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Efficiency of PVA supported silver nanoparticles in catalytic reduction of methylene blue

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Abstract

Silver nanoparticles were synthesized using polyvinyl alcohol (PVA) as a stabilizing agent. The chemical degradation of the organic dye, methylene blue, was studied using silver nanocatalyst. Effect of different concentrations of the catalysts and also the time dependence on the catalytic activity were investigated by using UV-Visible spectroscopy. The study of the absorbance with different concentrations helped to make the conclusion that, as concentration of the catalyst increases, the absorbance decreases gradually. This indicates that, as the concentration of the catalyst increases, corresponding increase in degradation occurs. Similarly the absorbance at different reaction time was also studied. It has been observed that as the time increases, the reduction of the dye also increases, this is observed from the corresponding decrease in absorbance. From the kinetic studies, the rate of the catalytic activity was calculated which showed that as the concentration of the catalyst increases, the rate of the catalytic reaction increases.

1. Introduction

Supported silver nanoparticles have wide variety of applications in various fields such as photonics, micro electronics, sensor fabrication, optics and catalysis (Badr and Mahmoud, 2007; Collier *et al*., 1997; Lee and El-Sayed, 2006; Sampaio *et al*., 2001; Smith *et al*., 2002). In particular, its application in catalysis is most important and it has drawn intense attention in recent years as catalyst in organic transformation reactions (Pandey *et al*., 2011). Silver nanoparticles supported on organic polymers provide high surface area. The unique properties like high surface area to volume ratio, low coordination number and easy access to a large number of active sites, makes the supported silver nanoparticles a good catalyst (Krstić *et al*., 2014). This is because of its combined property of high reactivity and selectivity. These type of supported metal nanoparticles shows catalytic activity towards various organic reactions such as coupling, cyclo addition, reduction of dyes, reduction of nitro phenols and so on (Krstić *et al*., 2014). In comparison to bulk counterparts, specially stabilized nanoparticles have significantly high catalytic activity.

Recently many researchers have been working on the nanoparticles for dye degradation. The treatment of the dye wastewater, which is harmful to the environment and the human health, is significantly important

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(Antonopoulou *et al*., 2014; Hai *et al*., 2007). Efficient degradation of dyes should be done to protect the environment from severe pollution problems. Several methods are widely used to treat the dye effluents which include adsorption tactics, biological degradation, photocatalysis, etc (Wang *et al*., 2013). Investigation on a solution to get rid of this problem has helped in the development of new, high performance heterogeneous catalysts. These catalysts are able to perform desired work more selectively and more efficiently (Eisa and Shabaka, 2013).

In the present study the aim is to find out whether it is possible to use supported silver nanoparticles as catalysts for the degradation of organic dyes. Dye degradation studies were done using methylene blue.

2. Experimental

AnalaR grade poly vinyl alcohol (PVA), silver nitrate ($AgNO_3$), sodium hydroxide (NaOH), sodium borohydride ($NaBH_4$) used were all of Merck, India; assay ≥ 99.9%. The PVA supported silver nanoparticles were prepared and characterized as reported earlier (Sagitha *et al.,* 2016).

3 Results and discussion

3.1 Study on catalytic properties - UV-Visible spectroscopic analysis

The UV- Visible spectra of organic dye methylene blue (Fig.1) gives a peak at 662 nm. Investigations on catalytic properties are done at five different concentrations of Ag nanoparticles (Fig. 2). As the concentration of silver nanocatalyst increases the absorbance decreases which indicates that degradation of methylene blue increases as the concentration of the catalyst increases. The absorbance *vs* concentration plot (Fig. 3) shows that as the concentration of the catalyst increases, the absorbance decreases linearly which indicates the efficiency of silver nanoparticles as a catalyst. The catalytic property of Ag nanoparticle at different time intervals was also carried out.

(a) 0.01 g Ag at 5 minute intervals of time

It has been observed that as the time increases (with the same concentration of the catalyst), the catalytic activity increases. This is understood from the decrease in absorbance with increase in time. For a 0.01 g of Ag nanoparticle the decrease in absorbance is occurring slowly with the small difference in absorbance (Fig. 4). The decrease in absorbance with increase in reaction time can be understood from the absorbance *vs* reaction time plot (Fig. 5).

