

A Benign Approach for Synthesis of Silver Nanoparticles and Their Application in Treatment of Organic Pollutant

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Abstract A facile fabrication of silver nanoparticles was carried out using tannic acid in the presence of sodium hydroxide in aqueous medium. This method of preparation is completely a green approach; free from harsh chemicals, only environmental benign solvents and nontoxic chemicals were utilized. The fabricated particles were characterized using various techniques including TEM, SAED, UV–visible spectroscopy, IR, XRD, and TGA. The estimated size of the prepared particles is of the range 7–15 nm with spherical shape exhibiting a prominent surface plasmon resonance band at 412.7 nm. The ensuing nanoscaled silver particles play a significant role in treatment of organic pollutants such as chlorpyrifos and methylene blue. Degradation of chlorpyrifos in the presence of silver nanoparticles was monitored successfully. Moreover, role of silver nanoparticles as catalyst in the degradation of methylene blue in the presence of sodium borohydride has been demonstrated in this work. The degradation reaction followed first-order kinetic, and the catalysis rate constant is 0.149 min^{-1} which is about 75-fold times than that of uncatalyzed reaction.

Keywords Tannic acid · Silver nanoparticle · Chlorpyrifos · Methylene blue · Degradation

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1 Introduction

Even though there is a wide spectrum of techniques for the generation of metal nanoparticles (NPs), interest in green routes for the preparation of nanomaterials is flourishing rapidly owing to environmental concern. Green synthesis is eco-friendly, less sophisticated, ease to scale up, and cost-effective and consume less amount of energy, chemicals, times [1], etc. On the other hand, chemical and physical methods of synthesis, generally, involved toxic solvents, capping agents, use of high temperature, etc. Utilization of environmental benign materials such as plants (leaves, stem, roots, etc.) extract, enzymes, micro-organisms, amino acids, and vitamins for the synthesis of NPs has various environment-friendly benefits. Tannic acid is a commercial form of tannin, a polymer of gallic acid molecules and glucose, having molecular formula $C_{72}H_{52}O_{46}$. This compound is widely distributed in species throughout the plant kingdom (gymnosperms as well as angiosperms) [2]. And it is polyphenolic in nature along with other suitable groups to form strong complexes with various macromolecules. Tannic acid has the potential to serve as reducing as well as capping agent in tailoring metallic NPs.

NPs play very important role in the area of degradation of organic pollutants because of its unique properties like large surface-to-volume ratio, small sizes which enable them to attach onto solid surface/matrices for the treatment of polluted water, waste water, etc. The synthetic pesticides and insecticides are like a boon to farmers because of ease availability, low cost, simplicity in application, effectiveness, and economic returns. Whatever progress that is made in the field of agriculture with the use of pesticides and insecticides has cost lots of environmental contaminations. Chlorpyrifos (CP) [O, O-Diethyl-O-(3,5,6-trichloro-2-pyridyl) phosphorothioate] is an organophosphate insecticide widely used in

different parts of the world. It contaminates soil and water by entering fresh water and saltwater ecosystem as spray drift [3]. About 24 km from the place of application of CP, the effects of CP can be sensed, and it was also reported that exposed to this, insecticide causes serious harm to human like headache, nausea, muscle twitching, convulsions, respiratory tract, cardiovascular system, and human birth defects, affects the male reproductive system, and in extreme case even leads to death [4–6]. When CP is oxidized by various oxidizing agents—ozone, dinitrogen tetroxide, peracid, chlorine, etc., S atom is replaced by oxygen in P=S (thiophosphoryl bond), resulting in formation of CP oxon. This CP oxon is more toxic than CP as it inhibits acetylcholinesterase (an enzyme for proper functioning of nervous system). CP interfered in the functioning of cholinesterase, an enzyme which plays an important role in the functioning of nervous system of both human and insects [7,8]. Besides this insecticide/pesticide, dyes are also one of the major organic pollutants which are released effluently and freely in the environment, thereby causing serious environmental and health problems. Methylene blue (MB) is a monoamine oxidase inhibitor; this dye causes hypertension, precordial pain, dizziness, mental confusion, headache, fever, staining of skin, nausea, vomiting, abdominal pain, fecal discoloration, bladder irritation, discoloration of urine, mutagenic to human [9–11], etc. So the degradation/elimination of such dyes, pesticides, and insecticides from the water system/environment is of serious concern now due to their chronic toxicity. Many works have been done in this field; one of the most effective and commonly used techniques is photocatalytic degradation in the presence of catalyst particles. Because of the properties of reusability and self-generating, photocatalysts have major advantages in comparison with other treatment materials [12].

In this work, we have tailored highly stable spherical Ag NPs in aqueous medium at alkaline condition employing tannic acid at room temperature. The synthesis methodology is completely a green aqueous approach with high atom economy. The synthesized nanoscopic Ag particles exhibit significant catalytic performance in the treatment of CP and MB which were used as model organic pollutants. The mechanism for the degradation of CP and MB is vividly explained.

2 Materials and Experimental Procedure

2.1 Materials

Silver nitrate (AgNO_3), tannic acid (TA) ($\text{C}_{76}\text{H}_{52}\text{O}_{46}$, $M_w = 1701$), sodium hydroxide, sodium borohydride (NaBH_4), and methylene blue were all purchased from Sigma-Aldrich, India. Chlorpyrifos of Cheminova India Limited was obtained from a local store. The chemicals were of AR grade and used

as such without any further purification. Double-distilled water (DDW) was employed for the preparation of solution.

