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Degradation of methylene blue using silver nanoparticles synthesized from *imperata cylindrica* aqueous extract

A A Fairuzi[1], N N Bonnia[1*], R M Akhir[1], M A Abrani[2], H M Akil[3]
[1]School of Physics & Materials Studies, Faculty of Applied Sciences, Universiti Teknologi MARA, 40460 Shah Alam, Selangor, Malaysia
[2]School of Chemistry, Faculty of Applied Sciences, Universiti Teknologi MARA, 40460 Shah Alam, Selangor, Malaysia
[3]School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

*E-mail: noornajmi@salam.uitm.edu.my

Abstract. The present study reports about the catalytic degradation of methylene blue (MB) by sodium borohydride ($NaBH_4$) in presence of silver nanoparticles (Ag NPs) as catalyst. Ag NPs was produced from green synthesis method using aqueous *Imperata cylindrica* extract. Formation of Ag NPs from the synthesis was confirmed by using UV-visible spectroscopy with the appearance of surface plasmon (SPR) bands around 427 nm. The agglomeration in microstructure of biosynthesized Ag NPs was revealed by field scanning electron microscope (FESEM). The synthesized of Ag NPs showed five diffraction peaks at 2θ values of 38.62°, 44.51°, 64.84°, 77.68° and 81.96° which corresponds to the (111), (200), (220), (311) and (222) planes of face-centred cubic. Energy dispersive X-ray analysis (EDX) revealed signals at the energy of 3 keV which indicates the presence of elemental silver that contributed to 68.44 weight % of the analysed sample. Upon addition of biosynthesized silver nanoparticles, the degradation of MB increases up to 92.06% within 14 min.

1. Introduction

Nanotechnology is the science of producing and utilizing nano-sized particles [1]. Ag NPs is useful various fields such as catalysis, optics, biomedical, pharmaceutical and sensor technology [2]. Although there are many methods that can be used to synthesize Ag NPs, most of them utilized toxic chemicals and may include the use of enormous energy. This scenario is not economic and cause serious pollution to environment. Synthesis of nanomaterials using biological entities is gaining attention as; biological methods are less expensive, nontoxic and environmentally acceptable "green chemistry" procedures [3]. The use of plant and plant extract in nanoparticles synthesis is advantageous compared to microbial based system because it eliminates the intricate process of maintaining cell cultures. In this study, Ag NPs nanoparticles were synthesized from aqueous extract of *I. Cylindrica* (Figure 1). This perennial grass lived well in Southeast Asia, the Philippines, China, and Japan [4]. *Imperata cylindrica* (L.) Beauv. or cogon grass is a plant in division of *Magnoliophytai*; class *Liliopsida*; order *Cyperales*; family *Poaceace/Gramieane* and genus *Imperata Cirillo*. Study of this plant by Krishnaiah et al. (2009) proved the traditional medicinal value *I. cylindrica* was due to presence of several bioactive constituents such as alkaloids, flavonoid, tannins and cardiac glycoside

[5]. These phytoconstituents is vital in biosynthesis of various metallic nanoparticles as reducing and capping agent.

Figure 1. Photograph of *I. cylindrica* plant.

In this study, the chemical and physical properties of biosynthesized Ag NPs were characterised. Silver nanoparticles as describe in previous study is a good catalyst. As an extension to previous study, catalytic ability of the Ag NPs synthesized from *I. cylindrica* extract was investigated. The investigation was carried out studying degradation of aqueous MB, an organic dye as model.

2. Experimental section.

2.1. Biosynthesis of Ag NPs

The leaves of *I. cylindrica* were collected from specialized area inside the Universiti Teknologi MARA, Shah Alam, Selangor, Malaysia campus. The collected leaves were cleaned thoroughly by distilled water and then oven dried at 60ºC for 48 hrs. The dried leaves were finely ground to powder using conventional food processor. Aqueous leaves extract was prepared by dissolving 5 g of the powder in 200 ml distilled water. The mixture was stirred and heated at 60 ^{0}C for 30 min and the leaves residue was filtered out from the extract. Ag NPs was synthesized by adding10 ml of the aqueous extract into 90 ml of 5 mM aqueous $AgNO_3$. The mixture was heated using water bath at 60 ^{0}C for 10 min. Appearance of brown colour marks the formation of Ag NPs.

