

Photocatalytic Activity of Gold and Silver Nanoparticles Synthesized by Using Coffee Flower Extract

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ABSTRACT

In this work, silver and gold nanoparticles (AgNPs and AuNPs) were synthesized via green synthesis using coffee flower (CF) extract as a source of reducing and stabilizing agents. The concentrations of HAuCl_4 and AgNO_3 were varied to be 2.5, 3, and 3.5 mM and 1.5, 2, and 2.5 mM, respectively, and five dilution ratios of CF extract to water were used. CF extract was analyzed for total phenolic content and reducing power. The obtained nanoparticles were characterized by UV-visible spectrophotometer and transmission electron microscope and were used as photocatalysts in colloidal form. The results showed that total phenolic content and reducing power of the extract were equivalent to 387.23 and 377.25 mg gallic acid/L. The optimum concentration of AgNO_3 was 3 mM and that of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was 2 mM, and the ratio of CF extract to water was 20:80. The average diameters of AgNPs and AuNPs were 35.21 and 12.18 nm, corresponding to absorbance peaks at 449 and 532 nm, respectively. The photocatalytic activities of uncoated, PEG6000-coated and alginate-coated AgNPs and AuNPs were investigated by decomposing 10 ppm methylene blue (MB) in 4 mL under UV light (250 nm, 6W). The degradation percentage after 120 min reached maximum levels of 39.6% and 35.47% by using non-coated AgNPs and alginate-coated AuNPs at loading of 0.16 mg. It was found that 0.04 mg of reused AgNPs and 0.11 mg of reused AuNPs was able to remove MB up to 11.54% and 22.90%, respectively.

Keywords: Coffee flower; Gold; Green synthesis; Nanoparticles; Photocatalytic activity; Silver

1. Introduction

Nanotechnology involves creation and management of materials or appliances at the level of atoms, molecules, or small parts in the range of 1-100 nm, resulting in materials

or appliance with new physical, chemical, or biological properties, which makes them advantageous to people and industries and increases their economic value [1].

Recently, various metal nanoparticles (NPs) have been investigated. Silver (AgNPs) and gold nanoparticles (AuNPs) have been increasingly applied in many industrial, medical, cosmetic, or food products [2]. For example, AgNPs and AuNPs were effective as anticancer, antibacterial agents, catalysts in wastewater treatment, and drug delivery agents [2-4].

Over the past decade, green synthesis has become a topic of interest for researchers and scientists worldwide because the plant extracts were used instead of harmful chemicals. The phytochemical analysis of some flowers showed that various compounds present in different flower extracts could act as oxidizing agents, reducing agents, stabilizing agents, or bio-templates to aid in the synthesis of NPs from biomaterials, especially metal or metal oxides NPs [5].

Every year in the coffee industry, approximately 30,000-40,000 flowers/adult trees fall to the ground without further uses, representing an abundant waste in the coffee industry [6]. Coffee flowers are not commonly used in cooking. They are, however, a rich source of bioactive compounds. Recently, the dried coffee flowers have been consumed in a form of tea, which was high in antioxidants that were believed to prevent cancer and help reduce fat in the blood [7]. Moreover, it was found that coffee flower extract contained carbohydrates of which the main constituent was glucose, followed by arabinose, galactose, xylose, mannose, and rhamnose [6]. A study reported that the body could take advantage of fructose in coffee flowers without causing residues [8]. Phenolic compounds in coffee flowers, which were the antioxidants, included gallic acid, chlorogenic acid, trigonelline, alkaloids, flavonoids, and anthocyanins. In addition to sugars and phenolic compounds, coffee flowers were mainly composed of water, lipids, and soluble proteins [7], all of which

played a role in the synthesis of NPs by acting as reducing and stabilizing agents.

Industrial waste is a major cause of water pollution, one of which is the pollution from waste dyes left in water, which were about 20% of the annual dye consumption. Because different types of toxic contaminants in the water will have adverse effects on human health and lead to waterborne diseases, many methods of wastewater treatment have been applied, such as biological treatment, adsorption, filtration, reverse osmosis, and others [9]. These methods were found to be relatively expensive and to slow the reaction rate [10]. In addition, the compounds in the wastewater produced by the dye industry have complex structures, making it difficult to remove them. Therefore, photocatalytic reaction has been considered for treating such wastewater because it was cheap, fast, and low in energy consumption.

Due to the nanoscale sizes of NPs, the energy band gap is generated. Once the NPs are excited via radiation, electrons in the valence band will move across the energy band gap to the conduction band. Both the electrons and generated holes could react with water molecules and produce the free radicals. The photocatalytic degradation of the dyes occurs when the free radicals attack the dye molecules by reduction and oxidation reactions [9].

