ENVIRONMENT-FRIENDLY METHOD FOR OBTAINING GOLD NANOPARTICLES BASED ON PLANT EXTRACT

JOLANTA PULIT*, MARCIN BANACH
Institute of Chemistry and Inorganic Technology, Cracow University of Technology, 24 Warszawska St, 31-155 Cracow

An environment-friendly way of nanogold particles receiving has been studied. The process is based on the chemical reduction method carried out in aqueous environment. Chloroauric acid was used as gold ions source. Knotweed extracts was used as a natural source of both a reducing and stabilizing agents. The total amount of polyphenols, ascorbic acid and anthocyanins have been analyzed and the effectiveness of free radical deactivation was determined. Obtained suspensions were analyzed by the Dynamic Light Scattering technique to determine the particles size and suspension stability which is specified by electrokinetic potential. Results confirmed that the size of obtained nanoparticles was included in the range from 20 to 200 nm.

(Received June 18, 2013; Accepted September 25, 2013)

Keywords: Nanogold, Green chemistry, Knotweed extract, Chemical reduction

1. Introduction

Nanogold is considered as one of the most useful commercial products belonging to the group of nanomaterials. Recently, its use has reached one of the highest level of cost-effectiveness [1]. Many years of research have contributed to the confirmation of the centuries-known thesis that gold has been shown to slow down the functioning of the bacteria. Therefore, in the daily exposure of human or animal organisms to microorganisms such as bacteria, viruses, or fungi, nanogold plays a key role in antiseptic action [2]. Medicine, nursing, cosmetology, dentistry and the construction industry belong to areas that take advantage of the nanogold benefits to the greatest extent [3].

Combining the nanoparticles with polymeric materials give new possibilities to design composites that are characterized by desirable mechanical, optical and electrical properties. With advanced techniques for preparing such composites, it is possible to direct the nanoparticles to the right place in compound, which is reflected in the final composite macroscopic performance, such as stability [4]. Nanoparticles that are added to the polymer material impact on the intensification of the phenomenon of light scattering, which causes that final composite is characterized by reduced light transmission and optical clarity.

In recent years, polymer composites with carbon nanotubes have gained a great commercial interest. Their high conductivity is a reason for this [5]. Kobayashi et al have been studying the Poly(butyl methacrylate) composite with colloidal silica. They showed that the addition of silica increases the glass transition temperature of the polymer matrix. It can be explained by the action of the nanoparticles as a barrier to polymer diffusion and that the polymer matrix layer adjacent to the surface of the colloidal silica, which is due to proximity with the nanomaterial is stiffer and this action is called as a "filler effect" [6].

Biocidal properties of polyacryl enriched with copper nanoparticles at 1% by weight were investigated. Studies have been conducted against Synechocystis sp. Two control samples were used: the first on was sample with bacteria which did not contain neither nanomaterial nor

* Corresponding author: jolantapulit@indy.chemia.pk.edu.pl

polymer, and the second one was polymer and bacteria, only. The second was particularly important as the influence of a polymerization photoinitiator to the growth of bacterial cells was investigated. The study showed that there were no significant differences between the control samples and the bacterial growth proceeded steadily over time. In case of composites with nanocopper, bacterial cell growth did not occur, and the number of cells remained at a constant level to the end of the study. The nanocopper concentration in the composite was not neutral, and as the concentration increases, the biocidal activity is greater [7]. Gold also has biocidal properties and it can be used in plastics processing.

Basing on Patent Application no 20120164202 there are known products such as foam, coated paper, textiles and polymer materials, which thanks to the addition of nanogold are characterized by surface antimicrobial action. Harris and co-inventors describe composites of styrene-ethylene-butadiene-styrene (SEBS), thermoplastic elastomer (TPE) and polyurethane (PU) with the gold nanoparticles. The patent disclose an innovative technology of polymer materials and other usable surfaces coating technique with nanogold in order to obtain the result desired product exhibiting biocidal properties [8].

