M. I. Skiba[1],
e-mail: margaritaskiba88@gmail.com
O. A. Pivovarov[1],
V. I. Vorobyova[2]
[1] Ukrainian State University of Chemical Technology
Gagarina ave., 8, Dnipro, 49005, Ukraine,
[2] National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"
Peremohy ave., 37, Kyiv, 03056, Ukraine

GREEN SYNTHESIS OF SILVER NANOPARTICLES AND THEIR CATALYTIC APPLICATION FOR THE DEGRADATION OF ORGANIC POLLUTANTS

A simple and rapid method of green synthesis of silver nanoparticles (AgNPs) was developed using aqueous extract of grape pomas (GP) obtained from by plasma-chemical extraction technique, and their catalitic potential was investigated. With this aim, the plasma-chemical obteained aqueous solutions of grape pomace and AgNO₃ (0.25-6.0 mM) were mixed (1:1 v/v), and heated for 10 mim. The synthesized GP-AgNPs were characterized by UV-visible spectroscopy, AFM, DSL analyses. The synthesized AgNPs showed an intense surface plasmon resonance band at 405-420 nm. The AgNPs were in highly uniform shape (everage size 20 nm). The role of pH in the green synthesis of silver nanoparticles (AgNPs) is investigated. The presence of silver nanoparticles with sun light was proven very effective for degradation of organic dyes. The reaction kinetics was found to be pseudo first order with respect to the dye concentration. The outcomes of the current study confirmed that the synthesized AgNPs had an awesome guarantee for application in catalysis and wastewater treatmen.

Keywords: silver nanoparticles, plasma discharge, aqueous extract, frute waster, methilen blu.

Introdaction. The sources of water pollution are categorised as either a point source or nonpoint source (diffuse sources). Point source water pollution occurs when the polluting substance is emitted directly into the water system, for example, a pipe that spews sewage directly into a river, while nonpoint source (NPS) pollution refers to diffuse contamination which occurs when pollutants enter a water system through runoff, for example, when fertiliser is washed into a river by surface runoffs. Water pollutants can be classified as physical (odour, colour, solids, or temperature), biological (pathogens), or chemical (organic or inorganic compounds) [1, 2]. Organic pollutants are of more concern than the other types because of their carcinogenic and mutagenic effects even after exposure to minute concentrations [3, 4]. Recently, applications of organic pollutants, such as dyes and deriva-tives of phenol, are escalated due to extensive use in various field such textile, paper, leather industries and the uncontrolled discharge of these organic pollutants into main stream water leads to environmental hazardousness. The color content in dye adsorbs and reflects sunlight entering the contaminated wastewater, thereby hindering photosynthesis and interfere the growth of aquatic species [5]. Moreover, the presence of the organic dyes in the ground water is unsuitable for irrigation and drinking. So elimination of these organic pollutants from wastewater has been now gained attention towards researchers.

Dyes can be of many different structural varieties like acidic, basic, disperse, azo, anthraquinone based and metal complex dyes as reported in works [6–8]. Due to this complexity in its structure, it is very difficult to degrade by traditional treatments (physical, chemical, biological). There are several chemical and physical methods such as photodegradation, chemical reduction, coagulation, reverse osmosis for treatment of dye containing effluents. These methods suffer from some disadvantages such as high cost, intensive energy and formation of hazardous by-products [7–8]. However, it is necessary to develop eco-friendly and highly efficient methods for reduction of organic dyes and nitroarenes. Nanoremediation has well improved the overallefficiency of the degradation process and is cost effective. Nanoremediation employs reactive nanomaterials for the transformation and detoxification of chemicals either through chemical. reduction or catalytic process [9].

Recently, metal nanoparticles (MNPs) have attracted attention for the treatment of wastewaters due to their number of active sites, strong electron transfers abilities, large specific surface area, high thermal stabilities and excellent activity and efficiency. Silver is the most widely used material due to its low toxicity and microbial inactivation in water [10–12] with well-reported antibacterial mechanism.