It was reported before about having a TiO₂ catalyst doped with silver and gold to boost up the photocatalytic activity to decompose ethanol under visible light [11]. However, the photocatalytic activities of the AgNPs and AuNPs themselves were out of focus. Therefore, in this work, both AgNPs and AuNPs synthesized from the coffee flower extract were investigated for their photocatalytic activities in decomposing methylene blue as a model dye. Both catalysts were applied in the form of colloids and the efficiency and limitation of this application would be discussed.

2. Methodology

2.1 Chemicals and reagents

Dried coffee flowers from 100% Arabica coffee flower were purchased from a retail shop in Chiang Mai. Silver nitrate (AgNO_3), as a precursor of silver ions, was supplied by Merck Ltd., Germany. Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), as a precursor of the gold ion, polyethylene glycols with MW of 6000 Da, and sodium alginate were supplied by Sigma Aldrich CO., USA. Phosphate buffer saline (PBS) was supplied by AMRESCO Inc., USA. Potassium ferricyanide and sodium carbonate were purchased from Kemaus Pty Ltd., Australia. Trichloroacetic acid was supplied by ITW Reagents Inc., Germany. Ferric Chloride anhydrous, Folin & Ciocalteus Phenol (FCP) Reagent AR, and gallic acid were supplied by Sisco Research Laboratories Pvt. Ltd., India. Methylene Blue were purchased from Ajax Finechem Pty Ltd., Australia.

2.2 Instruments

The absorbance spectra of the synthesized AuNPs and AgNPs colloids and those of methylene blue degraded during photocatalytic reaction were recorded using UV-Vis spectroscopy (model UV-5100, Metash). The collection of NPs was performed with a microcentrifuge (Wise Spin CF-10). The mixing of substances was done with an analog vortex mixer (Model VXMNAL, OHAUS). Furthermore, the morphology of the synthesized NPs was characterized using transmission electron microscopy (JEOL, JEM-2010).

2.3 Preparation of coffee flower extract solution

4 g of dried Arabica coffee flowers was immersed in 100 ml of hot water at 80°C for 10 minutes. The coffee flower (CF) extract solution was then diluted with distilled water at various ratios of 60:40, 50:50, 35:65, 20:80, and 5:95.

2.4 Determination of total phenolic content (TPC)

The total phenolic content (TPC) of the CF extract solution was investigated by comparing with the TPC of the gallic acid solution. Therefore, the calibration curve of gallic acid solution was constructed first.

0.75 mL of Folin-Ciocalteu reagent was diluted with distilled water and mixed with 0.1 mL of gallic acid solution at various concentrations in ppm. The mixture was vigorously mixed using a vortex mixer and left to stand for 5 min. The 0.75 mL of 10% sodium carbonate solution and 10 mL of distilled water were then added. It was mixed thoroughly and allowed to stand at room temperature for 90 min and then the absorbance was recorded at a wavelength of 725 nm. Subsequently, the procedure was repeated but replacing the gallic acid solutions with CF extract solutions.

2.5 Determination of reducing power

The reducing power of the CF extract solution was determined using the reported procedure [12]. As in the TPC experiment, the results were compared with those of gallic acid solutions.

1 mL of gallic acid solution at various concentrations was mixed with 2.5 mL of sodium phosphate buffer (pH 6.6) and 2.5 mL of 1% potassium ferricyanide solution. The sample was incubated at 50°C for 30 min, and 2.5 mL of 10% trichloroacetic acid solution was added. The mixture was centrifuged for 10 min. 5 mL of supernatant was sampled and mixed with 5 mL of distilled water and 1 mL of 0.1% ferric chloride solution. The sample was left at room temperature for 10 min and its absorbance was measured at 700 nm. After that, the experiment was done using the CF extract solutions instead of gallic acid solutions.

2.6 Synthesis of gold and silver nanoparticles (AuNPs and AgNPs)

To synthesize AuNPs, 2.5 mL of HAuCl₄ solutions at different concentrations, 1.5, 2.0, and 2.5 mM, were mixed with 2.5 mL of CF extract solutions at different concentration upon dilution with water. Each mixture was heated in a microwave oven at 800 watts for 10 seconds until the change of color from light yellow to purple-red was observed. The temperature measured at the end of the heating was around 80°C, after which the mixture was left at room temperature for 2 days.

In AgNPs synthesis, 2.5 mL of AgNO₃ solution at various concentrations, 2.5, 3.0, and 3.5 mM, were mixed with 2.5 mL of CF extract solutions. The mixtures underwent the same procedure as for AuNPs synthesis.