2.2 Fabrication of Ag NPs

For the synthesis of Ag NPs, 2 gm of AgNO_3 was dissolved in 100 ml DDW, and to this solution, 250 ml of freshly prepared 10^{-3} M solution of tannic acid was added followed by 10 ml of 0.2 M NaOH. The above mixture of the solutions was stirred for one hour at room temperature (25°C) with the help of a Tarsons magnetic stirrer. This reaction mixture was kept undisturbed for three hours. To extract the as-synthesized NPs, the reaction mixture was centrifuged and washed twice with ethanol. Later, the sample was dried at room temperature. Freshly prepared tannic acid solution and NaOH solution were used for the fabrication of Ag NPs.

2.3 Kinetic Study for the Degradation of Chlorpyrifos (CP)

Degradation of chlorpyrifos was monitored by using UV–Vis spectroscopy at a wavelength of 296 nm, a characteristic peak of CP, at room temperature. To 100 μl of 50 ppm chlorpyrifos (solution prepared in 1:1 ratio of water and methanol), 100 μl of freshly prepared aqueous dispersion of Ag NPs was added in a 3.5-ml capacity quartz cuvette. Total volume of the reaction mixture was made up to 3 ml by adding DDW, and this reaction mixture was studied using Perkin Elmer UV–Vis spectrophotometer.

2.4 Kinetic Degradation of Methylene Blue (MB)

Degradation of MB was assayed by adding 100 μl of (2%) Ag NPs to 100 μl of 10^{-4} M MB solution followed by 50 μl of 0.1 M NaBH_4 in a 3.5-ml capacity cuvette at room temperature, 25°C , by using UV–Vis spectroscopy. The reaction was analyzed by noting the disappearance in the absorbance of MB at 664.5 nm, a prominent characteristic peak of the dye. As above, the total volume was made up to 3 ml by adding DDW. To understand the role of Ag NPs in the degradation process, same kinetic study for the degradation process was carried out in the absence of NaBH_4 . 50 μl of DDW was added instead of NaBH_4 to maintain the volume of reaction mixture at 3 ml, and this uncatalyzed reaction was studied under irradiation of UV–Vis light.

2.5 Characterizations of Silver Nanoparticles

2.5.1 Ultraviolet Visible Spectroscopy

All UV–Vis spectra were recorded on PerkinElmer UV–Vis spectrophotometer fitted with a constant-temperature cell holder. The temperature of the cell holder was maintained

constant by circulating water around it by a water circulator from Ferrari fountain pump instrument. The absorption spectra of the prepared NPs were recorded by taking the aqueous dispersion of the NPs and scanned in the range of 200–800 nm.

2.5.2 Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED)

TEM and SAED pictures of the particles were taken with TECNAIG²-30 U TWIN transmission electron microscope operating at 300 KV. After preparation, the particles were centrifuged at 9000 rpm for 10 min, washed with DDW for three times, and dispersed in it by sonication for 4–5 min. A drop of dilute aqueous dispersion was put on the copper grid, and the grid was dried under ambient conditions. After complete drying of the grids, TEM and SAED patterns of the particle were taken.

2.5.3 Fourier Transformed Infrared (FT-IR) Spectroscopy

The particles were washed thoroughly, collected, and then dispersed in DDW after fabrication. Liquid FT-IR spectra of tannic acid and particles were recorded on IR-PerkinElmer, FT-IR system, Spectrum BX FT-IR in the range 400 to 4000 cm⁻¹. The transmission of the solvent, water, was finally normalized from the readings of the samples recorded.

2.5.4 X-Ray Diffraction (XRD)

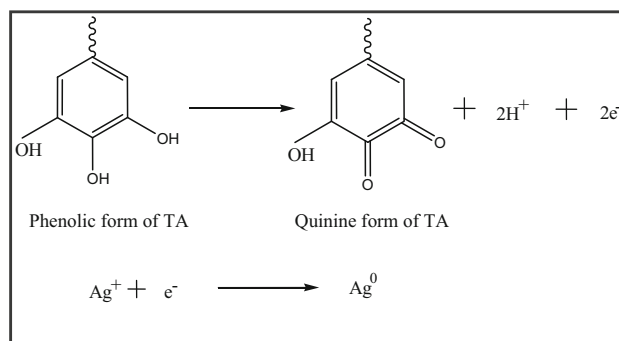
X-ray diffraction of sample was taken in a Phillip X'PERT XRD instrument, and dried powder sample was used to carry out diffraction experiment. The sample was scanned in the 2θ range of 30°–70°.

2.5.5 Thermo-Gravimetric Analysis (TGA)

The sample was monitored with PerkinElmer DTA/TGA/DSC instrument by taking an adequate amount of samples, which were dried at room temperature, on the sample holder of the instrument in nitrogen atmosphere. The change in weight of the subjected materials with respect to temperature in the range 0–1000°C was monitored.

