Shortleaf Spikesedge-Driven Silver Nanoparticles for The Reduction of Methylene Blue Dye

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Abstract

The textile industry is a heavy producer of wastewater, which may result in the discharge of toxic dyes into the environment. Methylene blue (MB) is an example of the most used dye in the textile industry. It is difficult to degrade MB under normal conditions due to its highly stable molecules. Therefore, a catalyst route is desired in MB reduction. The catalyst chosen in this work was silver nanoparticles (AgNPs) synthesised by a biological method utilising shortleaf spikedge extract (SSE) as a reducing agent. The formations of SSE driven AgNPs were monitored using visual observation (colour), ultraviolet-visible spectroscopy (UV-vis), and transmission electron microscopy (TEM). The different process variables (concentration of AgNO_3 , concentration of SSE, reaction time, temperature and pH) upon synthesis of SSE driven AgNPs were evaluated based on the absorbance of surface plasmon resonance (SPR) band. The TEM image showed that SSE driven AgNPs are highly dispersed with a quasi-spherical shape and an average particle size of approximately 17.64 nm. For the catalytic study, the reduction of MB was evaluated using two systems. A detailed batch study of the removal efficiency (%RE) and kinetics was done at ambient temperature, various MB initial concentrations, and reaction time. The batch study for System 2 clearly showed that SSE driven AgNPs exhibited 100% reduction of MB at 30–100 mg/L initial concentration (sample coding of MB30, MB50, MB70 and MB100) between 1.5 and 5.0 min reaction time. The kinetic data best fitted a pseudo-first-order kinetic model with the highest reaction rate of 2.5715 min^{-1} . The reduction of MB occurs via the electron relay effect. These findings demonstrate that the SSE driven AgNPs are a promising candidate with potential influence on coloured wastewater.

1.0 Introduction

Water pollution has become a major environmental issue globally, and this problem is detrimental due to rapid urbanisation and population growth. Rapid population growth increases the demand for water and the level of water pollution. Various human, industrial, commercial, domestic, and transportation wastes are discharged into water supplies regularly. Consequently, polluted water sources will cause serious health hazards.

Dyes have been extensively used for thousands of years for textile, food, pigment, paint, and other applications, and are still crucial in many industries. About 1.6 million tons of dyes are produced annually to meet industrial demands. However, around 10–15% of dyes are discarded with wastewater [1]. As a result, dyes have become significant water pollutants. Various technologies such as coagulation/flocculation [2], oxidation processes [3, 4], reduction [5], adsorption [6], membrane technology [7] and biological treatment [8] have been utilized to treat effluents especially coloring wastewater.

Methylene blue (MB) is an example of the most commonly used dye in the textile industry. MB is easily obtained because the dye is cheap and can be used for dyeing textiles. It is difficult to degrade MB under normal conditions due to its highly stable molecules [9]. Therefore, a catalyst route is desired for MB degradation. A catalyst is a substance that increases the reaction rate without modifying the overall

standard Gibbs energy change in the reaction, and the process is called catalysis [10]. Degradation by reduction is preferred to degrade MB using different catalysts. A suitable catalyst is needed for reduction to occur. In this work, silver (Ag) was selected as the catalyst in the form of nanoparticles.

Silver and their composite materials can degrade harmful contaminants, for example, heavy metal ions [11], pesticides [12], bacteria [13–15], and fungi [16]. Silver nanoparticles (AgNPs) have also been used as the catalysts to remove dyes; methylene blue [17, 18], 4-nitrophenol [19], methyl orange [20], congo red [21], betanin [22], and rhodamine B [23].

In this work, shortleaf spikeseed extract (SSE) was utilised as the reducing agent in the formation of AgNPs. Also known as *Kyllinga brevifolia*, SSE is often mowed or removed as waste in turf. The formation of SSE driven AgNPs was monitored by visual observation, ultraviolet-visible spectroscopy (UV-vis), and transmission electron microscopy (TEM). Furthermore, the photocatalytic activity of SSE driven AgNPs on MB under visible light irradiation was investigated.