There are several methods for the synthesis of MNPs through physical and chemical procedures [13]. The results showed that these methods suffer from several drawbacks such as requirement to costly and toxic capping agents or stabilizers, noxious organic solvents or dangerous materials, higher temperature to preparation the final product and etc. For this reason, the synthesis of MNPs by green methods has attracted interest for researchers [14]. Green synthesis of MNPs is an economical, eco-friendly and simple method in the synthesis route. A number of biomolecules act as reducing and protecting agents in the green synthesis of MNPs. Green/biosynthesis of MNPs were performed by using bacteria, fungi and plant extract. Green synthesis appears to be a cost-effective alternative to conventional physical and chemical method of MNPs synthesis and would be suitable for developing a biological process for large-scale production. Nowadays, plant extracts act as reducing and capping agents for the synthesis of nanoparticles, which is more advantageous than chemical, microbial synthesis.

The main goal is to determine the synthesis conditions properties of green-obtaining silver nanoparticles with the use of the grape pomace extract prepared by plasma-chemical extraction method and investigation on the decolorization of representative cationic phenothiazine dye in presence of nanocatalysts.

Material and methods

Materials

Silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), methylene blue were used without further purification. All materials used were of analytical grade.

Preparation and characterization of Grape Pomace Extract (GPE)

Grape pomace was stored in plastic bags at 4 C until treatment. Once in the laboratory, the grape pomace was dried at 100 C for 48 h, and ground to obtain a fine powder using a grinder. 40 ml of bidistilled water were added to 1 g of dry grape pomace powder and stirred. The resulting mixture was placed in a plasma-chemical reactor. The scheme and the principle of the plant operation are given in [15]. The mixture was treated CNP discharge for 5 minutes (at the amperage of I=120 mA and P=0.8 MPa), cooled and filtered. The freshly obtained aqueous extract was used immediately after its filtration.

Synthesis of silver nanoparticles (AgNPs)
$AgNO_3$ was dissolved in double distilled water to give a solution of 0.25–6.0 mmol/L. In a typical reaction procedure, 40 ml of grape pomace extract was added to 40 ml solution $AgNO_3$ under stirring 0.1 min. The final product was obtained as a colloidal dispersion. The mixture was then heated at 75° C for an appropriate time. The change in color of a mixture of $AgNO_3$ to brown indicates the synthesis of AgNPs. The strong SPR band at 400-440 nm in UV–Vis spectra thus confirms the formation of AgNPs. The AgNPs obtained by chemical synthesis were centrifuged at 5000 rpm for 5 min. The dried powders were then used for further characterization.

Characterizationtechniques

UV-visible spectra analysis was performed for all samples and the absorption maxima were analyzed at a wavelength of 200–700 nm using UV–visible spectrophotometer (UV-5800PC, FRU, China). Atomic Force Microscopic studies were conducted using WI Tec Alpha 300 RA instrument in the tapping mode.

Catalytic activity

The potential catalytic activity of synthesized silver nanoparticles in the decolorization of dyes is demonstrated using a cationic phenothiazine dye-MB. In a typical assay,10 mL of 10mM stock solution of MB were mixed with 3 mL of 1 mM freshly prepared $NaBH_4$ solution. The different samples were prepared. One blank sample was prepared without AgNPs. In experemental sample, 0.05 mL of as-synthesized colloidal AgNPs was further added into previously made mixture of MB and $NaBH_4$. The final volume of reaction mixture in all three samples was adjusted to 16 mL by adding ddH_2O. The experiment was carried out at ambient temperature. The evaluation of catalytic decomposition process were calculated by the differentiation of optical absorption spectra of a methylene blue. The solar light degradation of MB were observed in certain time intervals and by analyzing the reduction in the intensity of MB at a maximum absorption peak at 663 nm using UV-Vis spectrophotometer.

Results and disscution. One of the important techniques to elucidate the formation and stability of metal nanoparticle is UV-Vis absorbance spectroscopy [16]. The origin of intense color in the visible range for colloidal solution of silver nanoparticles can be attributed to Surface Plasmon Resonance (SPR) and the corresponding bands in the spectra are observed in and around 380-430 nm respectively.

