



Removal of silver nanoparticles using phytoremediation method

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Abstract

This paper presents on removal of silver nanoparticles using phytoremediation. In this study, floating macrophyte (*Pistia stratiotes*) was used for phytoremediation of silver nanoparticles. This study investigated the performance of *Pistia stratiotes* in the removal of silver nanoparticles using phytoremediation method. The silver nanoparticles were green synthesized by using *Muntingia calabura* sp. leaves as reducing and stabilizing agent. The silver nanoparticles were successful synthesized as a peak appeared at wavelength 450 nm by UV-Vis spectrophotometer, while *Pistia stratiotes* had been acclimatized in tank at laboratory. Similar size of *Pistia stratiotes* had been employed for investigation. Each selected *Pistia stratiotes* was placed in 5 L bottles water containing different concentration (0.5 ppm, 1.0 ppm, 2.0 ppm and 3.0 ppm) of silver nanoparticles. This study was evaluated using UV-Vis spectrophotometer for five days. The results showed that the highest removal was achieved 69.88% at concentration of 0.5 ppm. This percentage removal relatively decreased up to 55.61% as concentration increase at 3.0 ppm. These results prescribed that phytoremediation of silver nanoparticles by *Pistia stratiotes* can be considered to apply and implement in water environment for AgNPs removal.

Keywords :

phytoremediation, *Pistia stratiotes*, silver nanoparticles, UV-Vis spectrophotometer

1 Introduction

Silver nanoparticles (AgNPs) are widely used in various fields, including medical, food, health care, consumer, and industrial purposes, due to their unique physical and chemical properties. Silver nanoparticles have an unique optical, electrical, and thermal properties and are being incorporated into products that range from photovoltaics to biological and chemical sensors (Oldenburg, 2014). For examples conductive inks, pastes and fillers which utilize silver nanoparticles for their high electrical conductivity, stability, and low sintering temperatures. Other applications such as molecular diagnostics and photonic devices, which take advantage of the novel optical properties of these nanomaterials. A common application is the use of silver nanoparticles for antimicrobial coatings, textiles, keyboards, wound dressings, and biomedical devices now contain silver nanoparticles that continuously release a low level of silver ions to provide protection against bacteria (Oldenburg, 2014).

AgNPs are expected to flow into the environment as surface waters (e.g., lakes, streams, and rivers). The main pathway is through biosolids from wastewater treatment (Gottschalk et al., 2009).

An analysis of the wastewater from a sewage treatment plant indicated existence of AgNPs with a size of 9.3 nm and a concentration of 1900 ng/L (Hoque et al., 2012). Moreover, the concentrations of AgNPs in surface water and sewage treatment are increasing significantly (Fabrega et al., 2011; Gottschalk et al., 2010). In agriculture, AgNP-contaminated water may permeate into fields through fertilization and irrigation (Kaegi et al., 2013). The released AgNPs have the ability to permeate different media and eventually enter the plant rhizosphere (Dietz and Herth, 2011). Therefore, the AgNPs are inevitably taken up by crops and easily enter into the food chain (Dang et al., 2021).

Kalman et al. (2015) studied the bioaccumulation and trophic transfer of AgNPs in a simplified freshwater food chain comprising the green alga *Chlorella vulgaris* and *Daphnia magna*. After AgNPs were accumulated in algae, the Ag-contaminated algae were fed to *Daphnia magna* (Yan and Chen, 2019). Accumulation of Ag in *Daphnia magna* as food chain can be harmful to human health. Several studies have shown that AgNPs exhibit an extreme toxicity on nature and human body (Zahariev et al., 2016). Ag is in the form of silver ions, which are responsible for the toxic effects like: permanent discoloration of the skin (argyria) and eyes (argyrosis), damage to the liver and kidneys, gastrointestinal tract, respiratory and blood system (Panyala et al., 2008).

To prevent AgNPs accumulation in freshwater food chain related to human health, a remediation technology needs to be applied to AgNPs removal in waters. One of popular technology is phytoremediation. Compared to chemical and physical method, such as mesoporous silica as chemical adsorbent (Pongkitdachoti and Unob, 2018), conventional condensation and evaporation

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method (Haider and Kang, 2015), thermal-decomposition, combination of composite and magnetic field (Janacek et al., 2018), and combination of composite and magnetic material (Ul-Islam et al., 2017), phytoremediation is cost-effective, eco-friendly, and simple technique. Furthermore, phytoremediation technologies are available for various environments and types of contaminants (Greipsson, 2011; Nguyen et al., 2018).