After that, both AuNPs and AgNPs were characterized by UV-visible spectrophotometry, using the scanning range from 400 to 600 nm. For the case of uncoated nanoparticles, they were collected after centrifugation at 11,000 rpm for 10 min. The chosen samples of AgNPs and AuNPs were also investigated with a transmission electron microscope.

2.7 Coating AuNPs and AgNPs with polymers

The chosen coating polymers were PEG with molecular weight of 6000 Da (PEG6000) and sodium alginate. According to our previous study [13], for coating application, the PEG6000 solution was prepared at 10% w/v and alginate solution at 0.1% w/v. The AuNPs and AgNPs were each mixed vigorously with each polymer solution in a microcentrifuge tube using the vortex mixer. The coated nanoparticles were then collected after centrifugation at 11,000 rpm for 10 min.

2.8 Photocatalytic degradation of methylene blue (MB)

Nanoparticles before use were prepared as colloids dispersing in 0.2 ml water. Each nanoparticle weighed differently in the dispersion. It was 0.08 and 0.01 mg for uncoated AgNPs and AuNPs, respectively. PEG6000-coated AgNPs and AuNPs weighed 0.66 and 2.01 mg, respectively, while alginate-coated AgNPs and AuNPs weighed 0.06 and 0.16 mg, respectively.

The calibration curves were prepared by mixing the fixed amount of AgNPs and AuNPs, both coated and uncoated samples, with MB solution at various concentrations and the spectra were recorded using UV-Visible spectrophotometer. This was used for the measurement of the MB concentration changing upon photodegradation.

In the experiment of photocatalysis of MB solution, 4 mL of 10 ppm MB solution was mixed with 0.2 mL of AgNPs/AuNPs colloids, both coated and uncoated. The mixture was homogenized by the vortex mixer and treated under UV light (250 nm) at 6 watts for 120 min. The absorbance of the mixture at various times was measured with a UV-vis spectrophotometer at a wavelength of 350-750 nm.

The experiment was repeated using double and four-fold amounts of AgNPs and AuNPs, both coated and uncoated, to study the effect of catalyst loading.

3. Results and Discussion

3.1 Characterization of the CF flower extract solution

The CF extract solutions were reported to contain reducing and stabilizing agents [12], which could be useful in the synthesis of AuNPs and AgNPs. The total phenolic content (TPC) and the reducing power of the CF extract solutions prepared by dilution of the original extract solution with water were investigated and the results are shown in Fig. 1.

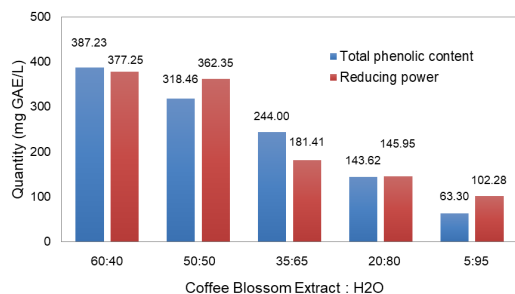


Fig. 1. The total phenolic content and reducing power of the CF extract solutions decreased upon dilution with water.

Fig. 1 shows that TPC and reducing power of the CF extract solution with the highest concentration were equivalent to 387 and 377 ppm gallic acid solutions, respectively. Obviously, both TPC and the reducing power of extracts decreased with more dilution with water.

Interestingly, TPC and reducing power were not much different from each other, especially at the highest concentration, implying that the phenolic compounds were the main reducing agents in the nanoparticle synthesis. It was reported that a phenolic compound could form a complex with gold ions before it was reduced. Furthermore, it could also act as the stabilizing agent for controlling the growth of nanoparticles [14].

3.2 Characterization of nanoparticles

The effects of CF extract and precursor concentrations on the synthesis of AgNPs and AuNPs are shown in Figs. 2 and 3, respectively.

Fig. 2 shows spectra of both AgNPs and AuNPs synthesized using fixed concentration of AgNO₃ at 3 mM and HAuCl₄ at 2 mM while varying the CF extract concentration. It can be seen for AgNPs that at the ratio of CF extract:water of 60:40 and 50:50, the absorbance peaks were at the highest wavelength (λ_{\max}) and the intensities were also highest, implying that the nanoparticles were the largest despite the highest amount. The ratios of 35:65 and 20:80 gave the similar λ_{\max} and intensities

while the ratio of 5:95 gave the lowest intensity. It seemed that the ratio of 20:80 was the optimal concentration of the CF extract solution because less volume of the extract was used when compared with 35:65.