3 Results and Discussion

Tannic acid, a polyphenolic phytochemical, serves a dual role as reducing and capping agent in this green protocol of synthesis of Ag NPs [13,14]. Tannic acid has antioxidant and chelating properties for several inorganic cations. Mechanism for the formation of Ag NPs using tannic acid can be explained as given in Scheme 1 [15,16]. It has 25 phe-



Scheme 1 Mechanism for the formation of Ag NPs

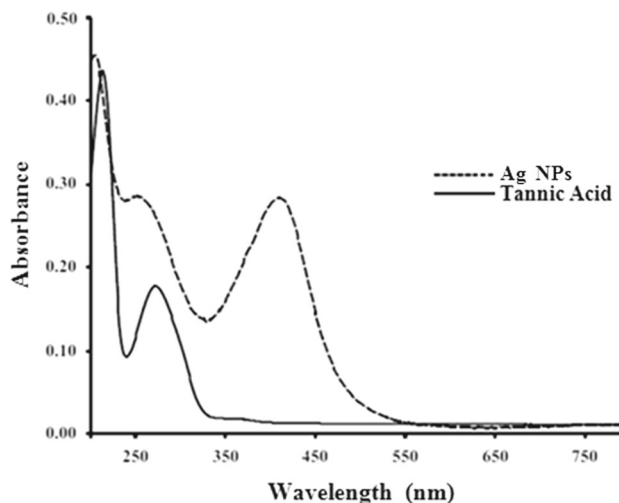


Fig. 1 UV-Vis spectra of Tannic acid and Ag NPs

nolic OH groups, but only 10 pairs of o-dihydroxyphenyl groups have the capacity to take part in the redox reactions to form quinines and donate electrons due to the chelating action of the adjacent hydroxyl groups and constraints on carbon valency [17–20]. Tannic acid is a weak acid; it partially hydrolyzes under mild acidic/basic conditions into glucose and gallic acid units. However, gallic acid is a good reducing agent but a weak stabilizing agent at alkaline pH medium, while glucose is a weak reducing agent and good stabilizing agent at alkaline medium. In alkaline pH medium of synthesis, gallic acid rapidly reduces AgNO₃ to Ag NPs and glucose stabilized it giving a large number of spherical Ag NPs. Many researchers have also reported that in acidic pH, rate of reduction in AgNO₃ is slow and this environment results in the direction-dependent growth, i.e., anisotropic growth of nanorod/nanowire [1,18,21]. The generated nanoscaled Ag particles are very stable in aqueous medium, and they remain without settling down more than 8 months, indicating that tannic acid performed as an efficient capping agent. These particles displayed distinct surface plasmon resonance bands at 412.7 nm as shown in Fig. 1. Surface morphology of the prepared Ag NPs was studied using TEM images. As

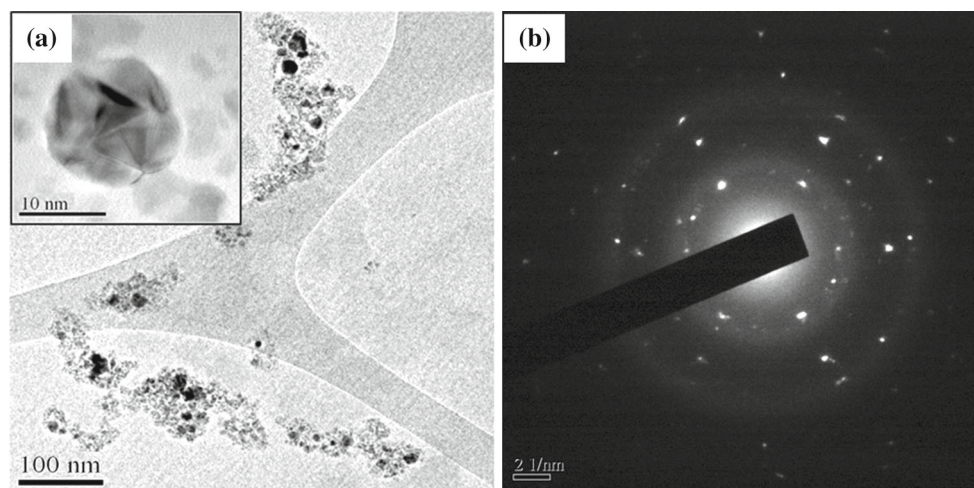


Fig. 2 **a** TEM image and **b** SAED pattern of Ag NPs; *inset* HRTEM images of the particles

such prepared NPs have spherical shape with size in the range of 7–15 nm. Crystalline nature of the particle is clearly predicted by the SAED pattern shown in Fig. 2b. The pattern presents well-dotted ring structure, indicating the crystalline behavior of the tailored Ag NPs. Additionally, FT-IR spectra of tannic acid and Ag NPs are provided in Fig. 3a, b, respectively. In IR spectra of tannic acid, band at 3400 cm^{-1} is of OH stretching of phenol group and methylol group. The absorption bands at 1732 and 1718 cm^{-1} are attributed to C=O stretching frequency of ketone and COOH. In IR of Ag NPs (Fig. 3b), stretching in range of $1500\text{--}1700\text{ cm}^{-1}$ is broaden and merged together, while band at 3400 cm^{-1} is missing, indicating that most of OH groups of tannic acid take part in reaction with metal ions [22]. IR bands at 1450 , 1323 , and 1197 cm^{-1} correspond to aromatic C=C and phenolic C–O stretching vibrations. From this, it can be concluded that majority of tannic acid is present in its oxidized form [23]. IR spectrum clearly indicates that tannic acid acts as reducing and capping agent providing stability to Ag NPs.

