THE GREEN SYNTHESIS OF SILVER NANOPARTICLES FROM *Morinda citrifolia* ROOT EXTRACT AND ITS METHYLENE BLUE DEGRADATION

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Abstract

This study evaluates the effects of ethanol and hot water extracts of *Morinda citrifolia* (*M. citrifolia*) root on the green synthesis of silver nanoparticles (MCAgNPs) for the photocatalytic degradation of methylene blue (MB). The MCAgNPs formation was confirmed by the UV-Vis spectroscopy. The synthesised silver nanoparticles in solution have shown maximum absorptions at 419 nm for MCEN and 429 nm for MHWN spectrophotometrically. The FTIR result showed that effective functional molecules such as hydroxyl, carboxylic, phenol, and amine groups are responsible for the formation of the nanoparticles. The photocatalytic activity of the synthesised silver nanoparticles was investigated by MB degradation under the sunlight. The synthesised MCAgNPs from ethanol extract (MCEN) was the most effective as it degraded the dye 92.6% at irradiation time of 360 min. The synthesised silver nanoparticles from ethanol *M. Citrifolia* root extracts exhibit excellent photocatalytic activity against MB molecules and can be potentially applied in water treatment systems.

Keyword: Green synthesis, methylene blue, *Morinda citrifolia*, photocatalytic degradation, silver nanoparticles

Introduction

Issues on–water pollution related to industrialisation have caused serious problems to the living community. An array of organic and inorganic dyes has contributed to the contamination of water resources. Dyes are widely used in the food, paint, textile, cosmetics, and paper industries (Kumar et al., 2021). The negative effects on the water system are due to the dye structure and its origin. These dyes have different structural forms such as basic, disperse, azo, diazo, and metal-complex dyes. The presence of benzidine and naphthalene makes these dyes carcinogenic. These dyes are constantly altered into carcinogens, and they enter the biological systems such as animals and humans through microbial degradation (Zafar et al., 2022). Hence, there are needs to treat the effluent-containing dyes before discharging them into the water resources. Nanotechnology offers a very efficient and effective approach to enhance the treatment and remediation of wastewater (Palani et al., 2023).

A nanoparticle is a small particle in the range of 1 to 100 nm in size. Thus, it has a large surface area, less resistance to diffusion, high adsorption abilities and faster rates of equilibrium (Shrestha et al., 2020). Based on all these properties, it can be used to eliminate dyes from the wastewater. Silver nanoparticles (AgNPs) are one of the common metal

nanoparticles that can be used to remove dyes from wastewater (Sana et al., 2022). The synthesis of AgNPs can be achieved by applying several methods such as physical, chemical, and photochemical procedures. Each of these methods has its distinct advantages and disadvantages.

Among all approaches, the chemical procedure is identified as efficient, convenient, and easily manageable (Yaaqob et al., 2020). However, the presence of a few noxious chemical types during nanoparticle synthesis adsorbed on the surface may have adverse effects on its application. To address these limitations, environmentally sustainable techniques were employed and referred to as "green synthesis," which are proven to be economically efficient. Compared to other green synthesis methods, synthesising nanoparticles with plant extracts has several advantages since plants are environmentally benign and simple to manipulate (Dikshit et al., 2021). Biological microorganisms or plant extracts are examples of green synthesis methods that can be used as a simple alternative to chemical preparation. The advantages of this technology encompass reduced time, exceptionally stable nanoparticles, and extensive biological resources (Roy et al., 2019).