Aforementioned above, this study attempts to show investigate the performance of *Pistia stratiotes* for silver nanoparticles removal using phytoremediation. The potential of *Pistia stratiotes* is also evaluated. Furthermore, the adsorption kinetics and isotherms of AgNPs on *Pistia stratiotes* are assessed.

2 Materials and method

2.1 Materials

Pistia stratiotes which is floating macrophyte is obtained from the pond near the IPASA laboratory. The *Pistia stratiotes* was obtained at the pond that had been take care by the laboratory staff. *Muntingia calabura* sp. leaves were obtained at the trees in UTM. The materials and solution for the process of synthesis were obtained and done at IPASA laboratory.

2.2 Sample collection and preparation

Pistia stratiotes are collected from the pond near the IPASA laboratory and transferred to a quarantined pond before use in experimentation. *Muntingia calabura* sp. leaves are obtained at the trees around UTM. Plants of similar shape and size are selected for use and washed several times with tap water before use. Plants are placed into different 5 L water bottles (Figure 1). Silver nanoparticles are added to each of the media.



Figure 1 The plants are placed in 5 L of water bottles containing silver nanoparticles

2.3 Green synthesis of AgNPs

The green synthesis is done to obtain the silver nanoparticles as a source of material for phytoremediation experiment. The procedure began with weighing 20 g of *Muntingia calabura* sp. leaves. After that, the leaves are washed and rinsed for three times to remove the impurities. The leaves are put into 500 mL flask and mixed with deionised water. The process is conducted by boiling the mixture at 100 °C for 30 minutes. The plant extract is then filtered.

Then, AgNO₃ solution (100 mL in volume) was prepared using AgNO₃ and the ultrapure water with a concentration of 0.15 M in a 500 mL flask. To initiate the synthesis process, 100 mL leaves extract were added slowly into the AgNO₃ solution. The mixture was

left overnight to perform the reduction of metal ions to the formation of AgNPs in the solution. The changes in colour were observed and the solution was checked using UV-Vis Spectrophotometer to determine the success formation of AgNPs (Figure 2).



Figure 2 UV-Vis spectrophotometer

2.4 Acclimatization and growth conditions

The silver-containing media is utilized in 500 mL containers with a hole in the lid. The media container is then placed into another box to shield the media from all light for the extent of the experiment. Roots are placed through the lid holes so that the roots are the only part of the plant to contact the media and the leaves remained above the media without media contact. Control solutions of the silver contaminated media are placed in the same dark environment.

2.5 Batch study

Initial to screen the plant for the next stage of study, the removal performance of the aquatic macrophyte was investigated through batch studies. The mechanism of the removal is investigated by studying the process of accumulation, absorption and uptake of the nanoparticles and silver ions by the plants.

2.6 Kinetic and isotherm study

Water samples are taken from the control solutions and plant media at 0, 3, 24, 72, 96 and 120 hours to test any changes in total silver concentration in the media during the experiment. Four different concentrations have been decided to be used in this study which are 0.5 ppm, 1.0 ppm, 2.0 ppm and 3.0 ppm. Each concentration has triplicate to get the average concentration. It may help in providing accurate results. The value of absorbance and wavelength would be obtained from the UV-Vis spectrophotometer test. The lowest peak of wavelength 450 nm that obtained from the result would be chosen to plot the calibration graph. The equation (1) would be produced from the graph of absorbance against concentration.

$$y = 0.1383x + 0.002 \quad (1)$$

Then, equation (1) is used to find the value of x which is equilibrium concentration.

$$removal\ rate(\%) = \left[\frac{C_0 - C_x}{C_0} \right] \times 100\% \quad (2)$$

Where C₀ : initial concentration of AgNPs

C_x : equilibrium AgNPs concentration in the solution.

3 Results and discussion

The results from UV-Vis spectrophotometer to determine the chemical structure of the substance are discussed herein. The

spectrophotometer is used to measure the intensity of light and the intensity is proportional to the wavelength. It is also used to

measure the absorption of a compound by the results.

