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A comparative study of gamma, electron beam, and synchrotron X-ray irradiation method for synthesis of silver nanoparticles in PVP

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ABSTRACT

A one-pot synthesis method has been developed for preparation of silver nanoparticles in aqueous poly (vinyl pyrrolidone) (PVP) solution by synchrotron X-ray radiation. The hydrated electrons (e_{aq}^-) and hydrogen atom radical ($H^{\cdot}$), products of radiolysis of water molecules by synchrotron X-rays brings about the reduction of the metal ions, resulting in homogeneous nucleation and nanoparticle formation. The nanoparticles were characterized by UV-visible spectroscopy and TEM analysis. A comparative study has been done to know the effectiveness of this synthesis method with that of gamma and EB- irradiation methods. In gamma radiation method the nanoparticle size obtained was ~8nm, whereas in synchrotron X-ray irradiation 10-15nm particles were obtained. Smaller size particles with narrow size distribution were obtained by γ-radiolysis and EB-irradiation than those obtained by X-ray radiolysis. The effects of different experimental parameters, such as concentration of Ag^+, PVP concentration on nanoparticle formation were studied. Copyright © 2013 VBRI press.

Keywords: Silver nanoparticles; synchrotron X-ray radiation; gamma irradiation; electron beam irradiation; PVP.

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Introduction

Metal nanoparticles have attracted considerable attentions to many researchers because of their unique optical, electronic, catalytic properties, which leads to their potential applications in diverse fields **[1]**. Wet-chemical routes such as direct reduction **[2]** are widely used for synthesis of metal nanoparticles. In these cases as a chemical reducing agent is added to the system, so that the reaction system contains by-products from these chemicals and also it is difficult to control the progress of the reaction in this method. Synthesis method using high energy radiation is being explored to broaden the range of experimental feasibility. The formation of metallic nanoparicles in solution initiated by γ-ray **[3-8]**, electron beam **[9, 10]** and X-ray **[11-18]** irradiation has been proved to be an alternative way to obtain dispersed nanoparticles. Synthesis of metal nanoparticles using high energy radiation like gamma and electron beam is well established techniques as reported in recent literature. Synchrotron radiation X-rays as an ionizing radiation source has been

little explored for fabrication of metal nanoparticles. The possibility of synchrotron X-ray source for the direct reduction of gold precursor solutions was first explored by Rosenberg and co-workers **[19, 11]**. The high flux and high energy of synchrotron X-rays can be utilized for reduction of metal ion precursor to generate metal nanoparticles in solution. The interaction of X-rays with aqueous medium is similar to that of γ-ray. The primary radicals produced from water radiolysis by X-rays are e_{aq}^-, H· and ·OH. The first two are reducing in nature and the later is oxidizing in nature. For reduction of metal ions to zero-valent state a total reducing condition is required. Hence isopropyl alcohol is added to the reaction system to scavenge ·OH radical. The advantage of using isopropyl alcohol is that the reaction product of isopropyl alcohol and ·OH radical, namely isopropyl radical is also reducing in nature. The advantages of X-ray irradiation method are, clean reaction system without reducing agents, controllable particle size by tuning the dose rate, rapid synthesis and high reduction yields due to the high X-ray flux.

In this work, silver nanoparticles (Ag np) are synthesized by high energy radiation, namely synchrotron X-ray, γ- ray and electron beam (EB) from silver nitrate ($AgNO_3$) precursor salt. When aqueous solution of $AgNO_3$, poly (vinyl pyrrolidone) (PVP, Mw 40,000Da) and isopropanol was exposed to ionizing radiation, Ag^+ is reduced to Ag^0 by reactive radical produced from water radiolysis. Ag^0 coalesce to give metal nanoparticles in presence of stabilizing agent PVP. The silver nanoparticles formed were characterized by UV-visible spectroscopy and TEM ananlysis.

