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Physicochemical parameters effect on biosynthesis and properties of copper nanoparticles

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Abstract: Plant extract obtained from green tea was used for the synthesis of nanoparticles under anaerobic and aerobic conditions at various ratios of the copper solution to the extract used. The smallest nanoparticles were obtained at a ratio of 1:10. The nanoparticles showed the maximum negative value of the zeta potential around pH 6. An increase in the temperature of reaction caused a decrease in the negative zeta potential value. Synthesis under nitrogen atmosphere favours the formation of smaller copper nanoparticles.

***Keywords*:** gallic acid, green tea extract, particle size, polyphenols, zeta potential, aerobic conditions, nitrogen atmosphere

1. Introduction

The synthesis of nanoparticles provides a desired size and shape of products, which determines their application in different areas of nanotechnology (Mott et al., 2007). Of approaches to synthesizing copper nanoparticles, biological methods based on microorganisms such as bacteria, fungi, algae, and yeast (Zikalala et al., 2018) are more environmentally friendly. Much attention has been paid to water plant extracts because they are relatively easy to obtain (Pinto et al., 2019). Green synthesis of copper nanoparticles based on naturally occurring plant extracts obtained e.g. from leaves and fruits seems a very promising method. Many of them were used for copper nanoparticles preparation: *Tilia* for the reduction of copper ions (Hassanien et al., 2018), and *Quisqualis indica* for fabricating copper nanoparticles (Mukhopadhyay et al., 2018). Recently, Sebeia and co-workers (2019) used *Nerium oleander* leaf extract for copper nanoparticles synthesis. Copper nanoparticles were also prepared with *Syzygium aromaticum* bud extract (Rajesh et al., 2018) and *Ziziphus spina-christ* (Khani et al., 2018). The majority of the plants – like *Azadirachta indica* – from which the extract is made are medical species (Nagar and Devra, 2018).

Plant extract contains natural organic compounds such as alkaloids, flavonoids, steroids, and others whose composition depends on both the plant species and preparation methods. It acts as ion reducer and nanoparticles stabilizer. Commercial green tea (*Camellia sinensis*) rich in polyphenols, flavonoids, amino and phenolic acids was used in the synthesis of silver nanoparticles (Sebeia et al., 2019). An appropriate extraction technique allows for obtaining an extract with maximum concentrations of active compounds (Das and Eun 2018). One of such uses microwaves, causing rapid and easy extraction of desired substances into water (Sokmen et al., 2017).

Currently, extracts from green and black tea are used for iron, silver, and copper synthesis (Asghar et al., 2018). The colour change in the reaction vessel points to the formation of nanoparticles in the solution. For instance, iron nanoparticle synthesis turns a bright green colour of $FeCl_3$ + tea extract solution into a dark brown. The possible synthesis reaction of metal nanoparticles can be described as:

$$M^{+} + Ar\text{-}OH = M^{0}_{nps} + Ar = O + H^{+}$$

where: M^+ - metal ion, M^0 – metal nanoparticles, Ar - aromatic ring.

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The physicochemical properties of green tea extracts strongly depend on the extraction method. The temperature was found to significantly influence the quality of tea extract (Xu et al., 2018). Generally, the higher the temperature is the higher concentrations of catechins, caffeine, and flavones in the green tea extract. The concentration of polyphenols gradually decreases with increasing duration of extraction. The synthesis of nanoparticles based on a special plant extract provides nanoparticles with various therapeutic benefits. For instance, the extract from *Tinospora cardifolia*, a popular natural herb used in Cu-nanoparticle synthesis, was formulated by Sharma and co-workers (2019). Synthesized nanoparticles capped with *Tinospora cardifolia* extracted compounds demonstrated a strong antimicrobial activity (Sharma et al., 2019). The experiments made with various parameters such as pH and temperature enabled us to determine the effect of the parameters of the Cu-nanoparticle synthesis on their size and stability.