Crystalline behavior of the fabricated nanoscopic Ag particles is further supplemented by XRD pattern given in Fig. 4. Peak at 38.7° is the characteristic peak of Ag NPs, which indicates the presence of silver. The XRD peaks at 2θ degrees of 38.7° , 47.5° , and 65.8° can be attributed to (111), (200), and (220) crystalline planes of face-centered cubic (fcc) structure of metallic silver, respectively [14]. Moreover, size of the Ag particles calculated from XRD data using Scherrer equation (Eq. 1) is 7.2 nm which is almost agreeable with the finding obtained from TEM images.

$$d = 0.9\lambda / B \cos \Theta_B \quad (1)$$

where d is the mean size of the ordered crystalline, λ is the wavelength of the X-ray, B is the full width at half maximum in radian, and Θ_B is the half of Bragg angle.

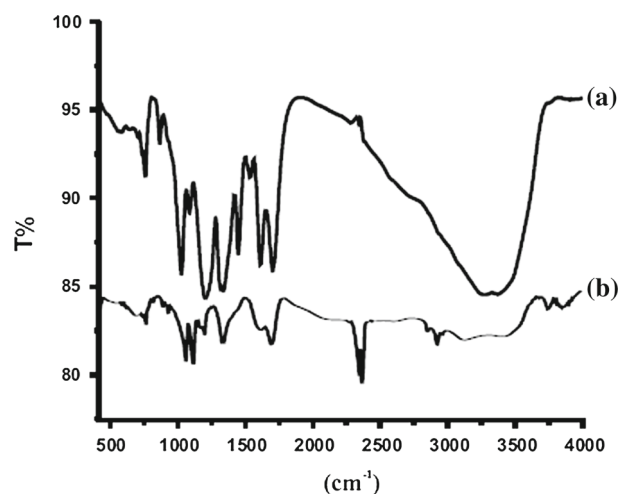


Fig. 3 FT-IR spectra of **a** tannic acid and **b** Ag NPs

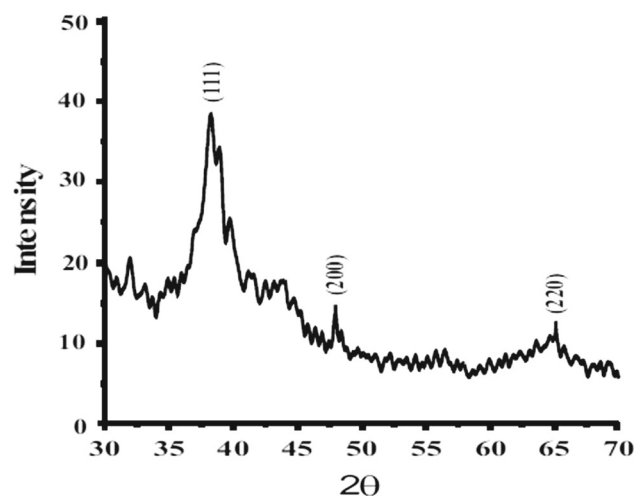


Fig. 4 XRD pattern of Ag NPs

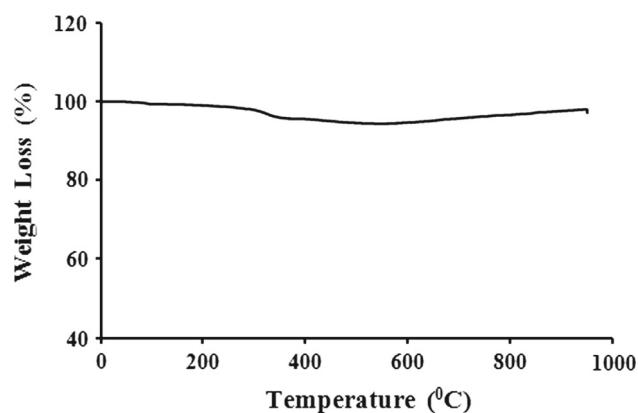


Fig. 5 TGA curve of Ag NPs

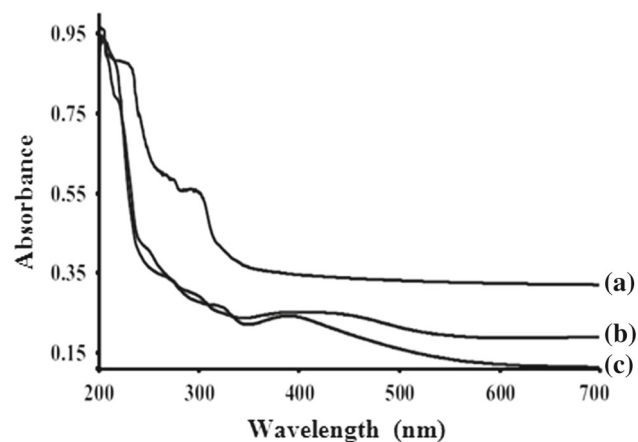


Fig. 6 Degradation of CP by Ag NPs **a** absorbance of CP, **b** after 24 h and **c** after 43 h

Further, Fig. 5 highlights TGA data of the tailored Ag NPs. The thermogram shows a slight decrease in weight of the particle even at very high temperature. Only 2.1% of weight loss occurs till 950°C, indicating the stability of the particles. This reduction in the weight of the particles may be attributed to the loss of adsorbed water molecules.

