Sustainable Environment Research 27 (2017) 245–250

Contents lists available at ScienceDirect

Sustainable Environment Research

journal homepage: www.journals.elsevier.com/sustainable-environment-research/

Original Research Article

A novel green synthesis of silver nanoparticles and their catalytic action in reduction of Methylene Blue dye

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ARTICLE INFO

Article history:
Received 20 December 2016
Received in revised form
21 February 2017
Accepted 25 April 2017
Available online 6 May 2017

Keywords:
Silver nanoparticle
Green synthesis
Fruit extract
Catalytic activity
Methylene Blue

ABSTRACT

Green synthesis processes are regarded as safer alternative to usual physical, chemical and microbial methods due to their cost effectiveness, environmental friendly nature and easy handling. In the present study, an eco-friendly and facile method for biogenic synthesis of silver nanoparticles (AgNPs) has been developed using fruit extract of *Gmelina arborea*, an abundantly available medicinal plant in North Eastern region of India. The prepared AgNPs were characterized by UV–Vis spectroscopy, transmission electron microscopy (TEM), selected area electron diffraction pattern and energy dispersive X-ray spectrum. TEM studies showed the as-synthesized AgNPs were stable, almost spherical and crystalline with the particles size varying from 8 to 32 nm. The average diameter of the particles was 17.0 ± 1.6 nm. The catalytic effectiveness of the prepared green catalyst, AgNP, was also investigated in catalytic degradation of Methylene Blue (MB) dye. The catalytic degradation reaction was completed within 10 min, signifying excellent catalytic properties of silver nanoparticles in reduction of MB.

1. Introduction

Development of environmental friendly and green processes for synthesis of noble metal nanoparticles is evolving into an important branch of nanotechnology. Metal nanoparticles exhibit unique chemical and physical properties including large surface/volume ratio, which are useful in different fields such as electronics, photonics, biomedical, catalysis etc. [1–4]. Among the various noble metals, silver is the metal of first choice due to their diverse properties especially high antimicrobial and catalytic nature [5,6]. A number of approaches, i.e., physical, chemical and biological methods have been used for the preparation of silver nanoparticles by several researchers. There is a growing need to develop eco-friendly processes to avoid the use of toxic and hazardous chemicals in their synthesis – also known as “Green synthesis”. Green synthesis of silver nanoparticles have advantages over the physical, chemical and microbial synthesis procedures, as this is cheap, eco-friendly, convenient single-step method, easily scaled up for large-scale synthesis and does not require high pressure, energy, temperature and toxic chemicals for production [7–10]. Many researchers reported the plant mediated green synthesis of silver nanoparticles using extracts of different plant parts such as root, stem, bark, leaf, fruit, bud, and latex as natural resources [11–14]. Various biomolecules found in these extracts, include polysaccharides, polyphenols, aldehydes, ketones, proteins/enzymes, amino acids and caffeine that can reduce metal ion and stabilize the nanoparticles to desired shapes and sizes [15,16].

Gmelina arborea is a fast-growing tree, occurring naturally throughout greater part of India and commonly known as Beech wood or locally termed as ‘Gamari’ in the Bodoland Territorial Area Districts area of Assam, a North Eastern parts of India [17]. *G. arborea* is one of the important medicinal plants of India and its root, fruit, bark and leaf are used as medicine for various diseases like diabetes, wound-healing, anti-diarrheal, antioxidant activity, antiulcer activity and are also used as temporary cures in the events like snake-bite, and scorpion sting [18–23]. Different phytochemicals like flavonoids, lignans, glycosides, alkaloids and proteins have been found in different parts of these plants [24].