2. Materials and methods

2.1. Green tea extract preparation

1 g of green tea was added to 50 cm^3 of deionized water at 80°C and maintained at this temperature for 30 min. Then, the cold extract was percolated through a 0.45 µm filter. The pure extract was stored in a refrigerator for max. 24 h.

2.2. Phenol content

The determination of polyphenol was carried out according to the international standard method ISO 14502-1:2005(E) which determines chemical characteristics of green and black tea. Briefly, 1 cm^3 of the diluted sample, 5 cm^3 of Folin-Ciocalteu reagent and 4 cm^3 of 7.5% Na_2CO_3 solution were added to a test tube. After 1 h of incubation, the Evolution 201 spectrometer (ThermoScientific) measured the absorbance (765 nm). The results were expressed as gallic acid equivalents (GAE).

2.3. Copper nanoparticles biosynthesis

The synthesis of Cu_{nps} was carried out as follows: the green tea extract was diluted to the concentrations of 2 mM, 4 mM, 20 mM (expressed as gallic acid equivalents). The extract in a proper ratio (of 1:1, 1:2, 1:10) was mixed with 2 mM copper sulfate solution. The synthesis was carried out at different temperatures (35-90°C) and pH (5, 8, 11) under aerobic conditions and nitrogen atmosphere.

2.4 Particle size measurements

The size of copper nanoparticles was measured with the effective optical method (dynamic light scattering DLS) and calculated using the Rayleigh approximation and Mie theory. The sonication is a preferred method for dispersing colloid particles. Sonic 0.5 (Polsonic Poland) with a power of 60 W was used. The nano-suspension was sonicated for a duration of 1 min.

2.5. Zeta potential measurements

The zeta potential of copper nanoparticles was determined at the constant ionic strength of 10^{-3} mM NaCl, at room temperature (22°C) as a function of pH. Measurements – a series of 12 for each sample to estimate the error – were taken with the NICOMP Particle Sizer 380 ZLS apparatus. The NICOMP 380/ZLS uses the method of electrophoretic light scattering to measure zeta potential. To the calculation of zeta potential Smoluchowski-Henry approximation was used.

3. Results and discussion

Copper nanoparticles synthesis was realized under both aerobic and anaerobic (nitrogen atmosphere) conditions with the latter being used to prevent the oxidation of organic compounds and nanoparticles.

3.1. Effect of copper to extract ratio

The first series of tests were run to determine the effect of the ratio of extract to copper ions on the nanoparticles size and zeta potential. Table 1 and Fig. 1 show the results.

Table 1. The particle size of copper nanoparticles depending on the copper to extract (Cu:E) ratio

Cu:E ratio	Initial pH	D (nm)
1:1	5.0	2536
	8.0	3018
	11.0	1740
1:2	5.0	2150
	8.0	1712
	11.0	101.4
1:10	5.0	3.06
	8.0	14.4
	11.0	17.3

The increase in the amount of extract relative to the number of copper ions causes a significant reduction in the size of the synthesised copper nanoparticles. This phenomenon can be explained by the increase in the number of organic compounds contained in the extract which play the role of dispersant reagents.

Zeta potential measurements are necessary to understand the surface potential and stability of Cu_{nps} suspensions. As can be seen in Fig. 1., the increase in the amount of extract caused an increase in the negative value of the zeta potential. This was clearly visible in the pH range of 6-7. The isoelectric point was located in the vicinity of pH 3, and its position changed slightly with the change in the ratio of Cu ions/extract. The greater negative value of zeta potential can be explained by the higher electrophoretic mobility of small copper nanoparticles.

