Journal of Chemical Technology and Metallurgy, 57, 1, 2022, 54-62

GREEN BIO-SYNTHESIS OF SILVER NANOPARTICLES AND THEIR CATALYTIC ACTIVITY FOR METHYL ORANGE DEGRADATION

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Received 16 October 2020
Accepted 30 March 2021

ABSTRACT

In the present work, silver nanoparticles (Ag NPs) synthetized with employing the aqueous extract obtained from grape pomace by plasma-chemical extraction technique was developed. The fabrication method was fast, low cost, and eco-friendly. The effect of silver ions concentrations, volume of extract and duration of synthesis for Ag NPs formation as well as their average particle size has been studied. The results demonstrated that synthesis provides the formation of Ag NPs for investigated concentrations of Ag^+ *(0.25 - 6.0 mmol* L^{-1}*) during 5 - 10 minutes. The prepared Ag NPs were with an average particle size about 25 - 31 nm. From the SEM and TEM images, the Ag NPs are found to be almost spherical. The catalytic effectiveness of the prepared green catalyst, Ag NPs, was also investigated in catalytic degradation of methyl orange (MO) dye. The catalytic degradation reaction under solar irradiation was completed (97 % - 98 %) within 3 - 6 min, signifying excellent catalytic properties of Ag NPs in reduction of MO.*

Keywords: silver nanoparticles, plasma-chemical extraction, grape pomace, volume of extract, catalytic degradation, methylene orange.

INTRODUCTION

In the past decade, the world has seen an exponential growth in the application of nanoscience and nanotechnology, leading to great strides in the development of new nanomaterials. Much attention has been paid to Ag NPs due to their unique properties [1, 2]. Silver NPs can be synthesized using different approaches, such as electrochemical methods, decomposition, microwave-assisted technique, and wet chemical procedures [3, 4]. However, the chemicals used in those methods are usually flammable and highly toxic, which limit their applications in many areas because they may pose risks to human health [5]. Therefore, there is an increasing need to promote a safe and environmentally friendly procedure to synthesize Ag NPs without using toxic chemicals.

Green nanotechnology integrates the principles of green chemistry and green engineering to produce eco-friendly, safe nanoparticles (NPs), that do not use toxic chemicals during a synthesis protocol [6, 7]. Green synthesis is defined as the use of environmentally compatible materials such as bacteria, fungi and plants for synthesis of nanoparticles [8, 9]. Various plants and agriculture waste has also been utilized for the synthesis of Ag NPs [10, 11]. Grape (*Vitis spp.*) is one of the most valued conventional fruits in the world. Grape crops are one of the main extended agro economic activities in the world with more than 50 million tons produced every year. More than 20 million tons correspond to European producers. Annually around 2.5 million tons of grape pomace is generated. Grape pomace (GP) mainly consists from peels (skins), seeds and stems. This biomass is rich in bioflavonoids, insoluble and soluble fibers, as well as proteins, all of which have potential applications in nanobiotechnology, such as in the synthesis of Ag NPs.

However, an analysis of the pertinent literature revealed challenging issues and shortcomings limiting the advancement of the green synthesis [10 - 12]. Major issues are associated with the source type and concentration of plant extracts and waste materials. Different extraction technique have been studied in an effort to increase a yield, including ultrasound-assisted extraction from grape stems, superheated liquid extraction from vine shoots, or fluidized-bed extraction from grape canes, UV or Vis and microwave ranges, plasma [13 - 20]. The contact non-equilibrium low-temperature plasma (CNP) is a promising option from the point of view of practical application [19 - 22]. Chemical transformations on the phase interface are conditioned by the combined effect [24 - 26]. These factors may increase the efficiency of extraction and concentration of the resulted extracts, and, as a consequence, the efficiency of further synthesis of Ag NPs.

Recently, applications of organic pollutants are escalated due to extensive use in various field such textile, paper, leather industries and the uncontrolled discharge of these organic pollutants into mainstream water leads to environmental hazardousness. There are several chemical and physical methods such as photo degradation, chemical reduction, coagulation, reverse osmosis for treatment of dye containing effluents [27]. These methods suffer from some disadvantages such as high cost, intensive energy and formation of hazardous by products. However, it is necessary to develop ecofriendly and highly efficient methods for reduction of organic dyes and nitroarenes. Nanoremediation has well improved the overall efficiency of the degradation process and it is cost effective. Nanoremediation employs reactive nanomaterials for the transformation and detoxification of chemicals either through chemical reduction or catalytic process [28].