2.2. Characterization of biosynthesized Ag NPs

The formation of Ag NPs was studied by measuring the absorption spectra of the mixture at a regular time interval using UV-visible double beam spectrophotometer (Perkin Elmer, Lambda 35 UV/Vis System) operated in 700 -300 nm range at a resolution 1 nm. X-ray diffractograms of the samples were recorded by X-ray diffractometer (Rikagu Ultima IV, Japan). FTIR spectrum biosynthesized Ag NPs was recorded in diffuse reflectance mode operated at a resolution 4cm^{-1} at wavelength of 4000 - 400 cm^{-1} (Thermo Scientific, Nicolet 6700). Morphology of the Ag NPs was obtained by field emission scanning microscope (FESEM) SUPRA-40 VP attached with energy dispersive X-ray (EDX) unit.

2.3. Dye degradation study

The experiment was conducted by adding 2 ml of freshly prepared NaBH4 solution (0.2 M) to 50 ml (10 mg l^{-1}) aqueous solution of MB at room temperature (30 ±1ºC). To this 1 ml of silver nanocatalyst were added and the reactants were mixed quickly. At a regular interval of time, 0.5 ml of the reaction mixture was withdrawn and diluted in 2.5 ml of distilled water. The absorbance of the mixture was monitored using UV–visible spectrophotometer at regular intervals of time. The degradation was also monitored without silver nanoparticles.

3. Results and discussion

3.1. UV-visible spectroscopic study

UV-visible spectroscopy characterization method was then used to monitor formation of Ag NPs and its properties. The absorption of light by the nanoparticles at different wavelengths provides an indication of particle size, while the breadth of the peaks signifies the particle size distribution [6]. The characteristic SPR band of Ag NPs is in the range of 400-450 nm [7]. Biosynthesized Ag NPs were evaluated at periodically for 60 minutes. Figure 2 shows the intensity UV- visible spectra of Ag NPs increase as the reaction time increase. This indicates the increased in concentration of the Ag NPs as time of reaction increased. The UV-vis spectroscopy showed that the nanoparticles started to form

after 15 min the reaction commence, as depicted by the appearance of surface plasmon bands around 427 nm. As the reaction continued, absorbance peaks became narrower and were shifted to shorter wavelength. These condition signifying that the particles became smaller and are getting monodispersed [8].

3.2. X-ray diffraction (XRD) analysis

The powder XRD pattern was recorded for the identification of phases exhibited by the biosynthesized Ag NPs. The synthesized of Ag NPs showed five diffraction peaks (Figure 3) at 2θ values of 38.62º, 44.51º, 64.84º, 77.68º and 81.96º which corresponds to the (111), (200), (220), (311) and (222) planes of face-centred cubic. The peak corresponding to the (111) plane is more intense than that of other planes suggesting the predominant growth of Ag NPs along (111) direction.

3.3. FESEM and EDX analysis

The silver colloid was oven dried at 90ºC for 72 hrs to remove water from the synthesized nanoparticles. The dried particles were brought to FESEM analysis. Micrograph (figure 5) of Ag NPs revealed agglomeration of the particles. The average particle size was 31 nm. EDX analysis displayed signal at the energy of 3 keV indicates that the silver has been correctly identified [9]. Elemental silver contributed 68.44 weight % of the analysed sample. A representative EDX spectrum is presented in figure 4.

