Research Journal of Recent Sciences _____ ISSN 2277-2502
Vol. 3**(ISC-2013),** 185-191 **(2014)** *Res. J. Recent. Sci.*

Synthesis of Silver Nanoparticles by Microwave irradiation and investigation of their Catalytic activity

Siby Joseph[1] and Beena Mathew[2]
[1]Department of Chemistry, St. George's College, Aruvithura, Kottayam, Kerala, INDIA
[2]School of chemical sciences, Mahatma Gandhi University, Kottayam, Kerala, INDIA

Available online at: www.isca.in, www.isca.me
Received 3rd November 2013, revised 4th January 2014, accepted 9th March 2014

Abstract

In this study, silver nanoparticles (AgNPs) have been synthesized in aqueous medium by a simple, efficient and economic microwave assisted synthetic route using hexamine as the reducing agent and the biopolymer pectin as stabilizer. The synthesized AgNPs were characterized by UV-vis. spectroscopy, Energy dispersive X-ray (EDX), X-ray diffraction (XRD) and Transmission electron microscopy (TEM) techniques. TEM images suggest that the nanoparticles are of spherical shape with an average diameter of 18.84 nm. The reduction of 4-nitrophenol to 4-aminophenol by $NaBH_4$ in aqueous medium was selected as a model reaction to investigate the catalytic activity of AgNPs. The pectin stabilized silver nanoparticles (AgNP-pectin) were found to exhibit very good catalytic activity and the reaction followed pseudo-first order kinetics. The rate of reaction was found to increase with increasing temperature and the activation energy was found to be 47.3 kJ mol^{-1}.

Keywords: Microwave, silver nanoparticle, pectin, 4-nitrophenol, catalysis.

Introduction

Much interest has been focused in recent years on the synthesis and stabilization of metal nanoparticles because of their exceptional chemical and physical characteristics and their promising applications in the fields of chemistry, physics, biology and medicine[1]. Among these, silver nanoparticles have received more consideration due to their tremendous applications in the fields of catalysis, optics, antimicrobials and sensors[2-5]. Various methods have been reported for the synthesis of silver nanoparticles. The most common method is reduction of a silver salt using chemical reducing agents such as sodium borohydride, citrate and other organic reagents in presence of a suitable capping agent such as polymers, dendrimers, hydrogels etc[6-8]. The main advantage of chemical reduction method is the shorter reaction time. However, the reagents used in this method as reducing and stabilizing agents are highly toxic and creates vast environmental problems. Hence in environmental sustenance, there is a need to develop environmental friendly synthetic strategies to avoid the toxic chemicals in the synthesis protocols.

The green synthesis of silver nanoparticles is advantageous over other methods as it is cost effective and eco-friendly and thus can easily scaled up for large scale synthesis. Now a days, plant extracts, natural compounds and microorganisms are used for the green synthesis of silver nanoparticles[9-11]. One main shortcoming of biological green methods is the longer reaction time. Microwave assisted synthesis is considered to be a valuable alternative in this regard. Microwave assisted synthesis using 'green' chemicals is getting more attention in recent times because of the eco-friendly nature, short reaction time, low energy utilization and improved product yield. Microwave irradiation provides rapid and even heating of the reaction medium and thus offers uniform nucleation and growth conditions for nanoparticles. Many successful reports on microwave assisted synthesis of silver nanoparticles are available recently[12-16].

Aromatic nitro compounds are found to have toxic effect on various life forms. Among these, nitrophenols are regarded as one of the most widespread and versatile organic pollutant. These pollutants are chemically very stable and so traditional water treatment methods are usually ineffective in removing them from water. Therefore, developing an efficient method for their removal is of immense importance. Nanocatalysis is a fast developing area of research in which metal nanoparticles are used as catalysts for wide range chemical reactions. Several research groups have investigated the reduction of nitrophenols using a number of noble metal nanoparticles as catalysts[17-20].

In this work, we report a rapid facile method for the synthesis of silver nanoparticles in aqueous medium using microwave irradiation. Here, silver nanoparticles are generated using hexamine as the reducing agent and the biopolymer pectin as stabilizer. Hexamine is a non-toxic, low cost and easily available material which is widely used for the treatment of urinary tract infection. It also finds application in food industry as a preservative. Pectin is a naturally occurring linear polysaccharide that is finding increasing applications in pharmaceutical and biotechnology industry. It is commercially extracted from citrus peels and apple pomace under mildly

acidic conditions. Chemically, pectin is the methylated ester of polygalacturonic acid. It is thought to consist mainly of D-galacturonic acid units joined by means of (1-4) α-glycosidic linkage. Pectin has several unique properties that have enabled it to be used as a carrier for a variety of drugs for controlled release applications. It has also been used successfully for many years in the food industry as a thickening agent, gelling agent and a colloidal stabilizer. As all the materials used in this synthetic method are non-toxic, this is a greener approach for nanoparticle synthesis. The synthesized AgNP-pectin was successfully used for reducing 4-nitrophenol into 4-aminophenol.

