Shape, size and dispersion of plant-driven silver nanoparticles for removal of methylene blue dyes

N Isa¹², W Z Wan Kamis¹, V Inderan², N I Husin², F N Ahmad³, N H Bashrom⁴ and Z Lockman⁵

¹Faculty of Chemical Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, 13500 Permatang Pauh, Pulau Pinang, Malaysia
²Department of Applied Sciences, Universiti Teknologi MARA, Cawangan Pulau Pinang, 13500 Permatang Pauh, Pulau Pinang, Malaysia
³Faculty of Mechanical Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang 13500 Permatang Pauh, Pulau Pinang, Malaysia
⁴School of Materials Engineering, Kompleks Pusat Pengajian Jejawi 2, Universiti Malaysia Perlis (UNIMAP), Taman Muhibbah, 02600, Arau, Perlis
⁵School of Materials and Mineral Resources Engineering, University Sains Malaysia Engineering Campus, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia

*norain012@uitm.edu.my

Abstract. Silver nanoparticles (AgNPs) were synthesized by green biological technique utilising kyllinga brevifolia extract (KBE) as reducing agents. The KBE was also found to be a good capping as well as stabilizing agent. The size, shape and dispersion of AgNPs were evaluated and compared with the results from the literature survey. The TEM image showed that KBE-driven AgNPs have quasi-spherical shape are highly dispersed with an average particle size ~17.64 nm. The catalytic activity of KBE-driven AgNPs on reduction of methylene blue (MB) using sodium borohydride (SB) was analysed using UV-vis spectroscopy. The MB removal was achieved 100% at pH 8-10. The efficient removal is proposed to be due to the process of reduction via electron relay effect.

1. Introduction

AgNPs have been exploited in a wide range of potential applications in environmental remediation, renewable energy, electronics, computers, biomedical devices and medicine [1]. Among all these applications, the use of AgNPs as nanocatalyst in the field of environment remediation is the most noteworthy. AgNPs can degrade harmful contaminants including methylene blue (MB) [2, 3], methyl orange [4], 4-nitrophenol [5], malachite green [6] and methyl red [7]. Currently, various techniques and methods have been reported for the synthesis AgNPs, including chemical techniques, physical techniques and photochemical reduction method [8]. However, these methods have many drawbacks such as costly, high energy consumption, scalability, toxic to environment, time consuming, uncontrollable particle sizes and size distribution [3].
Thus, researchers have the urge to switch to environmental-friendly methods of AgNPs synthesis without implementation of toxic chemicals. Various plant extract have been reported to produce AgNPs with diameters of < 10 nm from *Eichhonia crassipes* [9], 10 – 30 nm from *Albizia saman* [10], 30 – 60 nm from *Spirulina microalgae* [11], and > 60 nm from *Mussaenda erythrophylla* [12]. But there are still a lot of issues that need to be addressed in this field because of the diversity and the high potential of plants in producing nanoparticles with different shapes.

In this study, plant-driven AgNPs utilising *Kyllinga brevifolia* extract (KBE) as reducing agent has been implemented. The size, shape and dispersion of AgNPs were evaluated. *K. brevifolia* (figure 1) is weedy sedge that is becoming a problem in turf and ornamental planting in subtropical and warm temperate zone including Malaysia. For that reason, KBE was selected as source of biomolecule to produce KBE-driven AgNPs. The catalytic activity of KBE-driven AgNPs on the removal of methylene blue (MB) dyes was evaluated.

![Figure 1. Kyllinga brevifolia plant.](image)

2. Methodology

*K. brevifolia* plant was washed and shade dried for 5 days at room temperature. Dried *K. brevifolia* (5 g) was crushed into fine powder and soaked in 100 mL deionized water at 70 °C for 1 hr. This solution was considered as 100% KBE. AgNPs were prepared by adding 1 ml 100% KBE to 9 ml 2 mM silver nitrate solution at room temperature (20 ± 2 °C) for 90 mins reaction time. Average particle size, shape and size distribution were determined by Phillips CM12 TEM with Docu version 3.2 image analysis. For catalytic study, the reduction of 30-100 ppm of MB using 1 mL of 0.1 M of NaBH₄ in presence of 100 µL of AgNPs was carried out in 4.0 mL capacity quartz. A control (uncatalyzed) experiment was done without addition of AgNPs. The progress of the reaction was monitored by using Lambda 35 Perkin Elmer UV-vis spectrophotometer.

3. Results and discussion

3.1 Shape of AgNPs

Shape of AgNPs is one of the important information which crucially influences physical and chemical properties of AgNPs as catalyst in removal of pollutants. TEM is a powerful tool for characterization of shape and size of AgNPs. Even with low magnification, TEM can distinguish the different in contrast derived from the atomic weight and the lattice direction. Figure 2 shows the TEM images for various shape of silver synthesized from different method: (a) oval and spherical shape, (b) spherical shape, (c) mixture shape, (d) Ag bars, (e) Ag rods and (f) Ag pyramid. Method of preparation is very important to synthesis the different shape of AgNPs.

