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## GREEN SYNTHESIS OF SILVER NANOPARTICLES USING GRAPE POMACE WASTE FOR THE DEGRADATION OF PHARMACEUTICALS AND ORGANIC DYES

*The green synthesis of metallic nanoparticles paved the way to improve and protect the environment by decreasing the use of toxic chemicals. A simple and eco-friendly method for silver nanoparticles (AgNPs) synthesis employing the aqueous extract obtained from grape pomace by plasma-chemical extraction technique was developed. The reduction of silver ions in solution was monitored using UV-visible absorption spectroscopy. The synthesised nanoparticles were characterised using scanning electron microscopy (SEM) and dynamic light scattering measurement (DLS). The sizes of the spherical silver particles were found to be in the range of 27–33 nm. The effect of silver ions concentrations on the synthesis of silver nanoparticles and average particle size was investigated. As-prepared Ag NPs had an excellent catalytic activity as a catalyst for the degradation of ibuprofen, which was carried out in 50 s. The current findings are equally extendable for safeguarding the aquatic environment against the pollution caused by drugs and microbial activity via a facile, highly economical, rapid and efficient reduction/degradation method based on the catalytic potential of Ag NPs. The report emphasizes the effect of the size of silver nanoparticles on the degradation rate of hazardous dyes - methyl blue by NaBH<sub>4</sub>.*

**Key words:** green method, nanoparticle low-temperature nonequilibrium plasma, grape pomace extract, catalysis, methylene blue, ibuprofen

**Introduction.** Metal nanoparticles (NPs) have attracted a great interest both in the area of scientific research and industrial applications. Silver (Ag) NPs have generated substantial interest not only in fundamental research and development, but also at the industrial scale due to their excellent properties [1]. Hence, synthesis strategies that result in controlled AgNPs size, distribution, shape and stability are still an area of interest. Different methods have been employed in the production of nano-sized metallic silver particles with different morphologies and sizes [2].

Silver nanoparticles can be synthesized using different approaches, such as electrochemical methods, decomposition, microwave-assisted techniques, and wet chemical procedures [3]. Recently, the development of effective green chemistry methods has received much attention as an alternative approach to

synthesize metal nanoparticles, which can eliminate or minimize the generation of toxic or hazardous waste materials and establish a sustainable process.

### **Analysis of research and publications.**

The formation of NP with the use of plant extracts, as a rule, has two stages: preparation of the extract and its subsequent use as a reducing/stabilizing agent. Maceration of solid material with different solvents is the most common method to prepare extracts [4]. These techniques often involve several extraction steps, so take a lot of time. Different alternative extraction techniques have been studied in an effort to increase a yield, including e.g. ultrasound-assisted extraction from grape stems, superheated liquid extraction from vine shoots, or fluidized-bed extraction from grape canes, between others [5-7]. Some scientists additionally influence the reaction



mixtures directly at the stage of the NP formation by different types of radiation. Thus, a variety of radiation sources emitting in the gamma, UV or VIS and microwave ranges are used to synthesize AgNPs in the presence of plants extracts [8]. Among these, plasma-assisted extraction has low instrumental requirements and allows a simultaneous treatment of various samples in less time.

Among plasma-chemical discharges, contact nonequilibrium low-temperature plasma (CNP) is a promising option from the point of view of practical application [9]. Plasma discharge is generated between the electrode in the gaseous phase and a liquid surface, where another electrode is located. Therefore, chemical transformations on the phase interface are conditioned by the combined effect of: an electrochemical oxidation-reduction; initiated photolysis reactions, the UV radiation; a flow of charged particles from the gaseous phase to the surface of the liquid medium. These factors may increase the efficiency of extraction and concentration of the resulted extracts, and, as a consequence, the efficiency of further synthesis of AgNPs.

**The purpose.** The main goal is to determine the synthesis conditions and specific properties of green-obtaining silver nanoparticles with the use of the grape pomace extract prepared by plasma-chemical extraction method, their catalytically activity for the degradation of pharmaceuticals drugs and organic dyes.