It is also known a polymer-ceramic composite with embedded gold nanoparticles. Polyacrylic acid was used as a polymer material and hydroxyapatite was a ceramic insert. The combination of polyacrylic acid with hydroxyapatite and enrich it with nanogold gives the possibility of using such a composite in medicine and dentistry [9] .

There are many methods of nanogold synthesis described in details. Chemical reduction belongs to them [10]. It is preferable to base on this method as a process for the nanostructures obtaining relays upon mixing the solutions, which does not require the use of specialized laboratory equipment. Another advantage is the short time of synthesis and easiness of changing the process scale. The concept of this method is to reduce the gold ions to the zero oxidation state. However, atoms remaining in solution have a tendency to link with one another. Therefore, an important aspect is to determine when to stop the group of atoms and thus to prevent agglomeration of the particles leaving the size of them on the nano-level. In order to inhibit the growth of the particles a stabilizing factor (dispersant) is introduced into the system. This substance, due to the strong interaction with the surface of the metal particles, effectively opposes the proliferation of the particles. Appropriate choice of dispersant allows to manipulate the size of the obtained gold nanoparticles [11].

The aim of the work is to synthesize nanogold basing on chemical reduction method, using ellagic acid, ascorbic acid and anthocyanins as a reducing agents. The project is an eco-friendly concept, therefore, in the synthesis any synthetic compounds that would fulfill the role of the reducer and stabilizer will not be used. It was decided to use extracts of knotweed (*Polygonum aviculare)* as a natural source of these compounds. The complexity of these plants composition leads to the conclusion that it is a natural source of compounds with reducing properties, such as ellagic acid, gallic acid, ascorbic acid and anthocyanins, as well as other compounds belonging to the group of polyphenols, flavonoids and tannins. The extract includes other substances, whose nature allows for effective stabilization of the resulting nanogold suspension, and these are: mucous compounds, peptides and biopolymers [11,12]. The adsorption of these compounds on the surface of the nanoparticles prevents agglomeration. This action is in accordance with the principles of "green chemistry" because realization of process does not require to provide two distinct substances - reducing and stabilizing agents. The use of the aqueous extract of the knotweed ensures both reducing and stabilizing conditions.

2. Experimental

2.1. Materials

Chloroauric acid ($HAuCl_4$) and sodium hydroxide were purchased from Sigma Aldrich. All reagents were pure per analysis (p.a.). Redistilled water was used to prepare solutions. Knotweed herbs were purchased from Herbapol S.A. Company.

2.2. Methods

Primarily, knotweed extraction method was developed. Studies assumed checking out the extraction test results conducted at different conditions. Amount of plant material and time of extraction were changeable variables. Their valueswere within the range of 3 -12 g for knotweed mass and 3 – 8 h for time. Processes were conducted in the Soxhlet extractor. In obtained extracts amounts of polyphenols, ascorbic acid and anthocyanins have been analyzed and the effectiveness of free radical deactivation was determined. Having known that 5,25 g of plant material and 8 h of extraction process involves the most effective extraction process, the chemical reduction in order to get gold nanoparticles have been carried out. In order to perform the synthesis, an aqueous solution of chloroauric acid was mixed with the chosen knotweed extract. The concentration of chloroauric acid solution was so recalculated, to get the systems at about 50, 275 and 500 ppm of gold. The differences in the samples were generated by the final determination of pH value and samples incubation at different temperatures. The plan for preparation of nanogold suspensions is presented in the Table 1.

Table 1. Values of input variables in the process of nanosilver obtaining.

System No.	c_{HAuCl4} [mol/dm^3], x_1	pH, x_2	temp. [^{o}C], x_3
1	0.000264	6	20
2	0.000264	9	60
3	0.000264	12	40
4	0.002776	6	60
5	0.002776	9	40
6	0.002776	12	20
7	0.001454	6	40
8	0.001454	9	20
9	0.001454	12	60
10	0.001454	9	40

The resulting suspensions were studied spectrophotometrically. Particles sizes were determined by dynamic light scattering method (DLS) and a study on Malvern Zetasizer Nano test-CI provided information about the electrokinetic potential, which reflects the stability of the system.