2.0 Materials And Methods

Shortleaf spikeseed weed was collected from Bukit Mertajam, Pulau Pinang, Malaysia. For preparation of 100% concentration of shortleaf spikeseed extract (SSE), 5 g powdered shortleaf spikeseed weed was soaked in 100 mL of distilled water and heated at 70 °C for 1 hr. The preparation of shortleaf spikeseed driven silver nanoparticles (SSE driven AgNPs) was observed by appearance of characteristic of surface plasmon resonance (SPR), due to the combined vibration of free electrons of AgNPs in resonance with the light wave. The optimization studies were carried out for formation SSE driven AgNPs in order to find the optimum condition using SSE as reducing agent and AgNO₃ as metal precursor. As to ensure the results of the experiments were reproducible, the experiments were run in triplicates. In order to identify the optimum reaction time on formation of AgNPs, the different reaction time from 10 to 120 mins, concentration of AgNO₃ from 0.5 to 5.0 mM, SSE concentration from 100% was diluted to 10, 25, 50 and 75% respectively with different of temperature (4 ± 3 , 23 ± 3 and 65 ± 3) °C and pH 1 to pH 9. The formation of SSE driven AgNPs were evaluated by visual observation and UV-vis spectrophotometer. The optimised sample were further characterised using transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM).

For the catalytic study, several parameters were considered to investigate the performance of SSE driven AgNPs as a catalyst in MB removal. The experiments were run in triplicates to obtain reproducible results. A stock solution of 100 mg/L of MB dye (Fisher Scientific) was prepared and diluted to obtain concentrations ranging from 30 to 100 mg/L. In this study, two systems were applied to evaluate the performance of SSE driven AgNPs as a catalyst. In System 1, the performance of SSE driven AgNPs for MB removal was evaluated without the addition of any reducing agent. In this system, 3 ml of 30 mg/L MB was added to 100 µl of SSE driven AgNPs in 4.0 ml quartz cuvette. In System 2, 1 ml of 0.1 M sodium borohydride (SB) was added as a reducing agent in 3 ml MB with 100 µl of 2 mM SSE driven AgNPs as a catalyst. The control for this part was the addition of SB to MB without AgNPs as a catalyst. In this

system, the effect of initial MB concentration (30–100 mg/L) was evaluated. The reaction's progress was monitored using a Lambda 35 Perkin Elmer UV-vis spectrophotometer at the wavelength of 664 nm for initial condition and after 60 min reaction time. Figure 1 shows the summary of experimental set up for this study.

3.0 Results And Discussion

3.1 Formation of AgNPs

The formation of the SSE driven AgNPs was confirmed by the appearance of SPR band at 410–455 nm. Various effect of different synthesis parameters was investigated based on the SPR band and presented in here.

3.1.1 Effect of Reaction Time and pH on the SPR of AgNPs

To study the effect of reaction time, 2 mM silver nitrate with 100% SSE were used at room temperature (20.0 ± 3.0) °C without adjust the pH of solution. A SPR plot of the SSE driven AgNPs at different contact time was measured by UV-vis spectrophotometer is shown in Fig. 2a. As can be seen, SPR peak increases representing the formation of SSE driven AgNPs started and reaches a highest peak at for RT90 and RT120 samples. The sharp SPR peak at 430 nm for RT90 and RT120 samples indicated that narrow distribution of SSE driven AgNPs size at higher reaction time. It can be seen that there is no shift in SPR peak, it can be concluded that the formation of SSE driven AgNPs are also increase in time and become more homogeneous in size at 90–120 reaction time. Figure 3 shows the digital photographs of the colour change in the reaction solution taken from 10 min to 120 min. The reaction was slow and the colour of the synthesized colloidal AgNPs changed from yellow (RT10) to greenish brown (RT20 and RT30) to brown (RT60) to chocolate brown (RT90) and dark brown (RT120). The details of the sample's observation were listed in Table 1. From the observation, the pH of the solution increased from 6.04 at 10 mins to 7.76 at 120 mins reaction time. It obviously shows that the colour changes for the sample gradually become more intense in the same time pH of the solution was also increase. The rationale behind the increasing pH of solution is due to the ionization of the phytoconstituents in SSE.