Organic dyes are used in numerous industries like food, pharmacy, cosmetics, paints, plastics, paper and textiles. These synthetic dyes are harmful for human health and they are hazardous to

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Peer review under responsibility of Chinese Institute of Environmental Engineering.

http://dx.doi.org/10.1016/j.serj.2017.04.003
2468-2039/

environmental as well. Various conventional treatments like coagulation, filtration, adsorption and reverse osmosis have been used for dye removal. Nevertheless, it is difficult to remove these dyes from water, because of their aromatic structural stability. Nano-catalysts are one of the promising agents for the reduction of synthetic dyes [6,25–27]. Thus, in the present work, we have been investigating the degradation of Methylene Blue (MB) dye using the green-synthesized silver nanoparticles (AgNPs) as catalyst in the presence of sodium borohydride ($NaBH_4$). Green synthesis of AgNPs was done using *G. arborea* aqueous fruit extract as bio-reducing and bio-stabilizing agent. However, to the best of our knowledge, use of such a plant (*G. arborea*) for the synthesis of metal nanoparticle has been hardly explored till now.

2. Materials and methods

2.1. Materials

G. arborea fruits were collected from road side garden of National Highway (NH-31C) near Karigaon village of Kokrajhar District, Assam (India). Silver nitrate ($AgNO_3$) and Sodium borohydride ($NaBH_4$) were procured from SRL Chem, India whereas MB was from Merck, India. All the chemicals used in the present study were of analytical grade and used as such without any additional purification. Double distilled water (ddH_2O) was used to prepare aqueous solutions throughout the experiment.

2.2. Preparation of G. arborea fruit extract

100 g of fresh and good quality fruits of *G. arborea* were collected and thoroughly washed with ddH_2O. Washed fruits were cut into small pieces using clean stainless steel knife and seeds were removed. The small pieces of fruit were then ground in a mixture grinder by adding 50 mL of ddH_2O. The ground fruits were filtered using Whatman filter paper No. 1 and the supernatant was stored at refrigeration condition for further use.

2.3. Synthesis of AgNPs by aqueous fruit extracts G. arborea

AgNPs were synthesized by following the method adopted by Kumar et al. with minor modification [28]. For a typical synthesis, 30 mL of aqueous $AgNO_3$ (1.0 mM) was taken into a glass container (Actira, Merck) of 100 mL volume and 0.1 mL of fruit extract added into it. Sample was then heated on hot plate magnetic stirrer (REMI, India) at 60 °C with continuous stirring at 1000 rpm. Within 5 min, the color of solution starts changing from colorless to yellowish-brown. The formation of nanoparticles was investigated by UV–Vis spectra reading at regular interval of time. One blank sample was also prepared by taking 30 mL of distilled water instead of silver nitrate. The amount of fruit extract added varied from 0.1 to 1.0 mL.

2.4. Characterization of as-synthesized AgNPs

Progress of formation of silver nanoparticles was examined by UV–Vis spectroscopy (PerkinElmer, λ-35, USA) analysis. UV–Vis spectra of reaction mixtures having aqueous silver nitrate solution and *G. arborea* fruit extract were performed at regular time interval. The size, shape and crystallinity of the prepared silver nanoparticles were studied using transmission electron microscopy (TEM). A 2-d old sample was taken for TEM study, carried out on a JEOL JEM-1011 microscope, working at an acceleration voltage of 200 kV. Sample for TEM analysis was prepared by placing a small drop of colloidal silver solution on carbon coated copper grid of 300 meshes. The excess solution from the TEM grid was removed using a blotting paper and the grid was allowed to dry in ambient conditions prior to measurement. The crystalline nature and elemental composition of the green synthesized nanoparticles was characterized by selected area electron diffraction (SAED) pattern and energy dispersive X-ray (EDX) spectrum, respectively.

2.5. Study of catalytic action of prepared AgNPs against Methylene Blue

A potential application of metal nanoparticles is the catalysis of certain chemical reactions that would otherwise not occur. The catalytic activity of prepared AgNPs was assessed against a toxic dye (MB) as a substrate by $NaBH_4$. In a typical assay, 10 mL of 10 mM stock solution of MB were mixed with 3 mL of 1 mM freshly prepared $NaBH_4$ solution. Three different samples were prepared. In two samples, 1.5 and 3.0 mL of as-synthesized colloidal AgNPs was further added into previously made mixture of MB and AgNPs. One blank sample was also prepared without AgNPs. The final volume of reaction mixture in all three samples was adjusted to 16 mL by adding ddH_2O. The color of samples containing AgNPs was gradually changed with time from deep blue to light blue and finally became colorless. The reduction of MB was monitored at regular time interval (5 min) using UV–Vis spectrophotometer (PerkinElmer λ-35, USA). The experiment was carried out at ambient temperature, and at pH of 6.5. The values of absorption band maxima were recorded and compared.