The fabricated Ag NPs was utilized in the degradation of insecticide chlorpyrifos studied using UV–Vis spectroscopy. 50 ppm CP shows two peaks at 226.72 and 296 nm as shown in Fig. 6a, which might be due to the substitution in pyridine ring [5, 24]. As shown in Fig. 6b, the absorbance peak of CP at 296 nm continuously decreases with addition of Ag NPs. After 24 h, tremendous decrease in the absorbance of CP can be seen. A sharp peak at 320 nm was obtained after observing for another 19 h (as shown in Fig. 6c). This peak might be of the by-product formed in the process of degradation of CP.

FT-IR spectra of insecticide (CP) and insecticide treated with Ag NPs (Ag-CP) are displayed in Fig. 7a, b, respectively. FT-IR features of CP (Fig. 7a) at 740, 1090, and 1310 cm^{-1} can be attributed to stretching of C–Cl, P=S, and C–O, respectively. Doublet at 2860 cm^{-1} is of symmetric and antisymmetric stretching of the methylene groups [24–26].

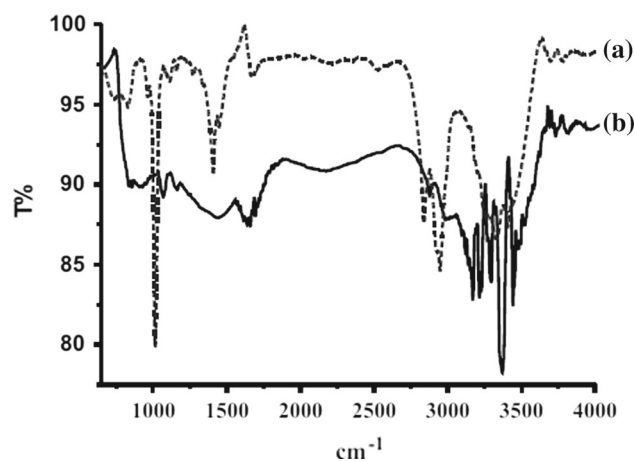
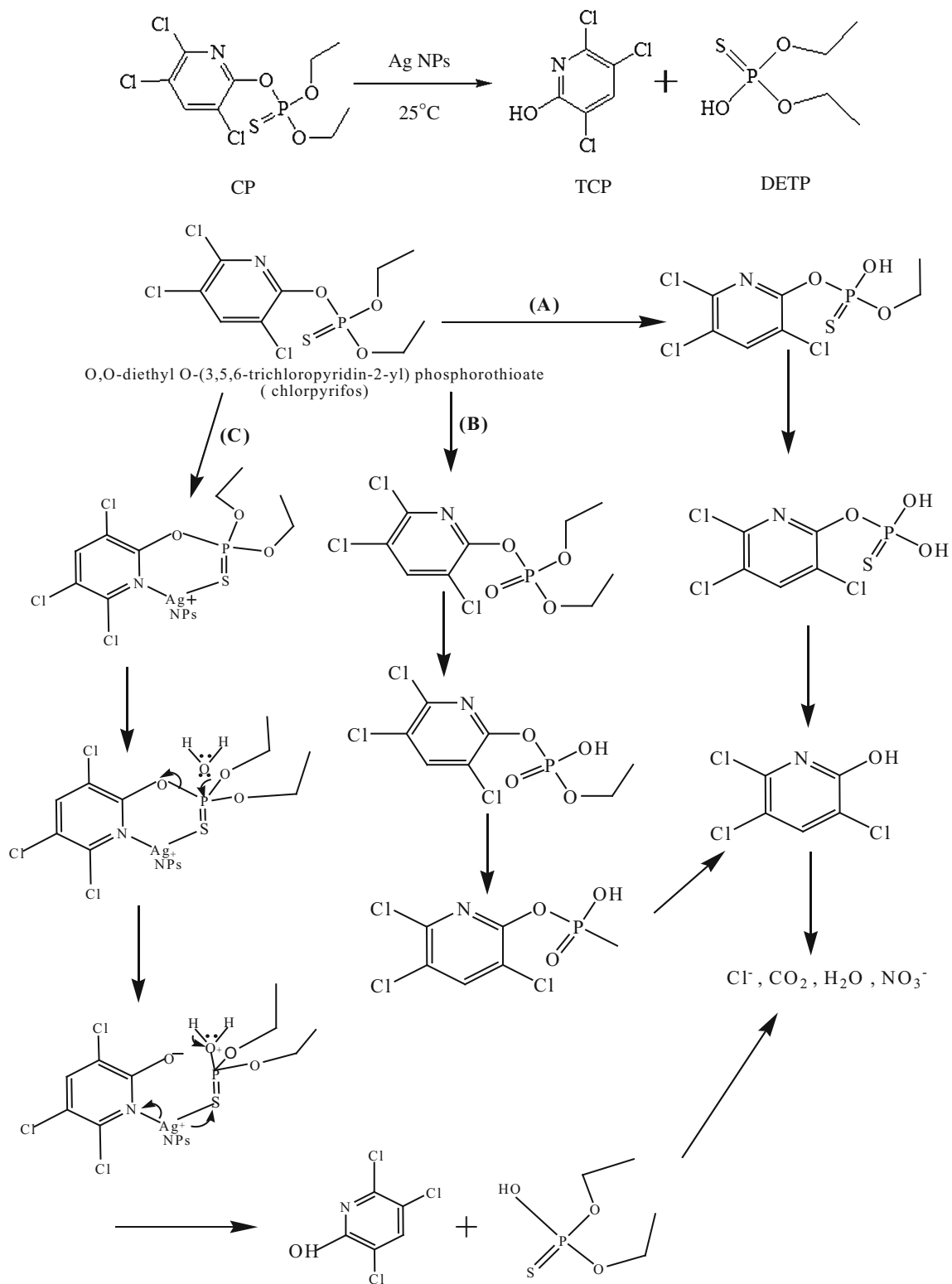


