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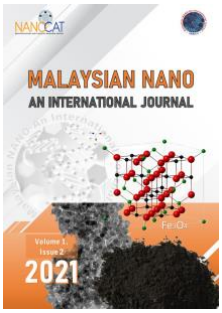

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Green Synthesis of Silver Nanoparticles Using Coffee Extract for Catalysis

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Abstract

The green synthesis method for producing metal nanoparticles has become more popular because it is more environmentally friendly and low cost. This study used a green approach to synthesize silver nanoparticles (AgNPs) using coffee Arabica bean's extract to reduce and stabilizing agents. The coffee extract was analyzed using GC-MS to identify the bioactive compounds in the extract, and Folin-Ciocalteu colorimetric test was done to find the total phenols in the extract. Later, the extract was used in the synthesis of AgNPs. Effects of synthesis parameters such as temperature, reaction time, pH, and amount of coffee extract on the formation of AgNPs were investigated. The formation of AgNPs was mainly observed using UV-Vis absorption spectroscopy. It was found that pH influenced the size of particles produced in which higher pH produce smaller particles than lower pH while other synthesis parameters mainly affected the yield of the AgNPs. The catalytic application of as-synthesized AgNPs was then evaluated in reducing methylene blue (MB) dye in a solution using NaBH4 as a reducing agent. The results show that the green-synthesized AgNPs were capable of catalyzing the reduction of MB dye in the solution.

Keywords: Green synthesis; Coffee extract; Silver nanoparticles; Methylene blue reduction; Catalysis

1. Introduction

Nanotechnology can be described as "engineering at a small scale" in which the particles involved are in the nano range between 1 to 100 nm. There has been an increase in the application of nanomaterials for the past decade due to their unique properties, such as the large surface area to volume ratio, which improves their optical, mechanical, and catalytic properties. Those properties can benefit many industries ranging from textile to medical devices [1]. One frequently studied nanomaterials with various applications is silver nanoparticles (AgNPs), a conductive metal with exceptional catalytic properties, high optical reflectivity, and good anti-bacterial performance [2]. Conventionally AgNPs are produced using a chemical route with the presence of harsh and robust reductants such as sodium borohydride or hydrazide with several steps that require heat treatment methods that often- produce hazardous by-products. To reduce the environmental impact, greener routes have been encouraged based on green chemistry principles, such as reducing hazardous chemicals and organic solvents [3].

Various approaches have been used for the green synthesis of AgNPs, including biological synthesis using bacteria, algae, and fungi and photosynthesis using plant extracts [4]. Synthesis of nanoparticles using microorganisms can result in either intracellular or extracellular products. However, the disadvantage of this method is that the production process requires a proper aseptic technique and a higher cost of product isolation. Therefore, many scientists prefer to use plant extracts due to various advantages such as being non-toxic, environmentally friendly, fast rate of growth, easy to scale up, and easy to obtain the extract. Furthermore, plant extracts can be obtained from various parts of the plant (seeds, leaves, or roots). Plant extract consists of carbohydrates, fats, flavonoids, polyphenols, and alkaloids capable of acting as reducing agents or stabilizers during the synthesis of nanoparticles [5].

Plant extracts contain a bioactive compound known as phytochemicals that can actively reduce metallic ions by reducing the ions, making complexes with them, and further reducing the complexes to form nanoparticles. This study chose coffee extract due to the presence of a wide range of phenolic compounds such as caffeine (one of the major alkaloids available in coffee extract), lipids, and chlorogenic acid, which can be used as stabilizing and reducing agents in the synthesis of AgNPs. In addition, it has been reported that the phytochemicals from plant extract can produce better morphology and consistent nanoparticles size [6]. Therefore, this study aimed to investigate the potential of coffee extract in producing AgNPs and investigate the synthesis parameters (temperature, time, amount of coffee extract, and pH) to the formation of AgNPs.

As the model reaction, the potential of as-synthesized AgNPs was evaluated using the methylene blue (MB) reduction in solution.