The main goal is to determine the synthetic conditions for green-obtaining Ag NPs using grape pomace (GP) extract prepared by plasma-chemical extraction method and to investigate the decolorization of representative cationic phenothiazine dye in presence of nanocatalysts.

EXPERIMENTAL

Materials

Silver nitrate (99.8 %, Kishida), methylene blue (MB), sodium borohydride ($NaBH_4$) purchased by Aqueous solutions of precursor were prepared using ultrapure water (Direct-Q UV, Millipore) and were utilized as starting materials without further purification.

Preparation of Grape Pomace Water Extract

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 plant operation for the plasma-chemical reactor are given in works [21, 23]. The mixture was treated CNP discharge for 5 minutes (at the amperage of $I = 120$ mA and $P = 0.8$ MPa), cooled and filtered by Millipore filter (0.45 m) and used for further experiments. Further, such extracts are mentioned as the plasma-chemically obtained grape pomace water extracts (PC GPWE).

In the second case, an aqueous-alcohol solution (30:70) was used to obtain an aqueous-alcohol extract. Other parameters as the ratio of powder to extractant and the duration of processing were unchanged.

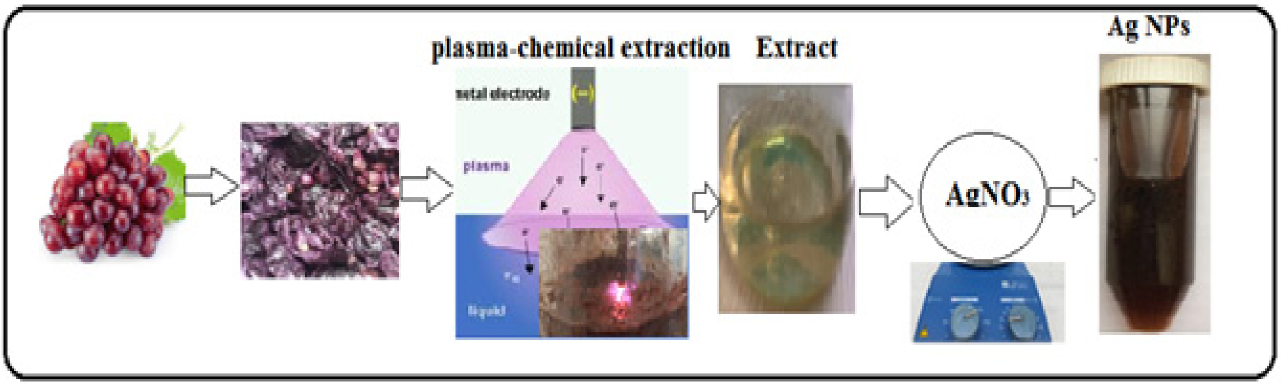


Fig. 1. Schematic illustration of the preparation of grape pomace water extract and Ag NPs.

Synthesis of Ag NPs

In a typical reaction procedure, grape pomace extract was added to $AgNO_3$ solution under stirring during 0.1 min (volume ratio (mL) 1:1). $AgNO_3$ was dissolved in bidistilled water to prepare the solutions with concentrations in the range 0.25 - 6.0 mmol L^{-1}. The 250 mL conical flask was then placed in a water-bath at 75°C. The temperature of the reaction mixture was maintained at this value for fixed times in a water-bath. The reaction mixture was removed from the water-bath and allowed to cool to room temperature (25°C). The final product was as a colloidal dispersion (Fig. 1). The strong SPR band at 400 nm - 450 nm in UV-Vis spectra additionally confirms the formation of Ag NPs.

Characterization technique

Spectra of colloidal solutions were obtained using the spectrophotometer UV-5800PC and quartz cuvettes in the wavelength range λ = 190 nm - 700 nm (FRU, China). Particle size was determined by the particle size analyzer Zetasizer Nano-25 (Malvern Instruments Ltd., Malvern, England). Microphotographs of NPs were obtained on scanning electron microscope JEOL JSM-6510LV (JEOL, Tokyo, Japan) and transmission electron microscope (TEM, JEM 2100). For TEM measurements, the one or two drops of silver sols was placed on the surface of carbon coated copper grid and the solvent was evaporated at room temperature before the experiment.