Morinda citrifolia (*M. citrifolia*) belongs to the Rubiaceae family. This plant is known to be used in traditional remedies such as hypertension, diarrhoea and atherosclerosis (Ali et al., 2016). *M. citrifolia* can be easily found in Southeast Asia as a small evergreen tree. The roots of *M. citrifolia* are rich in phenolic compounds such as protein, flavonoids, anthraquinones and terpenoids that are known to have antibacterial, antiviral and anticancer activities (Ali et al., 2016). The flavonoids and proteins that are present in this plant can act as a stabilising and reducing agent in the synthesis of silver nanoparticles. The polarity of solvents may influence the chemical structure of the compounds in the solute extracted. Therefore, the chosen type of solvent has a major impact on selectivity. We chose ethanol which is a moderately polar solvent that can extract variable compounds of lipids, phenolics, alkaloids and some proteins. Meanwhile, water is a highly polar solvent that can extract hydrophilic (water-soluble) compounds in the range of polysaccharides, sugars, amino acids, and certain vitamins (Lefebvre et al., 2021). This study aims to synthesise silver nanoparticles from the ethanol and water root of *M. citrifolia* extract to be used in methylene blue degradation.

Materials and Methods

Collection of plant material

The plant material, root of *M. citrifolia, was* gathered in the farm plantation in UiTM Jengka Campus, Pahang. The root of *M. citrifolia* was cleaned, air dried, grounded to powder form, stored and labelled neatly in an airtight plastic container until further use.

Preparation of *M. citrifolia* root extract

In the preparation of *M. citrifolia* root hot water extract (MHW), 20 g of dried sample was mixed with 300 mL of distilled water and heated at 100 °C for 15 minutes. For the preparation of *M. citrifolia* root ethanol extract (MCE), an amount of 20 g of dried powder was mixed with 300 mL of 90% ethanol at room temperature and stirred for 15 hours. Both solutions were filtered, and the extracts were stored in the refrigerator at 4 °C.

Synthesis of *M. citrifolia* Silver Nanoparticles

90 ml of 1 mM silver nitrate ($AgNO_3$) was added into two separated Erlenmeyer flasks which

initially contained 5 ml of *M. citrifolia* hot water extract (MHW) and 1 ml of *M. citrifolia* ethanol extract (MCE) respectively. Then, the mixtures were heated with continuous stirring for 30 minutes until the colour changed from light yellow to brown (Asimuddin et al., 2020). The synthesised MHW and MCE nanoparticles were labelled as MHWN and MCEN respectively. Upon completion, MHWN and MCEN were centrifuged for 15 minutes at 10000 rpm to discrete the sample, and the supernatant was further used in characterization and photodegradation analysis.

Characterization of MCAgNPs

UV-Vis Spectroscopy was conducted using SHIMADZU UV-1800 in the 200-700 nm range. FTIR analysis was investigated using Attenuated Transmittance Reflectance-Fourier Transform Infrared (ATR-FTIR) spectrometer (Perkin Elmer). The FTIR spectrum for MHW, MCE, MHWN and MCEN were recorded within the range of 4,000–400 cm^{-1}.

Photocatalytic Degradation of Methylene Blue (MB)

In two separated Erlenmeyer flasks, 10 mg of MHWN powder or 10 mg of MCEN powder was added into the 100 ml aqueous solution of MB (10 mg/L) and stirred continuously for 30 minutes. At a regular interval of time (15, 30, 45, 60, 90, 120, 180, 240 and 360 min), 2 mL of suspension was collected and filtered to evaluate the photocatalytic degradation of dye by using UV–visible spectrophotometer. According to the Beer–Lambert law, the concentration of MB is directly proportional to the absorption, so its degradation rate can be calculated using Equation (1)