The colorless aqueous silver nitrate solution became yellowish brown few minutes after the addition of fruit extract of GP at 75 °C on a hot plate. From Figure 1 it is clear that the SPR band of silver nanoparticles centered at 405-420 nm and increases as concentration of Ag^+ increases in reaction mixture.

Figure 2 indicates the SPR band of silver nanoparticles as functions of reaction time and gradually increases with heating time (reaction time).

Figure 2 – Dependence of absorbance (at λmax) of obtained colloidal solutions of silver on synthesis duration (τ, minutes) using plasma-chemically obtained grape pomace water extract and Ag+ concentrations (1 – 0.25 mmol/L, 2 – 0.5 mmol/L, 3 – 1.0 mmol/L, 4 – 3.0 mmol/L, 5 – 6.0 mmol/L)

Figure 1 – Absorption spectra of obtained colloidal solutions of silver using plasma-chemically obtained grape pomace water extract and Ag+ concentrations (1 – 0.25 mmol/L, 2 – 0.5 mmol/L, 3 – 1.0 mmol/L, 4 – 3.0 mmol/L, 5 – 6.0 mmol/L)

The effect of pH on the formation of AgNPs was evaluated by UV–visible spectroscopic studies and is given in Figure 3. From the figure, it is evident that the formation of AgNPs mainly depends on the pH of the reaction medium. Thereafter, for samples pH=2 λmax is near the normal absorption wavelength for silver nanoparticles and the absorbance broadening attains its minimum value among all conditions considered. The absorbance value was increased gradually with increasing pH range from 2 to 10 (3.5 initial pH), suggesting that the rate of formation of AgNPs is high in basic pH than in acidic pH.
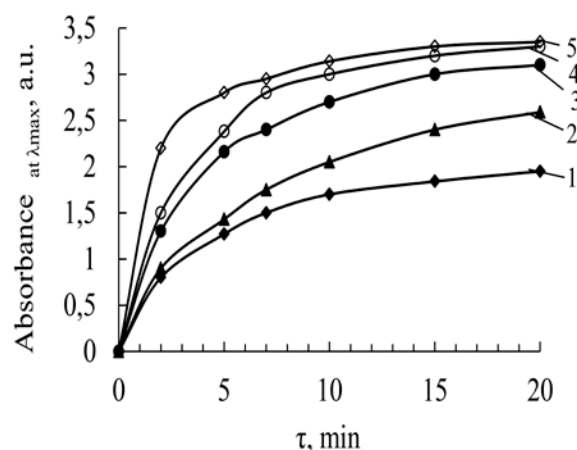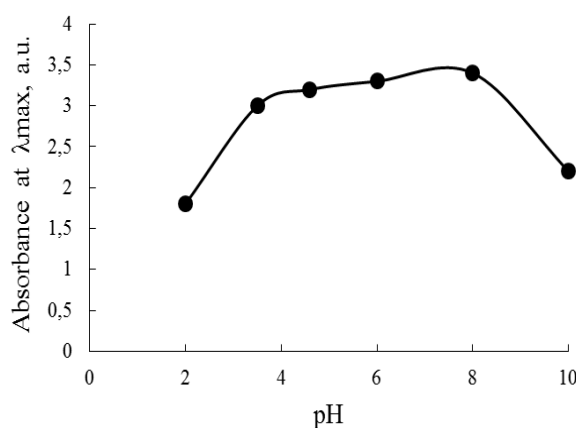

Figure 3 – The effect of pH on the formation of AgNPs using plasma-chemically obtained GPWE (C (Ag+) = 3.0 mmol/L, τ=10 min, ratio AgNO₃:extract, (mL)=1:1)

The formation of AgNPs occurs rapidly, in neutral, and the basic pH may be due to the ionization of the phenolic group present in the extract. The slow rate of formation and aggregation of AgNPs at acidic pH could be related to electrostatic repulsion of anions present in the solution.

The DLS pattern reveals that the mean size distribution of AgNPs was 24.01 nm and was found to be well dispersed in the colloidal solution with polydispersity index (PDI) of 0.71 (Figure 4).