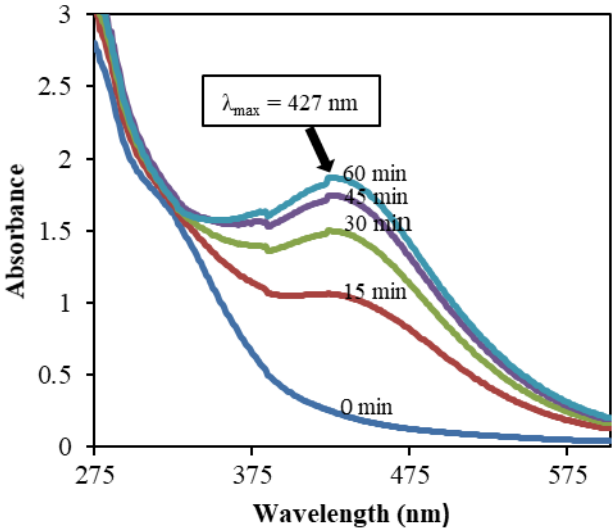

Figure 2. UV- visible spectra of Ag NPs

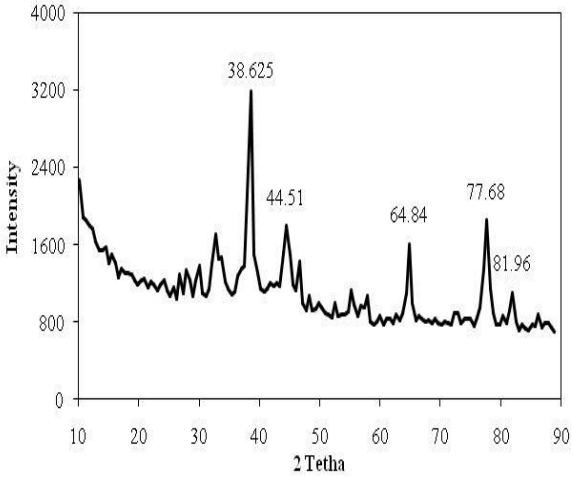

Figure 3. XRD pattern of Ag NPs

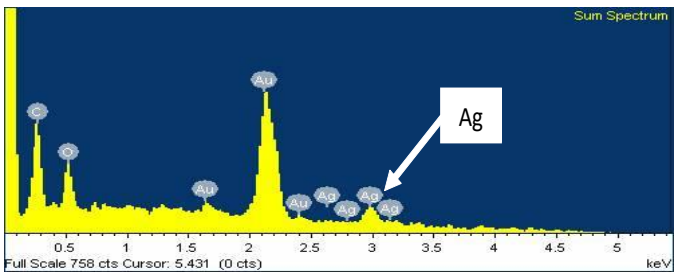

Figure 4. EDX spectrum of AgNPs.

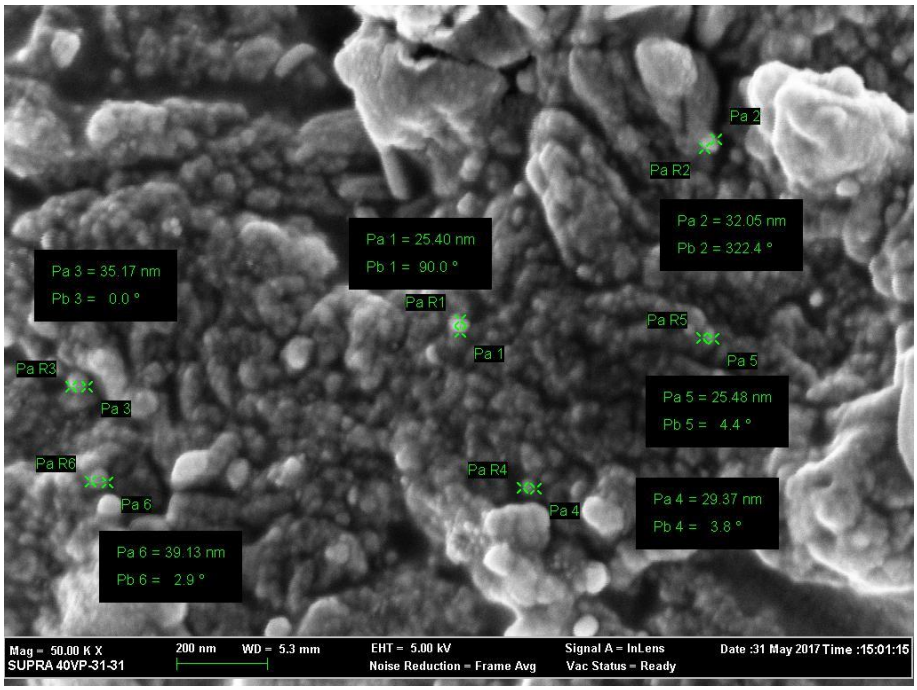

Figure 5. FESEM micrograph of biosynthesized Ag NPs.