Material and Methods

Materials: Silver nitrate ($AgNO_3$), hexamine, 4-nitophenol and sodium borohydride ($NaBH_4$) of analytical grade were purchased from Merck India Ltd. Pectin was obtained from Himedia Chemicals (Mumbai, India). Double distilled water was used for all experiments.

Synthesis of AgNP-pectin: In a typical synthesis, 0.1 g of pectin was dissolved in 90 mL of hot water in a beaker. To this, 10 mL of 0.05 M $AgNO_3$ solution was added so as to keep the concentration of $AgNO_3$ in the reaction mixture as 0.005 M and the solution was sonicated for 15 minutes. Then 0.07 g (0.005 M) of hexamine was added and sonicated for another 15 minutes. The reaction mixture was then placed in a domestic microwave oven (Sharp R-219T (W)) operating at a power of 800 W and frequency 2450 MHz and subjected to microwave irradiation for 5 min. Upon microwave irradiation, the colourless solution turned into yellowish-brown indicating the reduction of silver ions into silver colloids. The formation of AgNPs was monitored using UV-vis. spectrophotometry by analyzing the reaction mixture after different irradiation time.

Reduction of 4-nitrophenol to 4-aminophenol: The reduction of 4-nitrophenol to 4-amino phenol by $NaBH_4$ was used to study the catalytic activity of AgNP-pectin. To study this reaction, 2 mL of 4-nitrophenol (0.08×10^{-3} M) was taken in a quartz cuvette of 1 cm path length and to this 0.5 mL freshly prepared $NaBH_4$ solution (0.06 M) was added. Then 0.5 mL of AgNP-pectin hydrosol was added to start the reaction. The reaction was monitored by analyzing the absorption peak at 400 nm using UV-Vis spectrophotometer. The absorption spectra were taken in one minute intervals in the range of 200 - 600 nm at 26^{o}C.

Characterization: The UV-vis. spectra were measured on a Shimadzu UV-2450 spectrophotometer. The elemental composition studies were done by energy dispersive X-ray (EDX) spectroscopy using JEOL JSM-6390 scanning electron microscope with EDX attachment. X-ray diffraction measurements were carried out using PANalytic XPERT-PRO X-ray spectrometer. High resolution-transmission electron microscopic (HR-TEM) images were obtained using a JEOL JEM-2100 microscope.

Results and Discussion

Synthesis of silver nanoparticles (AgNPs): The indication for the successful formation of pectin stabilized silver nanoparticles (AgNP-pectin) is obtained from UV-vis. absorption spectral studies. The UV-vis. absorption spectra of the solution recorded at one minute intervals during microwave irradiation process are shown in figure 1. The UV-vis. absorption spectrum of pectin shows no apparent absorption in the range of 250-600 nm. But an absorption band was observed at about 416 nm after microwave irradiation for 3 min and the intensity of which became stronger with passage of reaction time. This prominent absorption band is attributed to the characteristic surface plasmon resonance (SPR) absorption of silver nanoparticles. Initially when $AgNO_3$ and hexamine were added to pectin solution, the solution remained colourless. But upon microwave irradiation, the colourless solution gradually changed to yellowish-brown indicating the formation of silver nanoparticles. The silver colloids are found to be stable for several months due to efficient capping by pectin molecules. These results indicate that hexamine is able to reduce Ag^+ ions into Ag nanoparticles and pectin is a good stabilizer for the generated AgNPs. Upon addition of $AgNO_3$ to pectin solution, Ag^+ ions get entrapped within the pectin chain because the polar -OH groups and electron rich oxygen atoms on the pectin chain act as templates for the incoming Ag^+ ions. Hexamine efficiently reduces these Ag^+ ions into Ag under the influence of microwave radiation which combines to form highly dispersed silver nanoparticles. The use of microwave radiation provides rapid initial heating and hence improved reaction rates[21].

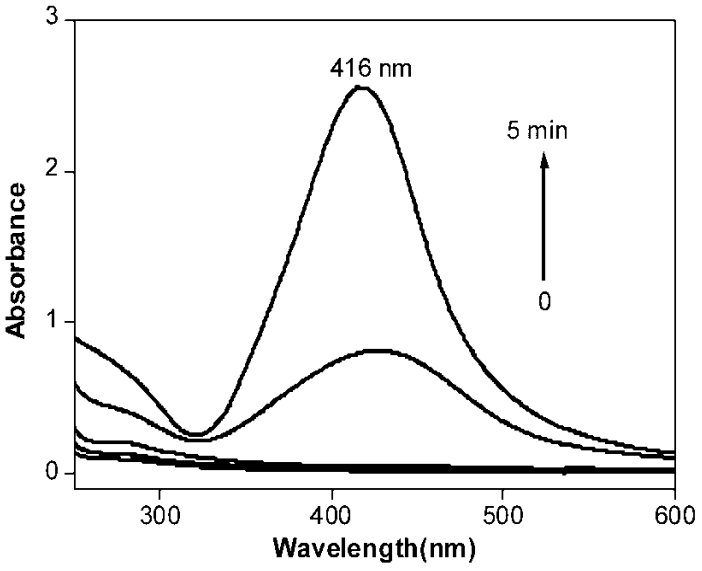


Figure-1
UV-visible absorption spectra of AgNP-pectin at different microwave irradiation time