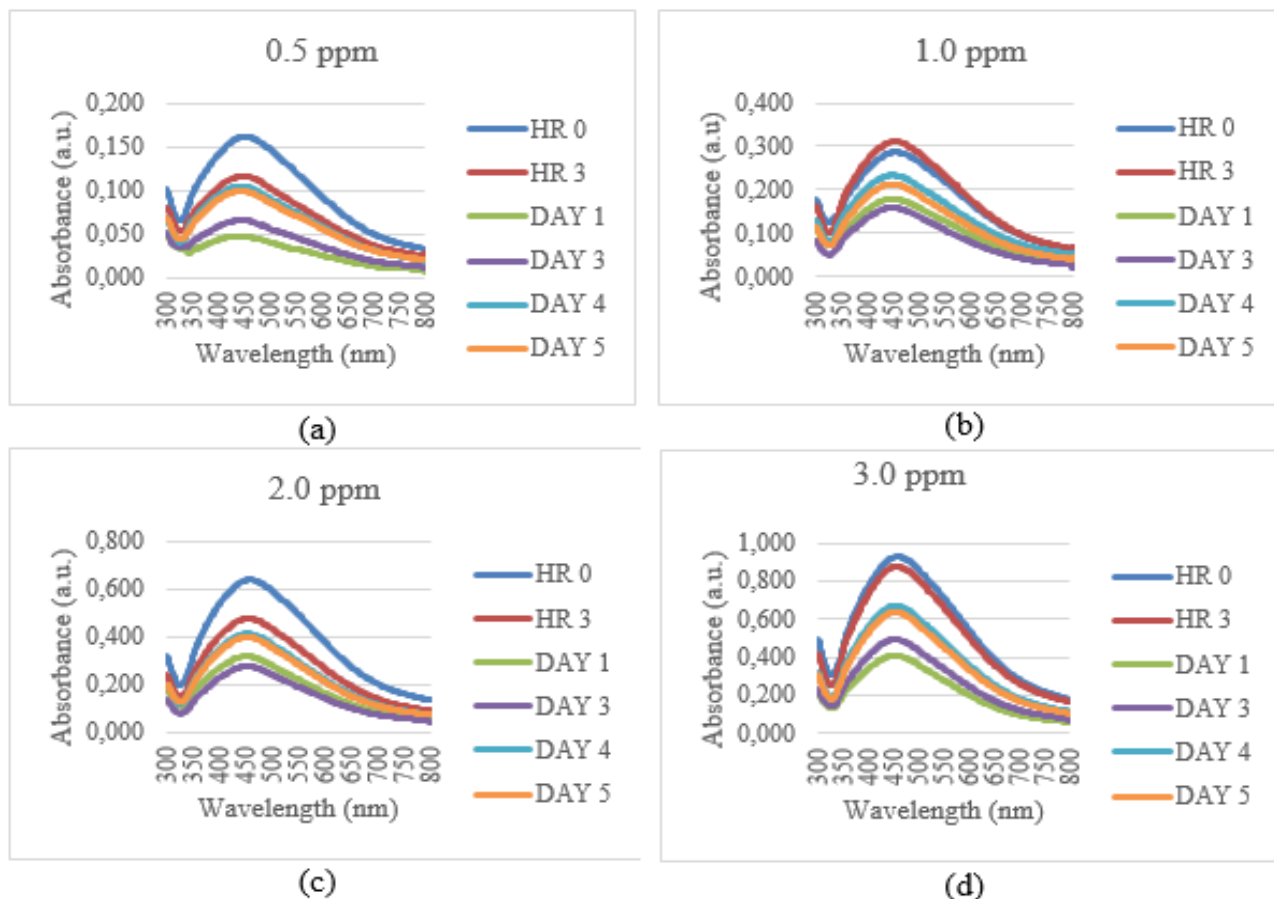


Figure 3 The graph of absorbance against wavelength for (a) 0.5 ppm, (b) 1.0 ppm, (c) 2.0 ppm and (d) 3.0 ppm

3.1 Green synthesis of AgNPs and its mechanism

The synthesis of AgNPs were done using plant extract which is *Muntingia calabura* sp. leaves. The results of the synthesis of AgNPs can be determined by the colour changes in the mixture solution of the plant extract. The colour of mixture solution changes from yellow to dark brown. The colour changes of the solution show that the formation of AgNPs is occur. It shows that the reduction of silver ion to the formation of AgNPs in the solution occurred. The reduction process of Ag^+ ion to Ag^0 and led to the formation of AgNPs (Vaidyanathan, 2010). The plant extract which is *Muntingia calabura* sp. act as reducing agent in the chemical reaction. The AgNPs synthesis was confirmed by the UV-Vis spectrum of surface plasmon resonance (SPR) at 450 nm of adsorption band (Ahmad et al., 2020).

