Decolorization of methylene blue dye in distilled and river water samples using citrate-stabilized silver nanoparticles

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This study investigated the decolorization of methylene blue (MB) dye in both distilled and river water samples using citrate-stabilized silver nanoparticles (cit-AgNP). Cit-AgNP was successfully synthesized using chemical reduction method with sodium borohydride and trisodium citrate as reducing and stabilizing agents, respectively. The resulting cit-AgNP solution was yellow in color with UV Vis absorbance peak at 393 nm, typical of AgNPs. TEM analysis confirmed the presence of spherical nanoparticles with average diameter 9.19 ± 4.91 nm. The calculated full width at half maximum (FWHM) of 59.42 ± 4.59 nm indicate good monodispersity. In the study, an initially prepared 20 ppm MB solution was added with $NaBH_4$ and cit-AgNP that acted as reducing agent and catalyst, respectively. This resulted in the decolorization of the blue MB solution in 10 minutes. The result is consistent with UV Vis analysis showing reduction of MB peak at 663 nm. The percent decolorization at 10 minutes is 94.45%. This is significantly higher than the 57.69% decolorization of MB solution with only $NaBH_4$ present and without cit-AgNP. To further examine its applicability, river water samples were used. Tests showed that at 10 minutes, 20 ppm MB solution using river water exhibited high percent decolorization at 94.33%. Statistical tests revealed the MB decolorization behavior in distilled water is not significantly different with its behavior in river water samples. Overall, the study showed successful synthesis and characterization of cit-AgNP and its potential as catalyst in the decolorization of MB in aqueous solutions.

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INTRODUCTION

Dyes are the most important chemicals used to add or change the color of materials. They are widely used in the textile, pharmaceutical, food, cosmetics, plastics, paint, ink, photographic and paper industries. The largest class of synthetic dyes are the azo dyes (Hsueh and Chen 2008). They are characterized by the presence of azo bonds (-N=N-), in association with aromatic structures. One of the most common azo dyes used in the synthetic textile fiber industry is methylene blue (MB), a heterocyclic aromatic azo dye (Oliveira et al. 2008). Due to their wide industrial application, they can potentially contaminate and damage nearby aquatic ecosystems. It is estimated that around 10% of the dyestuff in the dyeing process of textiles is released to the environment due to non-adherence in the fiber substrate (Puvaneswari et al. 2006). This results to reduced photosynthetic activities in aquatic ecosystems, depletion of dissolved oxygen and loss of biodiversity (Bhakya et al. 2015). In humans, MB has potentially neurotoxic effects on the central nervous system in high concentration (Vutskits et al. 2008).

The treatment of dye wastewater usually consists of conventional biological and chemical methods. However, most dyes are not biologically degradable and are resistant to microbial attack (Bhakya et al. 2015). Typical chemical treatments on the other hand, which include oxidation, ozonation and electrolysis, are generally economically unfeasible due to high cost of chemicals like ozone. These methods are also unable to completely remove recalcitrant azo dyes due to dye stability and they generate high sludge volume (Saratale et al. 2011). Therefore, there is a need to explore new emerging technologies

such as the application of nanotechnology in using nanocatalyst for dye decolorization in aqueous solution.

The use of nanocatalysts for improved dye decolorization presents an attractive alternative from conventional methods because of the ease of application, simplicity and rapid dye removal. Other advantages of photocatalytic decolorization using nanoparticles include quick oxidation and absence of polycyclic products (Rajabi and Farsi 2015).

Several researches on dye removal use nanocomposites which consists of at least two different materials that aim to combine beneficial characteristics of each of the constituent elements. For instance, a study in 2015 reported the use of a nanocomposite of silver, indium, nickel and sodium dodecyl sulphate as nanocatalyst in the decolorization of MB dye (Molla et al. 2015). Another study employed zinc, cadmium and titania nanocomposite as catalyst in the decolorization of Rhodamine B dye, a cationic dye like methylene blue (Li et al. 2011). In the synthesis of nanocomposite catalysts, some of the methods use multiple potentially toxic chemicals. Furthermore, most synthesis steps involve complex and time-consuming processes.