Fig. 7 FT-IR spectra of **a** CP and **b** CP treated with Ag NPs

After treating with Ag NPs, significant change in IR spectra of CP was observed (given in Fig. 7b). IR bands at 1650 and 1529 cm^{-1} were broader in case of Ag-CP as compared to CP spectra, indicating the formation of different carbonyl group [27]. Substantial shifts of $\nu_{\text{C-Cl}}$ and $\nu_{\text{P=S}}$ were observed in the IR spectra of Ag-CP, which clearly shows that halogen and sulfur atoms of CP strongly interact with Ag NPs resulting in adsorption of CP on NPs surface. From these results, it can be concluded that CP has been degraded through the formation of surface complex with Ag NPs. Possible mechanisms/pathways for the degradation of CP were reported earlier by Bootharaju et al. [7] and Vinod et al. [25] and are stated clearly in Scheme 2. Ag NPs formed surface complex by interacting/bonding with S and N groups of CP as they have lone pair of electrons. Due to the electron polarization in the surface complex, the side chain link to the pyridine ring may get weakened. The attack of water (nucleophile) at this electrophilic phosphorus site results in cleavage of P–O bond. Nitrogen withdraw electrons from a coordination bond (to Ag) to give trichloropyridinol (TCP), while diethyl thiophosphate (DEPT) might have formed after withdrawing sulfur electrons from the coordination bond.

MB is a heterocyclic aromatic dye commonly used in biology and chemistry. MB is used as role model dye for the degradation by Ag NPs. MB exhibits a prominent characteristic peak at around 664.5 nm in visible range. Degradation rate of MB in the absence of Ag nanocatalyst is very slow as indicated in Fig. 8a. The introduction of Ag NPs in the reaction mixture tremendously enhances the reaction kinetics. But with the addition of Ag NPs, the prominent peak of MB gets shifted to 680.9 nm which may be due to the change in solvent polarity [28]. Absorbance peak of MB continuously decreases, indicating the degradation of MB, and within 6 min MB is completely degraded as shown in Fig. 8b. This result clearly signifies the role of Ag NPs as catalyst in the degradation of MB. Reason of sudden decrease in absorbance of MB with addition of Ag NPs is that NaBH_4 reacts with



Scheme 2 Possible pathways for the degradation of CP by Ag NPs

metal to give H on the metal surface and transfer a surface-hydrogen species to metal surface, resulting in the increase in rate of reduction [29].



Absorbance is directly proportional to concentration, so degradation efficiency can be calculated as [30,31].

