm^{-1} and 989 cm^{-1} could be indicative of γ-terpinene and eucalyptol, respectively (Schulz et al., 2005). Not surprisingly, comparison of the absorption bands identified in the spectra of the aqueous leaf extracts and essential oils revealed that most of them were more intensive in the case of analyzed extracts. This points out that aqueous leaf extract contained higher amount of potential reducing agents than the corresponding essential oil. The only exceptions were the intensive bands in the range of 3000–2900 cm^{-1} in the spectra of the essential oils, corresponding to the saturated aliphatic groups that are the primary components of essential oils.

To confirm the preliminary identification of the chemical composition of aqueous leaf extracts and essential oils by ATR-FTIR, comprehensive GC-MS analyses were performed. The obtained results are included in the Supplementary Material. The following compounds were identified in *R. officinalis* aqueous leaf extracts and its essential oil: α-pinene, D-limonene, eucalyptol, borneol, camphor and boryl acetate. In *R. officinalis* aqueous leaf extract ethoxycitronellal and α-thujene were also found. β-phellandrene and caryophyllene were detected in the essential oil of this plant. Similar results were obtained by Hameed et al. (2015), who examined methanolic leaf extract of *R. officinalis*. Concerning *E. globulus* essential oil, α-pinene, eucalyptol, D-limonene, α-phellandrene, β-phellandrene, β-ocimene and γ-terpenine were identified and this corroborated suggestions of Sirvaityte et al. (2011). Due to large background noise, ethoxycitronellal was only identified in *E. globulus* aqueous leaf extract.

4. Discussion

In this study, we evaluated the potential of aqueous crude plant extracts and natural essential oils originating from the same plants for AuNPs biosynthesis. Two plant species were used in order to ensure that conclusions drawn from this work would not be species-specific. It was established that AuNPs were successfully synthesized using both aqueous leaf extracts and essential oils of *E. globulus* and *R. officinalis*. However, the quality of the resulting nanofluids was different. Aqueous leaf extracts yielded repeatedly smaller AuNPs, which were supported both by the blue-shift in the position