Experimental

Aqueous solutions were prepared using nano pure water (resistivity =18 MΩ. cm). All the chemicals used were of highest purity and were used as received. Poly (N-vinyl-2-pyrrolidone) (PVP) of molecular weights 40,000Da from Aldrich, 2-propanol and $AgNO_3$ from S. D. Fine Chemicals Ltd., Mumbai were used as received. Prior to use, glassware was cleaned with aquaregia (volume ratio HNO_3/ HCl = 1: 3) and thoroughly rinsed with nano pure water.

X-ray irradiations were carried out using BL- 07 (white beam, storage ring energy = 2.0 GeV, maximum current= 100 mA), Indus-2 synchrotron facility at RRCAT, Indore, India. The X-ray beam energy was 4-20kev and the X-ray beam size was (80×10) mm^2. The X-ray irradiation of samples was carried out in polypropylene press-fit cap storage vials. Gamma irradiations were carried out in ^{60}Co gamma chamber having a radiation dose rate of 4 kGy hr^{-1} determined using Fricke dosimetry **[20]**. The electron beam processing was carried out in 2 MeV, 20 kW industrial electron beam (EB) accelerator at BARC, Mumbai, India. Aerated aqueous solutions of precursor salt, PVP and isopropanol were irradiated with X-ray and EB. Whereas the precursor solutions were first deaerated by purging with high pure N_2 gas before subjecting to γ-irradiation. Absorption spectra were recorded on a Thermoelectron recording spectrophotometer. The dosimetry for the X-ray was carried out with a Fricke dosimeter with an estimated $G(Fe^{III})$ value of 13. Samples for TEM measurements were prepared by placing droplets of nanoparticle solution on carbon coated Cu grids and allowing them to dry. The average size of Ag nanoparticles was analyzed by counting over 100 individual particles in the TEM micrographs.

Results and discussion

Dosimetry

To measure the radiation dose as well as the dose rate delivered to the precursor metal ion solution, dosimetry of the X-ray irradiation was performed for a certain beam current by Fricke dosimeter **[15, 20, 21]** solution (aqueous solution of 1×10^{-3} mol dm^{-3} Fe^{II}, 1×10^{-3} mol dm^{-3} NaCl and 4×10^{-1} mol dm^{-3} = H_2SO_4). The dose rate measured for the X-ray irradiation was 31.6Gy/s (113.8kGy.h^{-1}) for 75mA current. Similarly dose rate of gamma irradiator was measured by Fricke dosimetry and was found to be 4.0 kGy.h^{-1}.

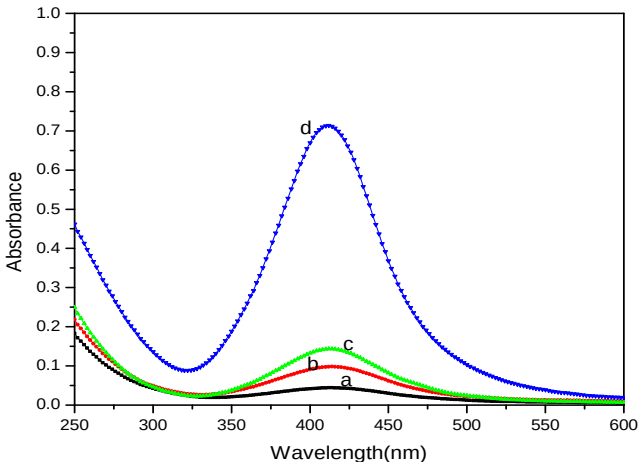

Fig. 1. Absorption spectra of aqueous Ag nanoparticles in PVP prepared by X-ray irradiation for different irradiation time: (a) 12s, (b) 23sec, (c) 41s, (d) 63s; $[Ag^+]= 2\times10^{-4}$ mol. dm^{-3}, [PVP]= 0.5%, [Isopropanol]= 2×10^{-1} mol. dm^{-3}, dose rate= 113.7kGy.h^{-1}.