(b) 0.05 g Ag at 5 minute intervals of time

The UV-Visible spectrum of 0.05 g Ag at different time interval is as shown in Fig. 6. It has been observed considerable changes in the absorbance when the concentration of Ag nanoparticles is increased from 0.01 to 0.05 g. The absorbance gradually decreases as the reaction time increases. This is more clearly understood from the absorbance *vs* time plot shown in Fig.7.

3.2. Kinetic study of catalytic degradation

The efficiency of the catalyst can be understood from corresponding rate constant values. The rate of catalytic degradation can be calculated using ln C_o/C vs time plot. The plot of ln C_o/C against corresponding irradiation time, has showed a linear relationship. The rate constant at two different concentrations (0.01 and 0.05g of nanocatalyst) are investigated. The rate constant for each concentration were evaluated from the slope of the straight line. The rate constant increases considerably as the concentration of the catalyst increases from 0.01 to 0.05 g (Figs. 8 & 9).

From Table.1 it is clear that the rate constant increases considerably with increase in the concentration of the nanocatalyst. This is because of the increase in the surface area of the active sites with the increase in the concentration of nanocatalysts. Hence the rate of the reaction also increases gradually. It is observed that, as the concentration of the nanocatalyst increases, the rate constant, and there by the rate of the reaction increases gradually.

Table 1 Rate constant of catalytic degradation of Methylene blue dye in presence of Ag nanoparticles.

Concentration of Ag nanoparticles (g)	Rate constant (min-1)
0.01	0.0065
0.0	0.0218