$$Degradation\ (\%) = \frac{100 \times (A_o - A)}{A_o} \quad (1)$$

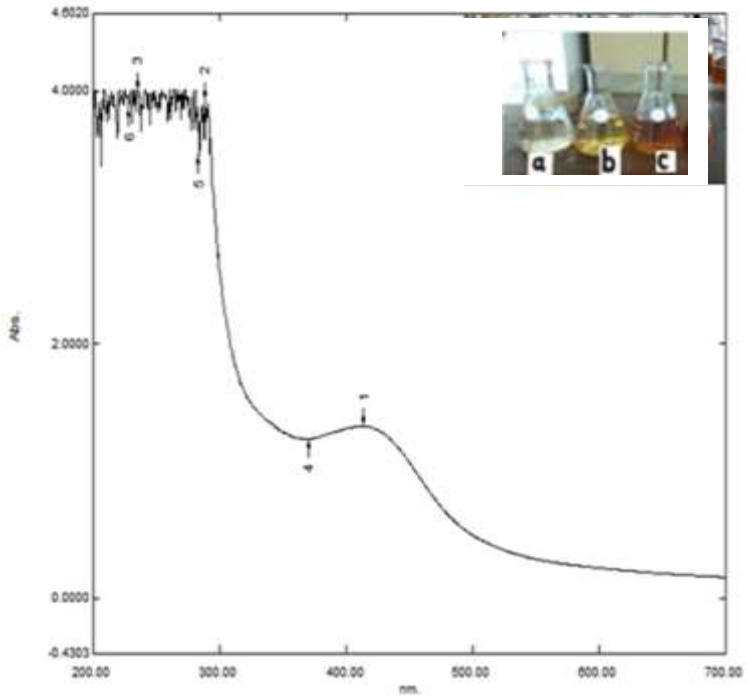
where A_o represents the initial concentration of the dye solution, and A represents the concentration of the dye solution after photocatalytic degradation.

Results and Discussion

Characterization of MCEN and MHWN

Figure 1 represents $AgNO_3$ solutions (Flask a), MC root extracts (Flask b) and synthesised MCEN/MHWN (Flask c). The production of the MCEN and MHWN occurred when the colourless solution of $AgNO_3$ (Flask a) changed to yellowish-brown colour. Colour changes are caused by the silver ions reduction due to the proteins and bioactive compounds present in each extract (Salih et al., 2022). The excitation of surface plasmon vibrations in the AgNPs initiates the colour formation (Al-kawaz & Al-Mashhedy, 2016). Similar findings by Sreelekha et al., (2021) and Patil et al., (2018) reported that the colour of the solutions was changed from colourless to yellow, brownish, and dark brown colour after the reduction of silver ions. The results of UV-Vis spectrometry show the presence of a surface plasmon resonance (SPR) absorption band with the maximum absorbance at 414 nm (**Figure 1a**) and 429 nm (**Figure 1b**), suggesting the formation of MCAgNPs. These results were consistent with the previous findings by other researchers (Morales-Lozoya et al., 2021, Paramesh et al., 2021, Suman et al., 2013). The different wavelength at the maximum absorbance for both extracts depends on the chemical composition used for the synthesis of MCAgNPs.

a)



b)