Catalytic degradation

In a typical assay, 10 mL of 10 mg L^{-1} stock solution of MO were mixed with 2 mL of 0.5 M freshly prepared $NaBH_4$ solution. Three different samples were prepared. In addition, one blank sample was prepared without Ag NPs. In two samples, 0.1 and 0.05 mL of as-synthesized colloidal Ag NPs 1.0 mmol L^{-1} was further added into previously made mixture of MO and $NaBH_4$. The experiment was carried out at ambient temperature. The evaluation of catalytic decomposition process was calculated by the differentiation of optical absorption spectra of a MO. The solar light degradation of MO was observed in certain time intervals and by analyzing the reduction in the intensity of MO at a maximum absorption peak at 464 nm using UV-Vis spectrophotometer. Pseudo-first order kinetics was carried out to evaluate the reaction kinetics of MO which is expressed in the followed equation:

$$\ln(A_t/A_0) = -kt \qquad (1)$$

where A_t is the dye absorbance for time t; A_0 is the dye absorbance for initial time and k is the rate constant.

RESULTS AND DISCUSSION

One of the important techniques to elucidate the formation and stability of metal nanoparticle is UV-Vis absorbance spectroscopy [1 - 16]. The origin of intense color in the visible range for colloidal solution of Ag NPs can be attributed to Surface Plasmon Resonance (SPR) and the corresponding bands in the spectra are observed in and around 380 nm - 430 nm, respectively [1 - 10, 29].

In our previous works it was shown, that Ag NPs are formatted after reaction with plasma-chemically obtained GPWE at heating around 2 min - 10 min [29, 30]. It was found that the rise of $AgNO_3$ concentrations from 0.25 to 6.0 mmol L^{-1} leads to an increase of the intensity of SPR peak. Additionally, it was visualized by the change of the solution color to brown.

In this paper, the influence of other factors on the formation of Ag NPs is considered. The effect of the volume of grape extract on synthesis of Ag NPs was studied at fixed concentration of $AgNO_3$ (mmol L^{-1}) on different volume of extract ($AgNO_3$: extract) : 10 mL : 5 mL = (2:1), extract = 2.5 mL (4:1) (b), extract = 1.25 mL (8:1), (c) (total volume 20 mL). UV-Vis spectra showed decrease in intensity of surface plasmon absorbance with decreasing extract volume (Fig. 2). However, as the PC GPWE volume decreases gradually from 5 mL to 2.5 mL - 1.5 mL this leads to a decrease in peak intensity of absorbance. It is known that the absorption peak characterizes the concentration of NPs in solution. It is possible that at higher amount the polyphenols in the PC GPWE had effectively reduced the Ag^+ ions to Ag^o. The lower values of the absorption intensity are due to the smaller number of formed NPs. It is also seen from the obtained spectra that with a larger amount of extract the peaks after 18 min of synthesis are wider and tend to form a shoulder in the long-wavelength region. This is usually due to the formation of larger particles and an increase in their polydispersity. With smaller amounts of extract, the curves are narrower. Such patterns can be explained as follows: in chemical synthesis, as a rule, some substances act as reducing agents and others as stabilizers of the formed particles. In green synthesis, the composition of the extract depends very much on