3. Results and discussion

UV-Vis spectrophotometry informed about the process progress. Thanks to this, the time after which no further changes in the samples were observed was determined. Spectrophotometric analysis confirmed the presence of the nanogold in some of received suspensions (Figure 1).

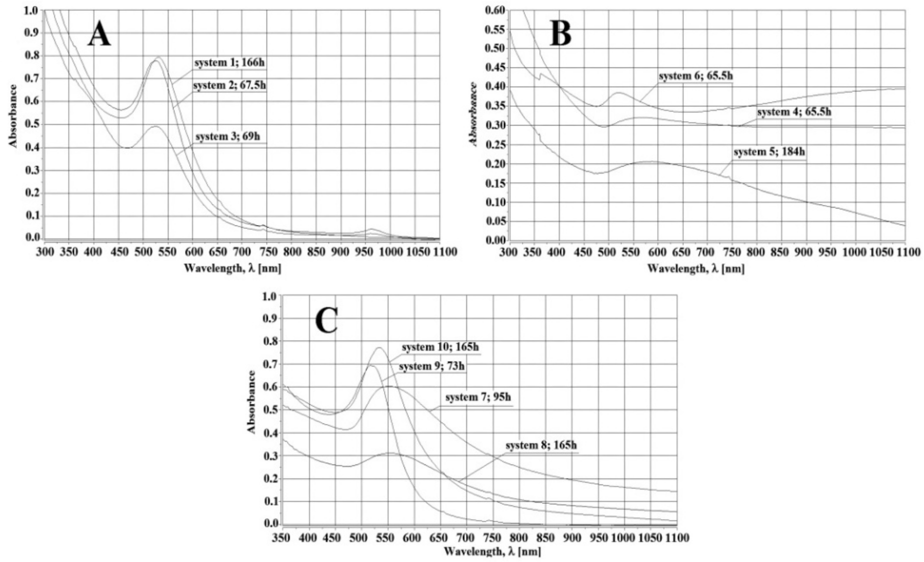

Fig. 1. UV-Vis spectra of nanogold received basing knotweed extracts (A – systems 1 – 3, B – systems 4 – 6, C – system 7 – 10).

Suspensions of nanogold were not obtained in all samples. In cases where the highest concentration of gold salt was used, supplied amount of reducing and stabilizing agent was insufficient and stable systems did not arise. The time required for the creation of a stable suspension in which no further changes are observed depends on the relation of amounts of the compounds contained in the extract to the amount of gold ions introduced into the reaction. With increasing amount of the extract to the chloroauric acid concentration, the time of the chemical reduction decreases, due to the intensification of the process and the formation of a larger number of smaller nanoparticles. The peaks maxima were uniformly located throughout the spectra of all samples and do not depend on the input variables values.

The study of particle size provided histograms which graphically illustrate the percentage of nanoparticles of a given size (Figure 2). The value of electrokinetic potential which is an expression of the suspensions stability was also determined (Fig. 3).