3. Results and discussion

3.1. UV–Vis spectroscopy of AgNPs

UV–Vis spectroscopy was used to follow the formation of silver nanoparticle by reduction of the aqueous silver ions during the exposure to the fruit extract of *G. arborea*. The colorless aqueous silver nitrate solution became yellowish brown few minutes after the addition of fruit extract of *G. arborea* at 60 °C on a hot plate magnetic stirrer. It is well known that this yellow color of the reaction mixture arises owing to excitation of Surface Plasmon Resonance (SPR) vibration in the silver nanoparticles [29]. Fig. 1a and b shows the UV–Vis spectra recorded from the silver nitrate-*G. arborea* fruit extract reaction mixture as a function of amount of fruit extract added and reaction time, respectively. From Fig. 1a it is clear that the SPR band of silver nanoparticles centered at 418 ± 3.0 nm and increases as concentration of fruit extract increases in reaction mixture. Fig. 1b indicates the SPR band of silver nanoparticles as functions of reaction time and gradually increases with heating time (reaction time). The inset of Fig. 1b corresponds to the plot of absorbance at λ_{max} (i.e., at 418 nm) against time of reaction and it shows that the reduction was almost completed within 4 h. Thus, the silver nanoparticles can be synthesized within 4 h by this green method.

3.2. TEM analysis

The size, shape and crystallinity of the prepared AgNPs were analyzed using TEM. High resolution TEM (HRTEM) images, SAED pattern & particle size distribution of the nanoparticles (prepared by using 0.5 mL of *G. arborea* fruit extract) are represented in Fig. 2. HRTEM images (Fig. 2a and b) show that most of the particles are almost spherical, while some of them are slightly elliptical in shape. The particle size distribution chart (Fig. 2c) shows the prepared nanoparticles having size range from 8 to 32 nm with the average diameter of about 17 nm. The indexed SAED patterns (Fig. 2d) of the AgNPs with bright spots indicate the crystalline nature of the silver nanoparticles. The patterns showed fringes with bright circular