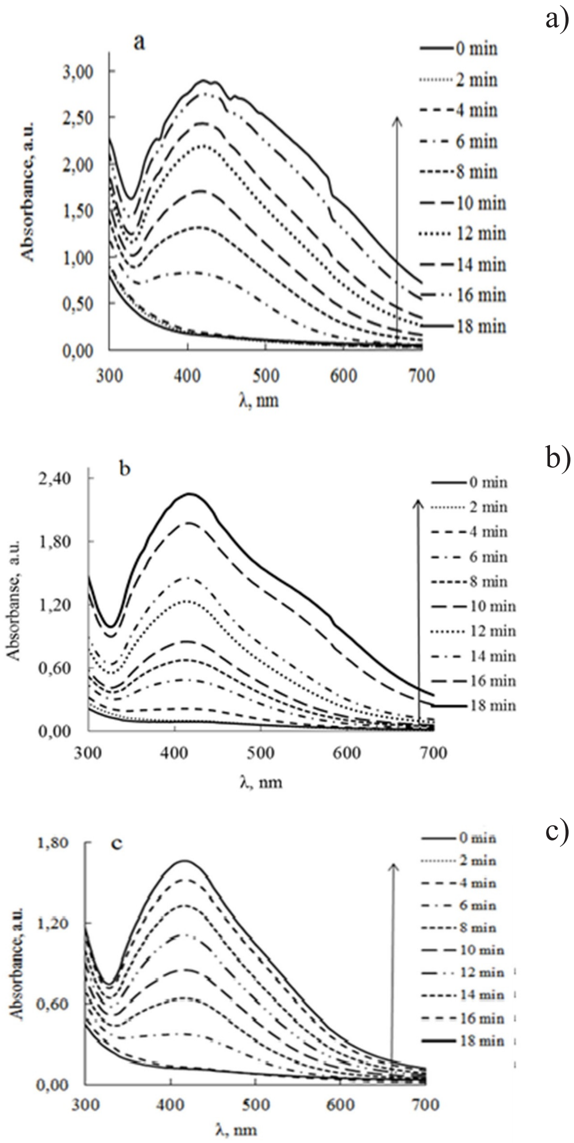


Fig. 2. The effect of volume of grape pomace water extract on synthesis of Ag NPs was studied at fixed concentration of $AgNO_3$ (1.0 $mmol.L^{-1}$) at different volume ratio of extract and $AgNO_3$ (mL) ($AgNO_3$: extract) 10 mL : 5 mL = (2:1) (a), 2.5 mL (4:1) (b), 1.25 mL (8:1) (c) (total volume 20 mL).

the method of extraction and it is exceedingly difficult to determine the composition of the extract reliably. Although a significant amount of literature has been devoted to this issue, it is only possible to predict which substances will act as reductants, as stabilizers or both, in green synthesis. In any case, the expansion of the peaks in Fig. 2 indicates an insufficient amount of stabilizer for the formation of a monodisperse colloidal system from the formed Ag NPs, while at lower concentrations more monodisperse systems are formed.

The DLS technique was used to determine the mean particle size at different volume of grape pomace water extract (see Table 1). The particle size distribution was evaluated under varying the ration of volume of grape pomace water extract and fixed Ag^+ concentration. As a result of the synthesis, Ag NPs with a not wide size distribution were formed. The obtained data indicate that the average diameter of the NPs formed at different volume of grape pomace water extract equals 22 nm - 32 nm and grows with the increasing of initial volume of grape pomace water extract.

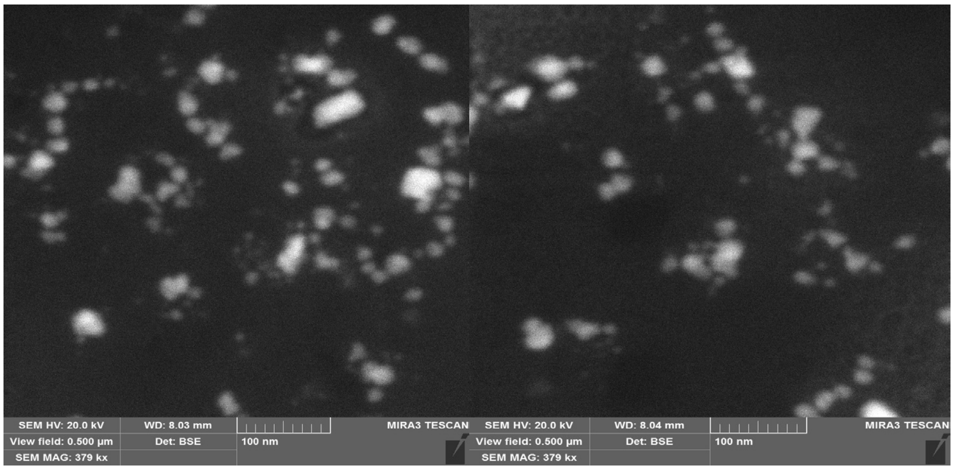
The SEM images of the prepared Ag NPs are shown in Fig. 3. As a rule, scanning microscopy allows the analysis of both the morphology of the samples and particle size. The morphology of the resulting samples indicates that relatively spherical NPs are formed at different volumes of grape pomace water extract. As for the dimensional characteristics, most of the literature shows that the results obtained using a particle analyzer and microscopic data usually do not match one hundred percent but are consistent with each other [22 - 30]. Our data indicates that the run-up of the formed NPs at a ratio of 1:1 is greater than at 1 : 8. This data is consistent with the data of photometric studies in Fig. 2, where when the amount of the extract decreases, there is a tendency to form narrower peaks.