$$R = (C_0 - C)/C_0 \times 100\% = (A_0 - A)/A_0 \times 100\%$$

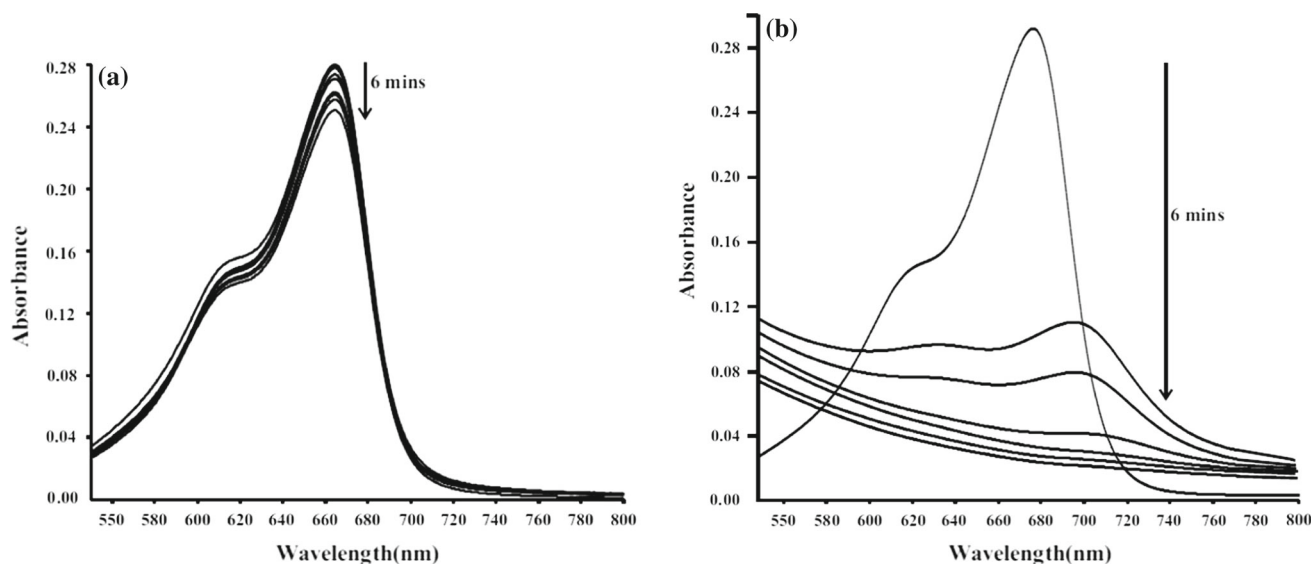


Fig. 8 Degradation of MB **a** uncatalyzed reaction and **b** catalyzed reaction

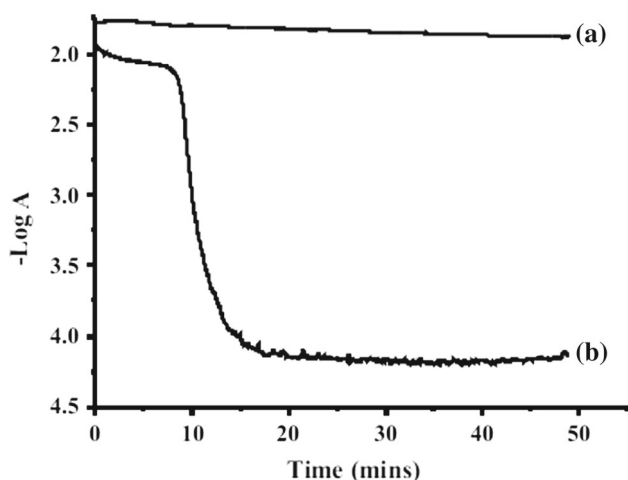


Fig. 9 Plot of $\log A$ versus time for the degradation of MB **a** uncatalyzed reaction and **b** catalyzed reaction

C_0 = initial concentration, A_0 = initial absorbance, C = final concentration, and A = final absorbance

Degradation efficiency of NaBH_4 in the absence of Ag NPs is 11 %, and it is increased to 96 % in addition of Ag NPs. Kinetic study for degradation of MB in the absence and presence of Ag NPs has been studied and is given in Fig. 9a, b, respectively. The plot of $\log A$ versus time can be approximated as straight line, implying that the degradation reaction of MB followed first-order kinetic. The rate of reaction for degradation of MB in the absence and presence of Ag NPs is 2×10^{-3} and 0.149 min^{-1} , respectively. The reaction rate for the catalyzed reaction is about 75-fold times than that of the uncatalyzed reaction. The high reaction rate in the presence of Ag NPs is accounted for their large surface-to-volume ratio, facilitating more active sites for the reactants molecules to interact and undergo the reaction. Thus, our report paves

a simple and facile route for the synthesis of highly stable spherical Ag NPs that possess excellent catalytic potential in the treatment of organic pollutants.

4 Conclusions

Method employed for the synthesis of Ag NPs is an eco-friendly approach. Water was utilized as environmental benign solvent, and Ag NPs prepared by employing tannic acid as reducing and capping agent in alkaline medium are very stable, i.e., for more than eight months. The generated nanodimensional particles have spherical morphology with size ranging from 7 to 15 nm and are well crystalline in nature. Such prepared particles have efficient catalytic properties, and it plays an eminent role in degradation of insecticide CP and MB dye at room temperature. UV–Vis irradiation in association of Ag NPs completely degraded CP within 43 h and MB in 6 min in the presence of NaBH_4 . Such synthesis technique can be extended in rational designing of other metallic and metallic oxide NPs that may find their importance in various types of applications.

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References

- Devendra, J.; Hemant, K.D.; Sumita, K.; Kothari, S.L.: Synthesis of plant mediated silver nanoparticles using papaya fruit extract and evaluation of their anti-microbial activities. *Dig. J. Nanomater. Biostruct.* **4**, 723 (2009)