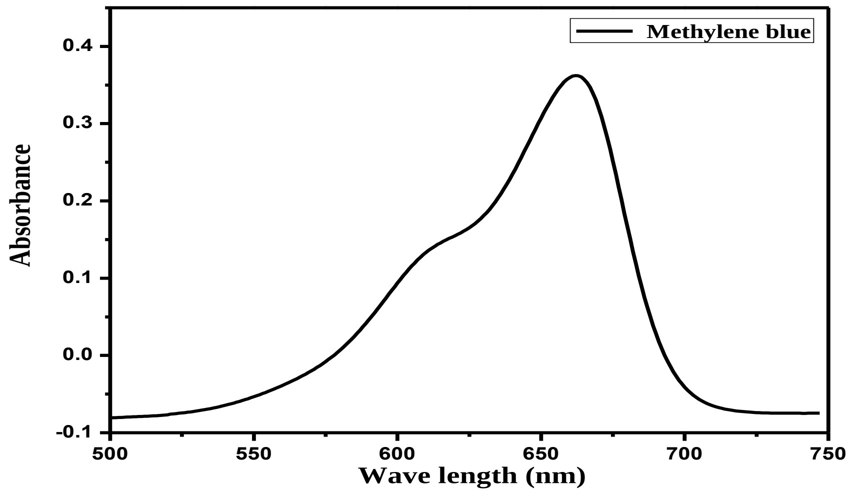

Fig. 1. UV-Visible spectrum of methylene Blue

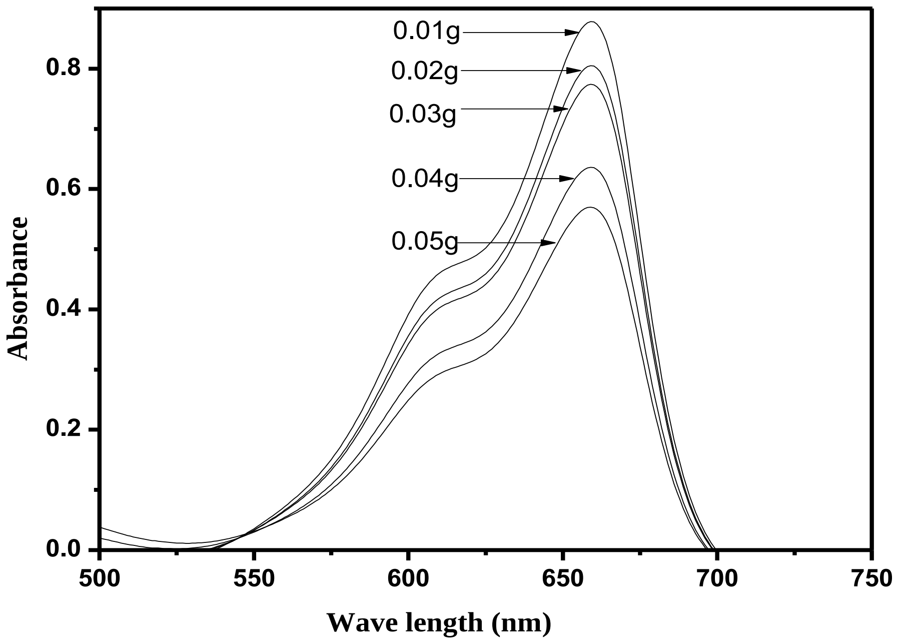

Fig. 2. UV – Visible spectrum of catalytic degradation of MB at different concentrations of Ag nanoparticles

