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Green synthesis, characterization and Photocatalytic Reduction of Congo red using Silver Nanoparticles from Millingtonia hortensis leaf extract

K. Muthu (karu.muthu@msuniv.ac.in)
Manonmaniam Sundaranar University
V. Thangapushbam
Manonmaniam Sundaranar University
P. Rama
Manonmaniam Sundaranar University
S. Sivakami
Manonmaniam Sundaranar University
M. Jothika
Manonmaniam Sundaranar University

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Abstract

Day-to-day increasing in the usage of organic dye and disposed waste has increases the environmental pollution. So there is an emergency need to removal of toxic dyes solution itself non-toxic. In the present work, green synthesis of silver nanoparticles (Ag NPs) from silver ions using the reducing and capping agent of *Millingtonia hortensis* leaf broth. UV-Vis absorbance spectral value at 423 nm was confirmed the product of Ag NPs. X-ray diffraction (XRD) analysis and selected area electron diffraction (SAED) pattern was confirm the crystalline nature of metallic silver. High resolution transmission electron microscope (HRTEM)analysis morphology of images identified the spherical shape particles with sizes from 20 to 50nm. The product of Ag NPs was applied as photocatalyst in the reduction/degradation of Congo red in the presence of $NaBH_4$ under different experimental conditions to confirm the pseudo first order kinetics. The Ag NPs was good photocatalyst in the reduction/degradation of Congo red within 14 min.

Introduction

Azo dye has commonly used the industries of paint, paper, plastics, textiles, food, cosmetics [1, 2] etc., for manufacturing of respective product. In the daily produced and usage of azo dye based materials and the excess of dyes wastewater has directly discharged in the natural sources of river and soil without pretreatment. The disposed wastewater was highly polluted the environment and to suffering the human health and ecosystems. The aromatic diazo dye of Congo red (sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid) has one of the periodically using colour reagents in leather, paper, textile, pharmaceutical, food industries and the wastewater of effluents is highly pollutant in water and soil [3]. Congo red (CR) dye is one of the highly carcinogenicchemicals in human beings and aquatic organismsof wastewater. Therefore, the several physico-chemical and biological techniques [4] such as photocatalyst, coagulation, electrochemical processes, adsorption, biological reduction/degradation [5–7] etc., to reduce/remove the toxicity dyes. Some methods do not completely to remove the dye from wastewater, fewer yields and more energy efficiency used. An alternative, recent researcher to develop the green chemistry method synthesized metal nanoparticles (MNPs) from corresponding metal ions using the reducing and capping agents of medicinal plant extracts.These methods synthesized MNPs areinvestigate the reduction/degradation of azo dye wastewater to maximum amount reduce the pollution. For example, *Abutilon indicum* leaves [8] extract used the synthesis of CuO nanoparticles and its catalytic degradation of CR dye, *Crocus Haussknechtiibois* bulb extract was used the green synthesis of Ag NPs and evaluated the degradation of CR [7], *Thunbergia grandiflora* flowers extract used the green synthesis of Ag NPs and their effective catalytic reduction of CR dye [9].

The plant part such as leaves, flower, bulb, etc., used the green synthesis of MNPs and its effective catalytic reduction of CR dye. Generally, plant extract contains secondary metabolites such as terpenoids, steroids, saponins, flavonoids, alkaloids, polyphenols, etc., which can act as reducing and capping in the synthesis of MNPs. One of the medicinal plant *Millingtonia hortensis*Linn., belongs to Bignoniaceae family. The leaves of *M. hortensis*are is using in folklore medicine for the treatment of antipyretic, sinusitis, cholagogue tuberculosis sinusitis, cholagogue, tonic, and asthma [10]. In the present study, the

medicinal valuable plant such as *M. hortensis* leaves extract was used the green synthesis of silver nanoparticles from silver nitrate. The product of Ag NPs was applied as photocatalyst in the catalytic reduction/degradation of diazo dye of Congo red in the presence/absence of $NaBH_4$.

Materials And Method

Extraction of Millingtonia hortensis **L., leaf broth**

The healthy leaves of *Millingtonia hortensis* L., was collected and washed with running tap water followed by distilled water to remove the dust. About 12 g of leaves were taken in 250 ml Erlenmeyer flask, add 100 ml triple distilled water and boiled at 80°C for 10 min and filtered through Whatmann filter paper. The obtained filtrate of leaf broth was stored and taken further process.

Green synthesis of silver nanoparticles from M. hortensis **L., leaf broth**

Green synthesis of Ag NPs was synthesized from aqueous silver ions (5mL of 10^{-3} conc.) using the reducing agents of *M. hortensis* leaf extract (0.5mL) at room temperature in the dark place. In the beginning, the colorless reaction mixture was slowly changed to yellowish brown within 10 min toindicate the formation of Ag NPs. This reaction was optimized by different volume of *M. hortensis* leaf extract and different concentration of silver ions. All the reactions were monitored by UV-Vis. spectrophotometer and determine the exact volume of extract and silver ions concentration. The optimized volume of *M. hortensis* leaf extract and silver ions conc. solution reaction mixture was recorded by UV-Vis. absorption spectra at different time intervals. The product of Ag NPs was confirmed and characterized by various spectral instrumental techniques.