X-ray diffraction (XRD) analysis: The crystalline nature of silver nanoparticles has been confirmed by X-ray diffraction studies. The XRD spectrum of AgNP-pectin is shown in figure 2 in which four distinct peaks can be observed at 2θ values of 37.86°, 43.94°, 64.17° and 77.12°. These peaks are indexed to the reflections of the (111), (200), (220) and (311) crystalline planes of face centered cubic (fcc) silver nanoparticles respectively (JCPDS file no.04-0783).

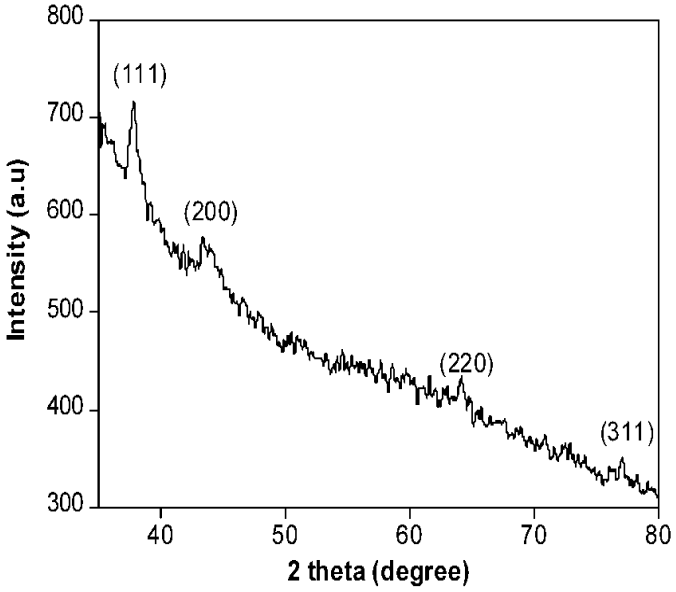


Figure-2
XRD pattern of AgNP-pectin

Energy dispersive X-ray (EDX) spectrum: The elemental description of the sample was obtained from energy dispersive X-ray analysis. In figure 3, the peaks located between 2 keV and 4 keV are directly related to the characteristic K and L lines of silver. The small maximum observed at about 0.3 keV is characteristic of carbon. The peak located at about 0.5 keV is due to oxygen. The carbon and oxygen signals arise from pectin which acts as capping agent for silver nanoparticles.

HR-TEM analysis: High resolution transmission electron microscopic analysis was conducted to look into the size and morphology of the synthesized silver nanoparticles. The TEM images of AgNP-pectin are given in figure 4. It is obvious from the images that the nanoparticles are more or less uniformly distributed and almost spherical in shape. They are also highly crystalline. The particle size histogram is shown in figure 4(b). The average particle size was observed as 18.84 nm ± 0.94. As can be seen, nearly 75 % of the particles have diameter between 16-20 nm and the size distribution plot appears to be almost symmetrical with all the nanoparticles coming within the range of 14-24 nm. The HR-TEM image (figure 4(c)) shows clear lattice fringes. This also reveals that the crystal growth of nanoparticles occurred mainly on the (111) plane. The selected area electron diffraction (SAED) pattern is shown in figure 4(d). The diffraction rings are visible clearly and these can be indexed to the (111), (200), (220) and (311) reflections of face centered cubic (fcc) silver nanoparticles. All these results give a clear indication of the highly crystalline nature of the silver nanoparticles synthesized by this method.