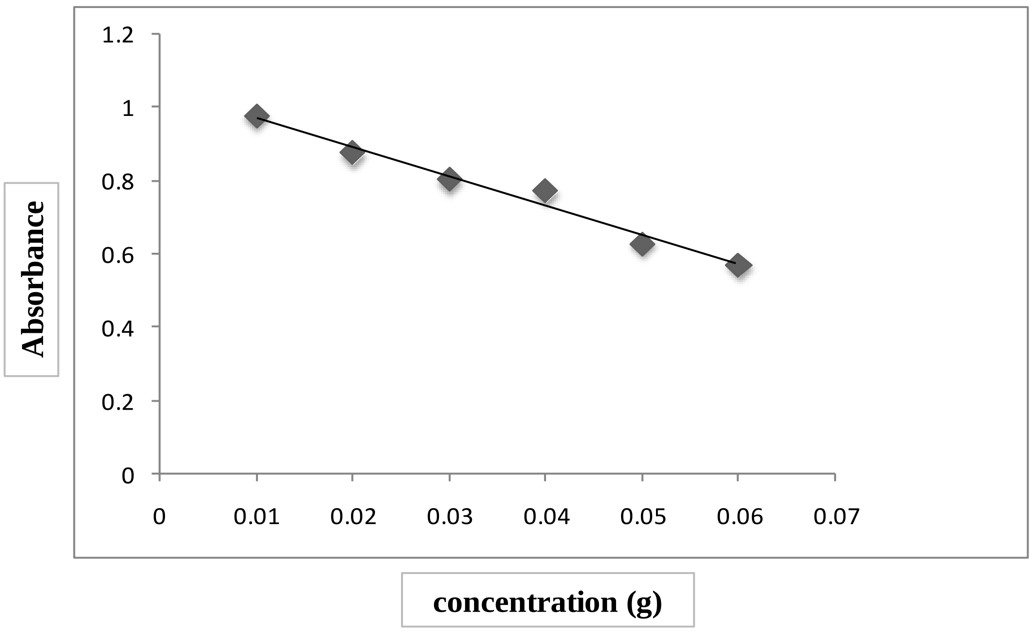

Fig. 3. Absorbance Vs concentration graph

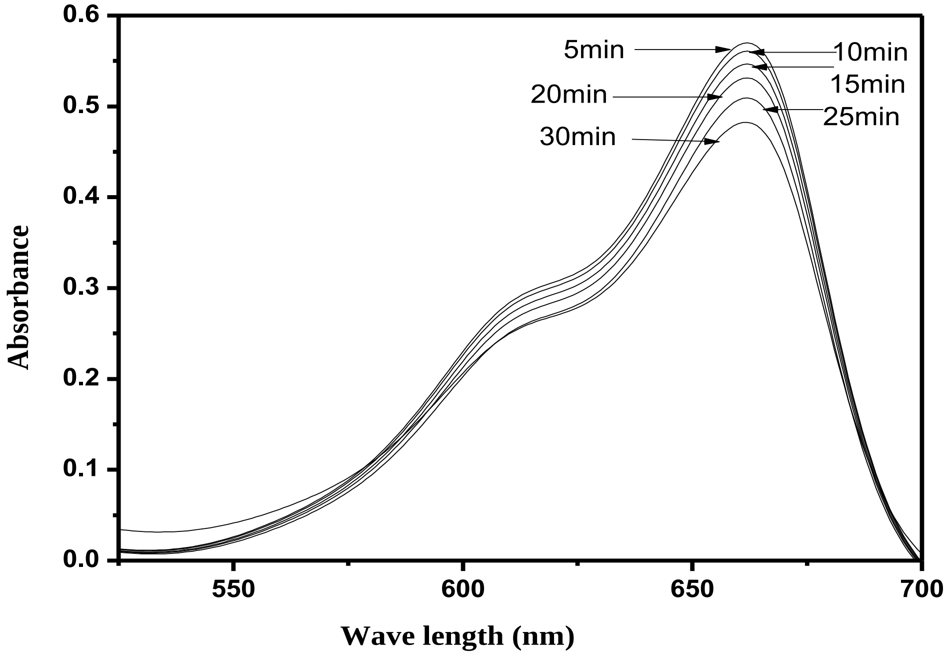

Fig. 4 UV-Visible spectrum of effect of time on catalytic activity of 0.01 g Ag

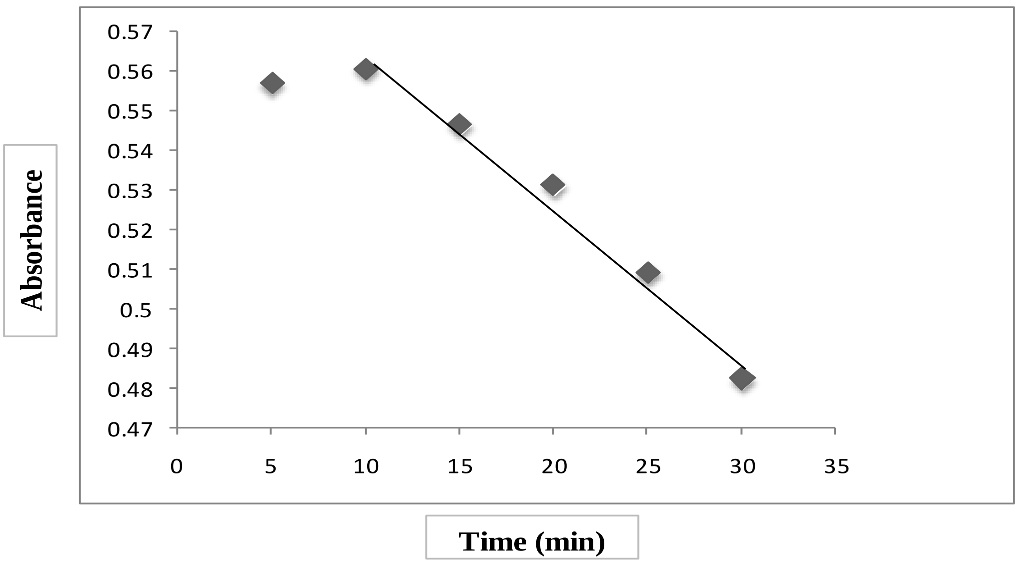

Fig. 5. Absorbance Vs time graph for 0.01 g Ag nano catalyst

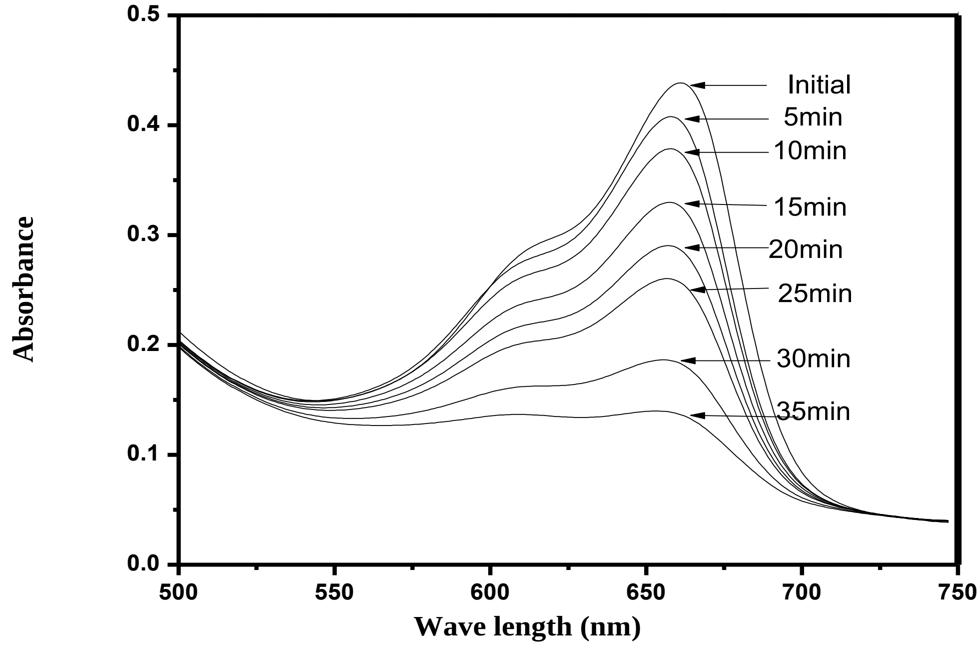

Fig. 6. UV-Visible spectrum of 0.05 g Ag at different time

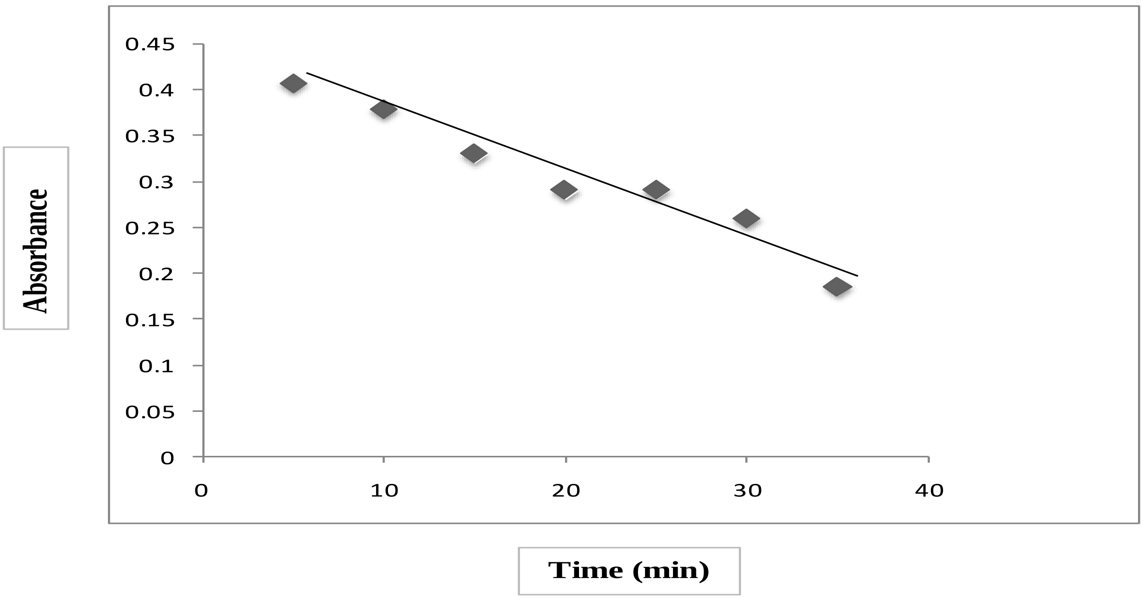

Fig. 7. Absorbance *vs* time graph 0.05 g Ag at different time interval

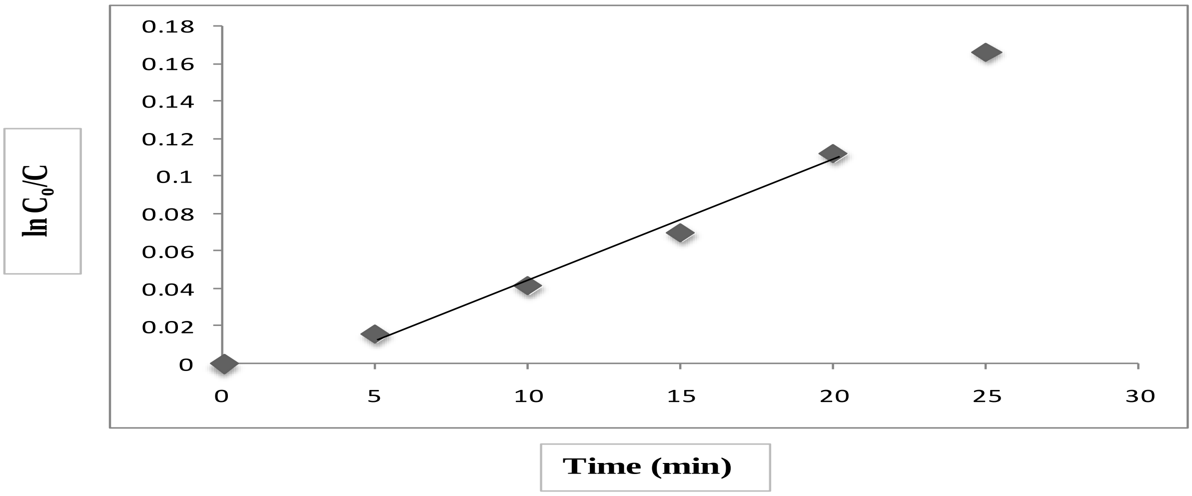

Fig. 8. lnC_o/C Vs time graph for 0.01g of nanocatalyst

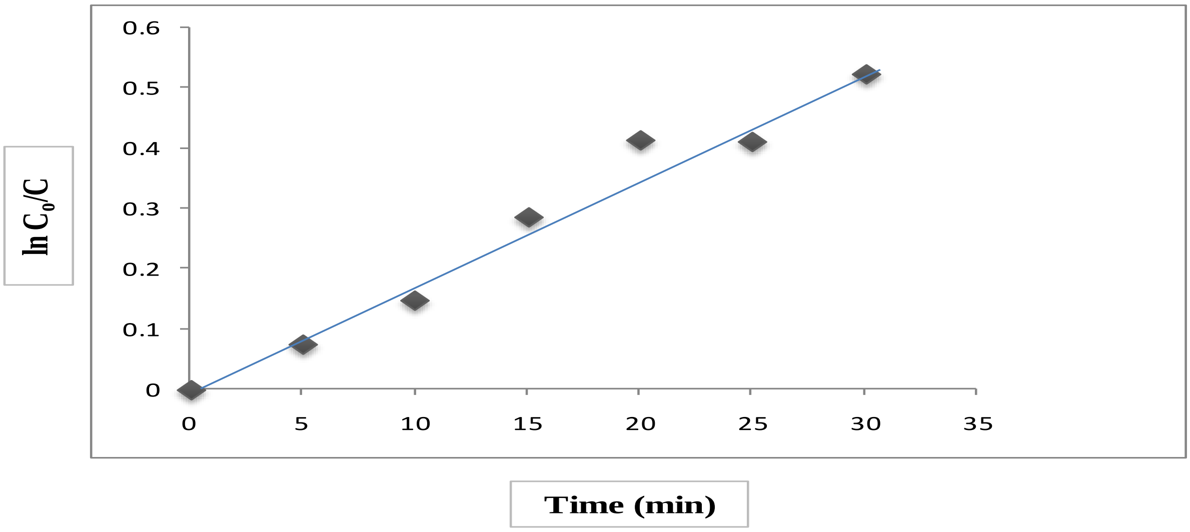

Fig. 9. lnC_o/C *vs* time graph for 0.05g of nanocatalyst

4. Conclusion

The chemical degradation of the dye was studied using silver nanocatalyst. Effect of different concentrations of the catalysts and also the time dependence on the catalytic activity were investigated by using UV-Visible spectroscopy. The study of the absorbance with different concentrations helped to make