**Experimental.** Silver nitrate (99.8%, Kishida), methylene blue, ibuprofen, sodium borohydride, were purchased from Merck Co. Ltd. (Darmstadt, Germany). Aqueous solutions of silver nitrate at different concentration were prepared using ultrapure water (Direct-Q UV, Millipore) and were utilized as starting materials without further purification.

The product of processing was provided by the open joint-stock company OJSC "VINNIEFRUIT" (Kalynivka, Vinnytsia oblast, Ukraine), which is engaged in the production of juices and soft drinks. The grape pomace was dried at 100 °C for 48 h and grounded to obtain a fine powder. The bidistilled water (40 ml) was added to 1 g of dry GP powder and stirred. The resulting mixture was placed in a plasma-chemical reactor. The scheme and the principle of the industrial operation for the plasma-chemical reactor are given in works [9-10]. The mixture was treated by CNP discharge for 5 minutes (at the amperage of  $I=120$  mA and  $P=0.8$  MPa), cooled and filtered. The freshly obtained GP water extract was used immediately after filtration. Further, such extracts are mentioned as the plasma-chemically obtained grape pomace water extracts (PC GPWE).  $AgNO_3$  was dissolved in bidistilled water

to prepare the solutions with concentrations in the range 0.25–6.0 mmol/L. In a typical reaction procedure, 40 ml of grape pomace extract was added to 40 ml of  $AgNO_3$  solution under stirring during 0.1 min.

Spectra of colloidal solutions were obtained by means of spectrophotometer UV-5800PC using quartz cuvettes in the wavelength range of 190-700 nm (FRU, China). Particle size of colloidal solutions was measured by means of the analyzer of particle size Zetasizer Nano-25 (Malvern Instruments Ltd., Malvern, England). Microphotographs of nanoparticles and particle sizes were obtained on scanning microscope JEOL JSM-6510LV (JEOL, Tokyo, Japan).

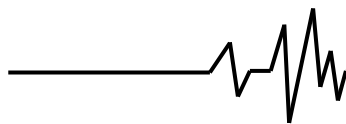
The catalytic effect of silver nanoparticles was monitored for the analgesics such as ibuprofen and paracetamol. The catalytic degradation of these analgesics was carried out in a standard quartz cell with 1 cm path length and about 3 ml volume containing Ag NPs. The reaction was performed in the presence of small quantity of  $NaBH_4$  only and AgNPs. The catalytic reaction procedures were as follows for ibuprofen and paracetamol. The amount of individual reagent was taken as 0.2 ml from 10 mg/L analgesic which was taken in quartz cell followed by the addition of 2.80 ml milli Q water and then by 0.1 ml of 0.02 M  $NaBH_4$ . After that, fixed amount of AgNPs solution was added to the above mixture. The absorption spectra were monitored by a UV/Vis spectrophotometer.

1 mL 100 mM sodium borohydride solution is added to 1 mL  $10^{-3}$ M methylene blue. The solutions are then made up to 10 mL using deionized water and vigorously stirred for 5 min. Then fixed amount of silver colloid is added to the solutions. The degradation of dyes is indicated by the decolorisation of the solution. Methylene blue initially blue in color in an oxidizing environment became colorless in the presence of reducing agent ( $NaBH_4$ ) indicating the reduction of methylene blue to leucomethylene blue (LMB).

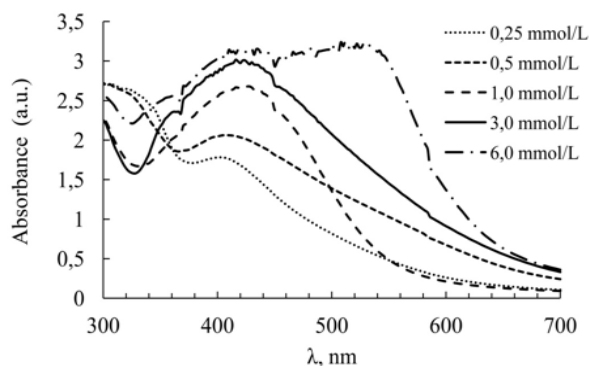
**Results and Discussion.** It is known that the "green" synthesis of nanoparticles is based on the use of reducing agents present in the composition of plant material [1-7]. These substances are characterized by their redox potential and are able to recover cations of the dissociated metal salts. In addition, they can simultaneously act as stabilizers of the obtained NPs.