3.4. Fourier transform infrared spectroscopy analysis

FTIR analysis on the biosynthesized Ag NPs was carried out to identify the functional groups responsible for the reduction of metal precursors ($AgNO_3$). The spectral (figure 6) analysis of the extract shows IR bands at 3253.70, 2922.30, 1594.00, 1397.53, and 1260.87 cm^{-1}. The bands corresponds to O-H vibration, C-H vibration, C=C groups or from aromatic rings, germinal methyls [7] and Amide III [8].

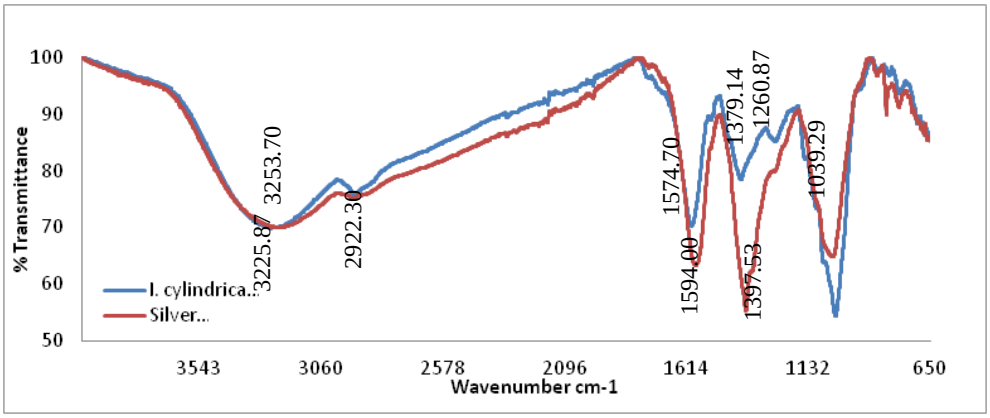

Figure 6. FTIR spectra of *I. cylindrica* extract and biosynthesized AgNPs

3.5. Catalytic activity of Ag NPs

A potential application of biosynthesized Ag NPs was as catalyst in the reduction of aqueous MB to Leuco MB in the presence of $NaBH_4$. Ag NPs act as an electron relay and initiate shifting of electron from BH_4^- ion (donor B_2H_4/BH_4^-) to acceptor (acceptor LMB/MB) and thus causing reduction of the dye. BH_4^- ion simultaneously adsorbed on the surface of NPs and thus electron transfer occurs from BH_4^- ion to the dye through NPs[12] .In aqueous medium, MB shows maximum absorption at 664 nm

and a shoulder peak at 615 nm. The reaction was monitored by UV-visible spectroscopy in the wavelength range between 300 and 900 nm at room temperature. The decrease of absorbance at maximum wavelength (664 nm) with time was followed spectrophotochemically (figure 7a and 7b). The intense blue colour of the MB solution faded and become colourless during degradation process. Percentage of degradation (table 1) was calculated as quantitative representation of the degraded dye.

$$Dye\ degradation\ (\%) = [(C_0 - C)/C_0] \times 100 \quad (1)$$

Where C_0 is the initial concentration of methylene blue solution and C is the concentration of the dye solution after t minutes of reaction. In the absence of biosynthesized nanocatalyst, the reduction process is negligible (dye degradation 1.02-2.61 %). Addition of biosynthesized silver nanoparticles improved the reduction process (dye degradation up to 92.06% within 14 min). Analysis of the kinetic data of degradation reactions reveals pseudo-first order reaction kinetics. The linear plot (figure 8) of ln $[C/C_o]$ versus time supports the kinetic theory, where the k value obtained was 0.137 min^{-1}.