Aside from nanocomposites, solutions of pure metal nanoparticles such as those of silver can also be used in catalytic reactions. Silver nanoclusters have displayed unique reactivity, selectivity and stability such that they are used as catalyst in various reduction and oxidation processes of compounds like nitroaromatics, alcohols and olefins to name a few (Dong et al. 2015). They have also been reported to catalyze the decolorization of dyes potentially through electron relay effect (Mallick et al. 2006). MB dye decolorization can be achieved through transforming the blue MB into its reduced colorless form, the leucomethylene blue (LMB). Adding a reducing agent however might not be enough to facilitate a rapid electron transfer process from the donor species to the acceptor species due to a large redox potential. An intermediate, such as silver nanoparticles, can therefore be introduced to serve as an electron relay center. This is possible if the silver nanoparticles have a redox potential intermediate that of the electron donor and acceptor system. As a relay center, the silver nanoparticles accept electrons from the donor, usually the reducing agent, and subsequently donate the electron to the dye being reduced (Ajitha et al., 2019). Aside from acting as electron relay center, AgNP that are negatively charged may adsorb cationic dyes such as MB due to electrostatic attraction or proximity. The presence of excited electrons at the surface of the nanoparticle may additionally facilitate the decolorization of the dye (Devi et al., 2016).

There are several studies that reported the use of silver nanoparticles (AgNP) for dye decolorization, most of which used plant materials to reduce and stabilize the AgNP (Khodadadi et al. 2017; Miri et al. 2018, Singh & Dhaliwal 2018; Sreekanth et al. 2016; Vanaja et al. 2014 and Vidhu & Philip 2014). Although biosynthesis of AgNP presents an appealing method due to the use of less chemical reagents, there are significant disadvantages to this method. For instance, there is significant variation in the plant extract matrix even within same species when collected from different sources which may present problems in the replicability of studies (Ahmed et al. 2016). Aside from that, since some of the plant material extract are taken from fruits and leaves, it competes with its natural use as food. Finally, additional pretreatment steps and equipment are required in the preparation of plant extracts such as size reduction, heating, centrifugation and filtration. Chemical reduction is still preferred due to established wet lab methodologies. The problem of replicability of the study is also addressed due to less variabilities in reagent composition. There is also potential for small to medium scale production. Finally, there are alternative non-toxic chemical reagents that can be used in stabilizing AgNP.

The focus of this work is the use of unmodified citrate-stabilized silver nanoparticles (cit-AgNP) for MB dye decolorization. Unmodified silver nanoparticles are those that have not undergone any post-synthesis modification or functionalization. This lessens the instrument and the reagents used in the process. Moreover, with a "one-pot" synthesis method, a simple mixing of the reagents in a single flask achieves both the reduction and stabilization of the AgNP. Finally, environmentally benign sodium citrate is used as capping agent instead of more common toxic chemicals.

In this study, the use of unmodified cit-AgNP as a nanocatalyst in the decolorization of MB dye was investigated. Its catalytic activity was studied by examining the changes in color and absorbance behavior of the MB solution through time. The percent dye decolorization of MB solutions with and without catalyst were also compared. Finally, its ability to catalyze MB decolorization in river water samples was investigated.

MATERIALS AND METHODS

Chemicals and Instruments

All chemicals used in the experiments were analytical grade and used as received. Absorbance values were determined using Thermo Scientific GENESYS 10S UV Vis spectrophotometer. The morphology and size of the nanoparticles were characterized using JEOL JEM 1010 transmission electron microscope (TEM). The nanoparticle size distribution analysis was performed using ImageJ software. All aqueous solutions were prepared with distilled water except solutions of river water samples. All glasswares were cleaned and dried prior to use.

Synthesis of cit-AgNP

The reduction of silver ions was based on the Creighton method (Creighton et al. 1979). Initially, 0.001 M silver nitrate solution was added dropwise to 30 ml of 0.002 M sodium borohydride solution that had been chilled in an ice bath and had been subjected to constant stirring at 400 rpm. Then, 5 ml of 0.001 M trisodium citrate was added dropwise immediately after the reduction process. The entire addition process took about 5 minutes, after which the stirring was stopped. The synthesized cit-AgNPs were then set aside for one hour.

Development of calibration curve

A calibration curve was generated to establish linear relationship between MB concentration and UV Vis absorbance. The calibration curve was generated by first preparing 0, 1, 3, 5, 8, 11, 15, 18 and 20 ppm MB concentration. UV Vis spectrophotometer was then used to obtain individual absorbance value at 663 nm MB peak. Then, a plot of absorbance against MB concentration was generated.