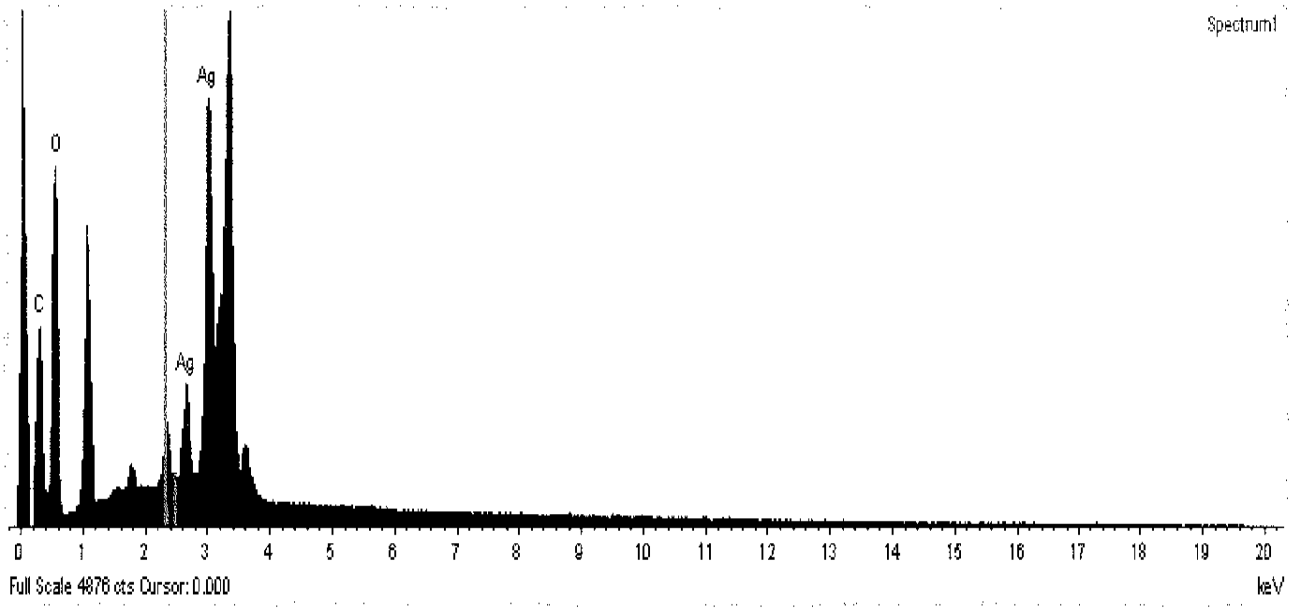
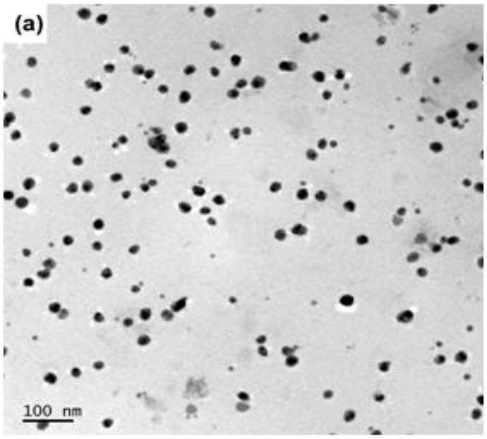
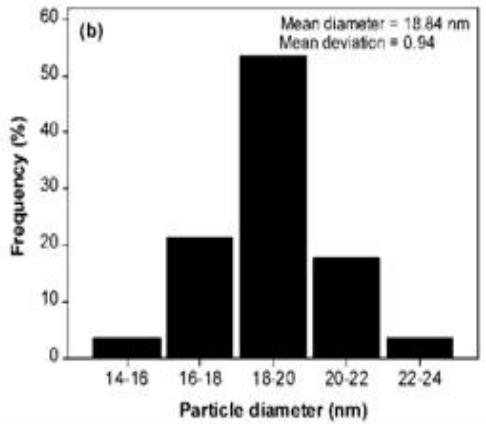


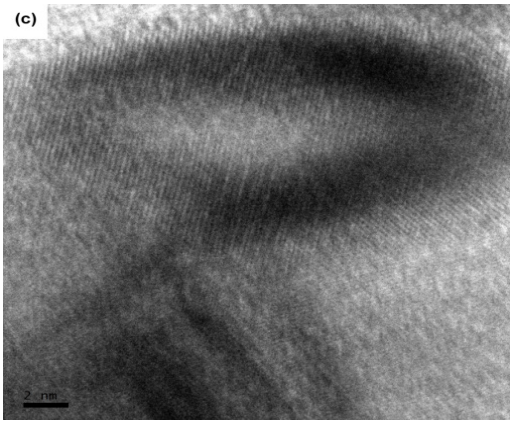
Figure-3
EDX spectrum of AgNP-pectin



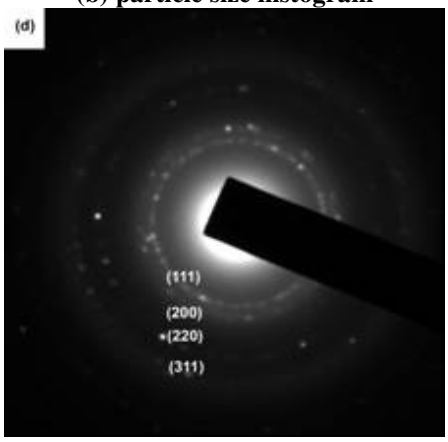
(a) TEM image



(b) particle size histogram



(c) HR-TEM image



(d) SAED pattern of AgNP-pectin

Figure-4
Catalytic reduction of 4-nitrophenol to 4-aminophenol

The catalytic competence of AgNP-pectin was studied by selecting the reduction of 4-nitrophenol to 4-aminophenol by $NaBH_4$ as a model reaction. The UV-vis. absorption spectrum of 4-nitrophenol has maximum absorption at 317 nm. Upon addition of $NaBH_4$, the yellow colour of the solution of 4-nitrophenol become more intense and the peak was shifted to 400 nm (figure-5). This is due to the formation of 4-nitrophenolate ions under the alkaline condition created on the addition of $NaBH_4$[22].