Fig. 1 shows the UV-Vis absorption spectra of Ag NPs obtained at different concentrations of  $AgNO_3$  (0.25–6.00 mmol/L) and in the presence of fixed amount of plasmochemically obtained aqueous extract (Ag NPs synthesized at 75 °C,  $\tau=10$  minutes).

The extract have a maximum absorption at 300 nm, which may be due to the functional



compound extracted from grape pomace. Analysis of obtained data showed that the Ag nanoparticles are formed using plasma chemical obtained aqueous GPE (Fig. 1). As can be seen, as concentration of silver nitrate changed from 0.25 to 1.0 mmol/L, the intensity of SPR peak was increased remarkably and the location of SPR peak was red shift from 410 nm to 428 nm. The increase in intensity suggests that more nanoparticles are formed. Thus it can be assumed, that although the silver nitrate concentration is increased, the particle size does not increase much. However, while the concentration of silver nitrate altered from 1.0 mmol/L to 3.0 mmol/L, the intensity of SPR peak was decreased slightly. The slightly increase of SPR intensity may due to exhaustion of reducing agent. With an increase in the concentration of silver ions to 6.0 mmol/L, the intensity of the peak slightly increases and there are obvious pair of absorption peaks at 424 nm and 430 nm, which indicates that aggregation occurs in this reactive system and the nanoparticles are well dispersed.



**Fig. 1. The UV-Vis absorption spectrum of silver nanoparticles synthesized using plasma chemical obtained aqueous GPE at various concentrations of AgNO<sub>3</sub>**

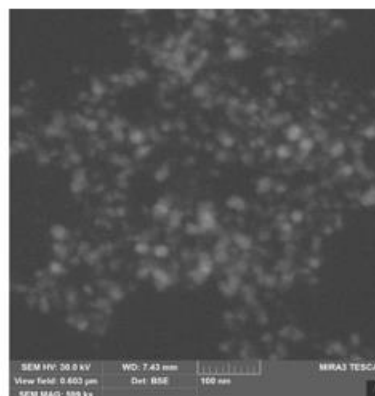
The DLS technique was used to determine the mean particle size (Table 1). The obtained data indicate that the average diameter of the nanoparticles formed equals 27–33 nm and slightly grows with the increasing of Ag<sup>+</sup> initial concentration.

**Table 1**

**Results from the particle size analyzer**

GPW Extract	C AgNO <sub>3</sub> , mmol/L	Average particle size d <sub>AgNPs</sub> , nm
PC GPWE	0.25	27.0
	0.5	28.2
	1,0	30.1
	6.0	33.0

The morphology of the synthesised AgNPs were investigated using scanning electron microscopy (SEM) analysis (Fig. 2). The AgNPs were spherical in shape with same size distributions.



**Fig. 2. SEM-images of obtained silver nanoparticles synthesis using plasma-chemically obtained grape pomace water extract (C (Ag<sup>+</sup>) = 3.0mmol/L)**

Many of pharmaceutical residues in water, wastewater, sludge and sediments are considered “emerging contaminants”. Analgesic drugs with more than 70 million global prescriptions annually are a special group of pharmaceuticals that exhibit “persistent toxic waste” character. Ibuprofen (IBP) is widely consumed analgesic drugs that are available without prescription and found commonly in domestic sewage as a persistent and environmentally stable pharmaceutical [11].