Table 1
Observation of the solution at different reaction times

Sample designation	pH at corresponding time	Observation
RT10	6.04	The colour of the solution was light yellowish.
RT20	6.12	The colour of the solution changed from yellowish to greenish brown.
RT30	6.25	The colour of the solution was greenish-brown and slightly intense than RT20.
RT60	6.43	The solution turned brown.
RT90	7.58	The colour of the solution was dark brown.
RT120	7.76	The solution turned to a darker brown with the highest recorded pH.

Further experiment is set up to understand the effect of pH on formation SSE driven AgNPs as stated in Fig. 2b. Actual pH of solution is 6.04 (sample HP6). pH of the solution was adjusted using 0.1 M NaOH (HP9) and H₂SO₄ (HP1, HP2, HP3). The addition of NaOH do not bring the negative consequence on formation of SSE driven AgNPs. Alas, the SSE driven AgNPs formed very fast within 5 minutes reaction time. However, the addition of acid solution (HP1, HP2 and HP3 samples), the SPR peaks shows lower and broader absorbance compared to pH 6 and 9, which can be due to larger size of AgNPs at acidic condition. When addition of H₂SO₄, pH of the solution decreased to pH 1, 2 and 3. At lower pH, suppression of the SSE driven AgNPs formation due to low availability of functional group of active compounds in SSE. As can be seen for HP9 sample, the SPR peak display sharper and blue shift from 430 to 413 nm indicated that the SSE driven AgNPs produced in alkaline condition have smaller size. When NaOH was added into the solution, pH was increased to pH 9. At higher pH, more distribution of functional group responsible for interaction with silver. In here, NaOH can serves as accelerator. When addition of NaOH, the rate of reaction is faster, so more nucleation produces a high concentration of nuclei thus smaller SSE driven AgNPs can be fabricated. Once nuclei are formed, growth occurs simultaneously. The SSE driven AgNPs will growth until the concentration has achieved the equilibrium solubility.

3.1.2 Effect of Concentration of Ag⁺ on the SPR of AgNPs

In order to investigate the effects of concentration of Ag⁺, the SPR peaks were measured using UV-vis spectra for different initial concentration of Ag⁺ from 0.5 to 5.0 mM at constant 100% concentration of SSE as shown in Fig. 2c. No significant SPR peak for CM0.5 and CM1.0 samples, indicating that at low concentration of Ag⁺ (0.5 and 1.0 mM) are not enough to induce the formation of AgNPs. For CM2.0 to CM5.0 samples, the SPR peaks were increased with increasing concentration of Ag⁺. At higher

concentration of Ag^+ (5.0 mM), the peak is shifted to the higher wavelength by about ± 8 nm. In addition to the red shift, the narrower SPR peak is also observed. The red shift happened due to the collision between the smaller AgNPs leading to particles growth. The red shift of the peak occurs as the conduction electrons in aggregated form become delocalised due to which SPR shifts to lower energies resulting in red shift of the SPR band.

3.1.3 Effect of Concentration of SSE on the SPR of AgNPs

The results of SPR peak for effect of SSE concentration are depicted in Fig. 2d. No obvious peak was observed for RA10, RA25, RA50 and RA75 samples for 10%, 25%, 50% and 75% concentration respectively. However, the increase of SPR peak with increasing SSE concentration can be explained by the increase in the amount of active ingredients in higher concentration of SSE. The results suggest that the highest formation of SSE driven AgNPs might obtained by using 100% SSE concentration. The blue shift of the SPR peak (424 nm) for RA100 sample might be due to the formation of smaller SSE driven AgNPs as the amount of SSE increased because the larger quantity of the SSE intensified the interaction surrounding the SSE driven AgNPs and increasing their stability. At low quantity of SSE for RA10 to RA75 samples, it cannot provide sufficient capping agents for nucleation of seeds for synthesis SSE driven AgNPs as well as failed to stabilize the high surface energy of AgNPs. Similar findings have been reported in other studies [24, 25].