The intensity of the peak at 400 nm due to 4-nitrophenolate ion remained almost unchanged even after several hours suggesting that $NaBH_4$ alone is unable to effectively reduce 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). But the reduction reaction started immediately after the addition of a small amount of AgNP-pectin catalyst. This is evident from the fading of the yellow color of the reaction mixture with time. The UV-vis. absorption spectra for the $NaBH_4$ reduction of 4-NP catalyzed by 0.025 mg/mL AgNP-pectin at 26°C is shown in figure 6. To pursue the progress of the reaction, the spectrum was recorded every 1 min after the addition of the catalyst to the reaction medium.

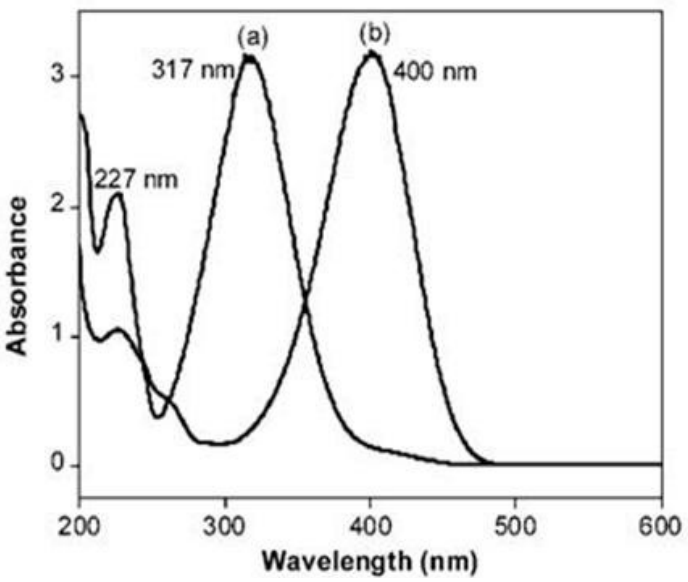


Figure-5
UV-vis. absorption spectrum of (a) 4-nitrophenolate ion, and (b) 4-nitrophenol

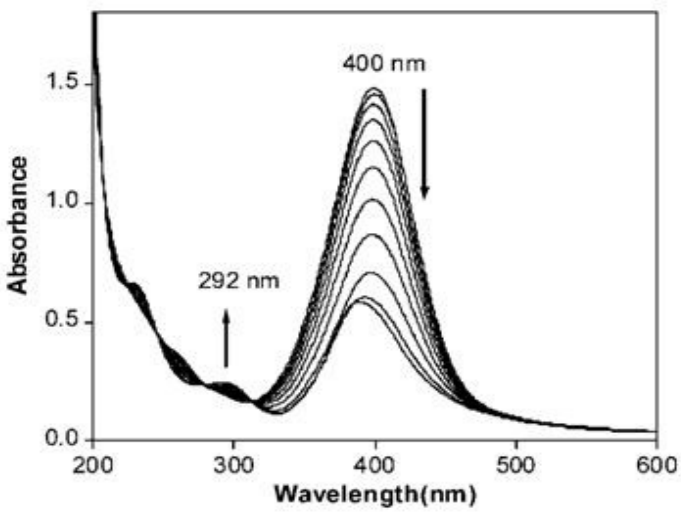


Figure-6

Successive UV-vis. absorption spectra for the $NaBH_4$ reduction of 4-nitrophenol recorded at 1 min intervals catalyzed by AgNP-pectin at 26°C. Conditions: [4-NP] = 0.08 × 10^{-3} M, [$NaBH_4$] = 0.06 M, [AgNP-pectin] = 0.025 mg/mL

It is apparent from figure 6 that, after the addition of AgNP-pectin catalyst, the intensity of the peak at 400 nm decreases continuously with time and a new peak appears at 292 nm whose intensity increases with elapse of time. This new peak is due to the formation of the product 4-aminophenol. The reaction was found to be complete in 10 min.

As reaction progresses, not only a decrease in the intensity of the peak at 400 nm but also a blue shift of the peak from 400 to 389 nm was observed. This peak is due to the surface plasmon resonance (SPR) of silver nanoparticles. In the intermediate stage of the reaction, the SPR band of silver nanoparticles is not observed because it is masked by the more prominent absorption band of 4-nitrophenolate ion. At last when all the reactant has reacted, this SPR band becomes observable. When AgNP-pectin is added as catalyst to the reaction mixture containing 4-NP and excess of $NaBH_4$, the borohydride ions injects electrons on to the catalyst surface and hence modify the catalyst. This leads to a blue shift in the SPR band of AgNP-pectin from 416 nm to 389 nm[23]. The mechanism of this reduction reaction involves the initial adsorption of both 4-nitrophenolate ions and BH_4^- ions on the catalyst surface. Due to the close proximity of the reacting groups on the catalyst surface, the reduction reaction becomes very easy. The catalyst helps this reduction process by conveying electrons from the donor BH_4^- ions to the acceptor 4- nitrophenolate ions.