- Simon, M.: The systematic distribution of tannins in the leaves of angiosperms: a tool for ecological studies. *Biochem. Syst. Ecol.* **21**, 833 (1993)
- Sulaiman, G.M.: Kinetic studies of catalytic photodegradation of chlorpyrifos insecticide in various natural waters. *Arab. J. Chem.* **3**, 127 (2010)
- Anoop, V.; Poonam, D.D.: Photocatalytic degradability of insecticide chlorpyrifos over UV irradiated titanium dioxide in aqueous phase. *Int. J. Environ. Sci.* **3**, 743 (2013)
- Xu, G.; Zheng, W.; Li, Y.; Wang, S.; Zhang, J.; Yan, Y.: Biodegradation of chlorpyrifos and 3,5,6-trichloro-2-pyridinol by a newly isolated *Paracoccus* sp. strain TRP. *Int. Biodeterior. Biodegrad.* **62**, 51 (2008)
- Qin, Z.; Xiaoyan, S.; Rui, G.; Qingzhu, Z.; Wenxing, W.: Mechanism study on OH-initiated atmospheric degradation of the organophosphorus pesticide chlorpyrifos. *J. Mol. Struct. Theochem.* **952**, 8 (2010)
- Bootharaju, M.S.; Pradeep, T.: Understanding the degradation pathway of pesticide, chlorpyrifos by noble metal nanoparticles. *Langmuir* **28**, 2671 (2012)
- Hossain, M.S.; Fakhruddin, A.N.M.; Chowdhury, M.A.Z.; Khorshed, A.M.: Degradation of chlorpyrifos, an organophosphorus insecticide in aqueous solution with gamma irradiation and natural sunlight. *J. Environ. Chem. Eng.* **1**, 270 (2013)
- Ramsay, R.R.; Dunford, C.; Gillman, C.K.: Methylene blue and serotonin toxicity: inhibition of monoamine oxidase A confirms a theoretical prediction. *J. Pharmacol.* **152**, 946 (2007)
- Mokhlesi, B.; Leikin, J.B.; Murray, P.: Adult toxicology in critical care: part 2: specific poisonings. *Chest* **123**, 897 (2003)
- Harvey, J.W.; Keitt, A.S.: Studies of the efficacy and potential hazards of M.B. therapy in aniline induced methaemoglobinaemia. *Br. J. Haematol.* **54**, 29 (1983)
- Mehmet, L.Y.; Tanju, E.; Necip, A.: A novel efficient photocatalyst based on TiO₂ nanoparticles involved boron enrichment waste for photocatalytic degradation of atrazine. *Chem. Eng. J.* **250**, 288 (2015)
- Tufail, A.: Reviewing the tannic acid mediated synthesis of metal nanoparticles. *J. Nanotechnol.* **2014**, 1 (2014)
- Zao, Y.; Xibo, L.; Xibin, X.; Binchi, L.; Jiangshan, L.; Weidong, W.; Yougen, Y.; Youngjian, T.: Green, effective chemical route for the synthesis of silver nanoplates in tannic acid aqueous solution. *Colloids Surf. A Physicochem. Eng. Asp.* **392**, 131 (2011)
- Anamika, D.; Swapan, K.D.: Tannic acid assisted one step synthesis route for the stable colloid dispersion of nickel nanostructures. *Appl. Surf. Sci.* **257**, 6889 (2011)
- Wei, D.W.; Qian, W.P.: Facile synthesis of Ag and Au nanoparticles utilizing chitosan as a mediator agent. *Colloids Surf. B Biointerfaces* **2**, 136 (2008)
- Bulut, E.; Ozacar, M.: Rapid facile synthesis of silver nanostructure using hydrolysable tannin. *Ind. Eng. Chem. Res.* **48**, 5686 (2009)
- Yoosaf, K.; Ipe, B.I.; Suresh, C.H.; Thomas, K.G.: In situ synthesis of metal nanoparticles and selective naked-eye detection of lead ions from aqueous media. *J. Phys. Chem. C* **111**, 12839 (2007)
- McDonald, M.; Mila, I.; Scalbert, A.: Precipitation of metal ions by plant polyphenols: optimal conditions and origin of precipitation. *J. Agric. Food Chem.* **449**, 599 (1996)
- Hagerman, A.E.; Riedl, K.M.; Jones, G.A.; Sovik, K.N.; Ritchard, N.T.; Hartzfeld, P.W.; Rielchel, T.L.: High molecular weight plant polyphenolics (tannins) as biological antioxidants. *J. Agric. Food Chem.* **46**, 1887 (1998)
- Sivaraman, S.K.; Elango, I.; Kumar, S.; Santhanam, V.: A green protocol for room temperature synthesis of silver nanoparticles in seconds. *Curr. Sci.* **97**, 1055 (2009)
- Tian, X.L.; Li, J.; Pan, S.L.: Facile synthesis of single crystal silver nanowires through a tannin-reduction process. *J. Nanopart. Res.* **11**, 1839 (2009)
- Aelenei, N.; Popa, M.I.; Novac, O.; Lisa, G.; Balaita, L.: Tannic acid incorporation in chitosan-based microparticles and in vitro controlled release. *J. Mater. Sci. Mater. Med.* **20**, 1095 (2009)
- Sreekumaran, N.A.; Pradeep, T.: Extraction of chlorpyrifos and malathion from water by metal nanoparticles. *J. Nanosci. Nanotechnol.* **7**, 1 (2007)
- Vinod, K.G.; Tanju, E.; Necip, A.; Mehmet, L.Y.; Hassan, K.M.: CoFe₂O₄@TiO₂ decorated reduced graphene oxide nanocomposite for photocatalytic degradation of chlorpyrifos. *J. Mol. Liq.* **208**, 122 (2015)
- Quintas, G.; Garrigues, S.; Guardia, M.D.L.: FT-Raman spectrometry determination of malathion in pesticide formulations. *Talanta* **63**, 345 (2003)
- Haidekker, M.A.; Brady, T.P.; Lichlyter, D.; Theodorakis, E.A.: Effects of solvent polarity and solvent viscosity on the fluorescent properties of molecular rotors and related probes. *Bioorg. Chem.* **33**, 415 (2005)
- Augustine, C.A.; Malay, C.: Degradation of pesticides chlorpyrifos, cypermethrin and chlorothalonil in aqueous solution by TiO₂ photocatalysis. *J. Environ. Manag.* **130**, 160 (2013)
- Tanyu, C.; Dacheng, Z.; Hexing, L.; Guohua, L.: Magnetically recoverable nanoparticles as efficient catalysts for organic transformations in aqueous medium. *Green Chem.* **16**, 3401 (2014)
- Wang, K.; Yu, L.; Yin, S.; Li, H.; Li, H.: Photocatalytic degradation of M.B on magnetically separable Fe₃O₄/Pc nano composite under visible irradiation. *Pure Appl. Chem.* **81**, 2327 (2009)
- Abdolahi, Y.; Abdullah, A.H.; Zainal, Z.; Yusof, N.A.: Photocatalytic degradation of p-Cresol by zinc oxide under UV irradiation. *Int. J. Mol. Sci.* **13**, 302 (2011)