3.1.4 Effect of Temperature on the SPR of AgNPs

The variation of effect of temperature (CT, RT and HT samples) on SPR peak of SSE driven AgNPs is shown in Fig. 2e. As can be seen, increase in SPR peak with respect to increase in temperature evidently depicts the higher formation of AgNPs at elevated temperatures. Most likely that occurs due to increase the reaction rate of the conversion of Ag^+ to AgNPs at higher temperature. The sharpness and blue shift from 430 to 421 nm due to the size of synthesized SSE driven AgNPs as with the higher temperature reduce in size. The results obtained agreed by previous work, which more AgNPs produced at higher temperature as example at 70 °C [26], 60 °C [27] and room temperature [28, 29].

3.1.5 Stability of SSE Driven AgNPs

After 12 months, the SSE driven AgNPs were seen to be as stable as when they were first made as seen from the dotted curve in UV-vis plot in Fig. 2f as well as do not show any precipitation or color change in the colloidal SSE driven AgNPs solution. Stability of synthesized SSE driven AgNPs can be obtained by either polymeric stabilization via adding stabilizer; sodium dioctyl sulfocuccinate [30], polymeric micelle [31–33] and sodium benzoate [34]. However, in this study, phytoconstituents in SSE coat these SSE driven AgNPs or form an organic matrix to embed them, thus preventing their aggregation and providing stability for a prolong period of time.

3.2 Morphology of SSE Driven AgNPs

The formation of SSE driven AgNPs was further confirmed by transmission electron microscopy (TEM) and transmission electron microscopy (HRTEM). TEM and HRTEM images of the morphology of SSE

driven AgNPs for RT120 sample are presented in Fig. 4. Based on the TEM image in Fig. 4(a), the colloidal SSE driven AgNPs has a quasi-spherical shape, and the particles are highly dispersed. From the histogram of the size distribution of AgNPs, the particle size of the AgNPs is in the range of 5–45 nm with an average size of approximately 17.64 nm, as shown in Fig. 4(b). From the HRTEM inset image in Fig. 4, it can also be seen that the AgNPs are capped with phytoconstituents, which are likely SSE, hence explaining the stability of the phytoconstituents from SSE. From our previous results [35], this plant is rich in carbohydrates, proteins, and plant sterols (campesterol and stigmasterol), which are considered the main reducing and stabilizing agents in forming SSE driven AgNPs. A lattice spacing of 0.235 nm was determined from the HRTEM of a single AgNP, associated with the (111) plane of the SSE driven AgNPs. This indicates the successful use of SSE as a reductant and a capping agent to avoid particle aggregation.

3.3 Catalytic Study of SSE Driven AgNPs

Figure 5 shows the MB removal efficiency in System 1 in the presence of only AgNPs. From the figure, the removal efficiency (%RE) in this system is very low (approximately 2%). It can be concluded that SSE driven AgNPs alone are insufficient in MB degradation. In System 2, the MB solution was mixed with SB as a reducing agent and SSE driven AgNPs as a catalyst. For the initial control study, the MB removal in the SB solution without AgNPs was evaluated using 30 mg/L MB, as shown in Fig. 6. No significant reduction could be observed even after 60 min.

The degradation of MB in System 2 was further investigated by treating MB at different initial concentrations of 30, 50, 70, and 100 mg/L corresponding to the sample coding of MB30, MB50, MB70, and MB100, respectively. AgNPs (2 mM, 100 μ l) were added to 0.1 M SB. For uncatalysed samples, a batch experiment was carried out by mixing SB with the aqueous solution of MB at the desired concentration without AgNPs. From the results, the %RE graph at different initial MB concentrations exhibited a sigmoid-shaped plot. The initial degradation was low at the initial stage with low MB concentration. This is due to the low driving force for MB removal initially, where a limited amount of MB interacts with the active sites of AgNPs at the beginning of the process. The reduction of MB by SB and SSE driven AgNPs catalysts is also preceded by time lag, also known as the induction time (t_0). t_0 is longer for a higher concentration of MB, as indicated in Fig. 7.