Characterization Of Synthesized Ag NPs

The product of synthesized Ag NPs was determined by UV-vis spectrophotometer (Perkin–Elmer Lamda 25 model) in the wavelength range 200–800 nm. FTIR spectra were analysis by JASCO FTIR spectroscopy using KBr disc technique in the range of 4000 – 400 cm^{-1} with the spectra resolution at 4 cm^{-1}. The product of Ag NPs was characterized using X-ray diffraction (XRD) analysis (PANanalytical X'PERT-PRO Powder XRD) in the 2θ range 20-80^{o}and scanning speed at 0.02 min per degree. Morphology of Ag NPs was investigated using high resolution transmission electron microscopy (HR-TEM) with selected area electron diffraction (SAED) pattern (TECNAI T30 G2 S-TWINFEI Company, Netherland, Serial No: D905, voltage 250 kV).

Photocatalytic Reduction/degradation Of Congo Red Dye Using Synthesized Ag NPs

The photocatalytic activity of green synthesized Ag NPs was investigated the reduction reaction of diazo dye CR in the presence/absence of $NaBH_4$. The aqueous solution 50 µL (0.1mM) of CR was mixed with 0.1ml (1mM) of $NaBH_4$ in a cuvette and then 25, 50 and 100 µL of Ag NPs was added and made upto 3.0ml triple distilled water. The reaction mixture was straightaway recorded by UV-vis absorption spectrum. For the controlled experiment has been carried out under same condition without addition of photocatalyst Ag NPs.

Results And Discussion

Green synthesis of Ag NPs was synthesized from 15ml of 1mM silver ions using the reducing agents 0.5ml of *M. hortensis* leaf broth. This reaction mixture was gradual colour changes from colourless to yellowish brown [11] within 10 min (Fig. 1A) to preliminary confirm the production of Ag NPs. An optimized this reaction at different volume of extract (0.1, 0.2, 0.3, 0.4, 0.5, 06, 0.8, and 1.0 ml) and silver ions (3.0, 5.0, 10.0, 15.0, and 20.0 ml) solution were recorded UV-Vis. spectrum (Fig. 1B). On the basis of spectral results shows to lower volume of the extract and silver ions to slow reaction and longer time to needed in the formation of Ag NPs. At higher volume of extract and silver ions solutions reaction were very fast form of the product on aggregated on the surface area. For the neutral volume of extract and silver ions has suitable in the green synthesis of Ag NPs and does not aggregated on the surface. The optimized volume at 0.5ml of plant extract and 15 ml of silver ions is most suitable in the synthesis of Ag NPs. Freshly taken the reaction mixture was periodically recorded by UV-vis spectra surface Plasmon resonance centered at 423nm which indicates the formation of Ag NPs (Fig. 2A).After, 5.5 hrs the maximum amount of silver nitrate was reduced to metallic silver by the overlapping of absorption intensity by UV-Vis spectra. The obtained UV-Vis spectra result values were plotting the wavelength of absorbance maximum (λ_{max} = 423 nm) against time (hrs). The curve should be clearly indicated that the absorbance maximum was increased that the speed of synthesis of the Ag NPs was very fast on the initial stage of reaction because the higher concentration of Ag^+ ions, becoming slower with the decrease in the concentration of Ag^+ ions as well as resulted higher concentration of the Ag NPs (Fig. 2B).

FTIR measurement of the *M. hortensis* leaf extract (3415, 2925, 1583, 1422, and 1047 cm^{-1}) and synthesis of Ag NPs (3442, 2924, 2854, 1719, 1636, 1382, and 1028 cm^{-1}) was (Fig. 3A) identified the functional group of phytochemicals. Both of the molecules show the wave numbers of vibrational regions at 2924 and 2925 $cm^{-1}$is due to the presence of C-H stretching of aromatic groups [12]. The peak at 1719 cm^{-1} is corresponding to carbonyl stretching group of amide linkage [13]. The sharp bands at 3415 and 3442 cm^{-1}represents to free overlapping hydroxyl groups (polyphenolic compounds or flavonoids) were identified by the leaf extract and Ag NPs. The appearance of intense bands at 1719 cm^{-1} is the carbonyl group have been indicating the reducing and stabilizing agents in the biosynthesis of Ag NPs. The wave numbers at 1636 and 1382cm^{-1} is representing to the carbonyl (C-O) stretching groups of amide I and amide II [14]. The band at 1583 cm^{-1} corresponds to the aromatic rings of the flavonoids or polyphenols. The absorption bands at 1047 and 1028 cm^{-1} corresponds to C-O-C (ether) linkage of

flavonoids compounds. From the above FTIR spectral results were represents to the presence of flavonoids in the plant extract and capping the Ag NPs.