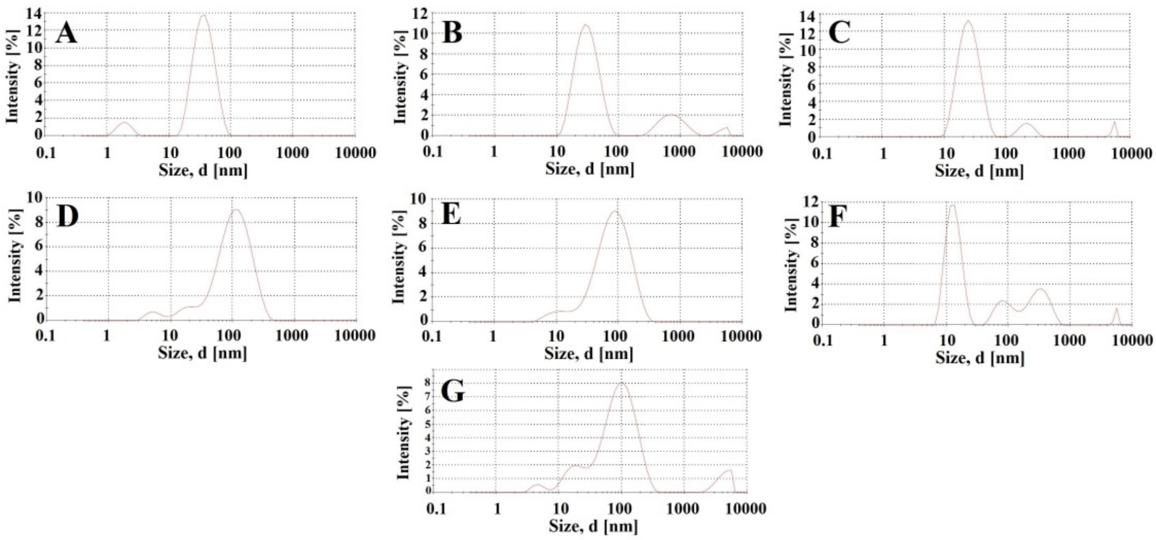

Fig. 2. Histograms of particle size for nanogold suspensions received basing on knotweed extracts (A – system 1, B – system 2, C – system 3, D – system 6, E – system 7, F – system 9, G – system 10)

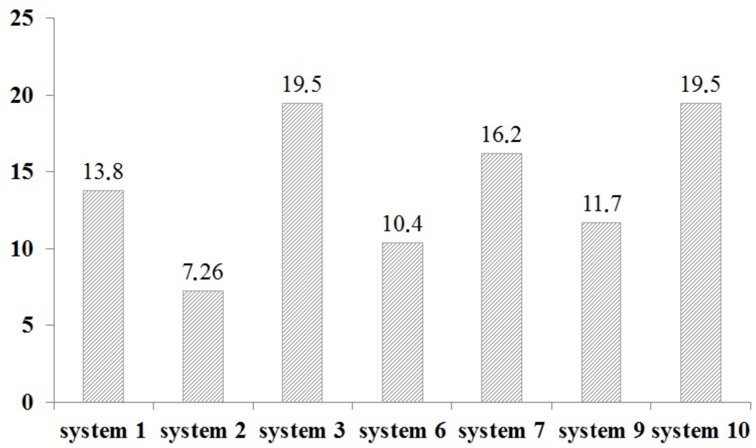

Fig. 3. Absolute values of electrokinetic potential.

It was found that all input variables have a significant impact on the diameter of nanoparticles. In the case of electrokinetic potential it was observed that none of the independent variable has any significant effect on the potential value. Basing on these analysis, the model was obtained which served to the setting the regression coefficients determined for the actual values of the factors significantly affecting the size of the nanoparticles. The equation is shown below:

$$y = -24,2081 + 56,1073x_1^2 + 21,4115x_2 - 24,3267x_2^2 + 27,7995x_3 - 31,3845x_3^2,$$

y – nanoparticles diameter [nm]
x_1 – $HAuCl_4$ concentration [mol/dm^3]
x_2 – pH
x_3 – temperature [°C]

After analysis it was found that the resulting model is valid and it may be advantageously used to estimate the size of the gold nanoparticles.

After centrifugation of suspensions, some powder form of nanogold was obtained. They were analyzed microscopically. Photos of selected nanomaterials are presented in the Figure 4.