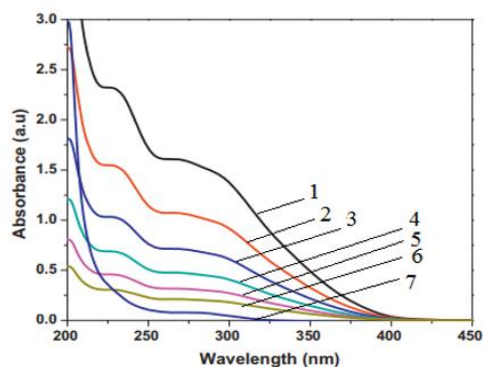
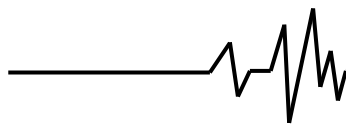
To explore the efficiency of Ag NPs in aqueous system for the degradation of ibuprofen (10 mg/L) that showed the surface plasmon resonance at 225 and 263 nm. Fig. 3 describes various aspects of catalytic degradation of ibuprofen in the presence of Ag NPs and NaBH<sub>4</sub> using UV–vis spectrometry as diagnostic tool.

Fig. 3 shows the degradation of ibuprofen (10 mg/L) using different quantities of Ag NPs (0.1–1.0 mL). This demonstrates that increase in the amount of Ag NPs favors to enhance the rate of reaction exponentially by providing more surface area and hence availability of more active sites for catalytic degradation of ibuprofen.

Generally, the degradation of ibuprofen using Ag NPs in the presence of NaBH<sub>4</sub> is an adsorption–degradation–desorption phenomenon.

At the initial stage, the ibuprofen and paracetamol molecules and BH<sub>4</sub><sup>-1</sup> ions would get adsorbed onto the surface of the Ag NPs where reductive degradation takes place via electron transfer process between the ibuprofen, paracetamol and BH<sub>4</sub><sup>-1</sup>.

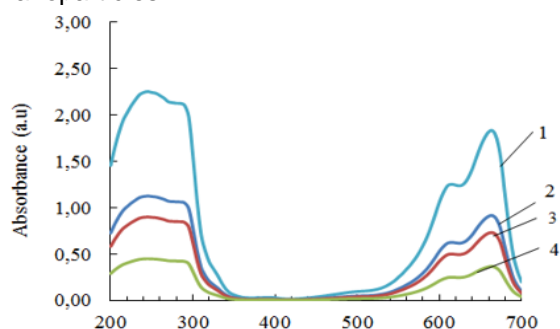
The catalyst Ag NPs is believed to serves as an electron transfer relay in this situation which concurrently accelerates the electron transfer rate and decreases the activation energy of reaction. Such rapid electron transfer sponsored by the large surface area of Ag NPs leads to complete degradation of ibuprofen molecules simultaneously with the recovery of the catalyst as the degraded molecules leave the surface of Ag NPs and diffuse into solution.



**Fig. 3 Degradation of ibuprofen drug in the presence of  $\text{NaBH}_4$  (0.02 M  $\text{NaBH}_4$ ) at fixed concentration of ibuprofen drug (10 mg/L) with varying amounts Ag NPs: 1 – 0 mL; 2–0.1 mL; 3–0.2 mL; 4–0.4 mL; 5–0.6 mL; 6–0.8 mL; 7–1.0 mL**

Dyes are a major class of synthetic organic compounds released by many industries such as paper, plastic, leather, food, cosmetic, textile and pharmaceutical industries. These effluents result in significant environmental pollution. Azo dye compounds were recognized as potential carcinogens. Abatement of dyes is a required part of wastewater treatment. The dye effluents are highly resistant to microorganisms so that their reduction by using conventional biological treatment is generally ineffective and also resistant to destruction by physical–chemical treatments in a high effluent concentration. We have investigated the size dependent catalytic degradation of organic dyes – methyl blue by  $\text{NaBH}_4$  in the presence of silver colloids.

The use of methylene blue, a heterocyclic aromatic dye, in the textile has increased in the last few years. The UV–visible band of MB monomer in water appears normally at 665 nm (Fig.4). The relative absorbance of band at 665 nm is plotted as a function of time to evaluate the reduction reaction rate in the absence of silver nanoparticles.