The crystalline nature of the AgNPs was analyzed by X-ray diffraction (XRD) pattern (Fig. 3B).The diffraction peaks at 38.14, 44.38, 64.44, and 77.36 corresponding to the lattice planes (111), (200), (220), and (311) have face centered cubic crystal structure of AgNPs. The XRD pattern results are corroborated with the data base of Joint Committee on Powder Diffraction Standards (JCPDS, file no. 89-3722). A few unassigned peaks were also marked in the vicinity of the characteristic peaks are due to the crystallization of bioorganic phase that occur on the surface of the NPs [15, 16]. The average sizes of the particles were calculated by Debye-Scherrer formula [17] results to confirm the particles sizes ~ 20 nm.

The morphology and particle size of the synthesized Ag NPs were viewed by TEM analysis. The lower and higher (Fig. 4A – 4E) magnification of TEM images of the Ag NPs shows predominantly spherical in shapes with sizes from 20 to 50 nm and some of the particles were found to be some distortion. The selected area electron diffraction (SAED) analysis of the four rings shows to be crystallographic plane (Fig. 4F) of face centered cubic crystal structure respectively reported [18]. These signals were correlated to XRD analysis and confirm the elemental silver [19].

Photocatalytic Activity Of Synthesized Ag NPs

The photocatalytic efficiency of green synthesized Ag NPs was determined for the reduction/degradation of Congo red in the presence of $NaBH_4$. The reduction/degradation reaction was visually confirm the change of colour from red to colourless indicates the as shown in Fig. 5D. The analysis of the Congo red dye discolouration reaction was monitored and recorded by UV-Vis spectra at different time intervals.From the UV-Vis spectrum of CR solution wavelength center at 498 and 350 nm has confirm the azo groups [20]Generally, $NaBH_4$ have been used as common reducing agent in the organic compound synthesis. In the absence of catalyst Ag NPs, and $NaBH_4$, only the plant extract was added to CR solution for reduction process recorded by UV-Vis spectra, the wavelength (498nm) absorption intensity does not any major changes upto 48 hrs and few more days (Fig. 5A.). Similarly, $NaBH_4$, plant extract and $NaBH_4$were added to the CR solution for the reduction reaction process. The UV-Vis spectraof CR wavelength at 498nm (π) absorption intensity do not any major change even after 48 hrs (Fig. 5B). Different concentration of green catalyst Ag NPs (25µL, 50µL, and 100µL) was added to the CR solution in the presence of $NaBH_4$ monitored by UV-Vis spectra (Fig. 6A, 6C & 6E). The CR solution wavelength at 498nm absorption intensity was steadily decrease at the end of reaction absorption intensity was almost negligible. The CR (two –N = N– groups) was reduction/degradation to hydrazine (two –NH–NH– groups) derivatives followed it may be broken the azo bonds to gives the colourless products of two molecules of naphthylaminesulphonic acid and 4,4’-diamino biphenyl[7, 21] and related to the reaction mechanism shown in the scheme 1. The complete decolouration of CR and $NaBH_4$in the presence of Ag NPs shows at 14 min, 10 min, and 6 min respectively. The reduction/degradation reaction kinetics was determining the first order kinetics with respects to CR and $NaBH_4$ in the presence of Ag NPs. Therefore

the reaction rate constant k was determined the linear plot of $\ln(A_t/A_0)$ versus the reduction time (Fig. 6B, 6D, & 6F) was found to be 0.1037, 0.1868, and 1901 for Ag NPs respectively. Recently, the plant extract mediated green/bio-synthesis of Ag NPs has been applied as the photocatalyst in the reduction/degradation of CR [22, 23]. Our synthesized NPs reduction time was much lowered to compare the other plant extract NPs.

Conclusions

In this study, green synthesis of Ag NPs was successfully synthesized using the reducing and capping agents of *M.hortensis* leaf broth. The product of Ag NPs was confirmed by change of colour and the UV-Vis spectra surface Plasmon resonance center at 423nm. FTIR analysis indicates the immersions of phytochemical functional group compounds in the reduction and capping of silver ions to metallic silver. The product of NPs was characterized by XRD result which confirmed the face-centered cubic crystalline phase of metallic silver. TEM images of the morphology was identified the spherical shapes with sizes at 20 to 50 nm. Further, the synthesized Ag NPs were examining as efficient catalyst with enhance the rate of reduction/degradation of environmental polluted CR (azo) dye. According to these results, green synthesis of Ag NPs procedure was relatively inexpensive, high yield and did not used any toxic chemicals and extensive catalytic applications in the different types of industries such as textile, chemicals, papers, paint, food, plastics, and many other industries.

Declarations

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Author Contributions Statement

KM has design this work, write and reviewed the manuscript. VT and PR have collected the plant, extraction, synthesis and characterization work. SS and MJ have to determine the catalytic activity.