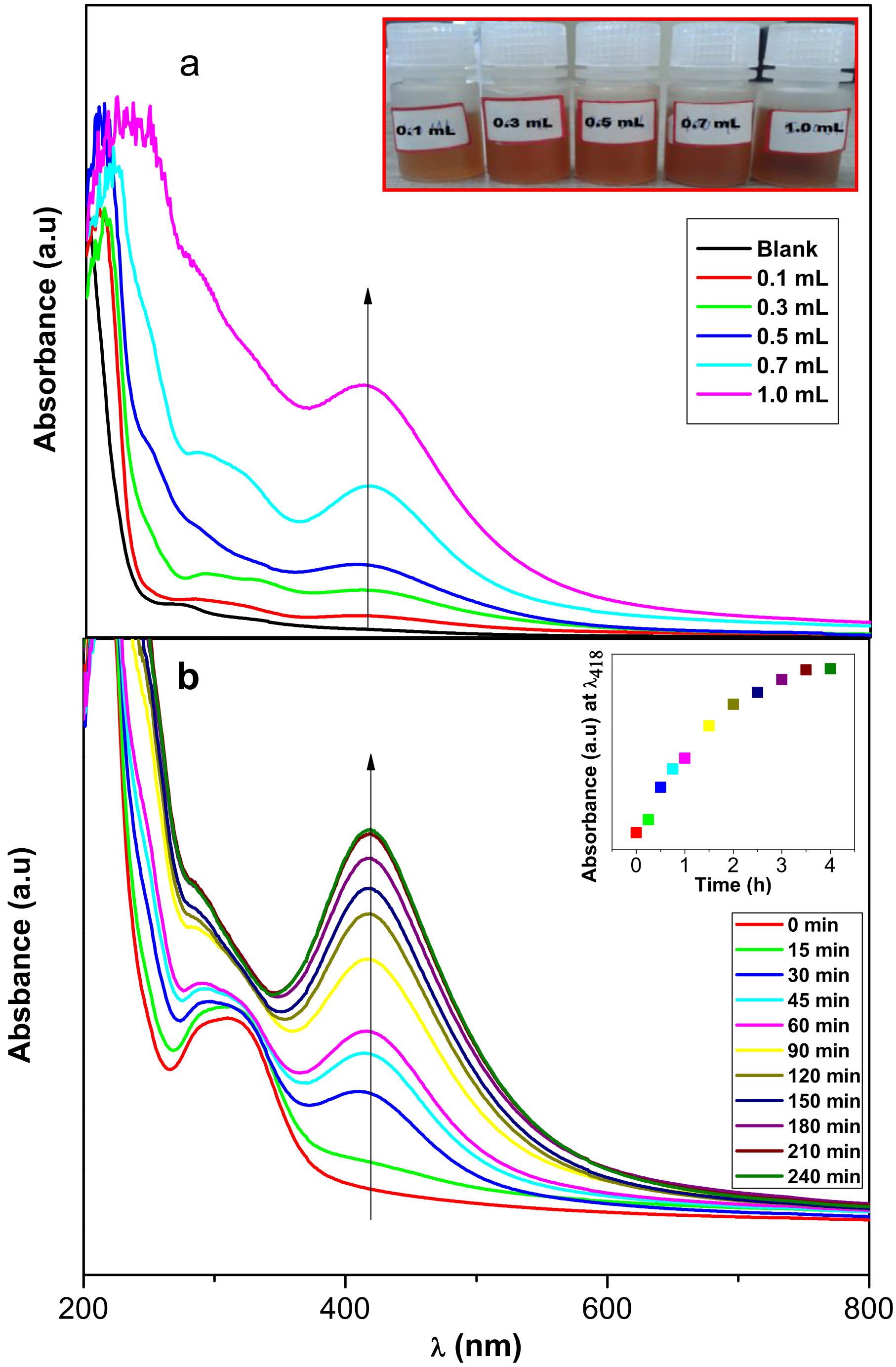

Fig. 1. UV–Vis absorption spectra of reaction mixture of aqueous $AgNO_3$ and GA fruit extract recorded (a) as a function of amount of GA fruit extract added; reaction time-60 min (Inset-as-synthesized silver nanoparticles), (b) as a function reaction time; sample containing 0.5 mL of GA fruit extract.

rings corresponding to the (111), (200), (220) and (311) planes of AgNPs.

3.3. EDX analysis

Elemental silver in the prepared nanoparticles was recognized by EDX study. A major peak around 3 keV was observed in EDX profile of silver nanoparticles confirming the presence of elemental silver in the prepared nanoparticles [30]. In addition to silver, the signal of Cu was also observed in the EDX spectrum (Fig. 3). The Cu signal might have come up from the carbon supported copper grid used for sample preparation.

3.4. Catalytic activity of prepared AgNPs

The catalytic ability of as-synthesized AgNPs was investigated using the reduction reaction of MB by $NaBH_4$ as a model reaction. MB is a basic aniline dye also known as methylthioninium chloride, which has many uses in diverse fields including biology and chemistry, as a stain and as a medicine [31–33]. MB has blue color in oxidized state and loses its color upon reduction forming colorless leucomethylene blue. The UV–Vis absorption spectra of reduction of MB by $NaBH_4$ in the absence of catalyst 'AgNPs' is shown in Fig. 4a. Fig. 4b and c shows the UV–Vis spectra of MB reduction by $NaBH_4$ in the presence of increasing amount of as-