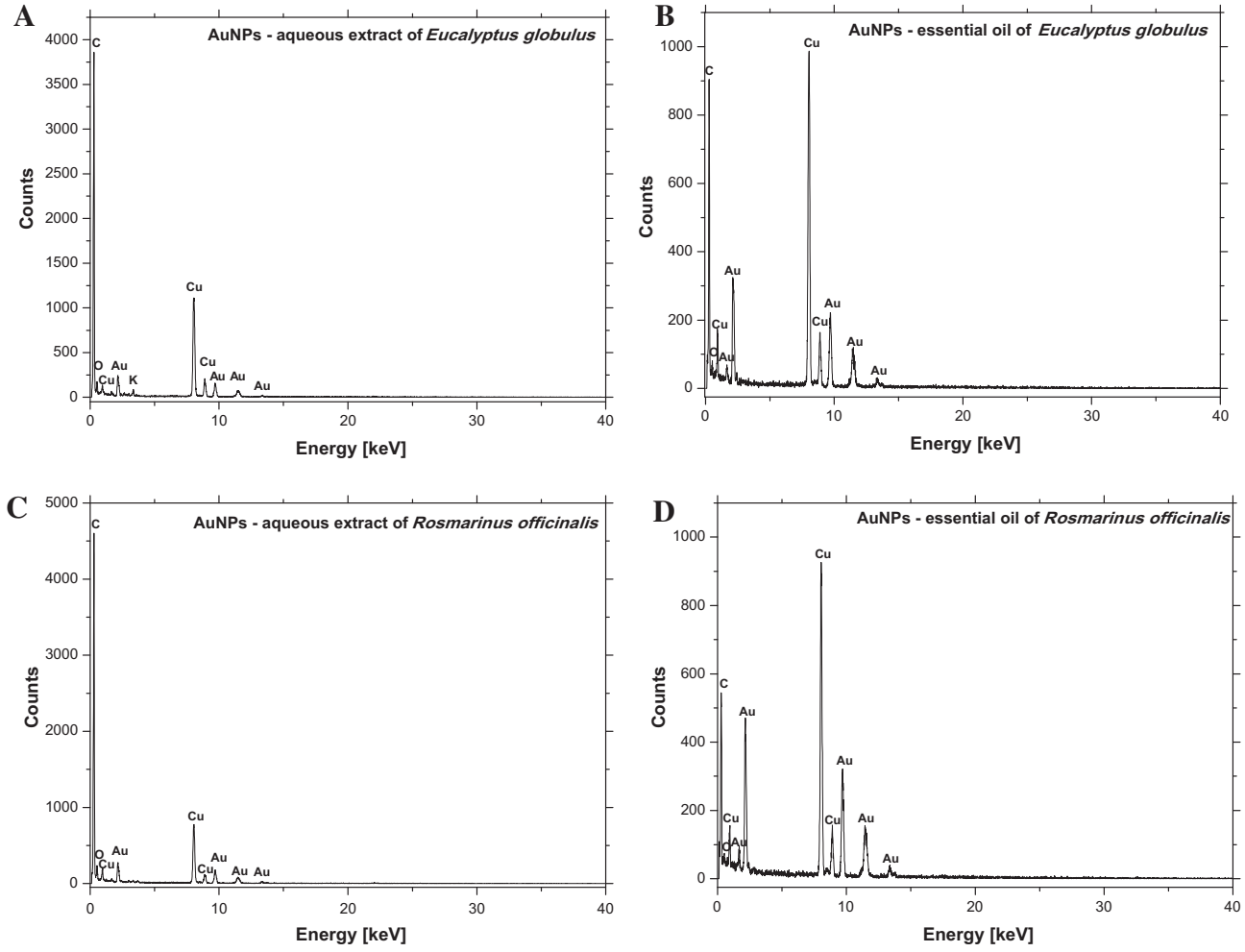

Figure 6 Element analysis of reaction mixtures containing biosynthesized AuNPs. EDX spectra are shown for AuNPs biosynthesized with (A) *E. globulus* aqueous leaf extract, (B) *E. globulus* essential oil, (C) *R. officinalis* aqueous leaf extract, (D) *R. officinalis* essential oil. Elements to which certain peaks correspond to are shown.