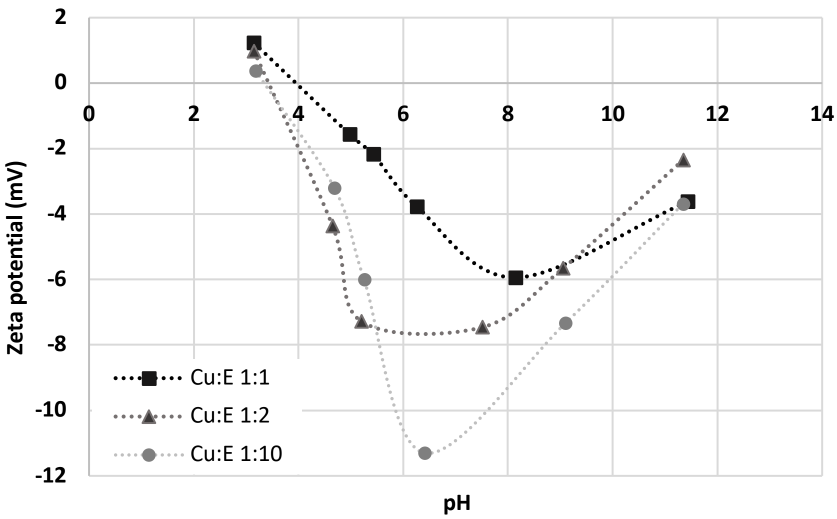

Fig. 1. Influence of reagent ratio on the zeta potential of copper nanoparticles (T=35°C, pH 11)

The more alkaline pH of the extract caused changes in the form of organic compounds in the extract, which were a reason for a colour change as shown in Fig. 2.

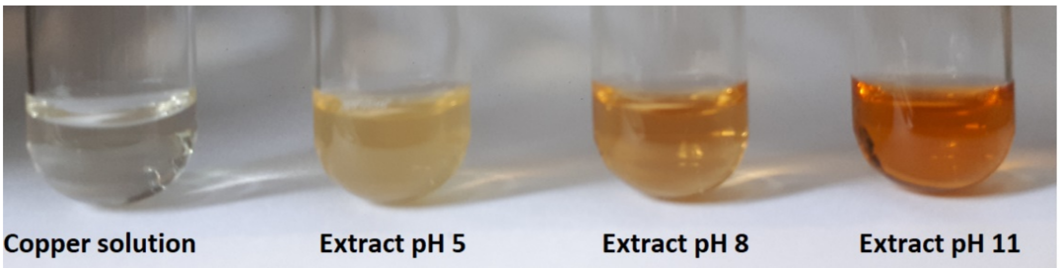

Fig. 2. Colour change of the green tea extract depending on the pH

The colour changed from a pale yellow to a yellowish-brown as a result of tea polyphenols degradation in alkali pH, mainly through oxidation and dimer formation.

3.2. The influence of temperature and reaction environment

The temperature and the atmosphere in which synthesis was carried out are important parameters. The final colour of Cu_{nps} suspension formulated at constant pH darkens with increasing temperature of the reduction reaction is presented in Fig. 3.

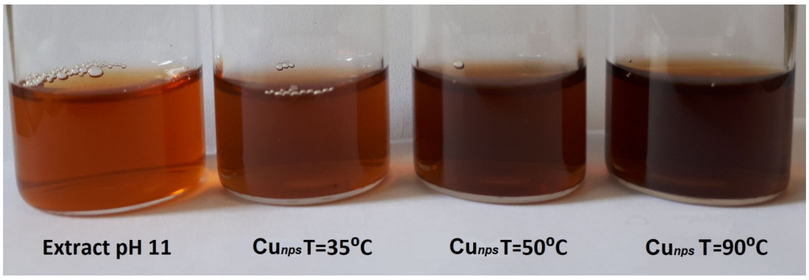

Fig. 3. Colour change of synthesized Cu_{nps} with a temperature of the reaction

The synthesis of nanoparticles is monitored by measurements of the UV-Vis spectrum. Figs. 4 and 5 present UV-Vis spectra of copper nanoparticles during synthesis – which was carried out in aerobic and anaerobic atmosphere – at different pH and temperatures (35°C and 50°C). It is well known that the optical properties of copper nanoparticles strongly depend on their shape and size.