TEM images of Ag NPs are presented in Fig. 4(a). The NPs are spherical with size ranging from 10 nm to 50 nm. Minute black spots were also visualized on the surface of metallic silver, indicating the presence of grape biomolecules on the surface of NPs. The size distribution curves of Ag NPs are given in Fig. 4(b).

In the above studies, an aqueous plasma-chemically derived grape cake extract was used. However, in the literature dedicated to the influence of the type of

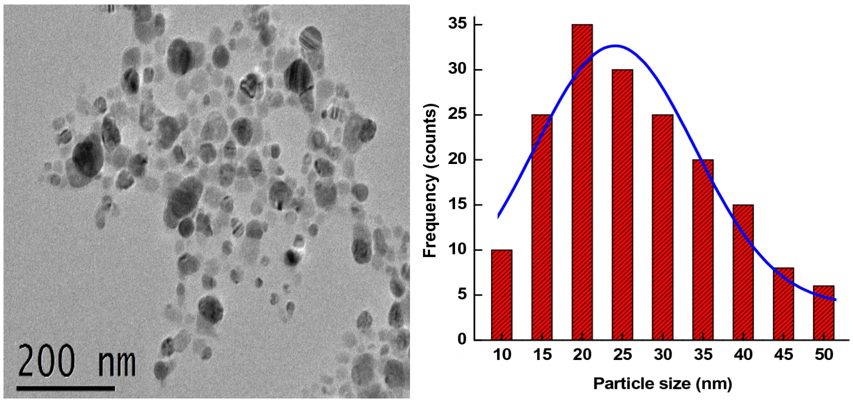
Table 1. The particle size of obtained Ag NPs at different volume of grape pomace water extract.

Ratio $AgNO_3$:extract, (mL)	C $AgNO_3$, mmol L^{-1}	Average particle size $d_{Ag\ NPs}$, nm
1:1	1.0	35.0
1:2		31.9
1:4		25.5
1:8		22.1



a) b)

Fig. 3. SEM-images of obtained Ag NPs at different volume of grape pomace water extract (C (Ag$^+$) = 1.0 mmol L^{-1}, τ = 10 min, (AgNO$_3$:extract) 10 mL : 10 mL = (1:1) (a), 1.25 mL of extract = (8:1) (b) (total volume 20 mL).



a) b)

Fig. 4. TEM-images of obtained Ag NPs with volume of grape pomace water extract (C (Ag$^+$) = 1.0 mmol L^{-1}, τ = 10 min, (AgNO$_3$: extract) 2.5 mL of extract = (4:1) and size distribution curves of Ag NPs.

extractant on the composition of the obtained extract [31 - 34]. It is noted that aqueous-alcoholic solutions at a ratio of 30 : 70 are preferred. Therefore, at this ratio, a plasma chemical extract of grape cake and Ag NPs were obtained. In the subsequent chemical synthesis, the ratio of AgNO$_3$: extract = 30 mL : 10 mL.

Fig. 5 shows the spectra of the dependence of the AgNO$_3$ solution and the plasma-chemically obtained aqueous-alcohol extract on the duration of heating. The obtained data show that the water-alcohol plasma-chemically obtained extract of grape cake after 10 min of synthesis when heated leads to the reduction of silver ions and the formation of Ag NPs. According to the spectra after 14 min of treatment, the most intense and narrow peak is observed at 410 nm. At 16 min - 18 min the tendency to aggregation of the formed particles is visible.

In recent times, degradation using biological sources has become a suitable alternative to remove dyes from the polluted water and soil. Researchers have been utilizing engineered metal NPs from different sources to degrade the dyes.

MO, an organic sulfosalt dye, has been widely used as an indicator in various fields. The excessive usage of this dye leads to several environmental and health hazards [35]. Reductants like NaBH$_4$ are being used to reduce MO to small organic molecules and non-toxic compounds.