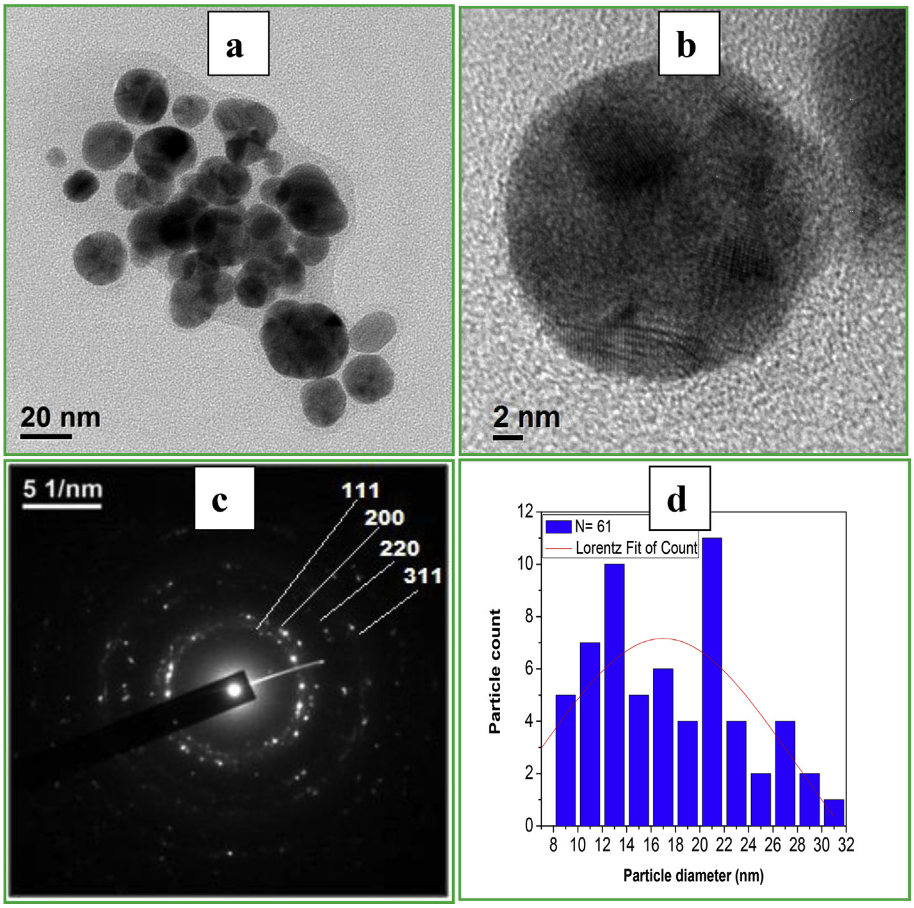

Fig. 2. TEM analysis of sample containing 0.5 mL of GA fruit extract (a) TEM image (b) HRTEM image of single spherical nanoparticles (c) The selected area electron diffraction (SAED) pattern; (d) Histogram showing particles size distribution of GA fruit extract capped AgNPs.