2. Materials and Methods

2.1 Preparing chemicals and coffee extract

Silver precursor (silver nitrate, $AgNO_3$), polyvinylpyrrolidone (PVP) and trisodium citrate ($Na_3C_6H_5O_7$), and reductant ($NaBH_4$) were purchased from Sigma Aldrich, while methylene blue (MB) was purchased from local suppliers. For all experimental works, solutions were prepared using ultrapure water (denoted by UPW; 18.2 MΩ.cm @ 25ºC). Beaker, volumetric flask, and other glassware were rinsed with UPW before use. For the preparation of coffee extract, brewed coffee Arabica seeds were purchased from a local store; then the extract was prepared by diluting 5 g of brewed coffee with 100 ml ultra-pure water, and the mixture was left to precipitate for 48 hours before it was filtered and ready to be used for the next stage.

2.2 Folin-Ciocalteu colorimetric test

The total phenol content inside the coffee extract was determined using Folin-Ciocalteu colorimetric method [7]. Briefly, 1 ml of coffee extract was placed in a 100 ml volumetric flask. Then, 70 ml of water, followed by 5 ml Folin-Ciocalteu reagent, were added into the flask. The flask was swirled for a while and incubated for 1 to 8 min at room temperature. After that, 15 ml sodium carbonate solution was added, followed by a volume of water until the volume reached 100 ml. All the solutions were mixed and incubated for 2 hours at room temperature. Lastly, 2 ml of the mixture were transferred to a 2 ml glass cuvette and was measured at 765 nm absorbance using a spectrophotometer. The amount of phenol was determined using the standard calibration curve prepared earlier. This curve is mainly to determine the corresponding gallic acid concentration of the samples.

2.3 Identification of coffee extract's compositions using GC-MS

The compositions of the coffee extract samples were analyzed using an Agilent 7890A gas chromatography equipped with an Agilent MSD 5975C mass spectrometer. A capillary column of 30 m x 0.25 mm with an internal diameter of 0.25 μm HP-5MS was used. Before analyzing the samples, the retention time was locked by changing column pressure using standard samples. A constant pressure model was then used for the entire analysis process. The gas chromatography (GC) oven temperature was programmed from 40 to 300°C via a ramp of 10°C min–1 and maintained at 40°C for 2 min and at 300°C for 15 min. The mass spectrum (MS) was

operated in full-scan mode from m/z, 50–700 for qualitative analysis or selected ion monitoring (SIM) mode for quantitative analysis. The inlet and MS transfer line temperatures were maintained at 250°C, and the ion source temperature was 300°C. Sample injection (1 µL) was done using splitless mode.

2.4. Synthesis of silver nanoparticles

The green synthesis of AgNPs was done in a 15 mL falcon tube. A certain amount of coffee extract was added with 4.4 mL UPW. Then, 0.10 ml of 0.04M $AgNO_3$ was added, and the tube was shaken before being incubated in a water bath at a certain temperature and reaction time. Effects of synthesis parameters (temperature, reaction time, amount of coffee extract, and pH) were studied by varying the parameters as follows (Table 1):

Table 1: Variation of synthesis parameters: (a) effects of temperature: (b) effects of reaction time; (c) effects of amount of coffee extract; and (d) effects of pH.

Temperature (°C)	**Reaction time (min)**	**Amount of coffee extract (mL)**	**pH**
45, 60, 85	10	0.5	No adjustment (pH 4)
60	15, 30, 45	0.5	No adjustment (pH 4)
60	45	0.5, 0.75, 1.0	No adjustment (pH 4)
60	45	0.5	• Acidic (pH 2) by adding HNO_3 • No adjustment (pH 4) • Basic (pH 10) by adding NaOH

2.5 Characterization of AgNPs.

The as-synthesized AgNPs were characterized using UV-Vis absorption spectroscopy (JASCO). Briefly, 0.5 ml of the sample was diluted with 1.5 mL UPW in the 3 mL quartz cuvette for the analysis. Samples of as-synthesized AgNPs for the study of pH's effects on morphology and size were further characterized by HRTEM. The High-resolution transmission electron microscopy imaging was performed using a 200 kV transmission electron microscope (TEM; JEOL JEM-2100 F, Tokyo, Japan).