Decolorization experiment

A prepared 20 ppm MB solution was subjected to decolorization using 0.2 M $NaBH_4$ as reducing agent and cit-AgNP as catalyst. First, 4 ml of 0.2 M $NaBH_4$ was added to a 50 ml of 20 ppm MB dye at room temperature. Then, 2 ml of cit-AgNP was added to obtain a final 17.86 ppm MB concentration in the mixture. The solution was mixed thoroughly in a vial and immediately transferred to different cuvettes and placed inside the set-up box with an equal distance of 20 cm from the 100 watts incandescent bulb at the center. The light inside the box was then turned on. The absorbance spectrum of the mixture was monitored from

300-700 nm using UV Vis spectrophotometer. Readings were done by drawing out samples from the box at a regular 1-minute time interval until the 10th minute. Experiment was repeated to obtain triplicate results. Decolorization of four types of solutions were compared namely: pure MB; MB-cit-AgNP (with catalyst only); MB-$NaBH_4$ (with reducing agent only) and the MB-$NaBH_4$-cit-AgNP (with reducing agent and catalyst) solution. The sketch of the set-up is presented in Figure 1.

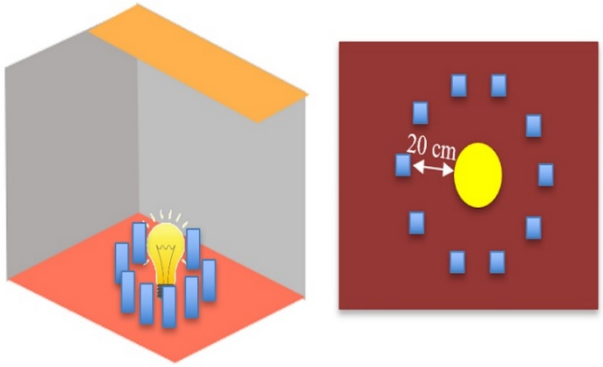


Figure 1: Diagram of the decolorization set-up consisting of MB solutions in cuvettes placed equidistant around a 100 W incandescent bulb.

Additionally, the percent dye decolorization was calculated using the following equation:

$$\text{Decolorization (\%)} = \frac{A_o - A}{A_o} \times 100\%$$

where A_o and A are the initial and final absorbance values read at the MB peak, respectively.

River water samples

River water samples were taken from creek of Brgy. Sapa, Miagao, Iloilo, Philippines. The collected samples were filtered to separate the solid particles. Filtered river water samples were then used to prepare a 20 ppm MB solution which was subsequently used for the decolorization process in order to verify the applicability of the study in a much more realistic environment.

RESULTS AND DISCUSSION

Characterization of cit-AgNP

Cit-AgNP was successfully synthesized using the modified Creighton method. As shown in Figure 2, a clear yellow colloidal solution was formed indicating the presence of grains of silver nanoparticles (Mahmudin et al. 2015). The UV Vis absorbance curve showed a peak at 393 nm further supporting the formation of cit-AgNP as AgNPs typically show a single visible extinction band near 400 nm. The calculated FWHM of the absorbance curve is 59.42 ± 4.59 nm. This suggests good monodispersity of the nanoparticles (Solomon et al. 2007).

The morphology of the cit-AgNP was also investigated using TEM analysis presented in Figure 3. The nanoparticles are spherical in shape with average diameter of 9.19 ± 4.91 nm. This is consistent with previous study showing that cit-AgNP with peak around 400 nm have particle size close to 10 to 15 nm (Ravindran et al. 2012). The obtained particle size is also in good agreement with the calculated FWHM value as particles with size around 10-14 nm have FWHM within 50-70 nm range (Solomon et al. 2007). Moreover, the TEM image shows that majority of the particles are relatively monodispersed and