the conclusion that, as concentration of the catalyst increases, the absorbance decreases gradually. This indicates that, as the concentration of the catalyst increases, corresponding increase in degradation occurs. Similarly the absorbance at different reaction time was also studied. It has been observed that as the time increases, the reduction of the dye also increases, this is observed from the corresponding decrease in absorbance. From the kinetic studies, the rate of the catalytic activity was calculated which showed that as the concentration of the catalyst increases, the rate of the catalytic reaction increases.

5. References

Antonopoulou, M., Evgenidou, E., Lambropoulou, D. and Konstantinou, I. (2014). A review on advanced oxidation processes for the removal of taste and odor compounds from aqueous media. *Water Res.*, **53**: 215-220.

Badr, Y. and Mahmoud, M.A. (2007). Photocatalytic degradation of methyl orange by gold silver nano-core/silica nano-shell. *J. Phys. Chem. Solid.,* **68**: 413–419.

Collier, P.C., Saykally, R.J., Shiang, J.J., Henrichs, S.E. and Heath, J. (1997). Reversible Tuning of Silver Quantum Dot Monolayers Through the Metal-Insulator Transition. *Sci.*, **277**: 1978–1981.

Eisa, W.H. and Shabaka, A.A. (2013). Ag seeds mediated growth of Au nanoparticles within PVA matrix: An eco-friendly catalyst for degradation of 4-nitrophenol. *React. Funct. Polym.*, **73**: 1510–1516.

Hai, F.I., Yamamoto, K., and Fukushi, K. (2007). Hybrid treatment systems for dye wastewater. *Crit. Rev. Environ. Sci. Technol.,* **37**: 315–377.

Krstić, J., Spasojević, J., Radosavljević, A., Šiljegovć, M. and Kačarević, Z. (2014). Optical and structural properties of radiolytically in situ synthesized silver nanoparticles stabilized by chitosan/poly(vinyl alcohol) blends. *Radiat. Phys. Chem.*, **96**: 158–166.

Lee, K.S. and El-Sayed, M.A. (2006). Gold and silver nanoparticles in sensing and imaging: Sensitivity of plasmon response to size, shape, and metal composition. *J. Phys. Chem.,* **110**: 19220–19225.