Pie chart from figure 3(a) revealed that from the literature survey extracted from table 1 with additional data from (2018-2019), the shape of AgNPs from green biological method using plant extract as reducing agent mostly is spherical shape. The shape of KBE-driven AgNPs synthesized from green biological method are quasi-spherical shape as shown in figure 3(b). Capping molecules in plant extract play an important role in controlling the shape of AgNPs.
3.2 Size of AgNPs
The catalytic performance of AgNPs is found to be size dependent. Pie chart from figure 4(a) and table 1 shows that the most reported diameter range of AgNPs is 11-30 nm. Smaller size AgNPs (< 10 nm) are more cytotoxic. When released into wastewater, they can be absorbed by aquatic life and can enter the cell and localize into the nucleus easily if they are transferred to human cell. Larger particles (> 100 nm) on the other hand has lesser toxicity [26]. So, fine-tuned of size of AgNPs is very important in enhancing the properties of AgNPs as catalyst for water treatment. The amount of reducing agent was reported to have an effect on the size of AgNPs [27]. Figure 4(b) shows the AgNPs prepared using KBE have the average particle size ~ 17.64 nm as shown in histogram (c). KBE have high concentration of carbohydrate, protein and plant sterol (stigmasterol and campesterol) that might be responsible as reducing agent in reducing Ag+ to Ag° [3, 28, 29].
Table 1. Biological synthesis of AgNPs using plant extract and their characteristics.

| Plants                          | Size and shape | Shape      | Ref. |
|--------------------------------|----------------|------------|------|
| Colocasia esculenta (leaf)     | 17.2 nm        | Spherical  | [19] |
| Cassia auriculata (flower)     | 10 – 35 nm     | Spherical  | [20] |
| Crocus sativus (flower)        | 15 nm          | Spherical  | [21] |
| Achillea millefolium L         | Less than 20 nm| Spherical  | [22] |
| Soymida febrifuga (stem bark)  | 20 – 30 nm     | Spherical  | [23] |
| Sterculia acuminata (fruit)    | 9.4 nm         | Spherical  | [24] |
| Abutilon indicum (leaf)        | 5 – 25 nm      | Spherical  | [25] |

3.3 Dispersion of AgNPs

The particle size distribution is contributing by particle size, shape of AgNPs reducing agent and capping agent. It has been reported that the larger TEM particles derive mainly by agglomeration [27]. The reducing power of reducing agents can control the dispersion of AgNPs. An excess of strong reducing agent is desired to produce small sized of AgNPs, which facilitates instant nuclei generation, resulting in the formation of monodispersed and uniform sized silver colloids [30].

Weaker reducing agent on the other hand resulted in the formation of relatively larger AgNPs with a wider size distribution. Capping agent provides colloidal stability in AgNPs through electrostatic and electrostatic repulsion, inhibiting the agglomeration. Figure 5(a) shows an example of AgNPs agglomeration after synthesis process by chemical reduction technique. The agglomeration was reduced when addition of as stabilizing agent as shown in figure 5(b).

Figure 5(c) shown that 52.38% of AgNPs produced from plant-driven AgNPs have highly dispersion. For this study, as shown in figure 3(b) and figure 4(b) in earlier section revealed that our AgNPs synthesized from the KBE as reducing agent have highly dispersions with wide size distribution. The particle size of AgNPs as obtained from TEM image is in the range of 5 - 45 nm with average particles size of ~17.64 nm.
3.4 Catalytic study of AgNPs on removal of MB dyes.

In view of the results obtained in figure 6, the removal efficiency (%RE) graph at different initial MB concentration has a sigmoid shape. At initial stage, the reduction of MB by NaBH₄ and AgNPs as catalyst is preceded by a time lag, called the induction time (tᵢ). The induction time, (tᵢ) is longer for MB with higher concentration as indicated in the figure 6(a). This trend was also in general agreement with other researchers [32, 33]. The cause of the delay may have originated to several factors as reported from previous research; diffusion of MB to AgNPs, removal of surface oxide layer on AgNPs, diffusion of NaBH₄ to AgNPs, decomposition of NaBH₄ on the AgNPs, reconstruction of AgNPs or scavenging of the dissolve oxygen [29].

![Figure 5](image)

**Figure 5.** (a) Agglomeration of AgNPs (b) AgNPs are highly dispersed after adding cationic surfactant (TEM images of (a) and (b) retrieved from [33]) (c) pie chart of dispersion of AgNPs.