The kinetics of this reaction can be followed quantitatively by monitoring the change in the intensity of the peak at 400 nm with time. In this study, the concentration of $NaBH_4$ largely exceeds that of 4-NP. As the initial concentration of $NaBH_4$ is very high, it remains essentially constant during the course of the reaction. So pseudo-first order kinetics with respect to 4-nitrophenol could be used to evaluate the reaction rate. The kinetics of the reaction can be represented using the equation ln [A] / [A_o] = - kt, where k is pseudo-first order rate constant, t is the reaction time, [A_o] is the concentration of 4-NP at time t = 0 and [A] is the concentration at time t. The value of [A] can be obtained from the absorbance of the peak at 400 nm.

To see how the amount of catalyst affect reaction rate, the above reaction was repeated by varying the concentration of AgNP-pectin hydrosol in the reaction mixture, keeping other parameters constant. As shown in figure 7, a linear relation between ln [A] and time has been observed in all the cases. This shows the pseudo-first order nature of the reaction. The first order rate constant k for these reactions is obtained from the slope of the linear plots.

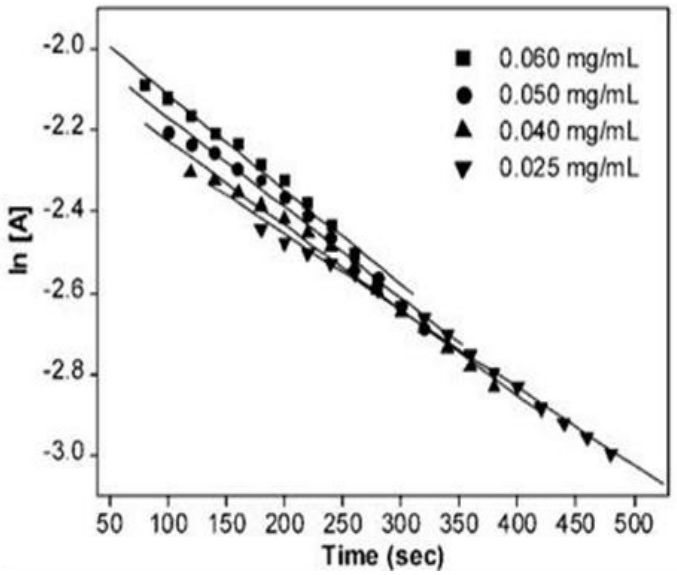


Figure-7

Plot of ln [A] against time for the reduction of 4-nitrophenol using varying amount of AgNP-pectin catalyst Conditions: [4-NP] = 0.08 × 10^{-3} M, [$NaBH_4$] = 0.06 M, Temperature = 26°C

The first order rate constant obtained from the slope of ln [A] versus time plot for different amounts of catalyst and the corresponding correlation coefficients are given in table 1.

Table-1

Pseudo-first order rate constants for the reduction of 4-NP using varying amount of AgNP-pectin catalyst

Conc. of AgNP-pectin (mg/mL)	Reaction time (min)	k ×10^{-3} (sec^{-1})	Correlation coefficient (R^2)
0.025	10	1.89	0.9934
0.040	8	2.09	0.9894
0.050	7	2.20	0.9800
0.060	6	2.33	0.9866

It is clear from the table that, these reactions are very fast and strictly follows pseudo-first order kinetics. The reaction time decreases with increase in the amount of catalyst. We can also see from figure 8 that the rate constant increases with increase in the concentration of the catalyst. Moreover, a strictly linear relation between rate constant and concentration of the catalyst can be observed.

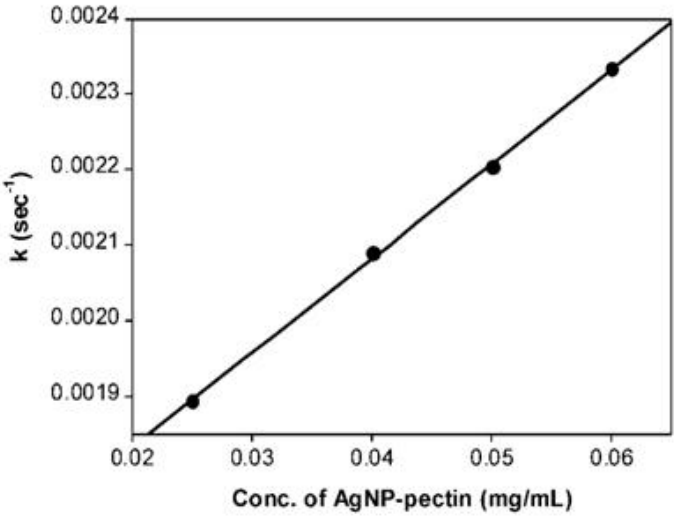


Figure-8
Plot of rate constant against amount of catalyst for the reduction of 4-NP. Conditions: [4-NP] = 0.08 × 10^{-3} M, [$NaBH_4$] = 0.06 M, Temperature = 26°C