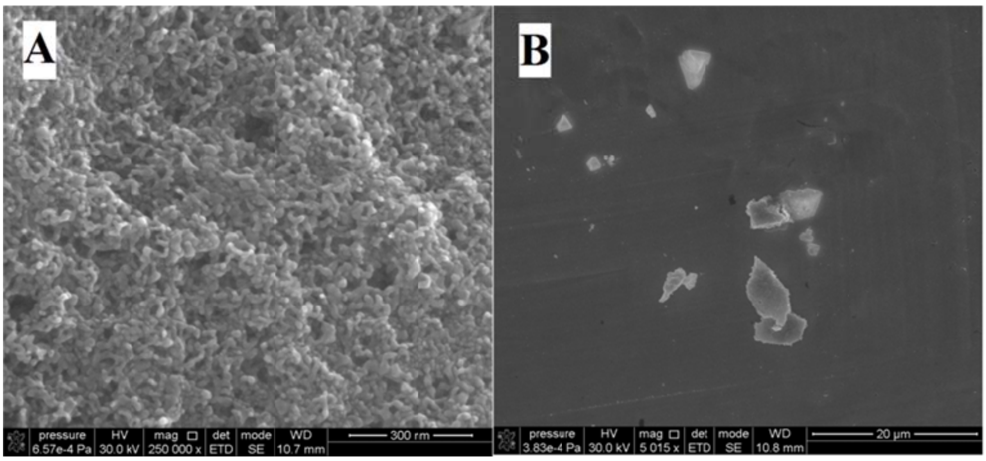

Fig. 4. SEM images of nanogold obtained basing on knotweed extracts (A – system 6, B – system 7)

Images were used to determine the gold nanoparticles shape. Basing on the photographs, it was found that nanogold obtained with the participation of knotweed extract is characterized by a longitudinal spherical and rectangular shape. Shape variability may be explained by a variety of process conditions. Received number of images is not sufficient to determine the mechanism of different shapes formation depending on the process conditions.

4. Conclusion

The possibility of obtaining stable nanogold suspensions in the way of a one-step reduction in aqueous medium using knotweed extracts as a both stabilizer and reducing agent source was has been confirmed. Basing on the results of UV-Vis analyzes, DLS and SEM the most favorable parameters of the process were determined.

Acknowledgements

The work is part of a project "Synthesis and application of innovative nanomaterials with antimicrobial properties" supported by National Centre for Research and Development under the contract no LIDER/03/146/L-3/11/NCBR/2012 for the period of 2012-2015.

References

[1] C. L. Brown, G. Bushell, M. W. Whitehouse, D. S. Agrawal, S. G. Tupe, K. M. Paknikar, E. R. T. Tieking, Gold Bull. **40**, 245 (2007).
[2] M. Horisberger, J. Rosset, J. Histochem. Cytochem. **25,** 295 (1997).
[3] F. K. Alanazi, A. A. Radwan, I. A. Alsarra, Saudi Pharm. J. **18**, 179 (2010).
[4] A. C. Balazs, T. Emrick, T. P. Russell, Science **314**, 1107 (2006).
[5] G. Schmidt, M.M. Malwitz, Curr. Opin. Colloid In. **8**, 103 (2003).
[6] M. Kobayashi, Y. Rharbi, L. Brauge, L. Cao, M. A. Winnik, Macromolecules **35**, 7387 (2002).
[7] K. C. Anyaogu, Stabilized Metal Nanoparticle-polymer Composites: Preparation, Characterization and Potential Applications, Bowling Green State University, Ohio 2008
[8] F. T. Harris, T. P. Davis, US patent No. 20120164202 (2012).
[9] A. Sobczak-Kupiec, D. Malina, B. Tyliszczak, M. Piątkowski, K. Bialik-Wąs, Z. Wzorek, Dig. J. Nanomater. Bios. **7**, 459 (2012).
[10] V. Reddy, Synlett, **61**, 869 (2006).
[11] A. Beer, M. Vivier, BMC Plant Biol. **8**, 75 (2008).
[12] G. K. Jani, D. P. Shah, V. D. Prajapati, V.C. Jain, Asian J. Pharm. Sci. **4**, 308 (2009).