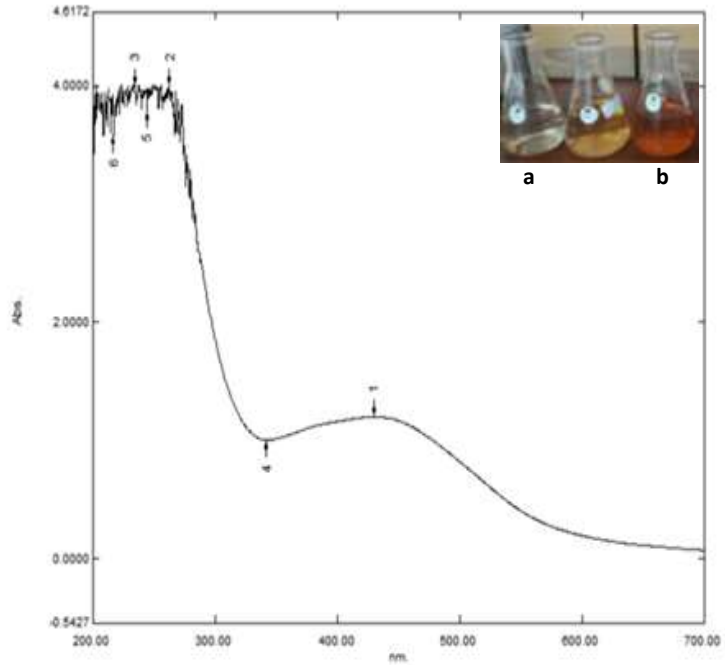


Figure 1 UV-vis absorption spectrum of (a) MCEN and (b) MHWN

The FTIR spectra of MCEN and MHWN are shown in **Figure 2**. The FTIR spectra of MCEN (**Figure 2a**) shows absorption bands at 3265 cm^{-1} and 1635 cm^{-1} when they were assigned with the hydrogen-bonded O-H stretch and C=C stretching, respectively. The FTIR of MCE (**Figure 2b**) shows intense bands at 3305 cm^{-1}, 2978 cm^{-1}, 2902 cm^{-1}, 1646 cm^{-1} and 1044 cm^{-1}, and they were slightly shifted to lower frequency and transformed to weak band and peak band disappearance. This observation may be due to the reduction process occurring during the production of MCEN. **Figure 3** shows strong absorption peaks of MHW (**Figure 3a**) at 3274 cm^{-1} and 1635 cm^{-1} were shifted to weak bands at 3235 cm^{-1} and 1634 cm^{-1}

(**Figure 3b**). New peaks appeared in the FTIR spectra of MHWN at 1394 cm^{-1} indicating the nitro groups, and 1187 cm^{-1} represents C-O stretch of carbonyl group (Fairuzi et al., 2018). The biomolecules presence in ethanol and hot water MC root extracts are responsible as the capping agent and stabilizer for MCAgNPs production.