Moreover, initially an induction time (the time taken to observe any appreciable change in the absorbance at 400 nm) was found for all the catalytic reaction when carried out under ambient condition and after that the rate increases gradually with time. The same observation was also made by several other researchers[19,23,24]. This is due to the surface oxidation of the catalyst in oxygen atmosphere resulting in the formation of oxide layer on the catalyst surface which may poison the catalyst. $NaBH_4$ reduces the oxide layer and regenerate fresh catalyst surface for the adsorption of reactants. Since $NaBH_4$ is taken in large excess, its consumption for the above process does not alter its concentration appreciably. Moreover, the hydrogen liberated during the reduction process scavenges O_2 and thus prevent the oxidation of the reduction product as well as the catalyst. The induction time (IT) was observed to decrease with increase in the catalyst concentration as well as temperature.

In order to study the effect of temperature on the rate of AgNP-pectin catalyzed reduction of 4-nitrophenol, the reaction was carried out at four different temperatures (22, 26, 30 and 33°C) and the pseudo-first order rate constant was calculated in each case. The activation energy (E_a) for the reaction can be calculated using the well known Arrhenius equation

$$\ln k = -E_a / RT + \ln A \quad (1)$$

In this equation, k is the rate constant, R is gas constant (8.314 $JK^{-1}mol^{-1}$), T is the absolute temperature and A is Arrhenius parameter. From the above equation, it follows that the plot of ln k versus 1/T should yield a straight line, the slope of which is equal to $-E_a/R$. From this, E_a can be evaluated. The values of ln k obtained in our study at different temperatures are plotted against 1/T in figure 9. As is clear, the value of k increases with increase in temperature showing that the reaction is accelerated by increasing temperature. From the Arrhenius plot, the activation energy for the reaction was calculated to be 47.3 kJ mol^{-1}.

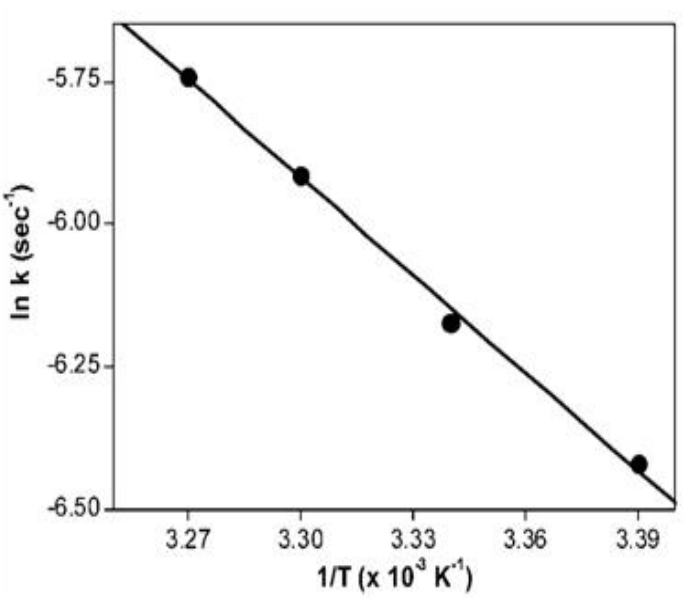


Figure-9
Arrhenius plot of lnk against 1/T for the reduction of 4-nitrophenol catalyzed by AgNP- pectin

Conclusion

In this work, we have reported a rapid facile microwave based method for the synthesis of silver nanoparticles in aqueous medium using the non-toxic hexamine as reducing agent and the easily available biopolymer pectin as the capping agent. The various characteristics of the synthesized silver colloids are analyzed by UV-vis., XRD, EDX and TEM analyses. The catalytic activity is investigated by studying the reduction of 4-nitrophenol to 4-aminophenol by $NaBH_4$. The reaction follows pseudo-first kinetics and the rate constant is found to increase as the concentration of the catalyst is increased. The temperature dependence of reaction rate is studied by conducting the reaction at four different temperatures. The rate of reaction is found to increase with increasing temperature and the activation energy is found to be 47.3 kJ mol^{-1}. Since this method is relatively simple, fast and environment friendly, this can be scaled up for the bulk production of silver nanoparticles.

Acknowledgment

The financial assistance provided by UGC (under FIP Scheme), Government of India is gratefully acknowledged.