2.6 Catalytic activity

The catalytic activity was prepared by mixing 0.5 ml of 0.05 M methylene blue with 2.45 ml of $NaBH_4$ as a reducing agent, and the mixture was shacked manually before adding 0.05 ml of the synthesized silver nanoparticles as the catalyst, then the UV–VIS spectra have been recorded at regular intervals of time to calculate the reaction rate.

$$\%\ of\ Decoloration\ =\ 100\ \times\ (\frac{C_o - C}{C_o}) \quad (1)$$

$$Kinetic\ Reaction\ rate = \ln\left(\frac{C_t}{C_o}\right) = -kt \quad (2)$$

3. Results and discussion

3.1 Phenol content and compositions of the coffee extract

The Folin-Ciocalteu analysis shows that the total phenol content in the coffee extracts to be 1496.5 mg GAE/L. Phenols may involve in the synthesis of AgNPs by interacting their carbonyl groups with silver ions (Ag^+) [8]. A reported study stated that the reduction of Ag^+ in the presence of phenols could happen in a two-step reduction, starting with the reduction of hydroxyl groups, and followed by the oxidation of the hydroxyl groups to the carbonyl groups, and later a release of reactive hydrogen, which is responsible for reducing the Ag^+ to Ag^0 [9]. Later, the carbonyl groups could prevent the agglomeration after binding with the surface of Ag^0 [10].

Meanwhile, for the GC-MS analysis, caffeine was found among the three highest compounds in the extract (as shown in Table S1 in the supplementary information). Based on the structure of caffeine (Figure 1), the reduction of Ag^+ to Ag^0 may be assisted by caffein molecules by contributing their electrons from the carbonyl groups and the nitrogen atom in the rings [11]. For instance, it was reported that secondary metabolites such as caffeine also functions as a capping agent in the synthesis of AgNPs, whereby the presence of the rings improves the stabilization of the AgNPs and prevents aggregation or inversion into Ag ions [12].

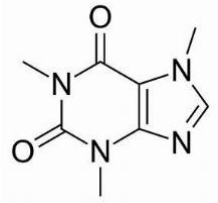

Figure 1: Chemical structure of caffeine

3.2 Effects of Synthesis parameters

3.2.1 Temperature

Temperature is an important parameter for the synthesis of metal nanoparticles, as the higher the temperature, the faster the reduction process. In some cases, the reduction can also happen with only a high temperature and without the presence of any reducing agent. In a reported study using persimmon leaf broth to synthesize AgNPs, both synthesis rate and final conversion to AgNPs increased when the reaction temperature increased [13].

In this study, the synthesis was carried for only 10 minutes with a temperature of 45^0C, 60^0C, and 85^0C. Based on the result in Figure 2a, the UV-Vis absorption peak of the coffee extract was analyzed first. It was found that there is no absorption peak within the wavelength of 350 to 600 nm. Meanwhile, based on the results in Figure 2b, the formation of AgNPs was observed with the presence of an absorption peak at about 403 nm when the synthesis was done at a temperature of 85^0C. However, for lower temperatures (45^0C and 60^0C), no distinctive peak of AgNPs was observed. The inset shows the color of the AgNPs solution after 10 mins of reaction. The incubation temperature affects the synthesis results because of the proportional relation with nucleation regions due to the rapid dissociation of ions when temperature increases [14]. However, using such a high temperature is not recommended for the synthesis of AgNPs because the high temperature affects the stability of the synthesized particles due to an increase in the kinetic energy of the synthesized AgNPs, and may cause a loss in the bioactive compounds by degradation.