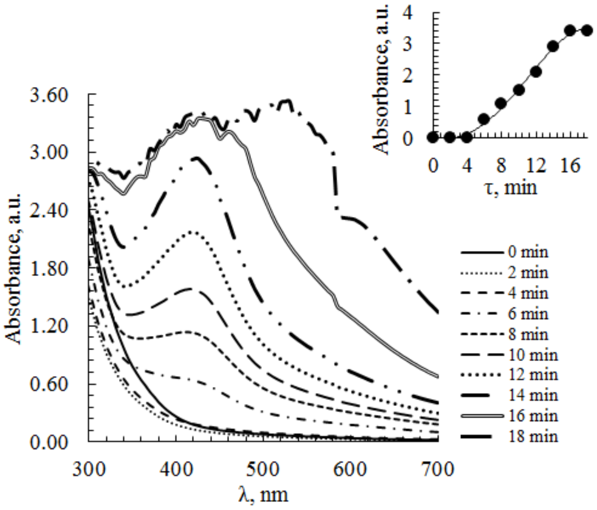


Fig. 5. UV-Vis spectra of Ag NPs formation with plasma-chemical prepared water-ethanol extract.

The catalytic activity of the synthesized AgNPs for the degradation of MO using $NaBH_4$ was evaluated. MO was selected as model dye for azo dye which is widely used as organic dyes in textile, printing and papera dyeing. According to the absorbance peaks of MO at 464 nm, time-dependent UV-Vis spectra are recorded in Fig. 6.

As control, absorption spectra of degradation of MO solution without nanocatalyst were measured at the same condition (under the solar light, at the maximum absorption peak around 464 nm wavelength using UV-Vis spectrophotometer). The blank experiments conducted without adding nanocatalyst showed no change in color as well as the intensity of λ_{max} at 464 nm. This shows that MO is not degraded by$NaBH_4$ alone in the absence of nanocatalyst. It is obvious that the intensity of dye declines quickly, indicating the dye is degraded through the catalysis of AgNPs (Figs. 6(a) and 6(b)). MO changes from yellow to colorless after catalytic degradation reaction for 4 min - 6 min. The rate of reduction reaction increases as the concentration of Ag NPs in the reaction mixture increases, respectively (Fig. 6(c)). It was also evident that in the presence of 0.05 mL of Ag NPs, ~ 90 % of reduction was completed within 6 min. In the presence of 0.1 mL of Ag NPs ~ 98 % - 100 % of reduction was completed within 4 min, (see Fig. 6).

The rate constants for MO were calculated by Eq. (1). The linear regression of lnA_t versus time (t) and the rate constant (k) for MO MO (k_{MO} = 0.44 min^{-1} and 0.74 min^{-1}) are illustrated in Fig. 6, respectively.

Compared with Ag NPs, MO is electrophilic and BH_4^- anion is nucleophilic. MO acts as electron captor and $NaBH_4$ acts as an electron donator in the redox reaction. Dye accepts electrons from the surface of Ag NPs which capture electrons from $NaBH_4$ [36]. Consequently, Ag NPs serve as electron relays which