It is observed for AuNPs that the optimal concentration of the CF extract solution was at the ratio of 20:80 because it gave the highest intensity and the lowest λ_{\max} , implying that the highest amount of the smallest particles was obtained.

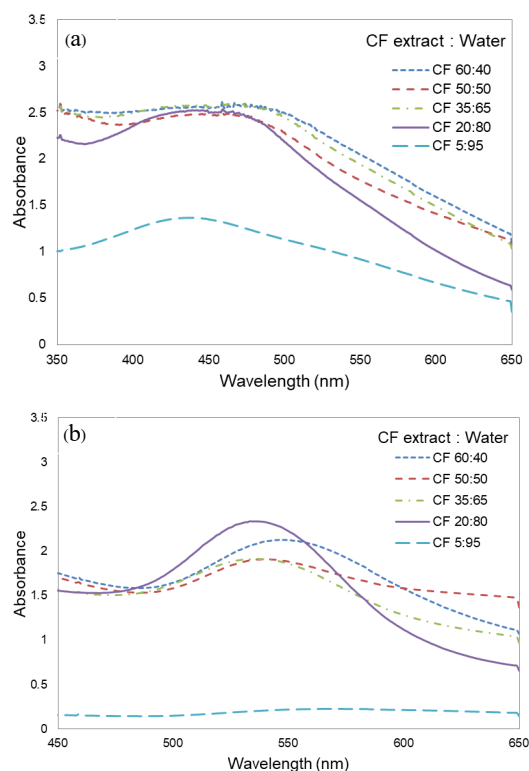


Fig. 2. Absorbance spectra of (a) AgNPs and (b) AuNPs synthesized using various concentrations of CF extract.

Fig. 3 shows the spectra of AgNPs and AuNPs in the experiments using the fixed CF extract concentration of 20:80 and varying the precursor concentration. It can be seen that the concentration of AgNO₃ at 3 and 3.5 mM gave the highest peak. Similarly, the concentration of AuHCl₄ at 2 and 2.5 mM also gave the similar highest peak. Therefore, the concentrations of AgNO₃ at 3 mM and

AuHCl₄ at 2 mM were chosen because less amount of chemicals was used.

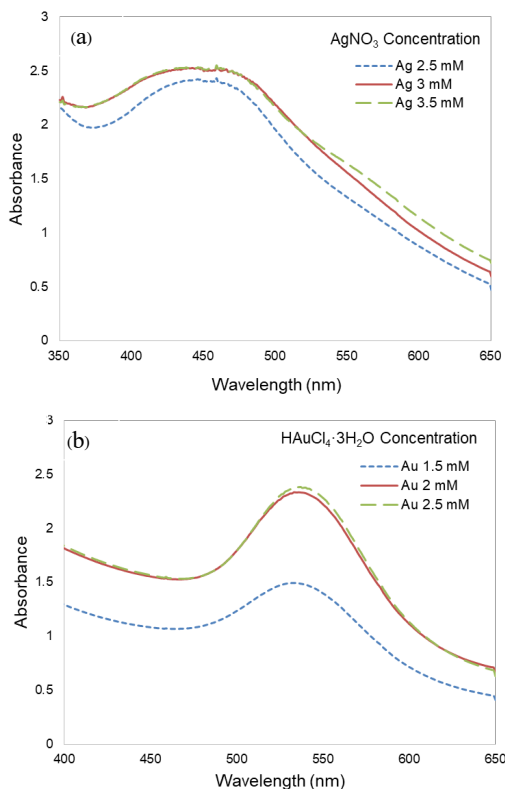


Fig. 3. Absorbance spectra of (a) AgNPs and (b) AuNPs synthesized using various concentrations of precursors.

AgNPs and AuNPs were then synthesized in a larger quantity using the chosen concentrations of the CF extract solution and the precursors. These chosen samples were later used for the test of photodegradation of MB.

The spectra in Figs. 2 and 3 could be studied in more detail as reported in Tables 1 and 2. Both tables show the wavelength of the maximum absorbance (λ_{\max}) ranged from 530-570 and 445-475 nm, respectively, corresponding to characteristic values of AuNPs reported in the literature around 520-

540 nm [13] and AgNPs reported in the literature around 375-460 nm [4].

The intensity of the peak (peak absorbance) gave the information about the amount of the nanoparticles, while position of the peak gave the information about the average particle size and its full width at half maximum (FWHM) could be related to the particle size polydispersity [14]. It can be seen in Table 1 that when decreasing the extract concentration, it seemed that the amounts of both AgNPs and AuNPs decreased while FWHM values (size polydispersity) of both increased from the reduction of reducing agent and stabilizing agent concentrations upon dilution. Table 2 shows the effect of precursor concentration. As the concentration of the precursor increased, the amount of the AgNPs and AuNPs increased and their size polydispersity increased.