The three-dimensional (3D) surface morphology and size analysis were obtained from AFM, shape and size distribution of the nanoparticles were done using software using the line analysis measurement in semi contact mode

(Figure 5). Particles with up to 20 nm size were found to be present in maximum quantity and the shapes of the particles are spherical.
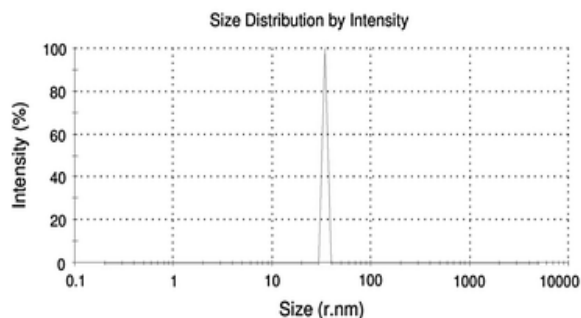

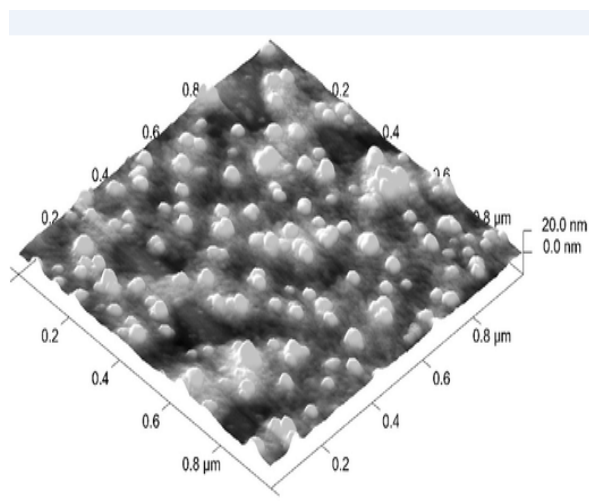**Figure 4 – Dynamic light scattering (DLS) pattern of synthesized AgNPs (C (Ag⁺) = 3.0 mmol/L, τ=10 min, ratio Ag-NO₃:extract, (mL)=1:1)**

Figure 5 – Three-dimensional AFM image of obtained colloidal solutions of AgNPs (C (Ag⁺) = 1.0 mmol/L, τ=10 min, ratio Ag-NO₃:extract, (mL)=1:1)

Methylene blue (MB) is a cationic thiazine dye which finds many uses in a wide range of fields including chemistry and biology. Methylene blue is widely used as a redox indicator in analytical chemistry and as an anti-malarial and chemotherapeutic agent in the aquaculture industry. It is also used in the analysis of trace levels of sulphide ions in aquatic samples. The aqueous solution of the oxidized form of methylene blue is deep blue in colour and its reduced form (leuco form) is colourless.

The reduction of methylene blue into its colourless form can be followed spectrophotometrically by monitoring the absorption maximum at 664 nm (Figure 6).
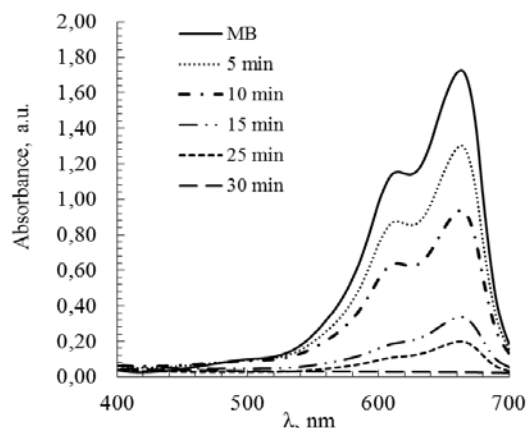
Figure 6 – UV–Vis absorption spectra for the degradation of methyl blue by NaBH₄ in the presence of 0.05 mL Ag NPs under the solar light

The blank experiments conducted without adding nanocatalyst showed no change in colour as well as 282 the intensity of λmax at 664 nm respectively in the case of methyl orange and methylene blue. This shows that they are not degraded byNaBH₄ alone or the degradation of them in the absence of nanocatalyst occurs at a negligibly slow rate which is difficult to identify.