![Figure 6](image)

**Figure 6.** (a) Removal efficiency of MB at different initial concentration (b) Removal efficiency at 6 mins contact time by AgNPs and control samples (without AgNPs).

After induction time, the % RE of AgNPs increased significantly and then plateau due to equilibrium at certain reaction time. As can be seen, AgNPs had an excellent catalytic activity with %RE 100 % MB with the equilibrium time 1.5 to 5.0 mins for MB30 to MB100 samples respectively. The excellent
catalytic activity in degradation of MB by AgNPs and NaBH₄ via electron relay effect are due to several reasons. Size effect of AgNPs do play an important role in degradation of dyes. The smaller size of AgNPs display a greater catalytic activity than a larger AgNPs [3]. In general, AgNPs have short-lives in aqueous solution as they rapidly agglomerate. It has been shown that plant constituents were attached on the surface of AgNPs prevent AgNPs aggregation, while the AgNPs surface can participate in MB removal.

4. Conclusion
Quasi-spherical shape and highly dispersed of KBE-driven AgNPs were successfully synthesized with the average crystallite size ~17.64 nm utilising KBE as reducing agent. AgNPs have shown excellent capability for reduction of 30 -100 ppm MB less than 5 mins reaction time with 100 % removal. The reduction mechanism of MB by NaBH₄ and AgNPs occurs via electron relay effect. The work suggests that ‘greener’ AgNPs can be produced from weeds that are often treated as waste.

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References
[1] Beyene H D Werkneh A A Bezabh H K and Ambaye T G 2017 Synthesis paradigm and applications of silver nanoparticles (AgNPs), a review Sustainable Materials and Technologies 13, p 18-23.
[2] Isa N Kian T W Kawamura G Matsuda A and Lockman Z 2018 Synthesis of TiO₂ nanotubes decorated with Ag nanoparticles (TNTs/AgNPs) for visible light degradation of methylene blue in Journal of Physics: Conference Series 1082, 1 p. 012105: IOP Publishing.
[3] Isa N and Lockman Z 2019 Methylene blue dye removal on silver nanoparticles reduced by kyllinga brevifolia Environmental Science and Pollution Research p. 1-14
[4] Vanaamudan A Soni H and Sudhakar P P 2016 Palm shell extract capped silver nanoparticles — as efficient catalysts for degradation of dyes and as SERS substrates Journal of Molecular Liquids 215, p. 787-794.
[5] Ismail M Khan M I Khan S B Akhtar K Khan M A and Asiri A M 2018 Catalytic reduction of picric acid, nitrophenols and organic azo dyes via green synthesized plant supported Ag nanoparticles Journal of Molecular Liquids 268, p. 87-101.
[6] Vandarkuzhalhi S A A Karthikeyan S Viswananathan B and Pachamuthu M P 2018 Arachis hypogaea derived activated carbon/pt catalyst: reduction of organic dyes Surfaces and Interfaces 13, p. 101-111.
[7] Bonigala B Kasukurthi B Konduri V V Mangamuri U K Gorrepati R and Poda S 2018 Green synthesis of silver and gold nanoparticles using stemona tuberosa lour and screening for their catalytic activity in the degradation of toxic chemicals Environmental Science and Pollution Research p. 1-9.
[8] Tran Q H and Le A T 2013 Silver nanoparticles: synthesis, properties, toxicology, applications and perspectives Advances in Natural Sciences: Nanoscience and Nanotechnology 4, 3 p. 033001.
[9] Oluwafemi O S Mochochoko T Leo A J Mohan S Jumbam D N and Songca S P 2016 Microwave irradiation synthesis of silver nanoparticles using cellulose from eichhornia crassipes plant shoot Materials Letters 185, p. 576-579.
[10] Daphedar A and Taranath T C 2017 Biosynthesis of silver nanoparticles by leaf extract of albizia saman (jacq.) merr. and their cytotoxic effect on mitotic chromosomes of drimia indica (roxb.) jessop Environmental Science and Pollution Research 24, 33 p. 25861-25869.
[11] Muthusamy G Thangasamy S Raja M Chinnappan S and Kandasamy S 2017 Biosynthesis of silver nanoparticles from spirulina microalgae and its antibacterial activity Environmental Science and Pollution Research 24, 23 p. 19459-19464.

[12] Varadavenkatesan T Selvaraj R and Vinayagam R 2016 Phyto-synthesis of silver nanoparticles from mussaenda erythrophylla leaf extract and their application in catalytic degradation of methyl orange dye Journal of Molecular Liquids 221, p. 1063-1070.

[13] Soliman H Elsayed A and Dyaa A 2018 Antimicrobial activity of silver nanoparticles biosynthesised by rhodotorula sp. strain at72 Egyptian Journal of Basic and Applied Sciences 5, 3 p. 228-233.