For the chosen samples of AgNPs and AuNPs, the FWHM values of the AgNPs and AuNPs colloids were approximately 89 nm and 56 nm, respectively. These LSPR results from UV-vis spectrophotometry could be confirmed with the results from TEM micrographs, as displayed in Fig. 4.

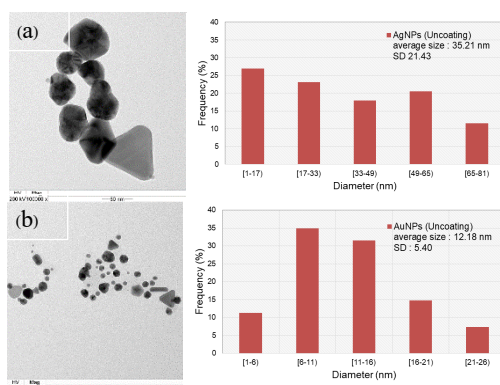


Fig. 4. TEM micrographs and size distributions of the chosen (a) AgNPs and (b) AuNPs samples.

Table 1. Results from spectra, λ_{\max} , maximum absorbance, and FWHM values of AgNPs and AuNPs synthesized using coffee flower extract when varying the extract concentration.

NPs	CF:H ₂ O	FWHM	λ_{\max} (nm)	Max Abs
AgNPs	60:40	66	472	2.59
	50:50	70	458	2.51
	35:65	87	475	2.57
	20:80	89	445	2.53
	5:95	95	439	1.37
AuNPs	60:40	59	547	2.13
	50:50	63	537	1.91
	35:65	54	533	1.91
	20:80	56	536	2.34
	5:95	115	569	0.22

Table 2. Results from spectra, λ_{\max} , maximum absorbance, and FWHM values of AgNPs and AuNPs synthesized using coffee flower extract when varying the precursor concentration.

NPs	Concentration (mM)	FWHM	λ_{\max} (nm)	Max Abs
AgNPs	2.5	84	449	2.42
	3	89	445	2.53
	3.5	92	445	2.53
AuNPs	1.5	52	534	1.50
	2	56	536	2.34
	2.5	57	542	2.37

TEM micrographs exhibited that AgNPs and AuNPs synthesized from CF extracts were polydisperse. The AgNPs colloid contained nanoparticles of spherical and other irregular shapes, while the AuNPs colloid contained, among spherical particles, triangular, pentagonal, and rod particles. Statistics from at least 100 particles showed that the average sizes of AgNPs and AuNPs were 35.21 ± 21.43 nm and 12.18 ± 5.40 nm, respectively. There have been no reported values for the optimal size of AgNPs and AuNPs for photocatalysis degradation. However, a literature on photocatalysis of nanoparticle [9] stated that smaller nanoparticles yielded larger surface area per volume, leading to more active sites for reaction to occur. In addition, for small particles, photo-electrons and holes could travel a shorter distance to reach the surface, thereby decreasing the recombination rate and increasing the efficiency of photocatalysis.

3.3 Photocatalytic degradation of methylene blue

It would be of interest to check first whether adsorption played some role in the

removal of MB from contaminated water. The preliminary study was done by mixing both 0.2 mL AgNPs and 0.2 mL AuNPs colloids with 4 mL of 10 ppm MB solution. The three situations were investigated up to 120 min, one with UV radiation, another under room light and the last one in darkness. The catalytic activities of both AgNPs and AuNPs are displayed in Fig 5.

Figs. 5 (a)-(b) revealed that MB could be removed by being adsorbed on both AgNPs and AuNPs up to 15 and 7%, respectively. Besides, the photocatalytic activities of AgNPs and AuNPs when exposed to UV light were the major mechanism in MB removal, as the removal percentages could be boosted to 39.6 and 27.5%, respectively. However, it seemed that AgNPs and AuNPs could also be photo-activated by room light at some degrees, more obviously for AgNPs. In a later experiment, the condition under UV treatment will be investigated in detail for the effect of catalyst loading.