Formation of colloidal Ag nanoparticles

An aqueous solution containing 2×10^{-4} mol dm^{-3} Au^{III}, 0.5% PVP (w/v) (M_w = 40,000 Da), 2×10^{-1} mol dm^{-3} isopropanol was irradiated by exposing the solution to X-ray beam for an absorbed dose of 2 kGy or for 63s. The formation of Ag nps was indicated by development of yellow color in the solution. Later the np solution was characterized by measuring UV-visible spectra after appropriate dilution. The formation of Ag nps with different irradiation time is shown in **Fig. 1**. With increase in radiation dose the yield increases which is confirmed from the increase in the absorbance value. The absorption maxima (λ_{max}) lies at 411nm and a dose of 2kGy (irradiation time=63s) is required for complete reduction of 2×10^{-4} mol $dm^{-3}Ag^+$ in aqueous PVP solution. In other experiments the dose delivered was calculated accordingly, depending on Ag^+ concentration. The TEM image of Ag nps prepared by X-ray irradiation is shown in **Fig. 2**. The size of particles was found to be 10-15nm as shown in **Fig. 2**. Also the Ag nps obtained by X-ray radiolysis have wide size distribution. The precursor solution for γ and EB-irradiations were at same concentration, but the solution

was deaerated before irradiated with γ-radiation. The interaction of ionizing radiation, such as γ-ray, X-ray and accelerated electron beam with aqueous solution is fully understood and well established today. Water being the major component of aqueous solution, most part of energy of the radiation is absorbed in water, which causes radiolysis of water. The radiolytic transient species, namely hydrated electron (e_{aq}^-), hydrogen atom radical ($H^\cdot$) and hydroxyl radical ($^\cdot OH$) are highly reactive in nature. The first two radicals can reduce many types of metal ions to lower valences and metal atoms. Finally these metal atoms coalesce to form metal nanoparticles in presence of a capping agent, such as polymers, ligands, surfactants etc. The $^\cdot OH$ radical being oxidizing in nature can oxidize back the metal atoms. Hence to scavenge $^\cdot OH$ radical, isopropyl alcohol is added to the system. The reaction product of isopropyl alcohol with $^\cdot OH$ radical is isopropyl radical. There is one more advantage of using isopropyl alcohol. The isopropyl radical hence produced is a reducing agent and it is capable of reducing metal ions like Ag^+. Under similar experimental conditions, the Ag np obtained by γ-radiolysis is shown in **Fig. 3**.

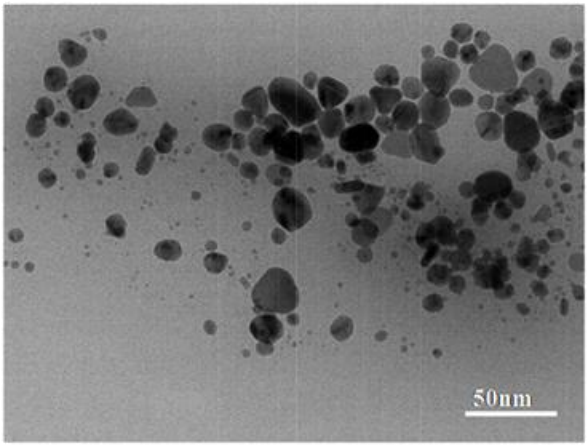

Fig. 2. TEM image of Ag nanoparticles in PVP prepared by X-ray irradiation.

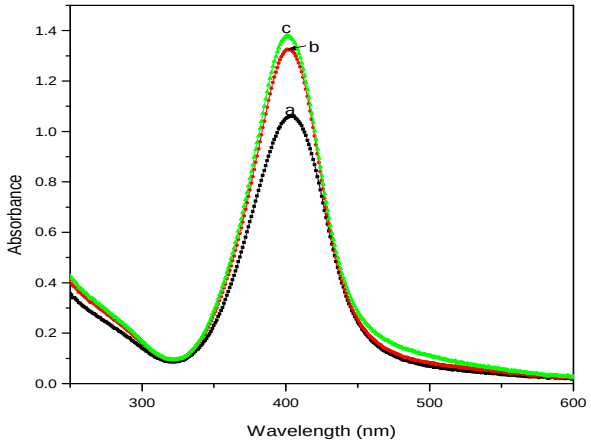

Fig. 3. Absorption spectra of aqueous Ag nanoparticles in PVP prepared by γ-irradiation for different absorption dose: (a) 1kGy, (b) 1.3kGy, (c) 1.6kGy; [Ag^+]= 2×10^{-4} mol. dm^{-3}, [PVP]= 0.5%, [Isopropanol]= 2×10^{-1} mol. dm^{-3}, dose rate= 4.0kGy.h^{-1}; The solution was two times diluted before taking spectra.