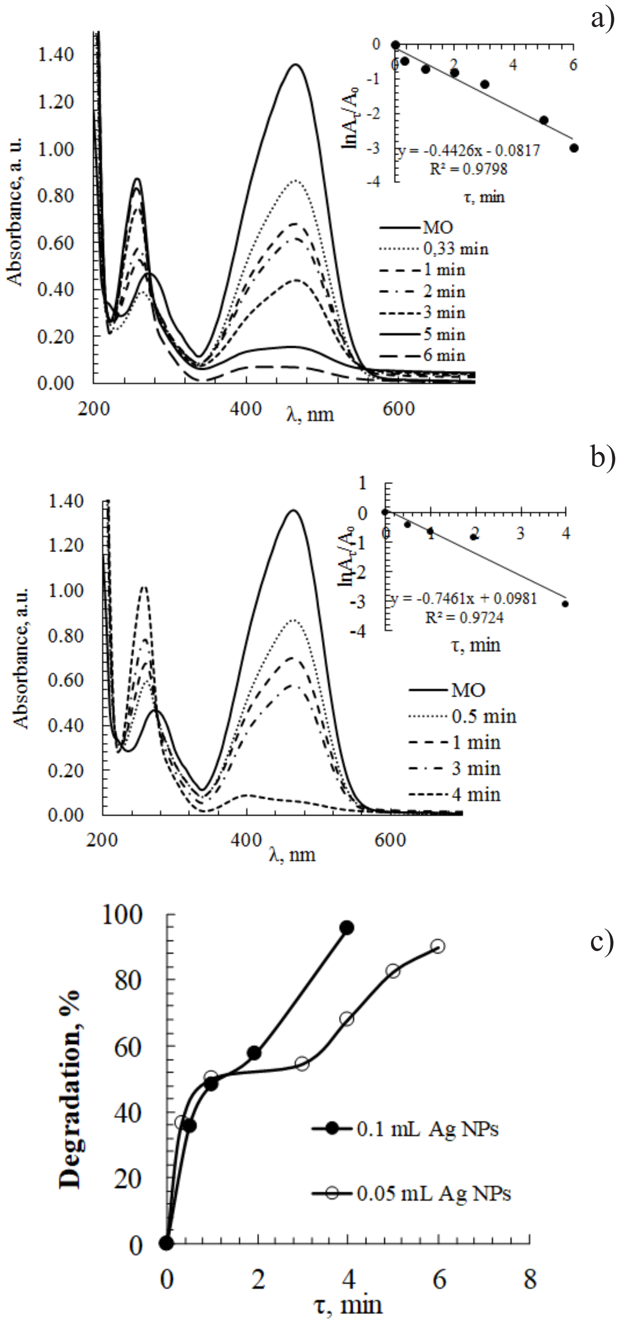


Fig. 6. UV-Vis absorption spectrafor the degradation of MO by $NaBH_4$ in the presence of (a) 0.05 mL, (b) 0.1 mL of Ag NPs under the solar light and degree of decomposition.

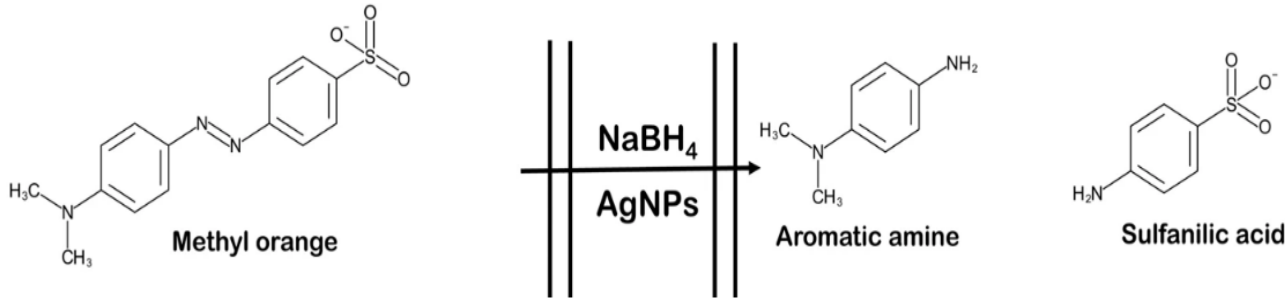


Fig. 7. Catalytic reduction of MO with $NaBH_4$ using Ag NPs in aqueous medium.

accelerate the redox reaction between MO and $NaBH_4$. The large surface area, good dispersion and excellent electrical conductivity of Ag NPs facilitate the electron transfer that increase the reduction and degradation of MO. Thus, Ag NPs serves as catalyst which strongly accelerates the redox reaction for dyes degradation to colorless small molecules, such as CO_2, H_2O and N, N-dimethyl-p-phenylenediamine [36, 37] (Fig. 7).

CONCLUSIONS

In the present study, stable silver nanocolloids were successfully prepared by a novel green route using plasma-chemically obtained water extract of grape pomace as a reducing and stabilizing agent. The procedure was relatively easy, rapid, inexpensive, eco-friendly and did not require any organic solvents or other toxic reagents. The UV-Vis spectrum of Ag NPs exhibited a surface plasmon absorption around 405 nm - 420 nm which originated from the formation of Ag NPs. The prepared Ag NPs were spherical in shape with the average particle size about 25 nm - 31 nm. Furthermore, this study demonstrated good catalytic activity of the prepared Ag NPs on reduction of MB dye at ambient conditions. The MO dye completely degraded within 3 min - 6 min, signifying the usefulness of the synthesized Ag NPs in effluent treatment (dye degradation) of pharmaceuticals, cosmetics, paints, plastics, paper, textiles, etc.

Acknowledgements

This work was supported by a grant of the Ministry of education and science of Ukraine (grant number 2044, 2019–2021) and program European Union (Harmonising water related graduate education /WaterH (www.waterh.net).

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