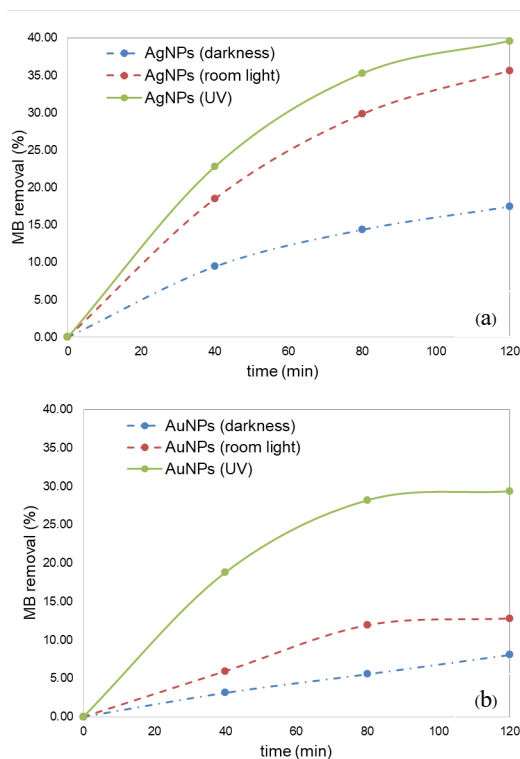
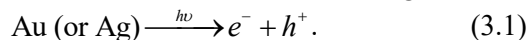


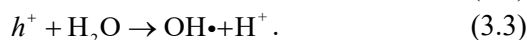
Fig. 5. The comparison was made for methylene blue removals (%) under UV exposure, room-light exposure and in the dark using (a) AgNPs and (b) AuNPs.

The mechanism of photocatalytic degradation of MB using AuNPs and AgNPs could be proposed similar to those of other nanoparticle photocatalysts [9] as the following.

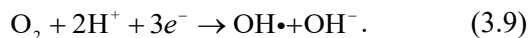
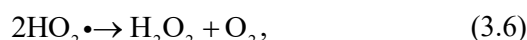
Photo-activation of AuNPs and AgNPs:



Oxidation to generate free radicals:



Reduction to generate free radicals:



After AuNPs or AgNPs were activated by photon, the photo-electron (e^-) and hole (h^+) were generated. The hole could undergo oxidation to produce hydroxyl radical $\text{OH}\cdot$ in Eqs. (3.2)-(3.3) while the photo-electron could undergo reduction through Eqs. (3.4), (3.7) and (3.9) with other side reactions, Eqs. (3.5)-(3.6) and (3.8), to produce superoxide radical ($\text{O}_2^{\cdot-}$), hydroxyl radical ($\text{OH}\cdot$), and hydroperoxyl ($\text{HO}_2\cdot$). All these free radicals are strong oxidizing agents which could decompose the structure of MB.

During these preliminary experiments, it was also found that the nanoparticles could be decomposed in some degree, probably by the oxidation that these free radicals generated during the photocatalysis process. The results are shown in Fig. 6(a) for the experiment using 0.2 mL of AgNPs and 4 mL of 10 ppm MB solution. The change of spectra was observed up to 100 min.

In Fig. (6), it can be seen from the spectra that there exist three prominent peaks. The peak at 453 nm represents the presence of AgNPs and peaks at 667 and 615 nm represent the presence of methylene blue. It was seen that during degradation of MB, both peaks at 667 and 615 nm decreased, implying the degradation of MB, and the peak at 453 also decreased, implying the destruction of nanoparticles.

It was then suggested that AgNPs and AuNPs be coated with PEG6000 and alginate for preventing nanoparticles from decomposition. The effectiveness of coating can be seen in Fig. 6(b) for PEG6000 and Fig. 6(c) for alginate as the peak of AgNPs remained the same during the photocatalytic experiment.