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Data availability: Any datasets used in this manuscript are available on request.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

Ethical approval: Not applicable

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Schemes

Scheme 1 is available in the Supplementary Files section

Figures

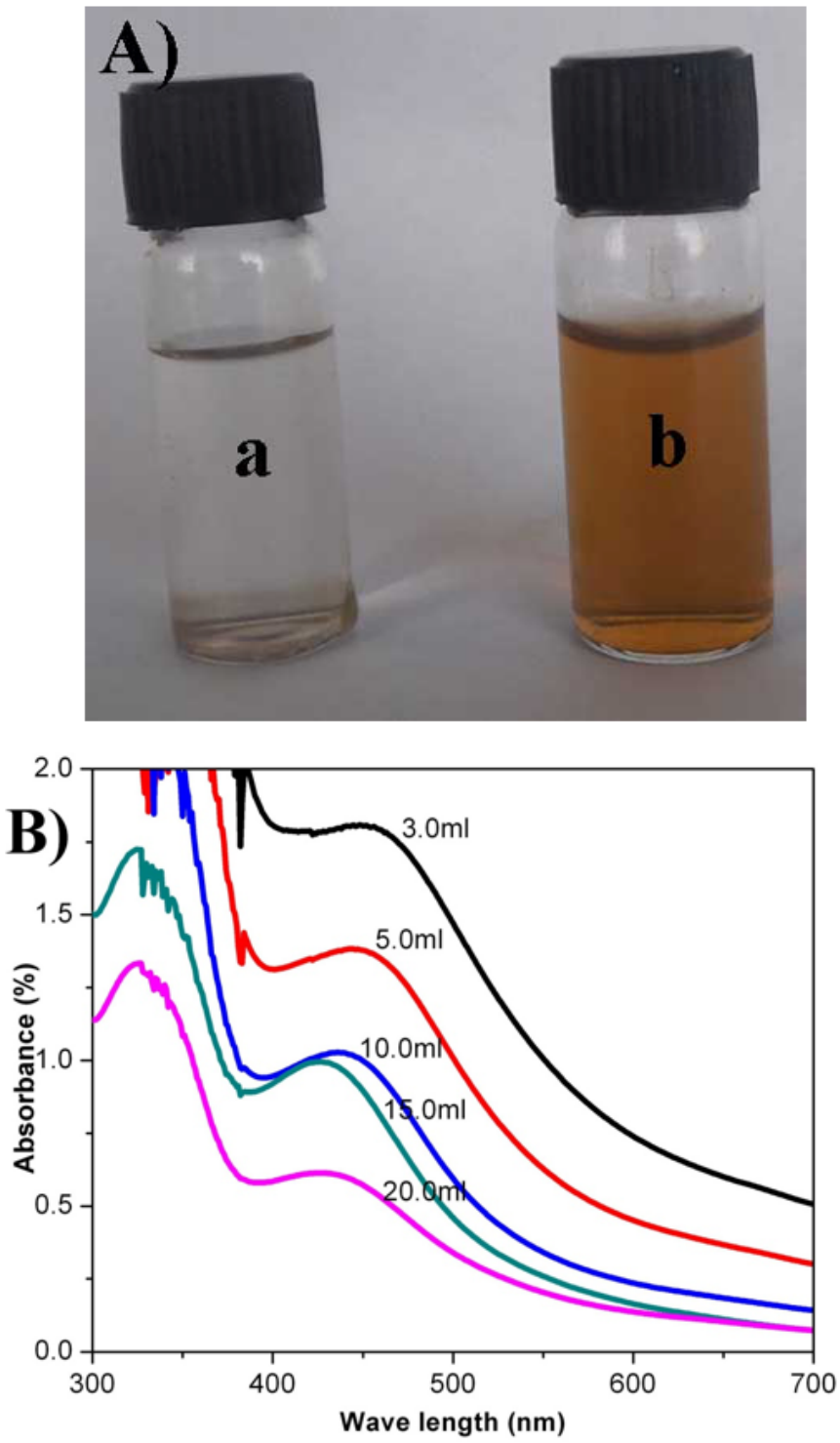


Figure 1

Biogenic Synthesis of Ag NPs from silver nitrate using *Millingtonia hortensis* L., leaf extract: A) Photo picture of the bottle solution from silver nitrate (1 mM) before (a) and after 10 min (b) and B) UV-Vis spectra of different concentrations of leaf extract and constant volume of silver nitrate.