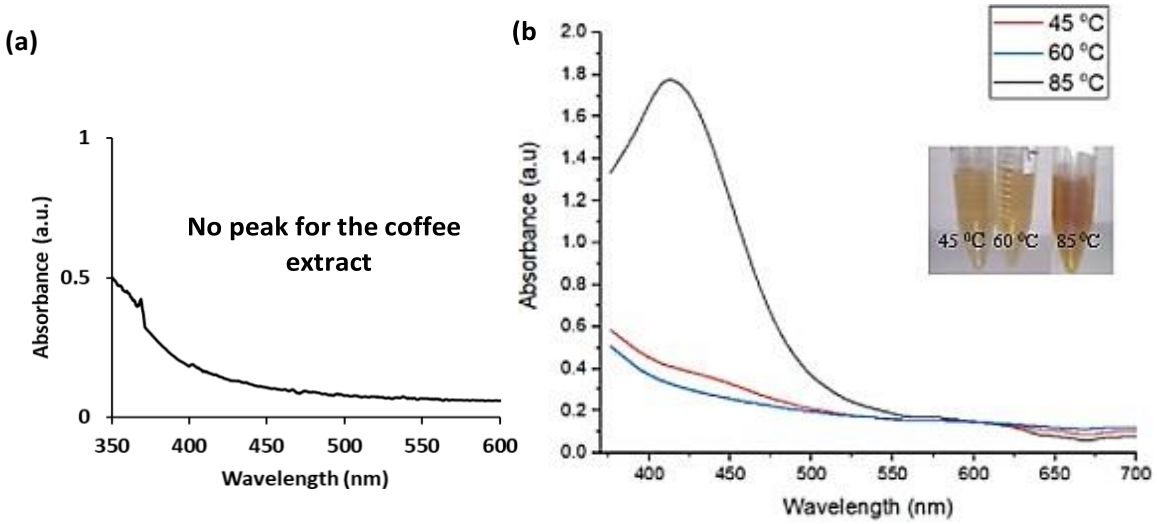

Figure 2: (a) UV-Vis absorption spectrum of coffee extract and (b) UV-Vis absorption spectra of as-synthesized AgNPs at different temperatures.

3.2.2 Reaction Time and Amount of Coffee Extract

Increasing reaction time was mentioned several times to increase the yield of metal nanoparticles [14]. Based on the results in Figure 3a, the yield of AgNPs increased with the increase of reaction time as more time allowed more reduction of Ag^+ happened for the formation of AgNPs. The color of the solution (inset image in Figure 3a) shows that the higher the reaction time, the darker the AgNPs solution, indicating the more AgNPs were formed. It can also be proven by the higher intensity of the UV-Vis absorbance peak. In addition, the size and shape of the AgNPs for all different reaction times can be said as similar due to the similar wavelength (about 430 nm) of their UV-Vis absorption peaks. The results also show that 15- min reaction time was insufficient to form AgNPs with a clearer UV-Vis absorption peak. The effect of reaction time and temperature is very crucial for the stability of the synthesized metal NPs. Using high temperatures to produce high yields over a short period of time might result in unstable metal NPs that are unsuitable for further applications [6]. Hence, the synthesis of AgNPs at 60^0C incubation temperature for 45 minutes was preferable to ensure the formation of stable AgNPs.

On the other hand, results in Figure. 3b show the effects of varying coffee extract amounts. For instance, a reported study that used Ziziphus jujuba leaf extract revealed the increase in the intensity of the UV-Vis absorption peak, indicating more formation of AgNPs when the amount of extract used was increased [15]. Similarly, in this study, it was found that the higher the amount of the coffee extract, the more AgNPs was formed, thus the higher the intensity of the UV-Vis absorption peak. The size and shape of the AgNPs were also considered to be similar as all the UV-Vis absorption peaks appeared at the same wavelength (about 430 nm). The amount of coffee extract increased the rate of reduction because more functional groups were available for the stabilization and reduction process in the synthesis of AgNPs. The color of the AgNPs was darker when increasing the amount of coffee extract (inset on Figure 3b).