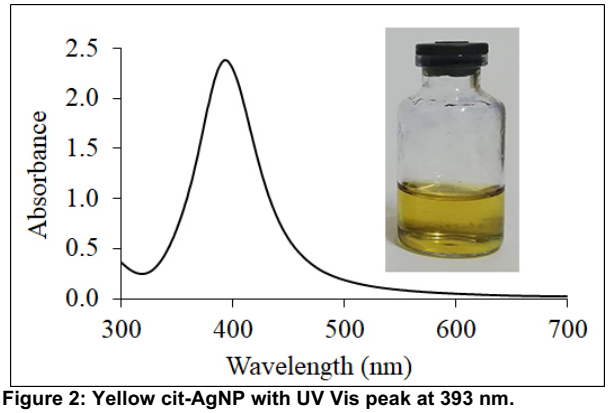
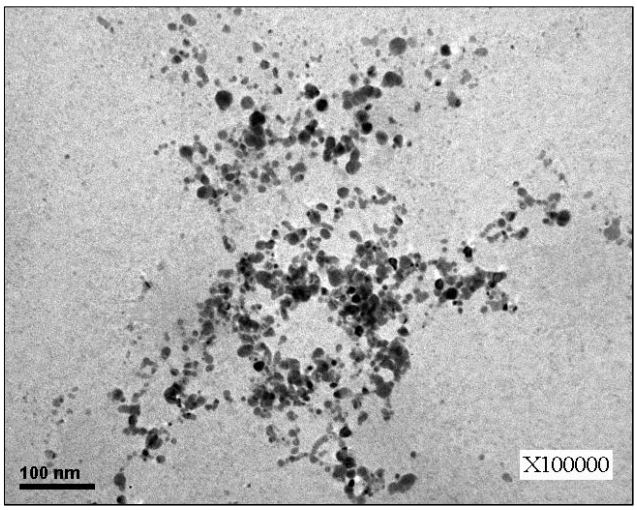
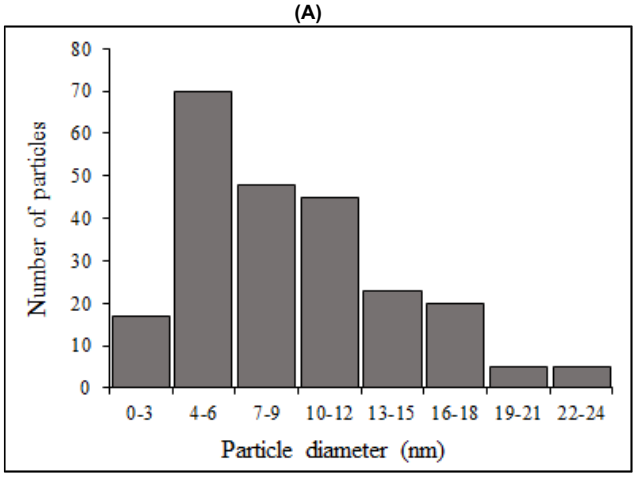


Figure 2: Yellow cit-AgNP with UV Vis peak at 393 nm.

unaggregated. This can be attributed to the presence of citrate ions on the surface of the AgNPs. A potential mechanism for interaction of a citrate ion with silver nanoparticle surface has been proposed where two of the carboxyl groups of citrate associate with the surface of the nanoparticle leaving two remaining free arms including one carboxyl group and one hydroxyl group (Munro et al. 1995). This can create a negatively charged cloud surrounding the AgNP preventing unwanted aggregation though electrostatic repulsion. It is important to ensure the dispersed state of the AgNP because its catalytic activity might be affected upon aggregation (Liao et al. 2018).



(A)



(B)

Figure 3: (A) TEM image of cit-AgNP at 100,000X magnification and (B) histogram showing distribution of particle size.

Decolorization of MB

The UV Vis absorbance curve of the prepared MB solution is shown in Figure 4. The peak was determined to be at 663 nm, consistent with the typical peaks of MB solutions (Yao and Wang, 2010).

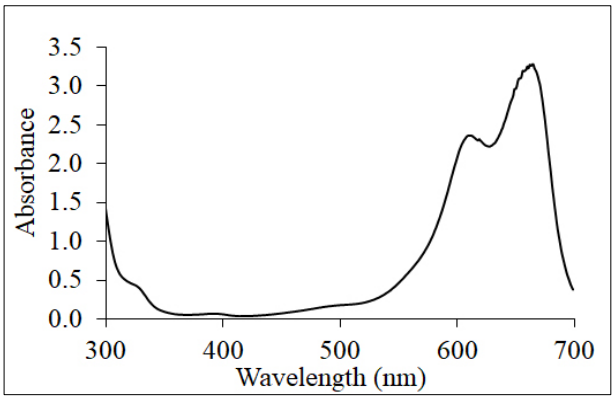


Figure 4: UV Vis peak of MB solution at 663 nm.

The calibration curve generated is presented in Figure 5. Based on the results, there is a strong linearity between UV Vis absorbance and MB concentration with coefficient of determination of 0.9954.