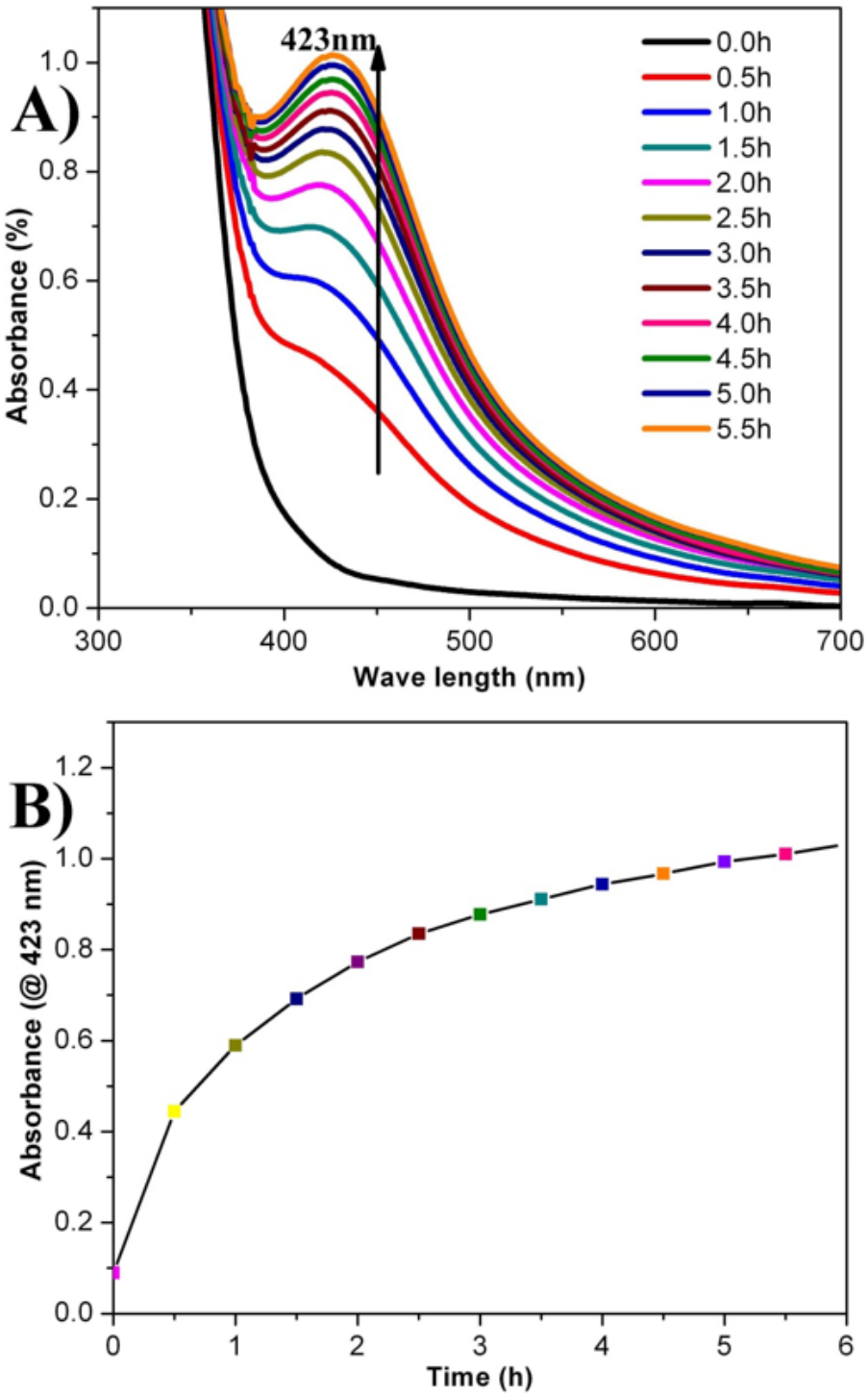


Figure 2

UV-Vis spectra of Biogenic Synthesis of Ag NPs from silver nitrate using *Millingtonia hortensis* L., leaf extract; A) Different time intervals; and B) Plot for Absorbance@423nm Vs Time intervals for the formation of Ag NPs.