As can be seen from the figure the absorption peak of Ag nanoparticles is narrow with λ_{max} at 401nm. This indicates smaller size particles with narrow size distribution were obtained by γ-radiolysis than those obtained by X-ray radiolysis. This was further confirmed by TEM picture of Ag nps synthesized by γ-irradiation (**Fig. 4**), which shows the average particle size of Ag nps was ~8nm. Similar results were observed in EB irradiation method as in γ-irradiation (**Fig. 7d**). The saturation dose in γ-irradiation method was found to be 1.7 kGy, which is close to that obtained in X-ray irradiation.

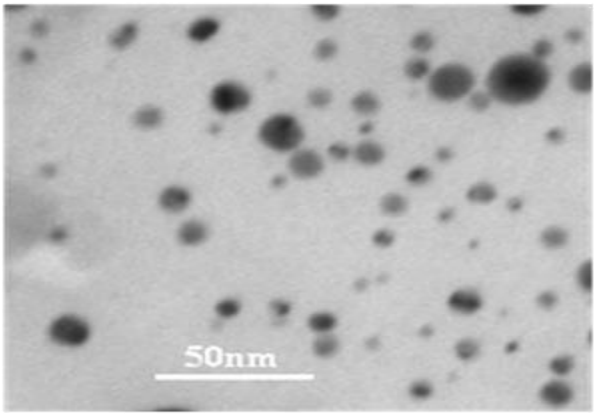

Fig. 4. TEM image of Ag nanoparticles in PVP prepared by γ-irradiation.

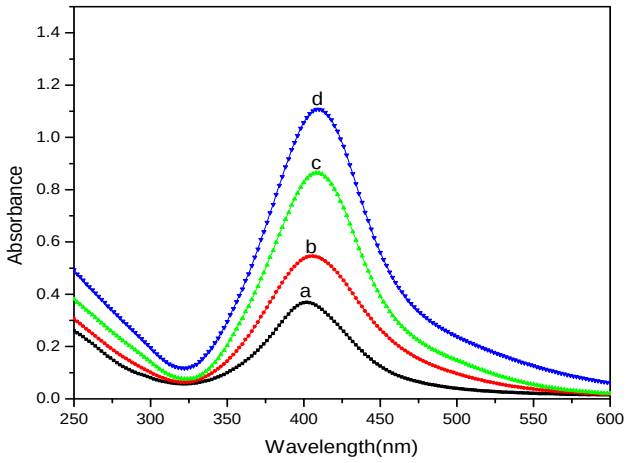

Fig. 5. Absorption spectra of aqueous Ag nanoparticles in PVP prepared by X-ray irradiation for different Ag^+ concentration: (a) 1×10^{-4} mol. dm^{-3}, (b) 2×10^{-4} mol. dm^{-3}, (c) 3×10^{-4} mol. dm^{-3}, (d) 4×10^{-4} mol. dm^{-3}; dose = 1.0kGy, 2.0kGy, 3.0kGy, 4.0kGy respectively; [PVP]= 0.5%, [Isopropanol]= 2×10^{-1} mol. dm^{-3}, dose rate= 113.7kGy.h^{-1}; The solution was two times diluted before taking spectra.

Effect of Ag^+ concentration variation on nanoparticle formation

The Ag^+ concentration variation from 1×10^{-4} mol dm^{-3} to 4×10^{-4} mol dm^{-3} in X-ray, γ-ray and EB irradiation methods are shown in **Fig. 5**, **Fig. 6** and **Fig.7** respectively. The concentrations of all other reactants are same as mentioned in section 3.2. The λ_{max} is red shifted with increase in Ag^+ concentration in X-ray (**Fig. 5**) and γ-irradiation (**Fig. 6**) method, whereas it is blue shifted in EB-irradiation method

(**Fig. 7**). This shows the Ag np size increases with increase in Ag^+ concentration in earlier two cases and it decreases in later case. The increase in particle size at higher precursor concentration is also observed in many cases **[22]**. But the decrease in size in EB-irradiation method is because the dose rate delivered by EB is very high, so that a large number of nuclei are generated in a small time. As the precursor concentration is limited, hence the final particle size is smaller. Also at higher precursor concentration the overall yield is more, hence the average particle size lies in a narrow range.