The delay may be due to several factors, as reported from previous research: removal of surface oxide layer on AgNPs [36], diffusion of MB into AgNPs [37], decomposition of SB on AgNPs [38], diffusion of SB into AgNPs [38], reconstruction of AgNPs [39], and scavenging of dissolved oxygen [40]. After the t_0 , the %RE of AgNPs increased significantly before reaching a plateau due to the equilibrium condition at a certain reaction time. The SSE driven AgNPs demonstrated excellent catalytic activity with the %RE of 100% at the equilibrium time of 1.5–5.0 min for MB30 to MB100 samples, respectively.

The excellent catalytic activity in the degradation of MB by SSE driven AgNPs can be due to several reasons. The first reason is the effect of AgNPs size; the smaller the size of AgNPs, the greater the catalytic activity [41]. The catalytic activity of AgNPs depends on its size and other properties, including

the uniformity of particles, shape [42], composition, the functionality of AgNPs, the concentration of AgNPs, the concentration of SB [36], and the effect of capping agent [37]. In general, AgNPs have a low shelf-life in an aqueous solution as they tend to agglomerate rapidly. The plant constituents attached to the surface of AgNPs could prevent the aggregation of AgNPs while allowing the SSE driven AgNPs surface to participate in MB degradation. Detailed information on the %RE at different initial MB concentrations is listed in Table 2.

<div>Table 2</div> <div>Removal efficiency and pseudo-first-order kinetics for catalysed and uncatalysed samples in System 2</div>					
Samples	1st order kinetic		2nd order kinetic		%RE
	k	R ²	k	R ²	
Catalysed					
MB30	2.5715	0.7704	0.2359	0.5531	100
MB50	2.3304	0.8523	0.1859	0.8984	100
MB70	1.6967	0.8758	0.0118	0.8745	100
MB100	1.4614	0.8006	0.0573	0.7454	100
Uncatalysed					
MB30	0.0050	0.4421	0.0002	0.4424	15
MB50	0.0067	0.9907	0.0016	0.9978	20
MB70	0.0085	0.9595	0.0001	0.9981	30
MB100	0.0135	0.9986	0.0002	0.9985	30

The removal kinetics of MB in an aqueous solution for various initial MB concentrations were also investigated for pseudo-first order and pseudo-second-order kinetics for the catalysed and uncatalysed samples, as shown in Fig. 8 and Fig. 9, respectively. The results showed that the degradation of MB followed the pseudo-first-order kinetics. The kinetic rate constants (*k*) for the MB30, MB50, MB70, and MB100 samples using the pseudo-first-order model are 2.5717, 2.3304, 1.6967, and 1.4614 cm⁻¹, respectively. The rate constants of AgNPs catalysed samples increased compared to the uncatalysed samples with a slightly flat trend. Interestingly, the catalysed samples' results are the highest compared to the available published studies, as shown in Table 3.

Table 3
Comparative analysis of MB reduction by AgNPs

Reducing agent for AgNPs synthesis	C ₀ of MB	Reducing agent	Size of NPs (nm)	Contact time	First-order (min ⁻¹)	Ref.
<i>Phoenix dactylifera L.</i>	0.67 mg/L	SB	28.66–39.40	60 min	0.137	(Laouini et al., 2021)
Jasmine flower	100 mL	-	10–40	120 mins	-	(Aravind et al., 2021)
Poly(ethylene glycol) methyl ether thiol	50 mg/L	SB	20	8 min	0.478	(Qi, Zhang, Qin, & Hu, 2020)
<i>Catharanthus roseus</i>	15 mg/L	Graphene oxide	1–26	30 min	1.4563	(Rohaizad et al., 2020)
<i>Cryptocarya alba</i>	10 mg/L	SB	3.5–25	1 min	-	(Recio-Sánchez et al., 2019)
<i>Barleria longiflora</i>	30 mg/L	-	2.4	45 min	-	(Cittrarasu et al., 2019)
<i>Ananas comosus</i>	40 mg/L	-	14–20	173 min	0.014	(Agnihotri, Sillu, Sharma, & Arya, 2018)
<i>Cuminum cyminum</i>	80 mg/L	SB	16	30 min		(Choudhary, Kataria, & Sharma, 2018)
<i>Gmelina arborea</i>	10 mM	SB	8–32	10 min	-	(Shi et al., 2018)
Shortleaf spikesedge	30 mg/L	SB	17.64	1.5 min	2.5715	(This work)

