



Short Communication

Visible Light Induced Photocatalytic Degradation of some Textile Dyes Using Silver Nano Particles

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Abstract

The preparation of stable, uniform silver nano particles by reduction of silver ions by polyvinyl alcohol is reported in the present paper. The samples have been characterized by SEM (scanning electron microscopy) which reveal the size of the nano particles as 50-100nm. These studies infer that the particles are spherical in shape. The UV-Vis spectra show that an absorption peak, occurring due to Surface Plasmon Resonance (SPR), exists at 420.226nm. Silver nano particles were prepared. Silver nano particles are used as a catalyst for the photocatalytic degradation of acid green 3GM and Blue ffs acid in the presence of H₂O₂. The kinetic study reveals that the photo catalytic degradation process is faster in the presence of silver nano particles/H₂O₂.

Keywords: Silver nano particles, photo catalytic degradation, hydrogen peroxide, dyes.

Introduction

Synthetic dyes are used extensively in numerous industrial processes. During various dyeing and finishing process, it is found that considerable amount of waste is generated. The discharge wastes containing dyes are toxic to micro organisms, aquatic organisms and human beings. These coloured dyes when discharged into rivers or lakes they cause non-aesthetic pollution, biological magnification eutrophication, toxicity and perturbation in aquatic life. These dye pollutant are chemically stable, so traditional water treatment methods are ineffective. Combination of UV radiation and hydrogen peroxide oxidation has been applied for the advanced oxidation degradation of dyes in waste water. UV/H₂O₂ process destroys the chromophore structure of these dyes, and leads to complete decolourisation of dyes. In the advanced oxidation process, the hydroxyl radical is formed which can oxidize the wide range of organic compounds and there is no sludge formation during different stages of treatment.

In the photo catalytic reactions, the semi conducting material absorbs light energy more than or equal to energy gap, which generates the holes and electrons, which further give rise to efficient oxidizers of organic dyes. For the degradation of organic dyes, nano silver used as a photo catalyst in aqueous medium which is a much needed process for the current issue. Smaller the particle size of the catalyst, especially in nano meters, better photo catalytic activity is imparted due to high surface area and high surface area to volume ratio values. We have focused our study on the oxidative degradation of two commercially used organic dyes Acid green 3GM (AG) and Blue Ffs acid (BFA) in aqueous medium in the presence of nano

crystalline silver as synthesized and characterized in the laboratory. UV-visible spectroscopy is employed to study the kinetic and reaction pathway of photo catalytic degradation of the dyes. In the figure 1 the molecular structure of the two dyes (AG and BFA) are given. The size characterizations on nano silver are measured using FE-SEM, and UV-visible spectrophotometer. The catalyst particle size and poly dispersity index are studied. The efficiency of H₂O₂ and nano silver catalyst for the degradation of the organic dyes are graded. The effect of variation in pH, solvent and ionic strength are carried out to optimize the oxidation rates in aqueous medium. Silver is known as a disinfectant for centuries. Presently, silver is an excellent candidate for antimicrobial finishes in textile sector. When silver metal has a size of nano level, the high specific surface areas and high fraction of surface atoms of silver nano particles will lead to bulk silver metal. Silver nano particles are one of the most commonly utilized nano materials due to their anti-microbial properties, high electrical conductivity and unique optical properties.

Material and Methods

Preparation of silver nano particles: In the synthesis of silver nano catalyst corresponds to silver nitrate for silver nano preparation. 0.001M of silver nitrate solution is taken in a beaker and stirred for 30 minutes. The temperature of the solution is raised to 80^o C using magnetic stirrer and capping agent poly vinyl alcohol (PVA). Then 0.001M of sodium borohydride solution (maintained under cold condition 5^oC) is added drop by drop, corresponding to silver salt solution and stirring is continued for 45 minutes. Characterisation of silver nano particles.

The photo absorption spectrum of Ag colloid dispersions were measured by VARIAN easy 50 Bio UV-Vis spectrophotometer. The synthesized silver nano particle is characterized using SEM technique. (Fig 2) The above SEM diagrams are taken in the micrometer scale where silver nano particles are having the size of 50-200nm size which is able to enhance the photo catalytic degradation property of silver nano particles figure 2.

Reaction catalysis: The catalytic degradation of the organic dyes were performed separately in a three necked round bottomed flask reactor. 100W tungsten lamp was let placing above the reactor in a chamber. For every 10ml of the aqueous solution, 1ml of 0.01M H₂O₂ and 1mg of catalyst were fed into the reactor and stirred continuously under visible light illumination. Small aliquots of the sample were collected at regular intervals of time. In the absence of light irradiation, the reaction was found to proceed feebly.