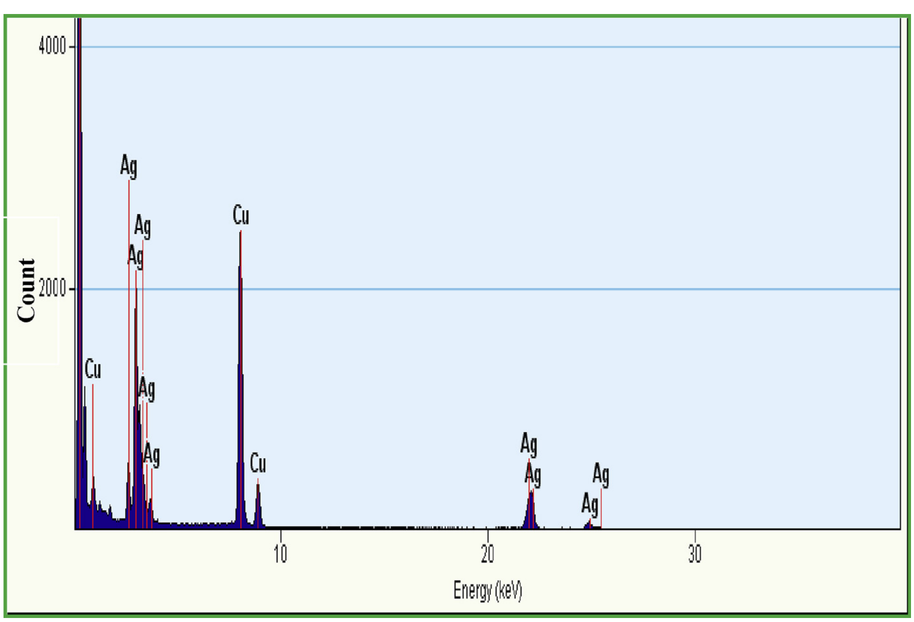

Fig. 3. EDX spectrum of prepared silver nanoparticles.

synthesized catalyst ‘AgNPs’, i.e., 1.5 and 3.0 mL, respectively. MB typically shows absorption maxima band at about 664 nm in aqueous solution due to π → π* and n → π* transitions [34]. The progress of the catalytic degradation can be easily pursued by decrease in absorption band maxima at 663 nm followed by concomitant formation of new band having maxima at 432 nm, which increases in intensity with time. It is clearly visible from Fig. 4a that the reduction rate of MB was significantly slower in the absence of AgNPs compared to that in the presence of them (shown in Fig. 4b and c). The rate of reduction reaction increases as the concentration of AgNPs in the reaction mixture increases, respectively shown in Fig. 4b and c. It was also evident that in the absence of AgNPs in reaction mixture only 30–40% of reduction was complete (Fig. 4a) within 30 min, but in the presence of 1.5 mL of AgNPs, 100% of reduction was completed within 30 min. In the presence of 3.0 mL of AgNPs the reduction was completed within 10 min only. A comparison between our findings and reported data of reduction time for 100% MB dye reduction in the presence of AgNPs synthesized using plant extract is shown in Table 1. These findings showed that MB reduction reaction became efficient after the addition of AgNPs in the appropriate proportion and the rate of reduction increased with increased concentration of AgNPs in the reaction mixture. This became more evident from Fig. 4d, which shows linear plots of ln A_t/A_0 versus time for reduction of MB using different concentration of AgNPs at ambient temperature. It revealed that the as-synthesized colloidal AgNPs performed as a mediator for electron transfer during reduction of MB by $NaBH_4$, and acted as an effective ‘green catalyst’.

Table 1
Comparison of time of 100% reduction time of Methylene Blue in presence of AgNPs synthesized using plant extract.

S. No.	Catalyst	Time	References
1	AgNPs/Seed extract	30 min	[35]
2	AgNPs/Bark extract	30 min	[36]
3	AgNPs/Leaf extract	20 min	[37]
4	AgNPs/Seed extract	8–19 min	[38]
5	AgNPs/Fruit extract	10 min	This work

3.5. Mechanism of MB degradation

The bond dissociation energy (BDE) plays an important role during chemical reaction in breaking and/or formation of new bond. Electron transfer takes place during the reaction between MB dye and $NaBH_4$, in which $NaBH_4$ acted as a donor and the dye as acceptor [39]. The addition of silver nanocatalyst in reaction mixture performed as potential intermediate between MB dye & BH_4^- ions. At first, it lowered the BDE and made the electron transfer between them more efficient. Thus, the rate of reduction of MB by $NaBH_4$ was increased in the presence of AgNPs. Clearly, as-synthesized colloidal AgNPs obtained from abundantly available