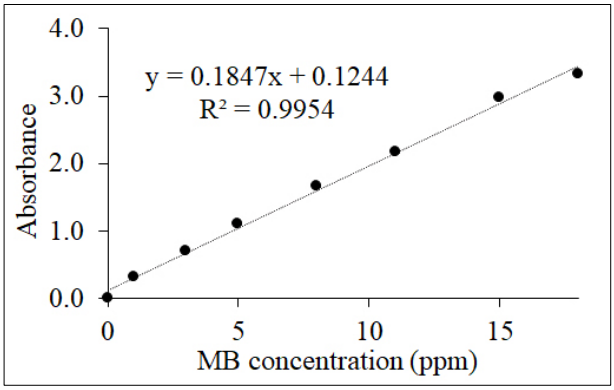


Figure 5: Calibration curve of absorbance at peak vs MB concentration showing strong linear relationship.

For the decolorization experiment, the absorbance spectra of the various treatments exposed to light were monitored over a 10-minute reaction time. The color of the solutions and the absorbance trend are shown in Figure 6. The results demonstrate that the decolorization of pure MB and MB with cit-AgNP exposed to light were very minimal with no substantial reduction in the absorbance at the characteristic 663 nm peak of MB. This observation is consistent with the blue color of the solution before and after the 10-minute reaction time. On the other hand, the exposure of the solution of MB with $NaBH_4$ and MB with both cit-AgNP and $NaBH_4$ resulted to a gradual decrease in the absorbance at 663 nm showing partial removal and almost complete color removal in the two solutions, respectively.

As expected, the pure MB solution displayed almost no reduction at the characteristic 663 nm peak implying almost no decolorization. This is due to the absence of a catalyst, sorbent or reducing agent that can alter the structure or reduce MB to LMB.

The solution of MB and cit-AgNP also showed very minimal decolorization. In literature, MB can be adsorbed by the cit-AgNP due to its high surface area and the presence of negatively charged citrate ions on the surface of the AgNP. Hence, the

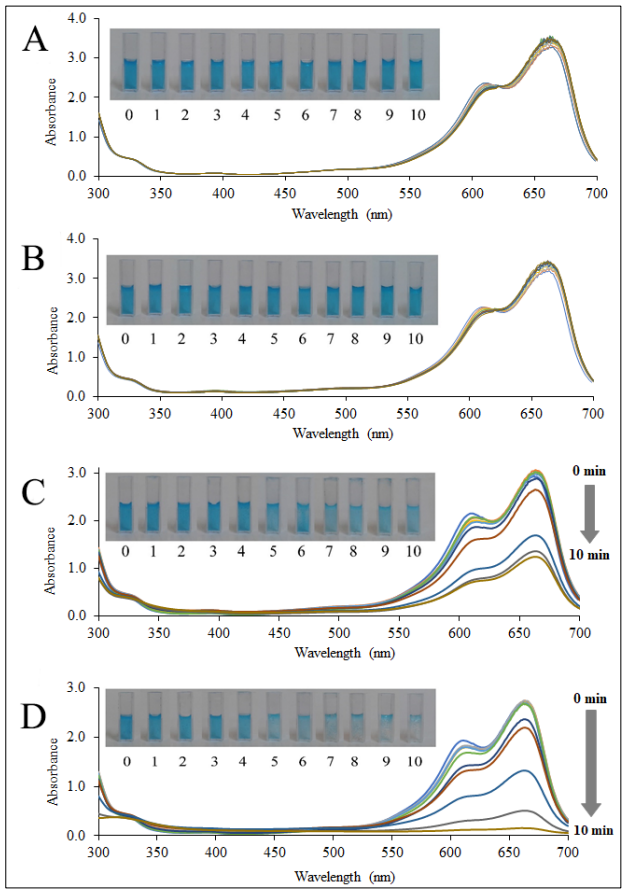


Figure 6: Decolorization of MB for 10 minutes in different set-ups: (A) pure MB, (B) MB with cit-AgNP, (C) MB with $NaBH_4$ and (D) MB with cit-AgNP and $NaBH_4$.

cationic MB dye has affinity towards the AgNP due to electrostatic attraction (Devi et al., 2016). For MB to be reduced at the surface of the AgNP to become colorless LMB, it can potentially interact with the excited conduction electrons at the surface of the AgNP due to the light irradiation (Sarina et al., 2013). However, this might not be the operative dominant mechanism because the minimal decolorization suggests that the present conditions are not enough to decolorize the MB solution. This implies that either there were simply too few dye molecules that were adsorbed and reacted at the surface of the cit-AgNP or there were too few conduction electrons to facilitate the reaction in the absence of a reducing agent.