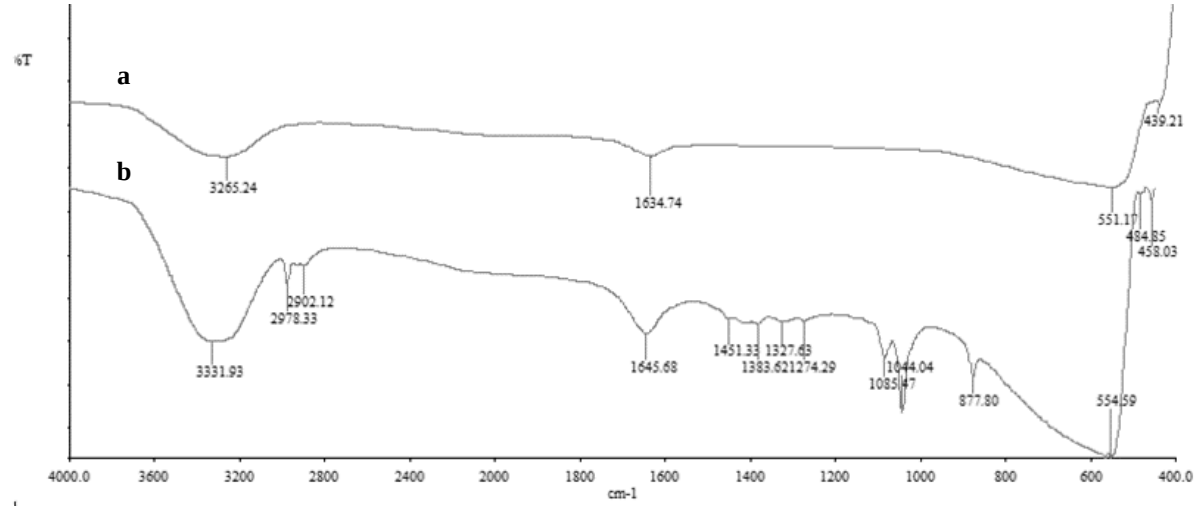


Figure 2 FTIR spectrum of (a) MCEN and (b) MCE

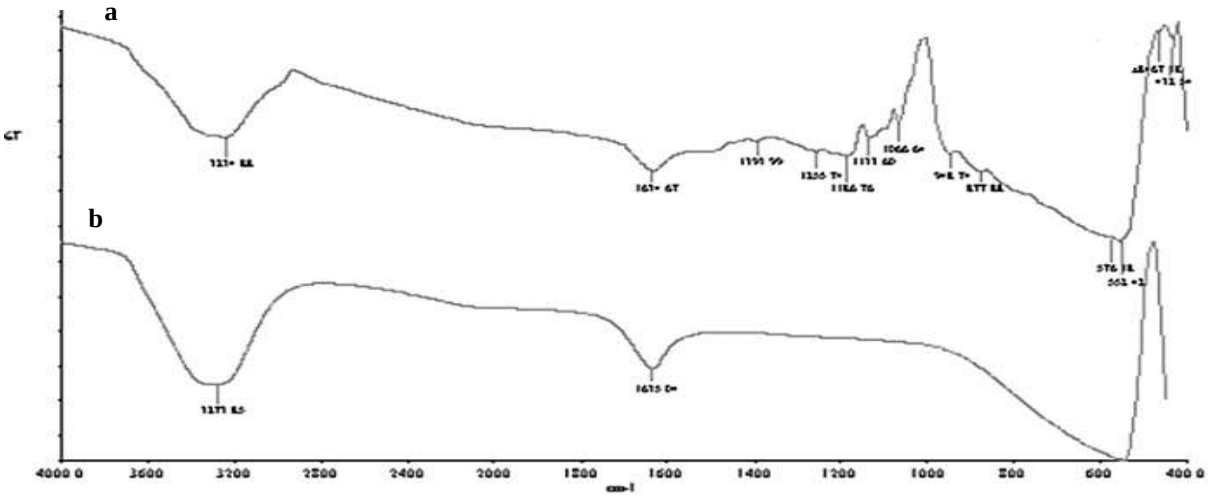


Figure 3 FTIR spectrum of (a) MHWN and (b) MHW

Catalytic Reduction of Methylene Blue by MCAgNPs

The catalytic performance of MCEN and MHWN were examined at their maximum absorption towards methylene blue (MB) as shown in **Figure 4**. Photocatalytic activity of both MCAgNPs towards the degradation of methylene blue was carried out at different times in the visible region. During the degradation of methylene blue, the absorption peak of methylene blue at 650 nm decreased gradually with the increase in exposure time (Aravind et al., 2021). The dark blue colour of MB in MCEN and MHWN changed to a light blue colour after 6 hours of sunlight exposure. **Figure 5** shows the degradation value of MCEN and MHWN in methylene blue solution at 10 mg/L, respectively. It was observed that with the time that the degradation was increased, both MCAgNPs were able to degrade methylene blue. The degradation of MCEN was slightly higher than MHWN at the initial time of reaction. The maximum decolourisation of MCEN and MHWN towards MB occurred at 360 min with 92.6% and 92.0%, respectively. The study by Jahnavi et al. (2014) found that more

numbers of secondary metabolite compounds have been extracted in ethanolic extract of *M. citrifolia's* fruits than its aqueous extract. The alkaloids and tannins that are not present in aqueous extract make it low in the concentration of -OH functional groups and resulting in less capability in silver ions reduction (Morales-Lozoya et al., 2021).