3.4 Mechanistic Aspect

Figure 10 shows the plausible reaction mechanism for MB reduction using SSE driven AgNPs as a catalyst in System 1 and System 2. In System 1, SSE driven AgNPs without any reducing agent could not reduce MB. In System 2, uncatalysed samples (MB with SB as a reducing agent and without SSE driven AgNPs) showed that SB could accept an electron from MB, reducing MB to leuco-methylene blue (LMB); however, the process was too slow. For catalysed samples, SSE driven AgNPs are considered as an electron relay in the redox reaction to transfer the electrons from the donor (i.e., SB) to the acceptor system (i.e., MB), where SSE driven AgNPs act as both the donor and acceptor of electrons (Fig. 10). Previous experimental results demonstrated that AgNPs accelerated MB reduction owing to the capability of AgNPs as an electron relay in MB reduction [43]. Based on this observation, it can be deduced that the redox potential of the AgNPs produced in this investigation is located between the redox potential of MB (E^0 (MB/LMB) = 0.01 V) and SB (E^0 ($\text{BH}_4^-/\text{B}_2\text{H}_4$) = -0.21 V).

4.0 Conclusion

SSE driven AgNPs were successfully synthesised via a biological method using SSE as a reducing agent. The TEM images verified the well-dispersed nanoparticles' formation having a quasi-spherical shape with size variation from 5 to 45 nm and an average size of approximately 17.64 nm. The synthesised SSE driven AgNPs were tested for MB reduction using two systems. System 1 (MB with AgNPs alone) showed no MB removal. In System 2, for uncatalysed samples, MB in the presence of SB as a reducing agent and in the absence of SSE driven AgNPs as a catalyst showed poor performance. Meanwhile, for the catalysed samples in System 2 (MB with SB as a reducing agent and SSE driven AgNPs as a catalyst), SSE driven AgNPs demonstrated excellent catalytic performance for MB reduction, but another reducing agent should be present (i.e., SB). The reaction rate for MB removal of this system is 2.5715 min^{-1} for 1.5 min reaction time for MB30 sample. SSE driven AgNPs showed outstanding performance in reducing MB to LMB via the electron relay effect in System 2.

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Figures

Figure 1

Summary of the experimental set up

Figure 2

(a) Effect of reaction time (b) effect of pH (c) effect of SSE concentration (d) effect of AgNO3 concentration (e) effect of temperature on the position of AgNPs SPR peak and (f) stability of SSE driven

AgNPs.

Figure 3

Digital photographs displaying the colour change of the solution reacted at different reaction times from 10 to 120 min

Figure 4

(a) TEM image, (b) histogram of size distribution, and HRTEM image of SSE driven AgNPs (inset).

Figure 5

Removal of MB in System 1 (only AgNPs)

Figure 6

Removal of MB in SB solution without AgNPs (Control) in System 2

Figure 7

The removal efficiency of MB at different initial MB concentrations (MB30, MB50, MB70 and MB100) for catalysed and uncatalysed samples in System 2

Figure 8

Pseudo-first-order kinetic plots for MB30, MB50, MB70 and MB100 in SSE-driven AgNPs catalysed and uncatalysed samples in System 2

Figure 9

Pseudo-second-order kinetic plots for MB30, MB50, MB70 and MB100 in SSE-driven AgNPs catalysed and uncatalysed samples in System 2

Figure 10

Schematic diagram of possible process mechanisms of MB removal in System 1 and System 2 (uncatalysed and catalysed solutions)