**Fig. 4. Effect of silver nanoparticles on the degradation of methylene blue to leucomethylene blue with varying amounts Ag NPs: 1 – 0 mL; 2 – 0.2 mL; 3 – 0.4 mL; 4 – 0.6 mL**

The decreasing trend of the absorption intensity indicates the reduction of MB, but in a slow pace. Increased degradation of MB has been achieved through the inclusion of silver colloid which is shown by a strong decrease in absorption intensity (Fig. 4).

**Conclusions.** For a healthy future of nanotechnology, green synthetic strategy should be adopted for nanoparticles synthesis by using the aqueous extract obtained from grape pomace by plasma-chemical extraction technique to get rid of hazards arising out of the use of chemical reducing agents and organic solvents. A straightforward and environmentally benign method for the synthesis of silver nanoparticles (AgNPs) is reported. Dynamic light scattering (DLS) was employed to measure the hydrodynamic size of nanoparticles in suspensions. The average size of formed silver particles is 27–33 nm.

### References

1. Sharma, G., Kumar, D., Kumar, A., Al-Muhtaseb, H., Pathania, D., Naushad, M., Mola, G. T. (2017). Revolution from monometallic to trimetallic nanoparticle composites, various synthesis methods and their applications: A review. *Materials Science and Engineering: C*, 71, 1216–1230.
2. Han, P., Martens, W., Waclawik, E.R., Sarina, S., Zhu, H. (2018). Metal Nanoparticle Photocatalysts: Synthesis, Characterization, and Application. *Part. Part. Syst. Charact*, 35 (13), 1–16.
3. Levard, C., Hotze, E. M., Lowry, G. V., Brown, G. E. (2012). Environmental Transformations of Silver Nanoparticles: Impact on Stability and Toxicity. *Environmental Science & Technology*, 46 (13), 6900–6914.
4. Plant-based green synthesis of metallic nanoparticles: scientific curiosity or a realistic alternative to chemical synthesis? / Peralta-Videa J. R., Huang Y., Parsons J. G., Zhao L., Lopez-Moreno L., Hernandez-Viezcas J. A., Gardea-Torresdey J. L. // *Nanotechnol. Environ. Eng.* 2016. Vol. 1.
5. New insights on the green synthesis of metallic nanoparticles using plant and waste biomaterials: current knowledge, their agricultural and environmental applications / Saratale R. G., Saratale G. D., Shin H. S. *Gardea-Torresdey J. L. // Environ. Sci. Pollut. Res.* 2018. Vol. 25 (11). P. 10164–10183.
6. Ulug, B., Turkdemir, M. H., Cicek A., Mete, A. (2015). Role of irradiation in the green synthesis of silver nanoparticles mediated by fig (*Ficus carica*) leaf extract. *Spectrochim Acta A Mol. Biomol. Spectrosc*, 135, 153–161.



7. Abdelghany, A. M., Abdelrazek, E. M., Badr, S. I., Abdel-Aziz, M. S., Morsi, M. A. (2017). Effect of Gamma-irradiation on biosynthesized gold nanoparticles using *Chenopodium murale* leaf extract. *Journal of Saudi Chemical Society*, 21 (5), 528-537. DOI:10.1016/j.jscs.2015.10.002

8. Ghiocel, A., Traian, Zaharescu E., Coroabă, A., Doroftei, F., Safrany, A., Vasile, C. Comparative study on gamma irradiation and cold plasma pretreatment for a cellulosic substrate modification with phenolic compounds /. // *Radiation Physics and Chemistry*. 2017. – Vol. 130. P. 52-61.

9. Pivovarov, A. A., Kravchenko, A. V., Tishchenko, A. P., Nikolenko, N. V., Sergeeva, O. V., Vorob'eva, M. I., Treshchuk, S. V. (2015). Contact nonequilibrium plasma as a tool for treatment of water and aqueous solutions: Theory and practice. *Russian Journal of General Chemistry*, 85 (5), 1339–1350.