Pandey, S., Pandey, S.K., Parashar, V., Mehrotra, G.K., Pandey, A.C., Mulik, U.P., Adamson, D.H., Schniepp, H.C., Chen, X., Ruoff, R.S., Nguyen, S.T., Aksay, I.A., Prud'Homme, R.K., Brinson, L.C. and Douglas, J.F. (2011): Ag/PVA nanocomposites: optical and thermal dimensions. *J. Mater. Chem.,* **21**: 17154.

Sagitha, P., Sarada, K. and Muraleedharan, K. (2016). One-pot synthesis of poly vinyl alcohol (PVA) supported silver nanoparticles and its efficiency in catalytic reduction of methylene blue. *Trans. Nonferrous Met. Soc. China.,* **26**: 2693−2700.

Sampaio, J.F., Beverly, K.C. and Heath, J.R. (2001). DC transport in self-assembled 2D layers of Ag nanoparticles. *J. Phys. Chem.,* **105**: 8797–8800.

Smith, G.B., Deller, C.A., Swift, P.D., Gentle, A., Garrett, P.D. and Fisher, W.K. (2002). Nanoparticle-doped polymer foils for use in solar control glazing. *J. Nanopart. Res.,* **4**: 157–165.

Wang, M., Tian, D., Tian, P. and Yuan, L. (2013). Synthesis of micron-SiO2 nano-Ag particles and their catalytic performance in 4-nitrophenol reduction. *Appl. Surf. Sci.,* **283**: 389–395.