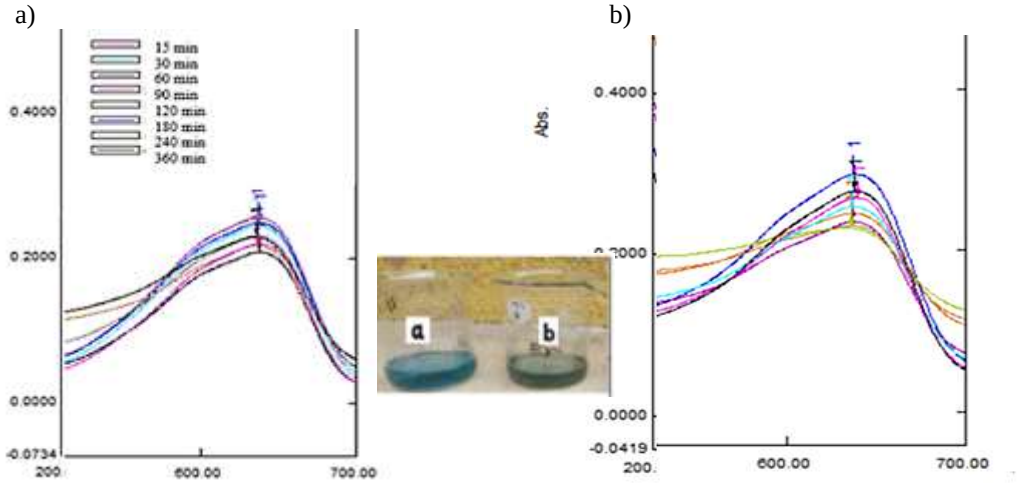


Figure 4 The absorption spectra of aqueous solution of MB treated with a) MCEN b) MHWN at different time intervals

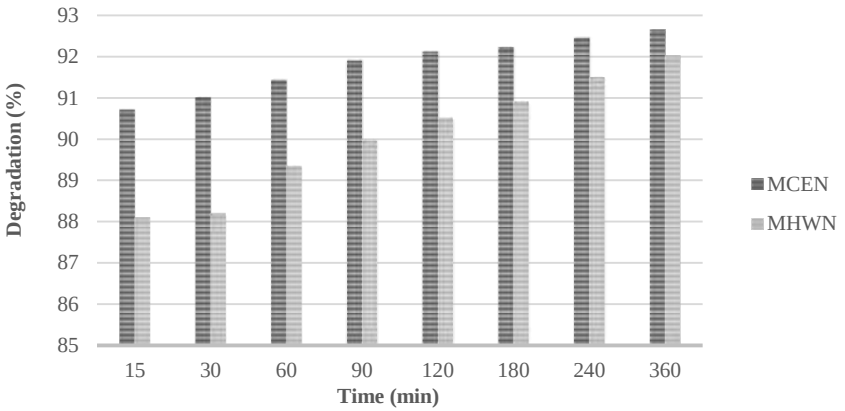


Figure 5 Degradation of methylene blue by 10 mg/L by MCEN and MHWN at different time intervals

Conclusion

M. citrifolia root extracts in ethanol and aqueous were used for the synthesis of silver nanoparticles (MCAgNPs). This study suggested various secondary metabolites present in both extracts are responsible for the reduction of silver ions and the stabilisation of MCAgNPs in colloidal solution. The characteristics of the synthesised MCEN and MWHN were confirmed by UV-Vis spectrophotometer and FTIR. The synthesised MCEN and MHWN were used as nanocatalysts for the degradation of MB dye. MCEN can efficiently degrade methylene blue greater than MWHN. More than 85% degradation was achieved in 15 minutes. In this study, the limitation of this research is in the control of the size and size distribution of AgNPs synthesised from this plant extracts and its stability. Optimisation using various synthesis parameters should be applied to achieve better control over the size, stability, and yield of AgNPs such as pH, temperature, reaction time, and concentration of reactants. In the future, surface functionalisation of AgNPs with biocompatible molecules or

polymers can also improve their stability, biocompatibility, and capabilities for biomedical applications.

Authors Contribution

Writing - Original draft preparation, Mat Hussin, Z; Literature review, Mohamad Jufly, F. H., Methodology - Yusof, N. S.; Writing - Review and editing, Daud, S.

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Conflict of interests

The author(s) confirm that this article content has no conflicts of interest.

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