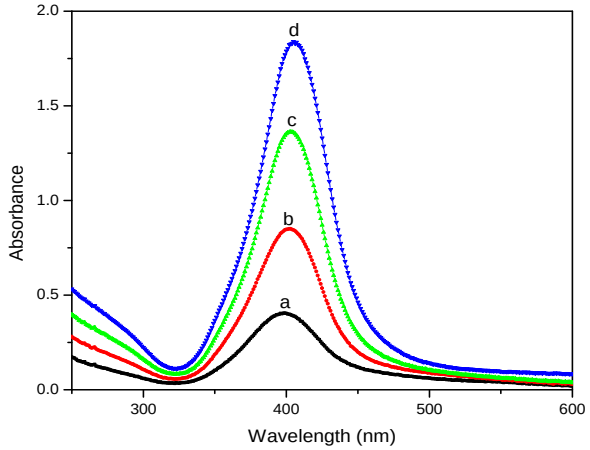

Fig. 6. Absorption spectra of aqueous Ag nanoparticles in PVP prepared by γ-irradiation for different Ag^+ concentration: (a) 1×10^{-4} mol. dm^{-3}, (b) 2×10^{-4} mol. dm^{-3}, (c) 3×10^{-4} mol. dm^{-3}, (d) 4×10^{-4} mol. dm^{-3}; dose= 1.0kGy, 2.0kGy, 3.0kGy, 4.0kGy respectively; [PVP]= 0.5%, [Isopropanol]= 2×10^{-1} mol. dm^{-3}, dose rate= 4.0kGy.h^{-1}; The solution was two times diluted before taking spectra.

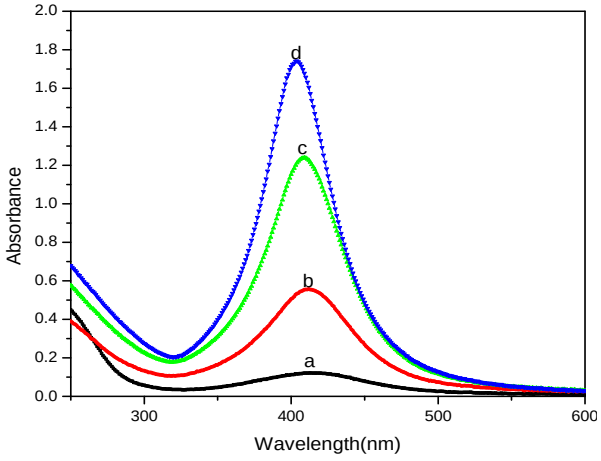

Fig. 7. Absorption spectra of aqueous Ag nanoparticles in PVP prepared by EB- irradiation for different Ag^+ concentration: (a) 1×10^{-4} mol. dm^{-3}, (b) 2×10^{-4} mol. dm^{-3}, (c) 3×10^{-4} mol. dm^{-3}, (d) 4×10^{-4} mol. dm^{-3}; dose= 1.0kGy, 2.0kGy, 3.0kGy, 4.0kGy respectively; [PVP]= 0.5%, [Isopropanol]= 2×10^{-1} mol. dm^{-3}, dose rate= 2.4kGy/s; The solution was two times diluted before taking spectra.