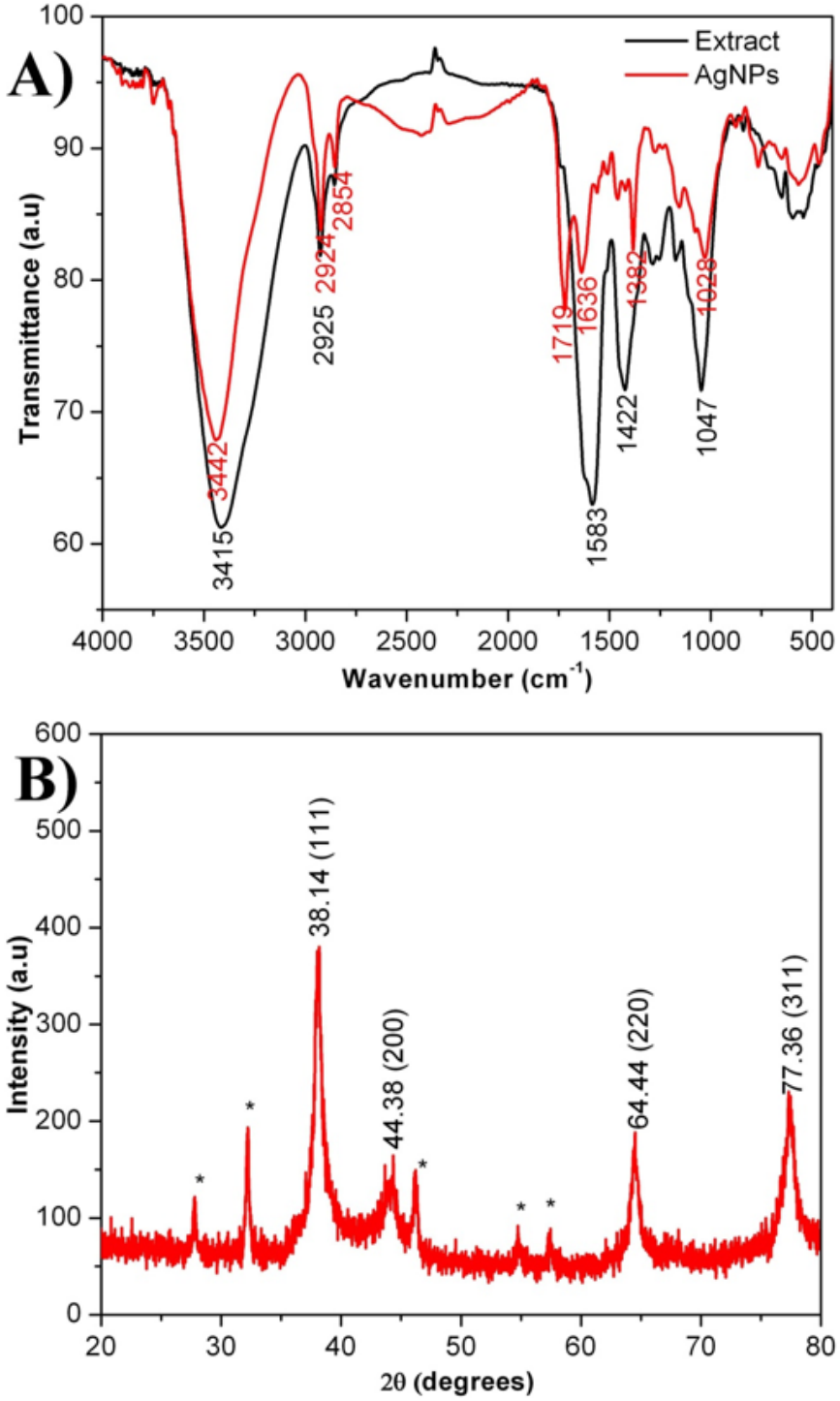


Figure 3

Biogenic Synthesis of Ag NPs from silver nitrate using *Millingtonia hortensis* L., leaf extract; A) FT-IR spectrum; and B) XRD spectrum.