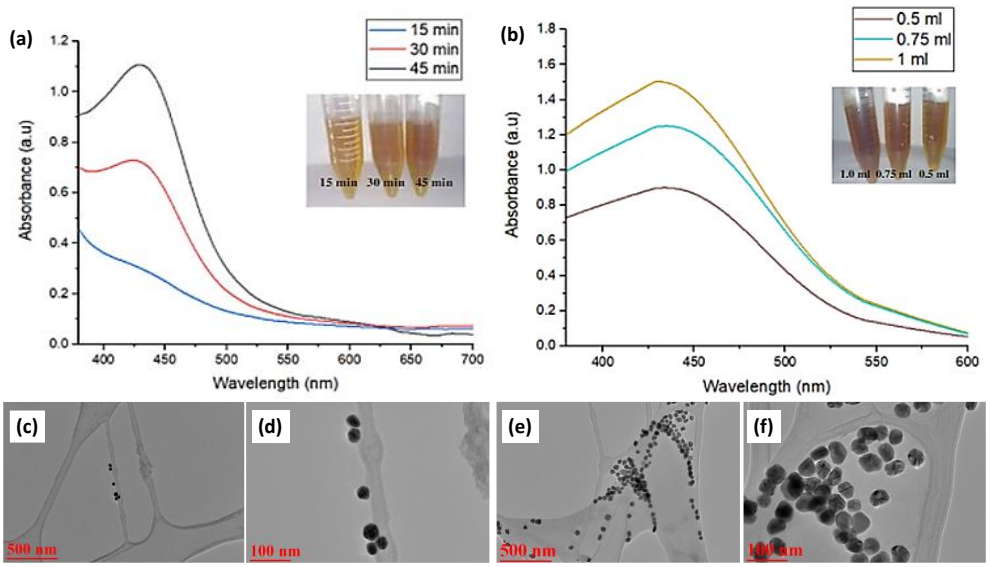

Figure 3: UV-Vis absorption spectra of as-synthesized AgNPs at (a) different reaction time and (b) different amount of coffee extract with 1496.5 mg GAE/L of total phenols content. HRTEM images of synthesized silver nanoparticles using (c-d) 0.5 mL coffee extract and (e-f) 1.0 mL coffee extract.

The pH of the mixture is among crucial parameters in the synthesis of metal NPs, especially when using plant extract. Different plants or parts of plants may have different pH ranges. It was reported that the yield of the AgNPs increased when pH was increased [16]. The nucleation is accelerated when the solution is alkaline. For instance, a reported study that used weed mimosa showed no formation of AgNPs at pH ranges of 2 to 4, but when the pH was increased, the quantities of reduced AgNPs were increased, and the size of the AgNPs decreased [17]. Another study also reported that when using a biological synthesis method such as plant extract, the pH should be checked as the pH can vary when extracting from different parts of the plant, which will highly affect the size and rate of reaction [18].

In this study, similar results were observed when varying the pH of the solution during the synthesis of AgNPs. As shown by the results in Figure 4a, the acidic solution (pH 2) showed almost no reduction of $AgNO_3$ and no color change indicating in the solution (inset of Figure 4a). The metal precursors are prone to oxidation rather than reduction at low pH, thus remaining as ions in the clear solution. When the solution was tested without any pH adjustment (pH 4), the formation of AgNPs can be observed with small amounts (based on the lower intensity of the UV-Vis absorption peak) but larger size (due to the higher wavelength of the UV-Vis

absorption peak). For the basic solution with pH 10, the UV-Vis absorption peak was shifted to a lower wavelength (410 nm), indicating the smaller size of the AgNPs but with a higher yield based on the higher intensity of the UV-Vis absorption peak.