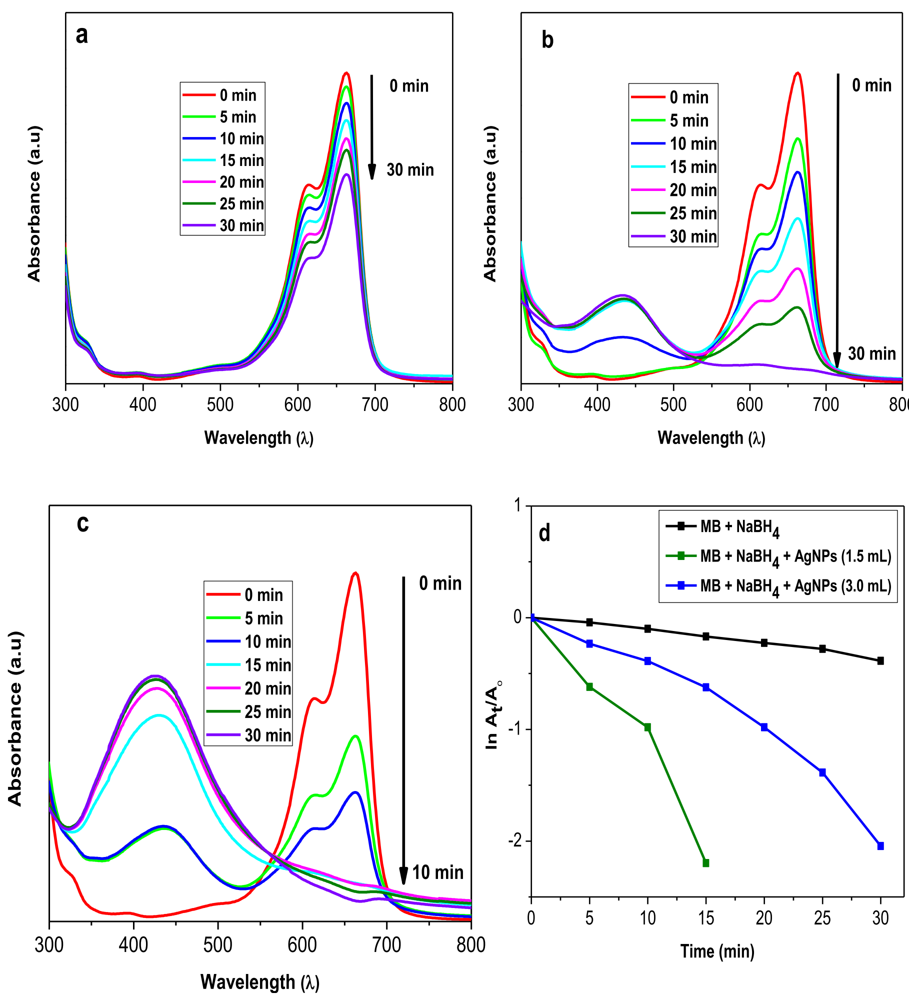

Fig. 4. Successive UV–Vis absorbance spectra at 5 min intervals showing reduction of MB by $NaBH_4$ at ambient temperature; (a) reaction mixture without AgNPs (b) reaction mixture with 1.5 mL of AgNPs (c) reaction mixture with 3.0 mL of AgNPs (d) Smooth plots of ln At/A0 against time for the degradation of MB at ambient temperature.

fruit extract showed promising results in catalytic reduction of an organic dye.

4. Conclusions

In the present study, stable silver nanocolloids were successfully prepared by a novel green route using aqueous fruit extract of *G. arborea*. The procedure was relatively easy, rapid, inexpensive, eco-friendly and did not require any organic solvents or other toxic reagents. Thus the synthesis process was advantageous over conventional methods of AgNPs synthesis. The prepared AgNPs were almost spherical in shape, crystalline in nature and with average diameter of 17.0 ± 1.6 nm. Furthermore, this study demonstrated good catalytic activity of the prepared AgNPs on reduction of MB dye at ambient conditions. The MB dye completely degraded within 10 min, signifying the usefulness of the synthesized AgNPs in effluent treatment (dye degradation) of pharmaceutical, cosmetics, paints, plastics, paper, textiles, and other chemical industries.

Acknowledgement

Authors are very much thankful to Prof. Uday S. Dixit, Ex-Director of CIT, Kokrajhar for his continuous support and encouragement toward successful execution of the present research work.

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