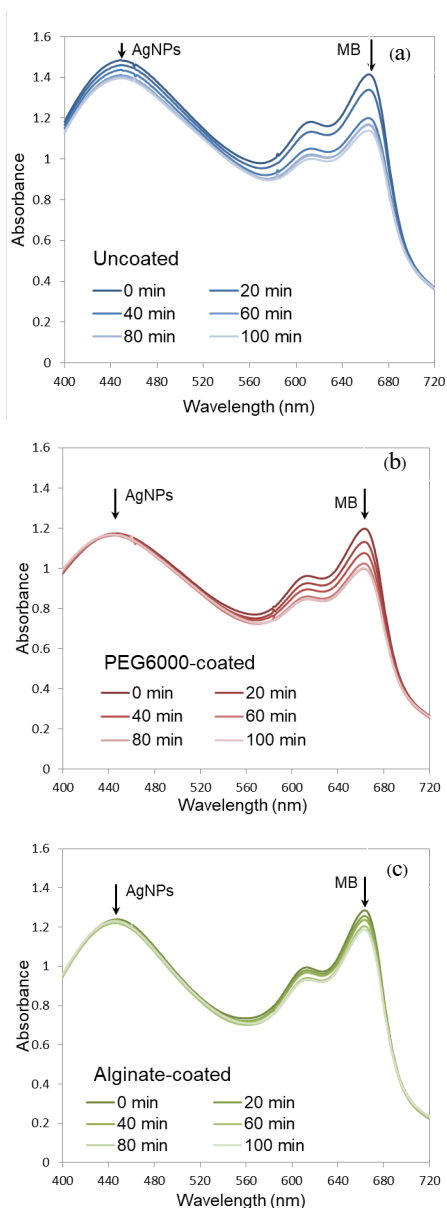


Fig. 6. The comparison of methylene blue removals after 100 min by using (a) uncoated AgNPs (b) PEG6000-coated AgNPs and (c) alginate-coated AgNPs.

The effect of catalyst loading was investigated next and the results are displayed in Figs. 7-9. Fig. 7 indicates that catalyst loading played a role in the photocatalytic reaction. In this experiment, AgNPs and AuNPs were loaded in three different quantities per 4 mL of 10 ppm MB solution. For both uncoated AgNPs and

uncoated AuNPs, in Fig. 7(a)-(b), the MB removal percentage after 120 min increased from 9.29% to 39.6% when AgNPs loading increased from 0.08 mg to 0.16 mg and decreased to 22.5% when the loading increased to 0.32 mg.

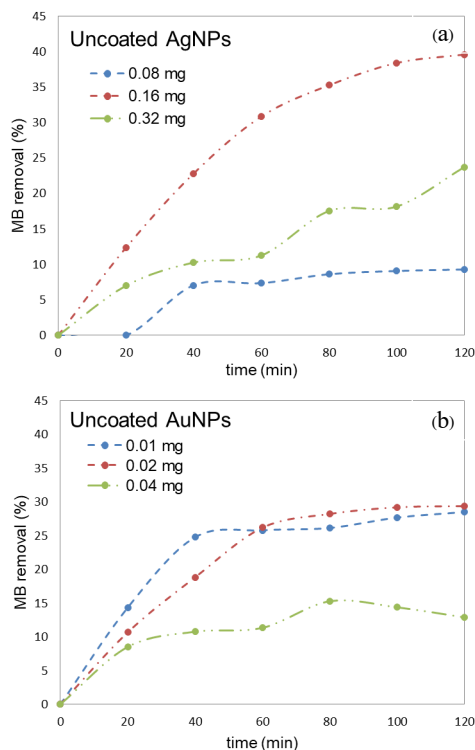


Fig. 7. The effect of nanoparticle loading on the removal percentage of methylene blue was investigated using (a) uncoated AgNPs and (b) uncoated AuNPs.

Similarly, the MB removal percentage after 120 min increased from 28.47% to 29.35% when uncoated AuNPs loading increased from 0.01 mg to 0.02 mg and then decreased to 12.5% when the loading increased further to 0.04 mg. Therefore, the catalyst could increase the rate of degradation when its loading increased. However, higher catalyst loading could decrease the transmittance of UV light to the liquid at a deeper distance, resulting in lower degradation efficiency.

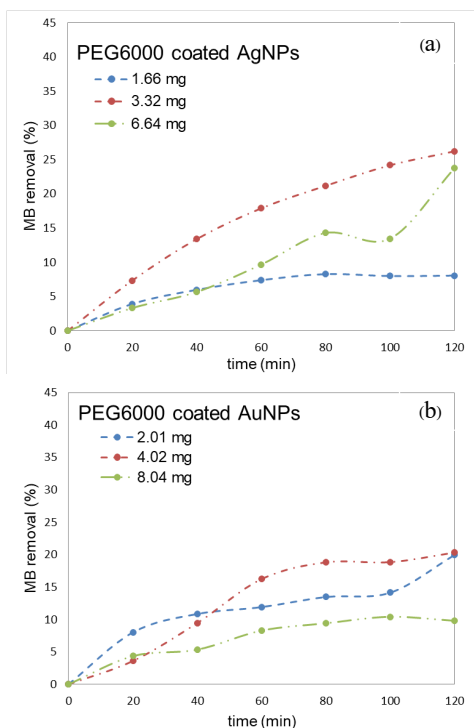


Fig. 8. The effect of nanoparticle loading on the removal percentage of methylene blue was investigated using (a) PEG6000-coated AgNPs and (b) PEG6000-coated AuNPs.

The same finding was observed for the case of using PEG6000-coated AgNPs and PEG6000-coated AuNPs in Fig. 8(a)-(b). It was seen that coating with PEG was found to lower the MB removal percentage since the polymer on the surface of the nanoparticles might interfere with photocatalysis despite the prevention of nanoparticle loss in the process.