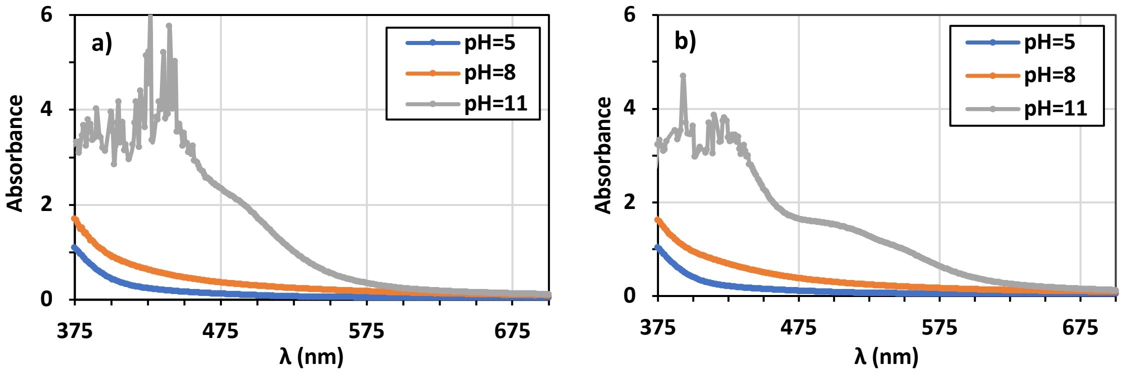

Fig. 4. UV-Vis spectra for samples synthesized at 35°C under aerobic conditions (a) and nitrogen atmosphere (b)

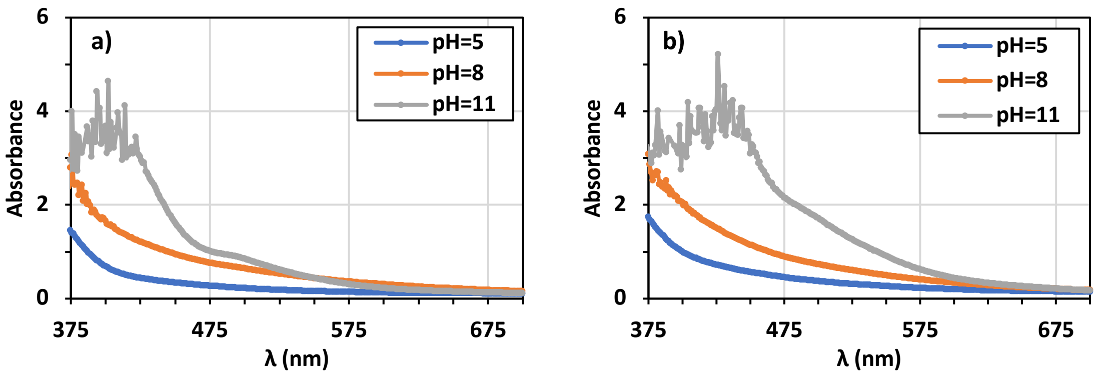

Fig. 5. UV-Vis spectra for samples synthesized at 50°C under aerobic conditions (a) and nitrogen atmosphere (b)

The synthesis of nanoparticles with diameters below 10 nm have been categorized as ultra-small (BRUMBAUGH et al., 2014). The synthesis of ultra-small Cu_{nps} with an aqueous extract of lemongrass stalks shows that the ultra-small nanoparticles are nonplasmonic. For these reasons, no apparent peaks are observed as in the synthesis of silver and gold nanoparticles.

The spectra of reacting suspensions showed an increase in absorbance within the 475-550 nm band, which indicates the presence of copper nanoparticles. Absorbance in the spectra within the range of 375-400 nm correlates with the oxidation products of green tea polyphenols. Li and co-workers (2015) showed, that catechin-Cu nanoparticles in pH 11 gave a maximum peak at 420 nm. When the temperature of the reaction was raised up to 50°C, the absorbance intensity became weaker as it was observed in Fig. 5a.