But the rate of degradation was greatly enhanced upon the addition of even a small amount of the catalyst indicating the immense catalytic effect of the synthesized silver nanoparticles in these reactions. This was evident from the fading and ultimate bleaching of the deep blue colour of methylene blue as well as the decrease in the intensity of λmax. When AgNP was added to the reaction mixture containing both MB and NaBH₄, the intensity of the peak at 664 nm began to decrease continuously with the passage of time. The catalytic degradation reaction under solar irradiation was completed (97-99 %) within 25-30 min.

Plot of Ln (A_t/A_0) vs time for catalytic degradation of methylene blue by AgNPs is depicted in Figure 7 and calculated degradation rate constant value of Methylene blue is 0.14 min^{-1}.

A probable mechanism for the photocatalytic degradationdyes by AgNPs remains proposed in Scheme 3. The impact on an SPR region on the photocatalytic performance under visible light exposure has clarifed by the charge transfer mechanism. In the charge transfer mechanism, excitation of the electrons (e⁻) into AgNPs, which transferred to the conduction band, hence to harvest the more charge carriers under visible light exposure to light consistent charge carriers excitation and it has been originating that this could contribute to numerous redox reaction.
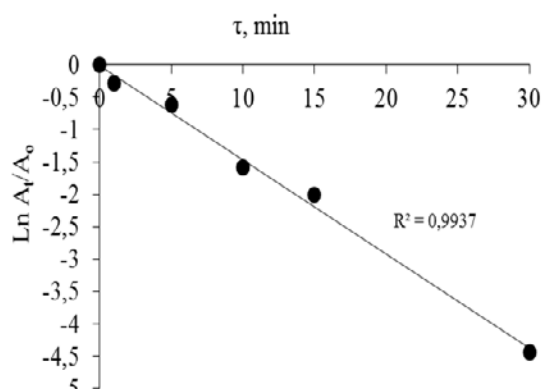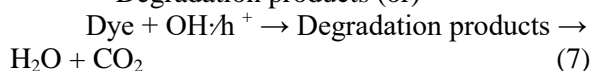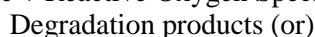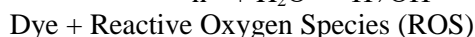
Figure 7 – Plot of Ln(A/A0) vs time for catalytic degradation of methylene blue

The surface of AgNPs traps to the photo-generated electrons as exposed typically by the Eqs. 1-7.

$$Ag\ NPs + Dye + solar\ light \rightarrow$$
$$Ag\ NPs + Dye + (e^-(CB) + h+(VB)) \quad (1)$$
$$Dye + OH \rightarrow OH^- + Products \quad (2)$$
$$Dye + OH \cdot \rightarrow H_2O + CO_2 \quad (3)$$
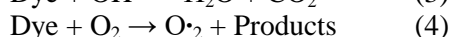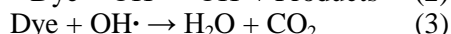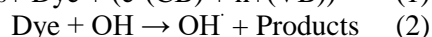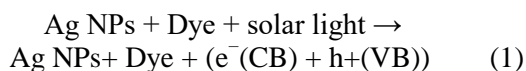$$Dye + O_2 \rightarrow O\cdot_2 + Products \quad (4)$$
$$Dye + h + \rightarrow H_2O + CO_2 \quad (5)$$
$$h^+ + H_2O \rightarrow H^+/OH\cdot \quad (6)$$
$$Dye + Reactive\ Oxygen\ Species\ (ROS)$$
$$Degradation\ products\ (or)$$
$$Dye + OH \cdot/h^+ \rightarrow Degradation\ products \rightarrow$$
$$H_2O + CO_2 \quad (7)$$
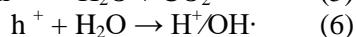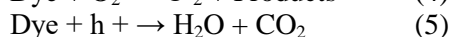
Accordingly, on the other hand, when AgNPs absorb visible light irradiation, the surface well electrons where they 4d band can be excited to the 5sp statuses might owe to the SPR efect by AgNPs profciently generated electron and hole pair (e^-/h^+). The electrons are eagerly accepted by the oxygen (O_2) molecules to form superoxide radicals $(O_2^{\cdot-})$ which encourage the degradation of dye molecules. Likewise, the holes generated in the 4d orbital react with adsorbed H_2O to produce hydroxyl radicals $(OH^\cdot)$, which bout the presence of dye molecules.