Interestingly, for alginate-coated AgNPs and alginate-coated AuNPs, Fig. 9(a)-(b), the smallest loading of catalyst yielded the highest MB removal percentage of 24.99% by using alginate-coated AgNPs of 0.06 mg and 35.47% by using alginate-coated AuNPs of 0.16 mg, possibly because the electrostatic stabilization with alginate was so efficient that nanoparticles could be dispersed more efficiently at this loading, leading to less blockage of UV-light.

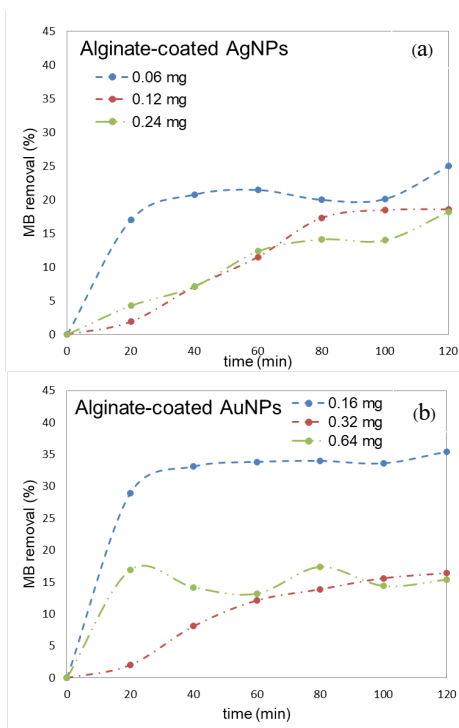


Fig. 9. The effect of nanoparticle loading on the removal percentage of methylene blue was investigated using (a) alginate-coated AgNPs and (b) alginate-coated AuNPs.

After 120 min of MB degradation, the alginate-coated AgNPs and alginate-coated AuNPs were removed by centrifugation and then they were reused without cleaning in another experiment of MB removal up to 100 min. The results are shown in Fig. 10.

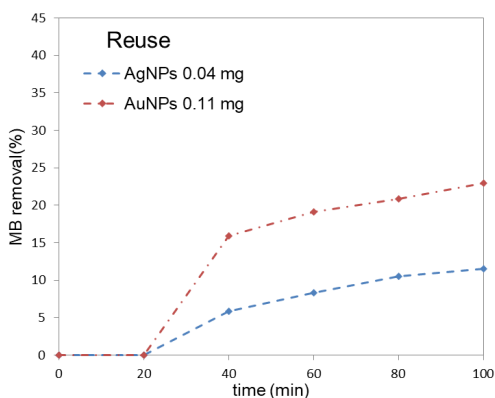


Fig. 10. The MB removal percentage up to 100 min when reusing the AgNPs and AuNPs without cleaning.

It was found that 0.04 g of reused alginate-coated AgNPs was able to remove MB up to 11.54%, and 0.11 g of reused alginate-coated AuNPs was able to remove MB up to 22.90%. However, centrifugation to remove the used catalysts was not efficient enough, resulting in lower amounts of AgNPs and AuNPs than the initial ones.

4. Conclusions

The AgNPs and AuNPs were successfully synthesized by using coffee flower extract as a source of reducing and stabilizing agents. Furthermore, the photocatalytic activities of the chosen AgNPs and AuNPs samples were investigated in the degradation of 10 ppm MB dye under UV light. AgNPs and AuNPs were stabilized by coating with PEG6000 and alginate. 39.6% and 35.47% of MB can be removed with 0.16 mg of AgNPs and AuNPs after 120 min. It was found that 0.04 mg of reused AgNPs and 0.11 mg of reused AuNPs were able to remove MB up to 11.54% and 22.90%, respectively.

During the investigation of the photocatalytic activities of the synthesized AgNPs and AuNPs colloids, it was found also that both nanoparticles could be excited under room light at some degree, more significantly for AgNPs. This could explain why both metals have been doped into other catalysts to boost the photocatalytic activity of the whole under visible light [11].

One limitation of using AgNPs and AuNPs colloids as catalysts was that they could lower the UV transmittance to a deeper level of liquid so a higher quantity of nanoparticles would increase this adverse effect. Therefore, any method that could disperse the nanoparticles at a lower quantity should be studied in more detail in the future. Another limitation could be observed from the saturation phenomena of MB removals in some experiments. Usually, when reaction proceeded, the removal percentage would increase along the reaction time if the catalyst were still active. Therefore, the

saturation might possibly be from adsorption of MB on the nanoparticle surfaces which could lower the efficiency of catalysts. This aspect should be investigated too.

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