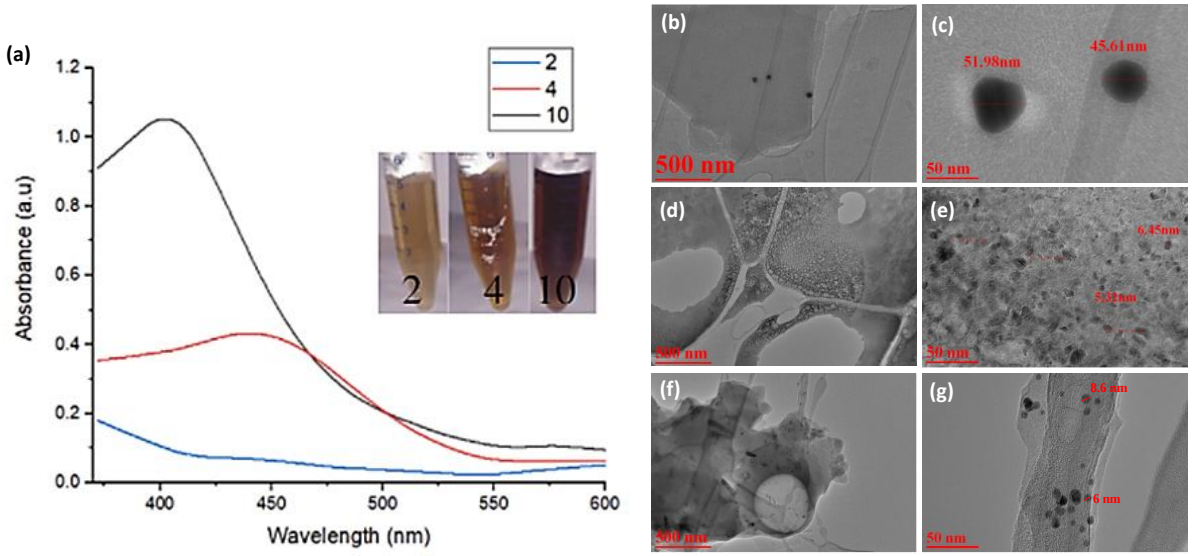

Figure 4: (a) UV-Vis absorption spectra of as-synthesized AgNPs at different pH and HRTEM images of AgNPs synthesized in (b-c) pH 4 solution, (d-e) pH 2 solution and (f-g) pH 10 solution.

The HRTEM images in Figure 4b-g also support the justification of the results by UV-Vis absorption. As shown in Figure 4b-g, the size of AgNPs synthesized in pH 4 solution was the biggest (45 nm and 52 nm), and their amount was the least than that of AgNPs synthesized in pH 2 and pH 10 solutions. Meanwhile, for AgNPs synthesized in acidic solution (pH 2), the presence of the AgNPs was almost negligible when using lower magnification (10k), as shown in Figure. 4d. However, when the magnification was increased to 100k, presences of smaller AgNPs can be observed (about 1 nm to 6 nm). As mentioned previously, at pH 2, oxidation is preferable to reduction process, and the products contain more Ag ions and Ag-biomolecules complexes. However, during the HRTEM analysis, some of them could be further reduced forming smaller AgNPs and Ag nanoclusters (AgNCs), as can be seen in Figure 4e. In addition, the HRTEM images (Figure 4f-g) also support that more and smaller AgNPs were formed when synthesized in basic solution (pH 10) as compared to those synthesized in pH 4 solution.

3.3 Catalytic activity

The potential use of the as-synthesized AgNPs in catalysis was evaluated using methylene blue (MB) reduction. MB is a redox indicator that turns into a colorless solution when exposed to reducing agents [19]. The reaction occurred because of the electron relay effect, where AgNPs act

as a donor of electrons for methylene blue to work as a redox catalyst [20]. The redox catalyst is activated because of the intermediated redox potential value between the acceptor and the donor of electrons, and the more positive the redox potential is, the reduction will occur faster.

Initially, the catalytic test was done by adding 0.1 ml of the as-synthesized AgNPs, but the reaction occurred too fast (in 10 seconds), and the bluish MB solution turned into a yellowish solution, probably due to the formation of more AgNPs after being reduced by the 2.6 mL $NaBH_4$ solution (Figure 5a). Therefore, for calculating the decolorization % and kinetic reaction rate, the amount of the AgNPs was reduced to half (0.05 ml), and the $NaBH_4$ solution was reduced to 2.45 mL. After 1 hour, the degradation was observed by UV-Vis absorption spectroscopy.