References

1. Murray R.W., Nanoelectrochemistry: metal nanoparticles, nanoelectrodes and nanopores, *Chem Rev*., **108**, 2688-2720 **(2008)**

2. Kundu S, Mandal M, Ghosh S.K. and Pal T., Photochemical deposition of SERS active silver nanoparticles on silica gel and their application as catalysts for the reduction of aromatic nitro compounds, *J. Colloid Interface Sci.,* **272**, 134-144 **(2004)**

3. Eychmuller A., Structure and photophysics of semiconductor nanocrystals, *J. Phys. Chem. B,* **104**, **(2000)**

4. Salata O.V., Applications of nanoparticles in biology and medicine, *J. Nanobiotechnol.* **2**, 3-9 **(2004)**

5. Ren X., Meng X., Chen D., Tang F. and Jiao J., Using silver nanoparticle to enhance current response of biosensor, *Biosens. Bioelectron.*, **21,** 433-437 **(2005)**

6. Rivas L., Sanchez-cartos S., Garcia-Ramos J.V. and Marcillo G., Growth of silver colloidal particles obtained by citrate reduction to increase the Raman enhancement factor, *Langmuir*, **17**, 574-577 **(2001)**

7. Murthy P.S.K., Mohan Y.M., Varaprasad K., Sreedhar B. and Raju K.M., First successful design of semi-IPN Hydrogel-silver nanocomposites: A facile approach for antibacterial applications, *J. Colloid Interface Sci.,* **318,** 217-224 **(2008)**

8. Esumi K., Isono R. and Yoshimura T., Preparation of PAMAM- and PPI- metal (silver, platinum and palladium) nanocomposites and their catalytic activities for reduction of 4-nitrophenol, *Langmuir,* **20,** 237-243 **(2004)**

9. Vigneshwaran N., Nachane R.P., Balasubramanya R.H. and Varadarajan P.V., A novel one-pot 'green' synthesis of stable silver nanoparticles using soluble starch, *Carbohydr. Res.*, **341**, 2012–2018 **(2006)**

10. Vidhu V.K., Aromal S.A. and Philip D., Green synthesis of silver nanoparticles using Macrotyloma uniflorum, *Spectrochim. Acta A,* **83,** 392–397 **(2011)**

11. Vigneshwaran N., Ashtaputre N.M., Varadarajan P.V., Nachane R.P., Par-Alikar K.M. and Balasubramanya R.H., Biological synthesis of silver nanoparticles using the fungus Aspergillus flavus, *Mater. Lett.*, **61**, 1413–1418 **(2007)**

12. Sreeram K.J., Nidhin M. and Nair B.U., Microwave assisted template synthesis of silver nanoparticles, *Bull. Mater. Sci*., **31**, 937-942 **(2008)**

13. Hu B., Wang S., Wang K., Zhang M. and Yu S., Microwave-assisted rapid facile "green" synthesis of uniform silver nanoparticles: Self-assembly into multilayered films and their optical properties, *J. Phys. Chem. C,* **112**, 11169–11174 **(2008)**

14. Chen J., Wang J., Zhang X. and Jin Y., Microwave-assisted green synthesis of silver nanoparticles by carboxymethyl cellulose sodium and silver nitrate, *Mater. Chem. Phys.*, **108,** 421-424 **(2008)**

15. Rastogi P.K., Ganesan V. and Krishnamoorthi S., Microwave assisted polymer stabilized synthesis of silver nanoparticles and its application in the degradation of environmental pollutants, *Mater. Sci. Eng. B,* **177,** 456-461 **(2012)**

16. Peng H., Yang A. and Xiong J., Green, microwave-assisted synthesis of silver nanoparticles using bamboo hemicelluloses and glucose in an aqueous medium, *Carbohydr. Polym,* **91**, 348-355 **(2013)**

17. Wunder S., Polzer F., Lu Y., Mei Y. and Ballauff M., Kinetic analysis of catalytic reduction of 4-nitrophenol by metallic nanoparticles immobilized in spherical polyelectrolyte brushes, *J. Phys. Chem. C,* **114,** 8814-8820 **(2010)**

18. Sen I.K., Maity K. and Islam S.S., Green synthesis of gold nanoparticles using a glucan of an edible mushroom and study of catalytic activity, *Carbohydr. Polym.* **91**, 518-528 **(2013)**

19. Nemanashi M. and Meijboom R., Synthesis and characterization of Cu, Ag and Au dendrimers-encapsulated nanoparticles and their application in the reduction of 4-nitrophenol to 4-aminophenol, *J. Colloid Interface Sci.,* **389**, 260-267 **(2013)**

20. Shin K.S., Choi J.Y., Park C.S., Jang H.J. and Kim K., Facile synthesis and catalytic application of silver-deposited magnetic nanoparticles, *Catal. Lett.,* **133,** 1-7 **(2009)**

21. Nadagouda M.N., Speth T.F. and Varma R.S., Microwave-assisted green synthesis of silver nanostructures, *Acc. Chem. Res*., **44**, 469-478 **(2011)**

22. Pradhan N., Pal A. and Pal T., Catalytic reduction of aromatic nitrocompounds by coinage metal nanoparticles, *Langmuir*, **17,** 1800-1802 **(2001)**

23. Pradhan N., Pal A. and Pal T., Silver nanoparticle catalyzed reduction of aromatic nitro compounds, *Colloids Surf. A,* **196**, 247-257 **(2002)**

24. Lu Y., Mei Y., Walker R., Ballauff M. and Drechsler M., 'Nano-tree'-type spherical polymer brush particles as templates for metallic nanoparticles, *Polymer,* **47**, 4985-4995 **(2006)**