Effect of PVP concentration variation on nanoparticle formation

In order to investigate the role of PVP in stabilization of Ag nps, the Ag nps were synthesized at different PVP concentrations. The PVP concentration was varied from 0.1% to 2% (w/v) in X-ray, γ-ray and EB irradiation methods are shown in **Fig. 8**, **Fig. 9** and **Fig. 10** respectively. The concentrations of all other reactants are same as mentioned in section 3.2. There is no appreciable shift observed in the λ_{max} position with increase in PVP concentration in X-ray (**Fig. 8**) and γ-irradiation (**Fig. 9**) method, whereas it is red shifted in EB-irradiation method (**Fig. 10**). Hence, there is a small increase in average particle size at higher PVP concentration in EB-irradiation method. In all the three cases the FWHM decreases with increase in PVP concentration. That means narrow size distribution of nps was obtained at higher PVP concentration in all cases.

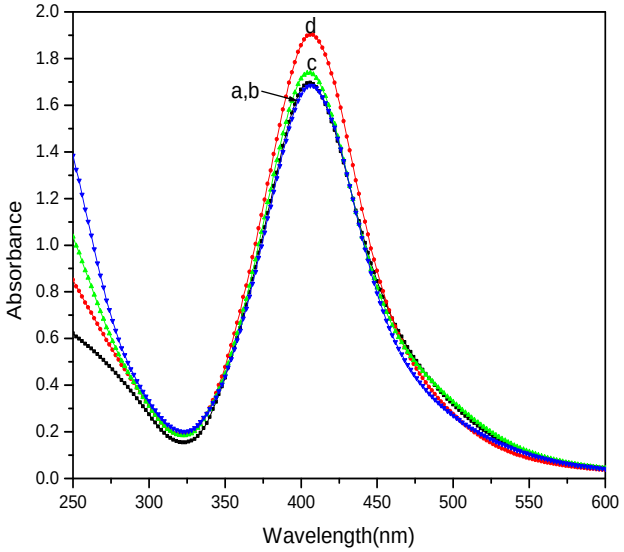

Fig. 8. Absorption spectra of aqueous Ag nanoparticles in PVP prepared by X-ray irradiation for different PVP concentration: (a) 0.1%, (b) 0.5%, (c) 1%, (d) 2% (w/v); [Ag^+]= 2×10^{-4} mol. dm^{-3}, [Isopropanol]= 2×10^{-1} mol. dm^{-3}, dose= 2.0kGy, dose rate= 113.7kGy.h^{-1}

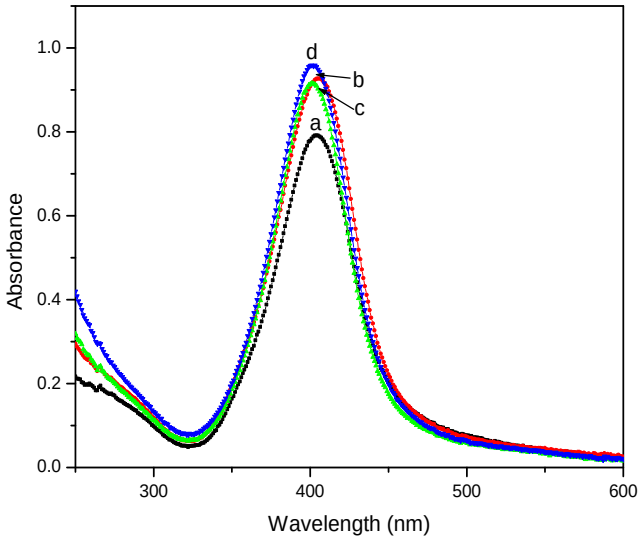

Fig. 9. Absorption spectra of aqueous Ag nanoparticles in PVP prepared by γ-irradiation for different PVP concentration: (a) 0.1%, (b) 0.5%, (c) 1%, (d) 2% (w/v); [Ag^+]= 2×10^{-4} mol. dm^{-3}, [Isopropanol]= 2×10^{-1} mol. dm^{-3}, dose= 2.0kGy, dose rate= 4.0kGy.h^{-1}; The solution was three times diluted before taking spectra.

Effect of dose rate on nanoparticle formation in EB-irradiation

The effect of dose rate was studied in EB-irradiation method by irradiating precursor solution at two dose rate conditions, i.e., 2.4 kGy/s and 1.2kGy/s. The absorption spectra of Ag np solution at different dose rate are shown in **Fig. 11**. As can be seen from the figure there is no shift in peak position observed with change in dose rate. Hence the size of nps produced by EB-irradiation is dose rate independent.