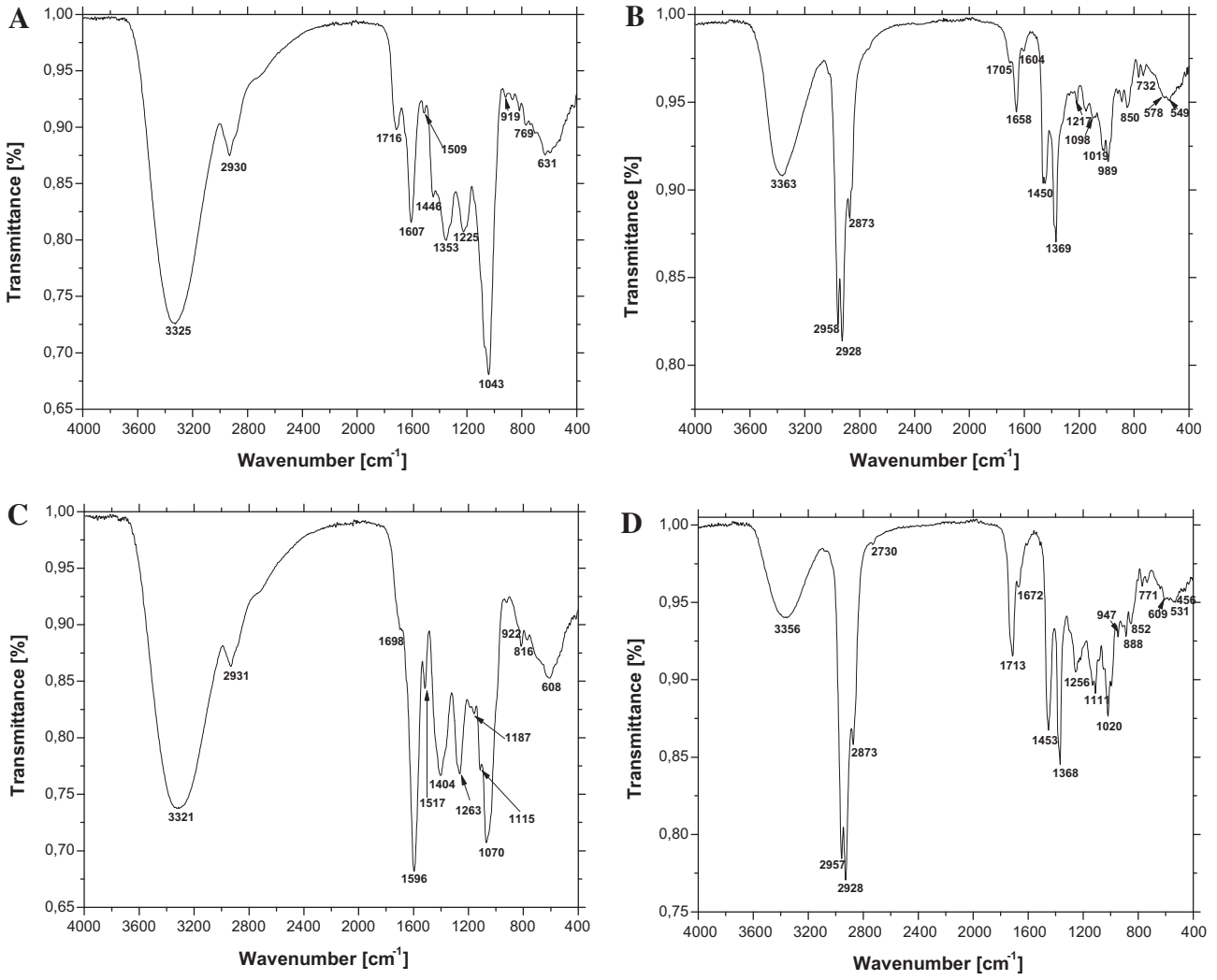

Figure 7 Identification of the functional groups involved in AuNPs bioreduction and stabilization. ATR-FITR spectra are given for *E. globulus* aqueous leaf extract (A) and essential oil (B), as well as for *R. officinalis* aqueous leaf extract (C) and essential oil (D).

of λ_{max} of the LSPR absorption band (Table 2) and the TEM micrographs (Figs. 2–5). Apparently according to the literature, the average size of AuNPs obtained via reduction with aqueous leaf extracts was within the range of 9.3–150 nm, whereas those synthesized by utilizing essential oils were of approx. 36 nm (Table 1). The results obtained in this study show that smaller AuNPs were synthesized using aqueous leaf extracts than the corresponding natural essential oils. The reason for the production of AuNPs of different sizes could be related to the variability in the types and amounts of potential reducing agents present in the used aqueous leaf extracts and essential oils. Previous works demonstrated that smaller NPs were produced when the ratio of reducing agents to metal precursors was increased (Chandra et al., 2014; Poojary et al., 2016). In our case, smaller AuNPs were obtained using aqueous leaf extracts that likely contained higher concentrations of potential reducing agents as compared to the corresponding essential oils. In addition, crude plant extracts could have yielded smaller AuNPs due to accelerated nucleation and growth as was previously suggested by Polte et al. (2010). In the case of plant essential oils, nucleation and growth of AuNPs were suspected to be slower, resulting in the formation of bigger nanostructures. Furthermore, the results obtained in the present study clearly showed that the types and amounts of potential reducing agents from aqueous leaf extracts and essential oils of *E. globulus* and *R. officinalis* affected the morphology of the generated AuNPs. A similar observation, but with other plant material, was described by An and Somorjai (2012). Accordingly, α-pinene, D-limonene, eucalyptol, camphor, borneol, bornyl acetate, and cis-3-hexanol that were present in aqueous leaf extracts used in the present work led to the production of smaller nanoparticles, but their coalescence was either observed. In the case of natural essential oils, the presence of natural stabilizing agents such as β-ocimene, γ-therpenine, β-phellandrene, α-phellandrene or α-pinene resulted in the production of well-dispersed AuNPs.

It should be mentioned that some additional factors could also be responsible for the differences in size, shape, and stability of AuNPs biosynthesized using extracts and oils originating from the same plant species. For example, it could be related to the geographical location from which the plants

were collected, which strongly affects their chemical composition as suggested by Pintore et al. (2002) and Lee et al. (2016). Reaction temperature and omnivorous solvents in which bioreduction occurred could also matter as reported by Rai et al. (2006), Lee et al. (2016) and Chandra et al. (2014). Biosynthesis of AuNPs with the aid of *E. globulus* and *R. officinalis* aqueous leaf extracts and essential oils was conducted at different temperatures and in two different mixtures of solvents. The potential reducing agents in the crude extracts were suspended in water, whereas in the case of essential oils, they were present in the water:ethanol solution.

5. Conclusions

In this work, synthesis of AuNPs using aqueous leaf extracts and essential oils of *E. globulus* and *R. officinalis* was described. Optical properties and morphology of biosynthesized AuNPs were established as strongly dependent on the applied form of reducing and stabilizing agents. It appears that natural compounds originating from *R. officinalis* and *E. globulus* can be used for effective green AuNPs synthesis. Smaller AuNPs, however, were obtained using aqueous leaf extracts of both plant species, possibly due to higher amounts of possible reducing and stabilizing agents in the crude extracts in comparison with the corresponding essential oils. Both plant extracts used are suitable for cheap, simple and environmental friendly one-step production of small-sized, spherical and stable AuNPs that are biocompatible and could be used for further biomedical applications.

Competing interest

The authors declare that they have no competing interests.

Author's contributions

AD, SB, PJ and PP planned all experiments and summarized the acquired data. AD wrote this paper. AM participated in drafting and reviewing of the manuscript. AD, SB, and KK performed AuNPs synthesis and carried out the UV/Vis measurements. AD assisted the TEM, EDS and ATR-FTIR measurements. WS obtained GC-MS data. AD analyzed the GC-MS spectra. PP and PJ supervised all works, gave the theoretical and inspiring advices, took a part in the discussion, and reviewed the manuscript.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2016.09.007.

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