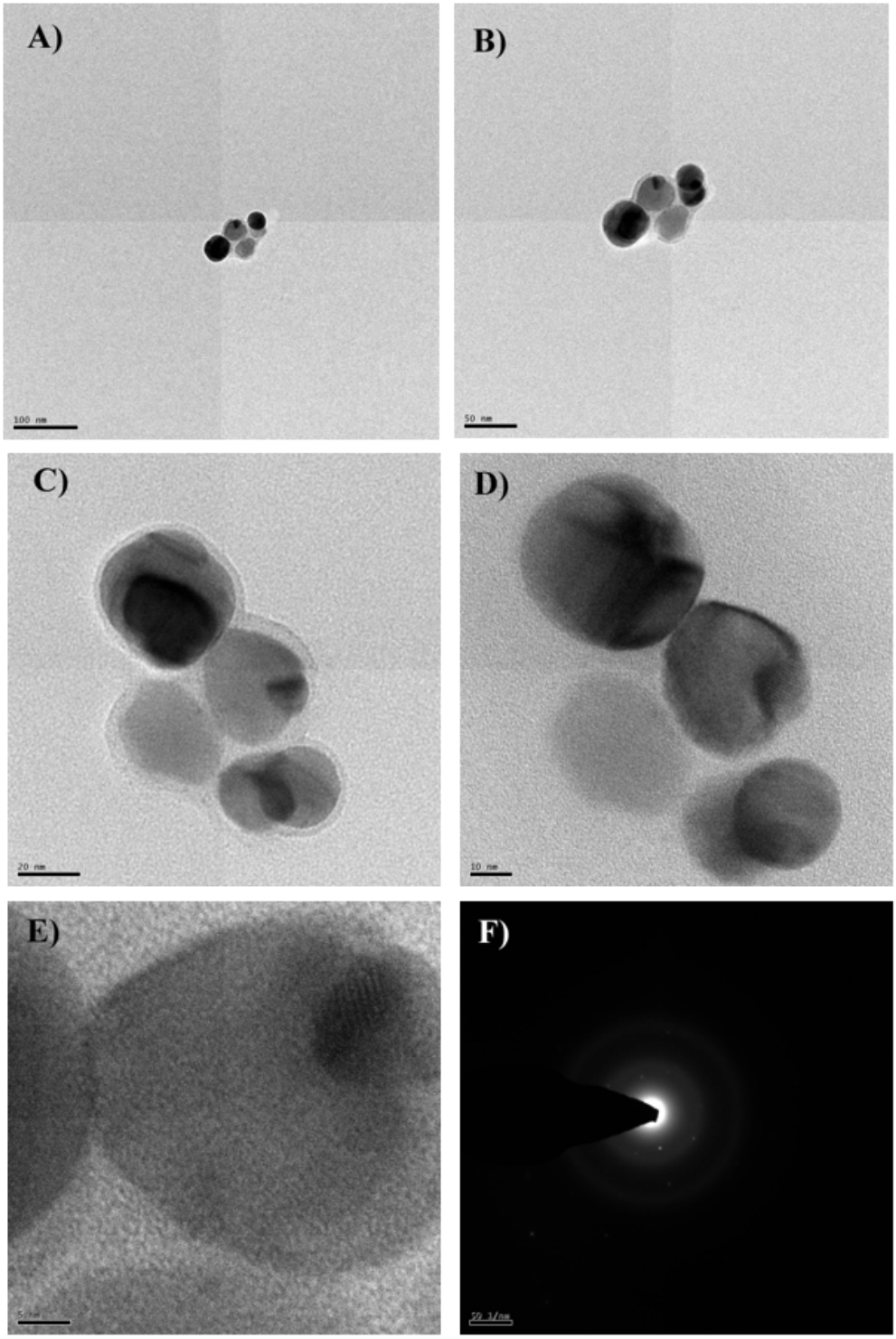


Figure 4

HRTEM images of Ag NPs: A) & B) Low magnetic images; C), D) & E) High magnetic images; and F) SAED pattern.

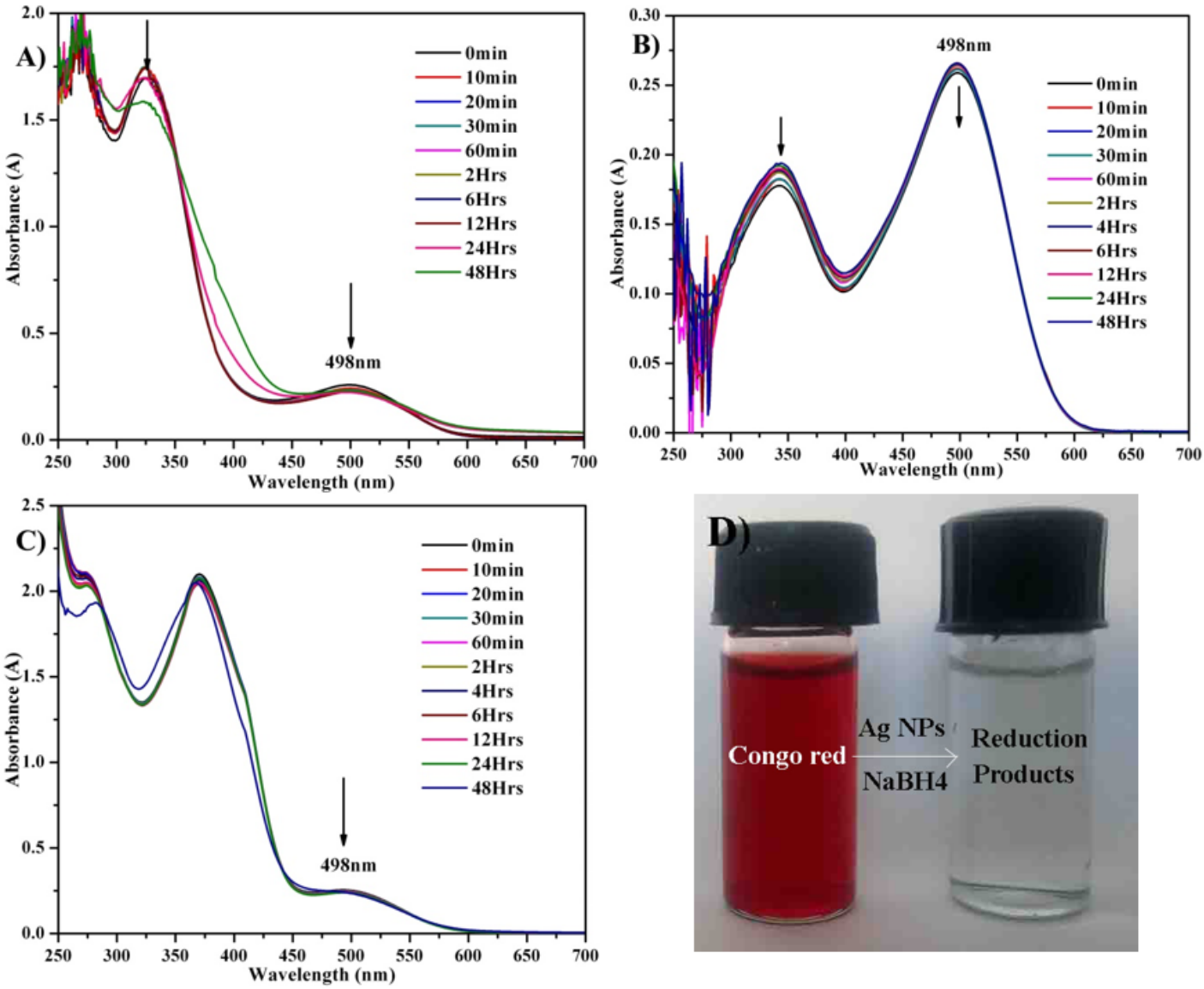


Figure 5

Catalytic reduction of Congo red using Ag NPs in the presence of $NaBH_4$: A) Congo red and extract; B) Congo red and $NaBH_4$; C) Congo red, extract $NaBH_4$; D) Colour change the reaction.