3.2 Kinetic and isotherm study

The experiment was carried out for 120 hours with four different concentrations which are 0.5 ppm, 1.0 ppm, 2.0 ppm and 3.0 ppm. Each concentration has triplicate. The graph of absorbance against wavelength for 0.5 ppm, 1.0 ppm, 2.0 ppm and 3.0 ppm are shown in the Figure 3.

From the graph, the concentration of the nanosilver at concentration 0.5 ppm and 3.0 ppm had decreased from 0 to 24 hours. while at concentration 1.0 ppm and 2.0 ppm, concentration of AgNPs had decreased from 0 to 96 hours. The percentage of removal could be obtained by using the equation percentage of removal.

3.3 The potential of *Pistia stratiotes*

The potential of *Pistia stratiotes* had been evaluated by determine the percentage removal of AgNPs at each concentration. The value of absorbance for each concentration in Table 1 is obtained from the lowest peak at wavelength 450 nm. To calculate the percentage removal, absorbance value gained from UV-Vis need to convert to concentration value by calibration graph. Calibration graph had been plotted as follow:

Table 1 The value of absorbance for each concentration

Concentration (ppm)	Absorbance (a.u.)
0	0
0.5	0.047
1.0	0.159
2.0	0.274
3.0	0.409

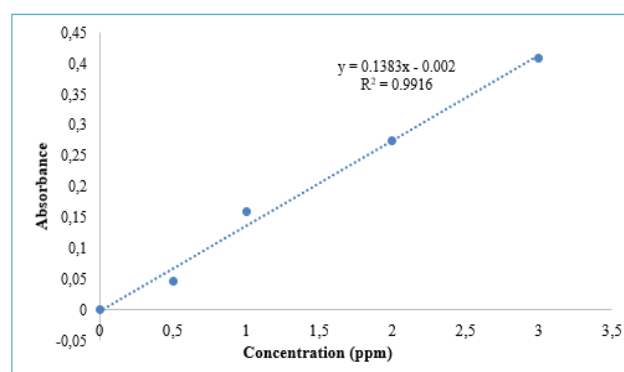


Figure 4 The graph of absorbance against concentration

From that, the graph of absorbance against concentration are plotted in Figure 4 to convert absorbance value into concentration value and gained the equation (1). Use equation (1) to find the value of X which is equilibrium concentration of silver nanoparticles (Table 2).

Table 2 The value of X for each of the concentration

Concentration (ppm)	Y	C	m	X
3.0	0.924	0.002	0.1383	6.6956
	0.409	0.002	0.1383	2.9718
2.0	0.634	0.002	0.1383	4.5987
	0.274	0.002	0.1383	1.9933
1.0	0.286	0.002	0.1383	2.0848
	0.159	0.002	0.1383	1.1641
0.5	0.161	0.002	0.1383	1.1762
	0.047	0.002	0.1383	0.3543

Then, the percentage removal of silver nanoparticles for each of the concentration are obtained using equation (2). The result of the removal rate for each of the concentration is shown as in Table 3.

Table 3 The removal rate for each of the concentration

Concentration (ppm)	C ₀	C _x	$\frac{C_0 - C_x}{C_x}$	Percentage removal (%)
3.0	6.6956	2.9718	0.5562	55.6156
2.0	4.5987	1.9933	0.5666	56.6562
1.0	2.0848	1.1641	0.4416	44.1618
0.5	1.1762	0.3543	0.6988	69.8770

The results showed that *Pistia stratiotes* have higher percentage removal at lowest concentration. Study showed that, the percentage removal of AgNPs decreased as the concentration increased. Concentration of 0.5 ppm of AgNPs, the removal was 69.87%. then, the percentage removal was decreased from 44.16%, 56.65% and 55.62% as concentration increased 1.0 ppm, 2.0 ppm, and 3.0 ppm, respectively. However, at concentration 1.0 ppm, might be had an error since the result was not follow the trend, which the removal efficiency decreased by increasing of the pollutant concentration (Naghipour et al., 2018).

4 Conclusion

In general, findings from this work confirmed that the *Muntingia calabura* sp. leaf extract has the potential as the biological alternative for AgNPs production. The synthesis of AgNPs using *Muntingia calabura* sp. leaves as plant extract is identified by colour changed from light brown to dark brown. Study showed that *Pistia stratiotes* had higher potential removal at lower concentration of AgNPs with period time of 24 hours. Thus, phytoremediation of AgNPs by *Pistia stratiotes* can be considered to apply and implement in water environment for pollutant removal.

Declaration of competing interest

The authors declare no known competing interests that could have influenced the work reported in this paper.

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