10. Skiba, M., Pivovarov, A., Makarova, A., Pasenko, O., Khlopytskyi, A., Vorobyova, V. (2017). Plasma-chemical formation of silver nanodisperssion in water solutions. *Eastern-European Journal of Enterprise Technologies*, 6 (6 (90)), 59–65.

11. Zulfiqar, A.T., Sirajuddin, Memon, N., Agheem, M.H., Junejo, Y., Hassan, S.S., Kalwar, N.H., Khattak, M.I. (2011). Selective, simple and economical lead sensor based on ibuprofen derived silver nanoparticles. *Sens. Actuators B – Chem.*, 430–437.

### **«ЗЕЛЕНИЙ» СИНТЕЗ НАНОЧАСТОК СРІБЛА З ВИКОРИСТАННЯМ ВІДХОДІВ ПЕРЕРОБКИ ВИНОГРАДУ ДЛЯ ДЕГРАДАЦІЇ ФАРМАЦЕВТИЧНИХ ПРЕПАРАТІВ ТА ОРГАНІЧНИХ БАРВНИКІВ**

Зелений синтез металевих наночастинок є шляхом поліпшення та захисту навколишнього середовища за рахунок зменшення використання токсичних хімікатів.

Розроблено простий і екологічний спосіб синтезу наночастинок срібла (Ag НЧ) з використанням водного екстракту, отриманого з відходів переробки винограду методом плазмохімічної екстракції. Відновлення іонів срібла в розчині контролювали за допомогою УФ-видимої спектроскопії. Синтезовані наночастинок були охарактеризовані за допомогою скануючої електронної мікроскопії (СЕМ) і вимірювання динамічного розсіяння світла (ДРС). Встановлено, що розміри

сферичних частинок срібла знаходяться в діапазоні 27–33 нм. Досліджено вплив концентрацій іонів срібла на синтез наночастинок срібла та їх середній розмір.

Синтезовані НЧ проявили каталітичну активність як каталізатор для деградації ібупрофену за 50 с. Показано каталітичні властивості наночастинок срібла щодо деградації метилового синього в присутності  $\text{NaBH}_4$ .

**Ключові слова:** зелений метод, наночастинок, низькотемпературної нерівноважна плазма, екстракт виноградних відходів, каталіз, метиленовий синій, ібупрофен

### **«ЗЕЛЕНИЙ» СИНТЕЗ НАНОЧАСТИЦ СЕРЕБРА С ИСПОЛЬЗОВАНИЕМ ОТХОДОВ ПЕРЕРАБОТКИ ВИНОГРАДА ДЛЯ ДЕГРАДАЦИИ ФАРМАЦЕВТИЧЕСКИХ ПРЕПАРАТОВ И ОРГАНИЧЕСКИХ КРАСИТЕЛЕЙ / М.И.**

Зеленый синтез металлических наночастиц является путем улучшения и защиты окружающей среды за счет уменьшения использования токсичных химикатов. Разработан простой и экологичный способ синтеза наночастиц серебра (Ag НЧ) с использованием водного экстракта, полученного из отходов переработки винограда методом плазмохимической экстракции.

Восстановление ионов серебра в растворе контролировали с помощью УФ-видимой спектроскопии. Синтезированные наночастицы были охарактеризованы с помощью сканирующей электронной микроскопии (СЭМ) и измерения динамического рассеяния света (ДРС).

Установлено, что размеры сферических частиц серебра находятся в диапазоне 27-33 нм. Исследовано влияние концентрации ионов серебра на синтез наночастиц серебра и их средний размер. Синтезированные НЧ проявили каталитическую активность в качестве катализатора для деградации ибупрофена за 50 с. Показано каталитические свойства наночастиц серебра деградации метилового синего в присутствии  $\text{NaBH}_4$ .

**Ключевые слова:** зеленый метод, наночастицы, низкотемпературная неравновесная плазма, экстракт виноградных отходов, катализ, метиленовый синий, ибупрофен



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