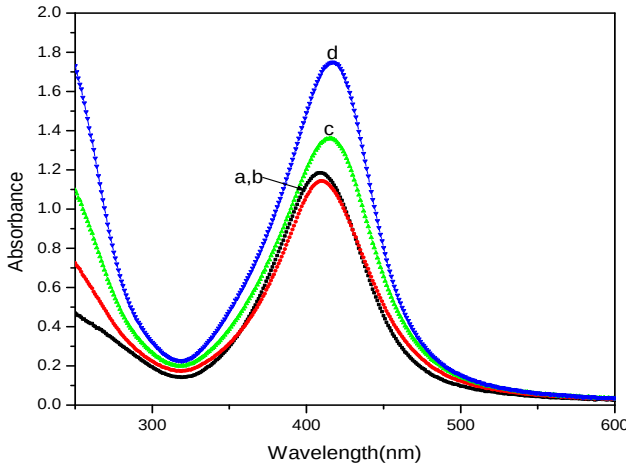

Fig. 10. Absorption spectra of aqueous Ag nanoparticles in PVP prepared by EB- irradiation for different PVP concentration: (a) 0.1%, (b) 0.5%, (c) 1%, (d) 2% (w/v); $[Ag^+]= 2\times10^{-4}$ mol. dm^{-3}, [Isopropanol]= 2×10^{-1} mol. dm^{-3}, dose= 2.0kGy, dose rate= 2.4kGy/s; The solution was two times diluted before taking spectra.

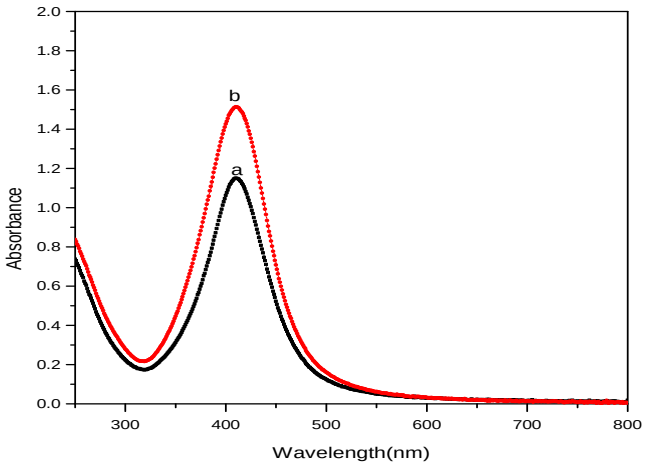

Fig. 11. Absorption spectra of aqueous Ag nanoparticles in PVP prepared by EB- irradiation for different absorption dose rate: (a) 2.4kGy/s, (b) 1.2kGy/s; $[Ag^+]= 2\times10^{-4}$ mol. dm^{-3}, [PVP]= 0.5%, [Isopropanol]= 2×10^{-1} mol. dm^{-3}, dose rate= 2.0kGy.

Conclusion

Radiolytic methods have proved to play an important role in the development and modification of metal nanostructures. In this study it has been shown that X-ray irradiation induced reduction of aqueous metal ions leading to the formation of metallic nanoparticles as in the case of gamma radiolysis. Hence synchrotron X-ray radiation having high flux and high energy offers a tool for generation of metal nanoparticles in aqueous solution. However, the particle size distribution appears as more polydispersed compared to the one obtained when using gamma ray irradiation and EB-irradiation. In gamma radiation method the nanoparticle size obtained was ~8nm, whereas in synchrotron X-ray irradiation 10-15nm particle were obtained. This can be due to the gamma irradiation chamber is designed to irradiate the sample homogeneously the whole volume solution and in the X-ray irradiation geometry, restriction in beam size leads to a non homogeneous energy deposition along the beam-solution interception. This results in an inhomogeneous rate of reduced Ag along the beam. The same reason holds in case of EB- irradiation as gamma irradiation.

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