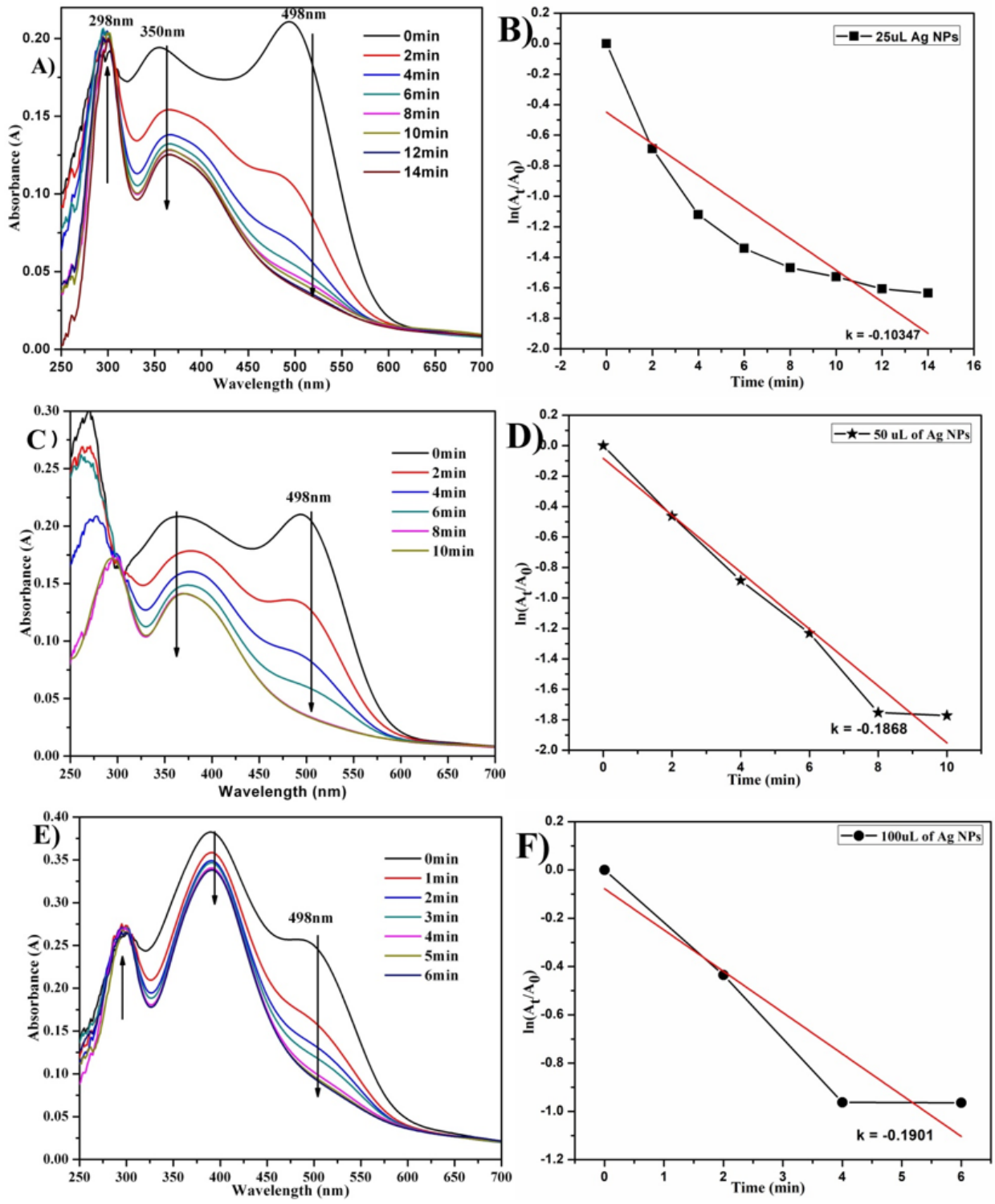


Figure 6

A) Congo red, 25µL Ag NPs and $NaBH_4$; B) kinetic plots of ln(*At*/*A*0) versus time; C) Congo red, 50µL Ag NPs and $NaBH_4$; D) kinetic plots of ln(*At*/*A*0) versus time; E) Congo red, 100µL Ag NPs and $NaBH_4$; and F) kinetic plots of ln(*At*/*A*0) versus time.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- GA.png
- Scheme1.png