Table 2 presents the results of particle diameter measurements of copper nanoparticles fabricated at different temperatures and different pH. The syntheses were realized under aerobic and anaerobic conditions. The size of nanoparticles synthesized in the nitrogen atmosphere was smaller and did not exceed 6 nm. Larger particles were obtained under aerobic conditions and in this case, also no significant influence of sonication was observed. Samples obtained under aerobic conditions are more likely to agglomerate after treatment using ultrasound, which is more intense at higher temperatures. The sonication is a preferred method for dispersing colloid particles. However, also agglomeration of metal nanoparticles was observed (Pradhan et al., 2016) as an effect of van der Waals interactions.

Table 2. pH values and particle sizes for samples synthesized at different temperatures

Reaction conditions	**Initial pH**	**D (nm)**	**D_{ultra} (nm)**
	35°C		
Aerobic	5	3.06	2.66
	8	14.4	28.7
	11	17.3	5.20
Anaerobic (nitrogen)	5	2.41	2.54
	8	1,76	1.68
	11	5.24	5.24
	50°C		
Aerobic	5	6.12	12.5
	8	56.0	264
	11	7.76	10.2
Anaerobic (nitrogen)	5	2.64	3.00
	8	5.12	3.20
	11	5.18	5.74

D – particle diameter, D_{ultra} – particle diameter after 1 min of sonication

The temperature of the Cu_{nps} synthesis has influenced the values of zeta potential. Fig. 6 presents zeta potential measurements at temperatures of 35°C, 50°C and 90°C. The suspension pH was changed

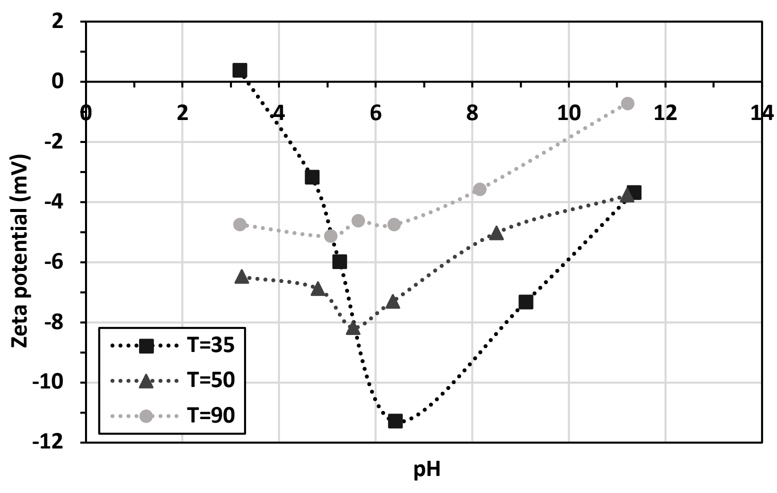

Fig. 6. Influence of the reaction temperature on the zeta potential of copper nanoparticles (aerobic conditions, Cu:E = 1:10, nanoparticles fabricated at pH 11)

within the range of pH 2 to 12. An increase in the temperature of the Cu nanoparticles synthesis caused a decrease in the negative value of zeta potential. The curves showing changes of zeta potential as a function of pH, for temperatures of 50°C and 90°C changed their shape. The isoelectric points are likely located at a very acid pH and were not determined. These experiments showed that the anaerobic condition of copper nanoparticles synthesis yields in products with smaller dimensions.

4. Conclusions

The synthesis of metal nanoparticles with the use of plant extracts is becoming very popular due to the ease of obtaining a plant extract and the absence of harmful effects on the environment. The following conclusions can be drawn from the collected experimental data:

- the water extract of green tea leaves contains a large number of polyphenols and for this reason, is a good reagent to fabricate copper nanoparticles.
- the size and zeta potential of copper nanoparticles depend on the conditions of synthesis such as the ratio of the extract to the Cu^{2+} concentration, pH, and temperature.

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