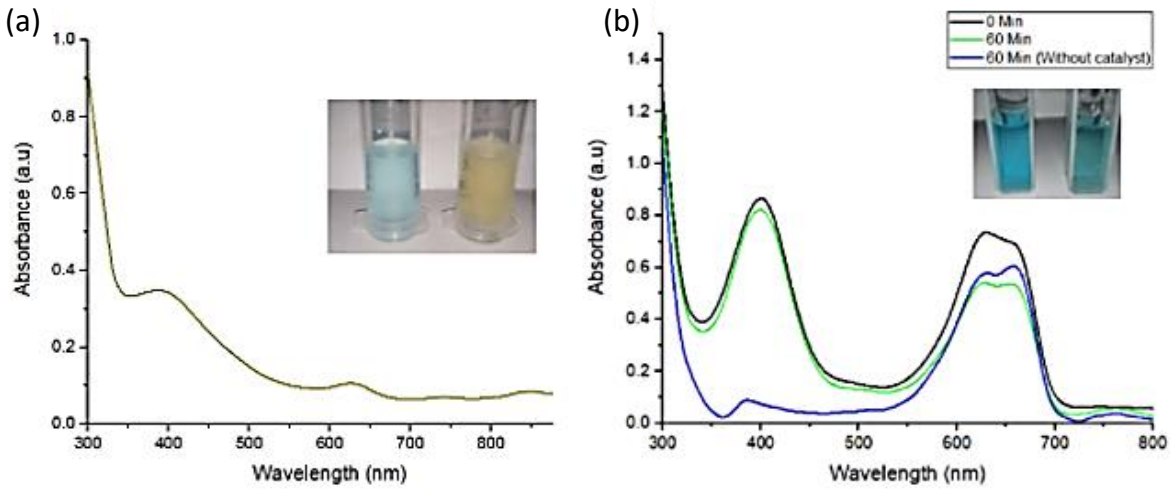

Figure 5: (a) UV-Vis absorption spectrum of MB after fast degradation by AgNPs and $NaBH_4$ (2.6 mL) in excess of $NaBH_4$ Decolourization in 10 seconds using 0.3 ml MB, 2.6 ml $NaBH_4$, and 0.1 ml catalysis, and colorless MB on the right. b) Degradation of methylene blue by silver nanoparticles in excess of $NaBH_4$. Decolorization over 60 minutes period time using 0.5 ml MB, 2.45 ml NaBH4, and 50 µl catalyst, and the decolorization without adding AgNPs for comparison.

Based on the UV-Vis absorption spectra in Figure 5b, the UV-Vis absorbance peak at 665 nm was decreased gradually, and the bluish color of MB started to reduce. The decolorization percentage during this period was 26.7%, and the reaction rate was $5.175 \times 10\text{-}3s^{-1.}$ The reaction was relatively slow compared to the control experiment (without AgNPs) due to the reduced volume of AgNPs solution. In addition, another peak was observed at 400 nm could be due to the reaction between $NaBH_4$, and the catalyst, which caused more production of AgNPs. It can be

speculated when the $NaBH_4$ was consumed for the formation of AgNPs, less of the reducing agent was available for the reduction of MB, thus leading to lower enhancement of the catalytic reaction of AgNPs (Table 2). Light activation might also be needed to enhance the catalytic activity of AgNPs.

Table 2: Reaction rate and decolorization percentage calculated after 1 hour

Experiment	Reaction rate	Decolorization %
With catalyst	5.175×10^{-3}	26.7 %
Without catalyst	3.75×10^{-3}	19.3 %

4. Conclusions

This study investigated four important parameters (temperature, reaction time, amount of coffee extract, and pH) to synthesize AgNPs. The results showed that increasing temperature, time, and amount of extract resulted in an increasing amount of AgNPs. Meanwhile, pH affected both size and amount of AgNPs. The as-synthesized AgNPs also showed potential as a catalyst in the reduction of MB. However, the green synthesis of AgNPs should be studied further to achieve a controllable system that allows control of shape and size, and this method needs to be optimized for scale-up. On the other hand, the effect of light to activate the AgNPs could also be investigated as AgNPs are semiconductors that can function as photocatalysts.

Competing interest

The authors declare no conflict of interest.

Acknowledgments

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