For the set-up with MB and $NaBH_4$, as expected, the solution was partially decolorized because $NaBH_4$ is a reducing agent which can donate electrons to transform the blue MB to colorless LMB. However, for the 10-minute reaction time, only partial decolorization was achieved.

For the solution with MB, $NaBH_4$ and cit-AgNP, the results show almost complete decolorization after 10 minutes. In terms of the mechanism, since both catalyst and reducing agent are present in the solution that resulted into its successful decolorization, this can be potentially explained by the Langmuir-Hinshelwood model. According to the model, the reducing agent (BH_4-) and the dye (MB) can be adsorbed at the surface of the catalyst through affinity, physical sorption or hydrogen bonding. Then, electron from the reducing agent (BH_4-) is transferred to the dye (MB) which reduces it to its colorless LMB form. The catalyst AgNP assists in the process as the transfer medium. Once the LMB products are formed, they can desorb from the surface and return to the bulk solution (Ma et al. 2017; Shah et al. 2017).

Aside from the reagents present in the solutions, additionally, the light could have also contributed to the decolorization process. Based on literature, light irradiation can potentially excite energetic conduction electrons at the surface of the cit-AgNP and interact with the dye molecules adsorbed at its surface. However, this is dependent on the number and energy of the conduction electrons and the number of dye molecules at the surface of the cit-AgNP (Sarina et al., 2013). The results suggest that both the reducing agent and catalyst are necessary to achieve high rate of decolorization which is achieved potentially through cit-AgNP acting as an electron relay center for the $NaBH_4$ and the MB dye (Mallick et al., 2006).

To properly compare the effect of the presence of catalyst in the decolorization of MB dye, the percent decolorization was determined and shown in Figure 7. The graph shows that the solution with catalyst registered an appreciable decolorization in as early as the 4th minute. Furthermore, in the 10th minute, the percent decolorization of the solution with catalyst is at 94.45% which is substantially higher than the 57.69% decolorization in the solution without catalyst. The results support the catalytic activity of cit-AgNP to have better decolorization effect on the MB solution.

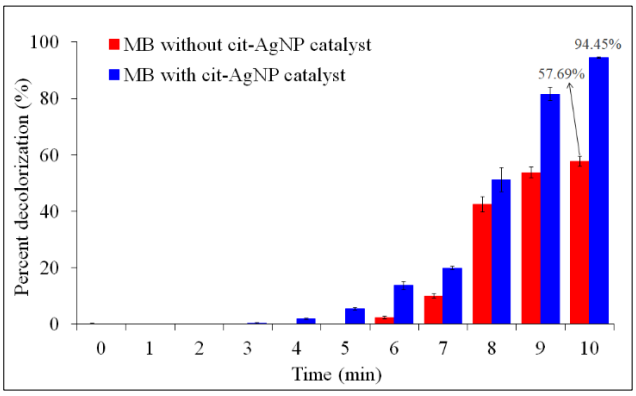


Figure 7: Comparison of percent decolorization of MB with and without cit-AgNP catalyst.

The result of the study was compared to several researches that used AgNP for MB decolorization. Table 1 shows the comparison in terms of the nanoparticle used, particle size, the initial MB concentration, reducing agent for decolorization, exposure time and percent decolorization.

Table 1: Comparison of result of this work with studies using AgNP for MB decolorization