[14] Ahn E Y Jin H and Park Y 2019 Assessing the antioxidant, cytotoxic, apoptotic and wound healing properties of silver nanostructures green-synthesized by plant extracts Materials Science and Engineering: C, 03/26.

[15] Darmanin T et al. 2012 Microwave-assisted synthesis of silver nanoprisms/nanoplates using a “modified polyol process” Colloids and Surfaces A: Physicochemical and Engineering Aspects 395, p. 145-151.

[16] Wiley B J et al. 2007 Synthesis and optical properties of silver nanobars and nanorice," Nano letters 7, 4 p. 1032-1036.

[17] Murphy C J and Jana N R 2002 Controlling the aspect ratio of inorganic nanorods and nanowires Advanced Materials 14, 1 p. 80-82.

[18] BWiley B J Im S H Li Z Y McLellan J Siekkinen A and Xia Y 2006 Maneuvering the surface plasmon resonance of silver nanostructures through shape-controlled synthesis J. Phys. Chem. B 110, 32 p. 15666-15675.

[19] Barua S Thakur S Aidew L Buragohain A K Chattopadhyay P and Karak N 2014 One step preparation of a biocompatible, antimicrobial reduced graphene oxide–silver nanohybrid as a topical antimicrobial agent RSC Advances 4, 19 p. 9777-9783.

[20] Muthu K and Priya S 2017 Green synthesis, characterization and catalytic activity of silver nanoparticles using cassia auriculata flower extract separated fraction Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 179, p. 66-72.

[21] Bagherzade G Tavakoli M M and Namaei M H 2017 Green synthesis of silver nanoparticles using aqueous extract of saffron (crocus sativus L.) wastages and its antibacterial activity against six bacteria Asian Pacific Journal of Tropical Biomedicine 7, 3 p. 227-233.

[22] Khodadadi B Bordbar M and Nasrollahzadeh M 2017 Achillea millefolium L, extract mediated green synthesis of waste peach kernel shell supported silver nanoparticles: Application of the nanoparticles for catalytic reduction of a variety of dyes in water Journal of colloid and interface science 493, p. 85-93.

[23] Sowmyya T and Vijaya L G 2017 Spectroscopic investigation on catalytic and bactericidal properties of biogenic silver nanoparticles synthesized using soymida febrifuga aqueous stem bark extract Journal of Environmental Chemical Engineering 6, 3 p. 3590-3601.

[24] Bogireddy N K R Kumar H A K and Mandal B K 2016 Biofabricated silver nanoparticles as green catalyst in the degradation of different textile dyes Journal of Environmental Chemical Engineering 4, 1 p. 56-64.

[25] Mata R Nakkala J R and Sadras S R 2015 Biogenic silver nanoparticles from abutilon indicum: their antioxidant, antibacterial and cytotoxic effects in vitro Colloids and Surfaces B: Biointerfaces 128, p. 276-286.

[26] Maddinedi S B Mandal B K and Anna K K 2017 Tyrosine assisted size controlled synthesis of silver nanoparticles and their catalytic, in-vitro cytotoxicity evaluation Environmental Toxicology and Pharmacology 51, p. 23-29.

[27] Rossi M Della Pina C Falletta E and Matarrese R 2008 Chapter 12 - gold nanoparticles: from preparation to catalytic evaluation in Metal Nanoclusters in Catalysis and Materials Science p. 253-262.
[28] Isa N Bakhari N A Sarjo S H Aziz A and Lockman Z 2017 Kyllinga brevifolia mediated greener silver nanoparticles in AIP Conference Proceedings 1901, 1 p. 020012: AIP Publishing.

[29] Isa Sarjo S H Aziz A and Lockman Z 2017 Synthesis colloidal kyllinga brevifolia-mediated silver nanoparticles at different temperature for methylene blue removal in AIP Conference Proceedings 1877, 1 p. 070001: AIP Publishing.

[30] Agnihotri S Mukherji S and Mukherji S 2014 Size-controlled silver nanoparticles synthesized over the range 5–100 nm using the same protocol and their antibacterial efficacy Rsc Advances 4, 8 p. 3974-3983.

[31] Sharma A and Tapadia K 2016 Silver nanoparticles-based nano-drop spectrophotometric determination of cationic surfactants coupled with hydrophobic interaction; an application to pharmaceuticals and environmental Oriental Journal of Chemistry 32, 5 p. 2641.

[32] Das R S Singh B Mandal A Banerjee R and Mukhopadhyay S 2015 Kinetics of palladium nanoparticles catalyzed reduction of methylene green by hydrazine: role of induction period in determining mechanistic pathway Inorganica Chimica Acta 428, p. 185-192.

[33] Choi S Jeong Y and Yu J 2016 Spontaneous hydrolysis of borohydride required before its catalytic activation by metal nanoparticles Catalysis Communications 84, p. 80-84.