Table 1. Degradation percentage of MB

Time (min)	% Degradation	
	Ag NPs	Control
2	15.39	1.02
4	25.00	2.61
6	34.74	2.55
8	46.84	1.80
10	56.39	2.59
12	86.69	2.53
14	92.06	1.90

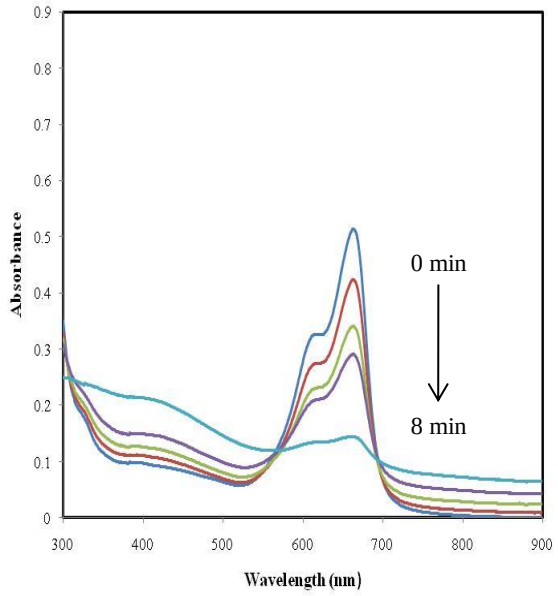

Figure 7a. Absorbance spectra of MB with nanocatalyst

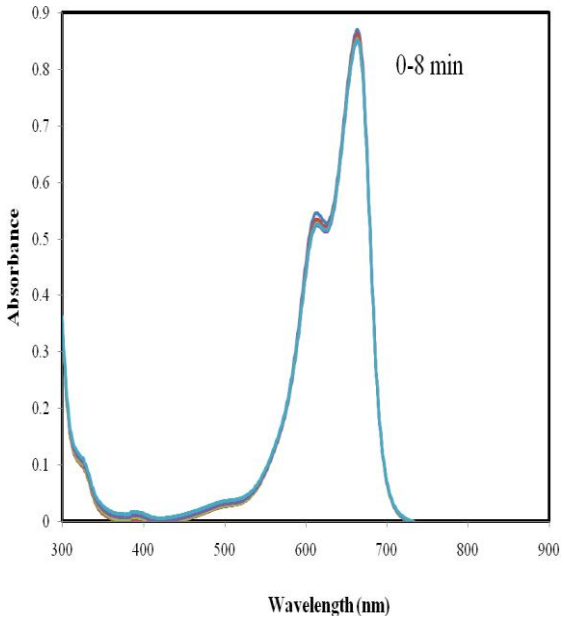

Figure 7b. Absorbance spectra of MB without nanocatalyst (control)

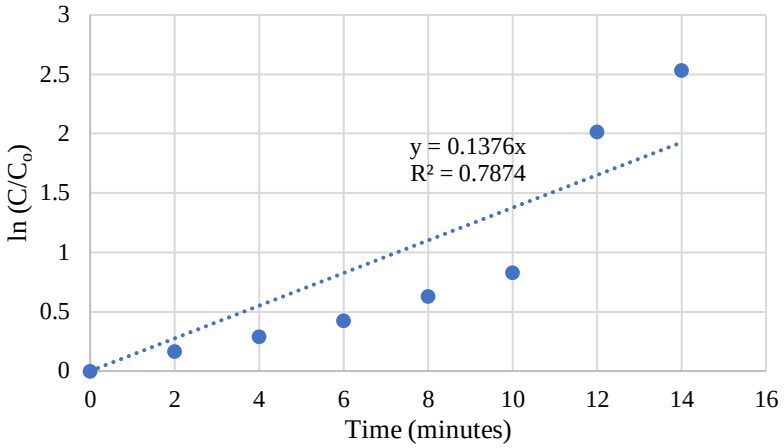

Figure 8. Kinetic studies of MB degradation catalysed by Ag NPs

4. Conclusion

The biosynthesized Ag NPs degrade (presence of $NaBH_4$) 92% MB within 14 min. Catalytic properties of Ag NPs synthesized from aqueous extract of *I. cylindrica* in degrading organic dye was demonstrated.

Acknowledgments

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