Nanoparticle	Size (nm)	Prepared MB concentration (ppm)	Reducing agent (decolorization)	Time (min)	Decolorization (%)	Reference
Bark extract-AgNP	17.5-66.5	0.32	$NaBH_4$	30	~100	Sreekanth et al. 2016
Fruit extract-AgNP	30	10	-	30	70.20	Miri et al. 2018
Kernel shell-AgNP	< 20	10	$NaBH_4$	13	~100	Khodadadi et al. 2017
Leaf extract-AgNP	79-96	10	-	4,320	95.3	Vanaja et al. 2014
Stem extract-AgNP	15-25	60	-	180	82.8	Singh & Dhaliwal 2018
Seed extract-AgNP	22-32	320	$NaBH_4$	< 19	~100	Vidhu & Philip 2014
Graphene oxide-AgNP	10-49.5	0.32	$NaBH_4$	15	~100	Sreekanth et al. 2016
Polyvinyl alcohol-AgNP	10-13	*	$NaBH_4$	35	< 100	Sagitha et al. 2016
AgNP/TiO_2 nanotubes	5 nm AgNP on 200-400 nm long nanotubes	20	-	150	81.2	Viet et al. 2018
AgNP/PSNM**	7-29 nm AgNP on 295.60 nm PSNM sphere	9.60	$NaBH_4$	11	~100	Liao et al. 2018
Citrate-AgNP	9.19	20	$NaBH_4$	10	94.45	This study

**not indicated*
*** poly(styrene-N-isopropylacrylamide-methacrylic acid)*

The results in Table 1 show that cit-AgNP is as good or even better than some of the reported methods in terms of reaction time. The improved performance of the cit-AgNP can be potentially attributed to its higher surface area to volume ratio due to its smaller particle size relative to the other synthesized AgNPs. Having a larger surface area means it can accommodate the adsorption of more reductant and dye molecules and subsequently enhance its potential as electron transfer center as it is able to reduce more MB molecules at a time. One can also notice that studies that incorporated $NaBH_4$ as reducing agent have relatively achieved decolorization at a quicker period. For plant extract-reduced AgNPs, it is possible that due to the cocktail of compounds present in the extract, this could have interfered in the sorption or electron relay transfer mechanism. For this study however, aside from the quicker decolorization time, other significant advantages include having simpler method of cit-AgNP catalyst synthesis using "one-pot" mixing method, reduction of equipment requirement, and removing the need to process plant materials for extracts resulting to less reagent composition variability.

River water samples

To test the potential of cit-AgNP in catalyzing MB decolorization in simulated water samples, a solution of MB was prepared using river water instead of distilled water. Table 2 shows the percent decolorization of MB after 10 minutes. The resulting color of the MB solutions before and after exposure to light in the presence of cit-AgNP and the UV Vis spectra are shown in Figure 8.

Table 2: Decolorization of prepared 20 ppm MB with cit-AgNP as catalyst at 10 minutes.

Distilled water	River water
94.45%	94.33%

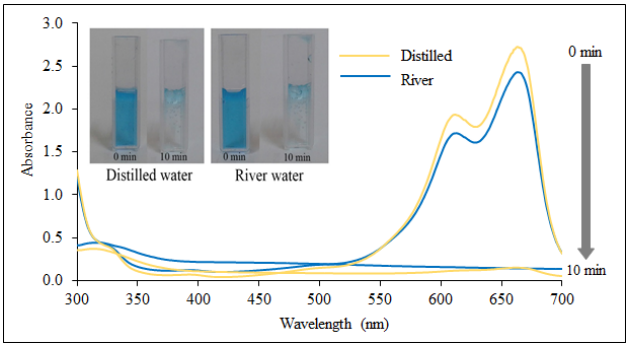


Figure 8: Decolorization of prepared 20 ppm MB in distilled water and in river water samples.

The results show that for river water tested, the percent decolorization is 94.33%. Running a one-way analysis of variance comparing the percent decolorization using distilled and river water matrix, the p-value returned is 0.89 which is greater than alpha ($p > 0.05$). This means that there is not enough evidence to conclude that the means of the responses for distilled and river water are statistically significantly different from each other at 95% confidence interval. This also implies that the presence of other possible contaminants in the river water such as microorganisms, dissolved salts and other organic compounds had minimal effect on the ability of cit-AgNP to catalyze the MB decolorization process in the river water sample.

CONCLUSION

In summary, cit-AgNP was successfully synthesized using chemical reduction method and characterized using UV Vis and TEM analysis. The cit-AgNP successfully decolorized an MB dye solution in 10 minutes with high percentage decolorization of 94.45%. This is significantly higher than the 57.69% decolorization for MB without catalyst loading. Finally, cit-AgNP was also successful in catalyzing the decolorization of MB in river water samples. Overall, cit-AgNP showed potential as a nanocatalyst in MB dye decolorization.

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CONTRIBUTIONS OF THE AUTHORS

The conceptualization of the study and funding was secured by FEA. All authors contributed in the design of the methodology, data gathering, analysis, and writing.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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