Conclusion. In this study, a simple and convenient method is developed for the preparation of silver nanoparticles. The prepared AgNPs were almost spherical in shape, crystalline in nature and with average diameter of 20 nm. These synthesized silver nanoparticles were used as catalysts in the process of degradation of hazardous dyes in a cost effective manner. In the presence of silver nanoparticles as catalysts, the degradation efficiency is increased due to their very high surface area as well as accelerate migration rate of electrons/hole to the surface of the nanoparticles. The MB dye completely degraded within 10 min, signifying the usefulness of the synthe-

sized AgNPs in effluent treatment (dye degradation) of pharmaceutical, cosmetics, paints, plastics, paper, textiles, and other chemical industries.

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М. І. Скиба[1]**,** *к.т.н.,*
А. А. Півоваров[1]**,** *д.т.н., професор,*
В. І. Воробйова[2]**,** *к.т.н.*
[1] Український державний хіміко-технологічний університет
просп. Гагаріна, 8, м. Дніпро, 49005, Україна
[2] Національний технічний університет України «Київський політехнічний інститут
імені Ігоря Сікорського»
просп. Перемоги, 37, м. Київ, 03056, Україна

ЗЕЛЕНИЙ СИНТЕЗ СРІБНИХ НАНОЧАСТОК І ЇХ КАТАЛІТИЧНЕ ВИКОРИСТАННЯ ДЛЯ ДЕГРАДАЦІЇ ОРГАНІЧНИХ ЗАБРУДНЮВАЧІВ

У статті представлено використання виноградної макухи для зеленого синтезу наночастинок (AgNPs) з водних розчинів іонів металів відповідних попередників. Нині існують нагальні проблеми утилізації відходів агропромислового комплексу, раціонального природокористування і переходу до використання екологічно чистих та енергоефективних технологій. Тому існує тенденція до використання «зелених» технологій для отримання наноматеріалів, які вважаються екологічними та ресурсозберігаючими. Дослідженням доведено ефективність використання харчових відходів як відновлюючого та стабілізуючого агента при формуванні наночастинок дорогоцінних металів моно- та біметалічних структур. Біологічну сировину добували у водному середовищі під короткочасним впливом низькотемпературної плазми. На основі комплексного аналізу складу екстракту було доведено, що гідроксильні, карбонільні й карбоксильні функціональні групи органічних сполук екстракту виноградної кісточки відповідають за відновлення іонів металів та стабілізацію отриманих продуктів. Плазмохімічні одержані водні розчини виноградних жмихів і AgNO₃ (0,25-6,0 мМ) змішували (1:1 об.) і нагрівали протягом 10 хв. Синтезовані GP- AgNPs аналізувалися УФ-видимою спектроскопією, AFM, DSL-аналізами. Синтезовані AgNPs демонстрували інтенсивну поверхневу плазмонову резонансну смугу при 405-420 нм. AgNPs були в дуже рівномірній формі (розмір середнього рівня – 20 нм). Досліджено роль pH у зеленому синтезі наночастинок срібла (AgNPs). Наявність наночастинок срібла із сонячним світлом виявилася дуже ефективною для деградації органічних барвників. Кінетика реакції була псевдопершої черги щодо концентрації барвника. Результати цього дослідження підтвердили, що синтезовані AgNPs мають приголомшливу гарантію застосування у каталізаторах та очисних спорудах.

Ключові слова: наночастинки срібла, плазмовий розряд, водний екстракт, фруктові відходи, метилен блю.