Results and Discussion

Kinetic studies: The aqueous solutions of organic dyes with known concentration are irradiated with, visible light using tungsten lamp which is compatible with solar radiation both in the presence of hydrogen peroxide and silver nano particles. After the start of the irradiation at regular intervals of time 5ml aliquots of the solution are subjected to UV-spectral scan. The completion of the oxidative degradation of the dyes is known from the gradual decrease of the absorbance value approaching the base line. The time of completion of oxidative degradation varies with the chemical structure of the organic dyes. From the time dependence UV-spectra profiles, OD Vs time plots are drawn. The limiting regions in the exponential plots indicate the completion of reactions. It was found that in the presence hydrogen peroxide the oxidative degradation was detected on the substrates and the rate of oxidative degradation is enhanced in the presence of silver nano particles in the present work. The photo catalytic disappearances of dyes are found initiated only upon the incorporation of hydrogen peroxide and silver nano particles. From the OD Vs time readings, the kinetic plots consisting of log [OD₀/OD_t] Vs time are generated. The first order rate coefficient (k) values are obtained from the slope values of the kinetic plots, multiplied with 2.303. The best fit linear plots are found in the kinetic analysis for the first order reaction under pseudo conditions only.

Spectral studies: In most cases the peak present in the visible region (more than 400nm) are chosen for the time dependence study on the spectra. In figure 3 time dependent UV-spectra for the organic dyes are presented. When the visible light was switched off, no variation in the UV- spectra with time was recorded. Therefore presence of visible light seems to trigger oxidative degradation soon after the visible light irradiation. Using these time dependent spectra absorbance Vs time plots were prepared.

The kinetic plots for the rate co-efficient determination was successfully generated using log OD₀/OD_t Vs Time data. Such kinetic plots are given in the figure 4.

In table 1 the pseudo first order rate coefficient values determined from the figure are given for the organic dyes. It was found that, among the organic dyes used, the rate coefficient value of was found to be the highest for acid green 3GM and least value is for Blue ffs acid in the presence of hydrogen peroxide. In the presence of silver nano particles the rate coefficient value was found to be the highest for acid green 3GM and the least value for the Blue Ffs Acid.

The silver nano particle is synthesized and characterized by using UV-visible spectrophotometer and Scanning electron microscope. In the UV- visible spectrophotometer a characteristic peak at 420nm shows the formation of silver nano particles and also in the SEM analysis 50-200nm size particles are formed which confirms the formation of silver nano particles.

The acid green dye has the wavelength of 560nm and it undergoes photo degradation in the presence of hydrogen peroxide. This is plotted as graph at various intervals of time. It is observed that the absorbance value decreases with time.

Conclusion

The photo catalytic oxidative degradation of the four pesticides by visible light irradiation was employed which is a green chemistry reaction. Silver nano particles as synthesized in the laboratory and size characterized to be 50-100nm particles are chosen as the photo catalyst for the visible light interactions. The trend in the overall rate coefficient values among the organic dyes found to be Acid green 3GM > Blue ffs acid.

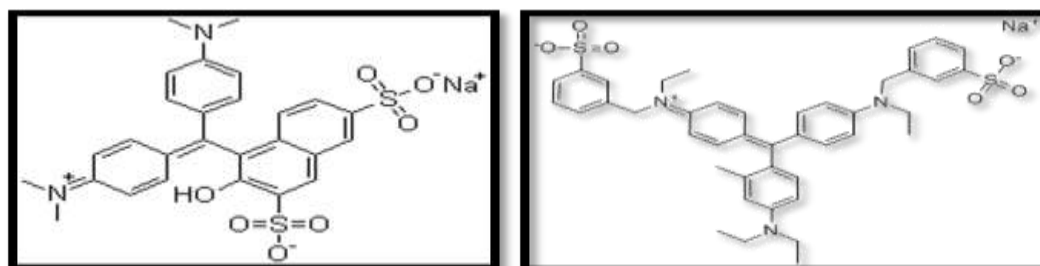


Figure-1
Molecular structure of AGM and BFA

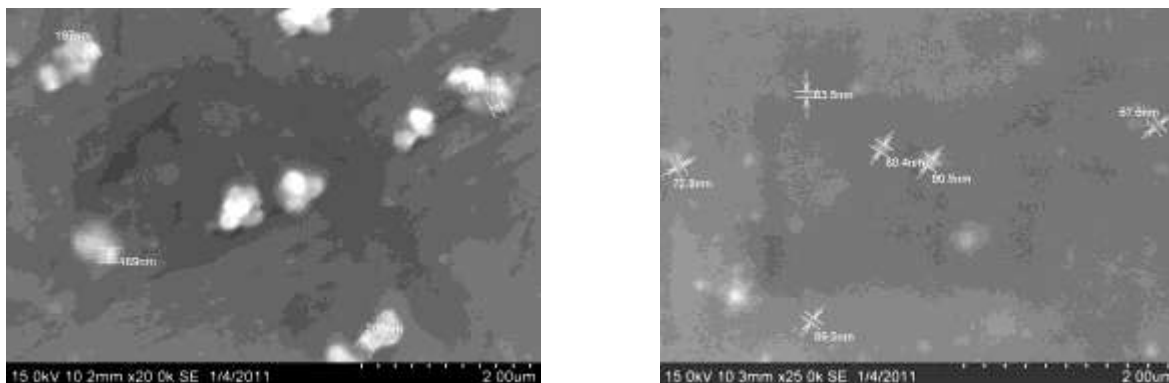


Figure 2
SEM image of Silver nano particles

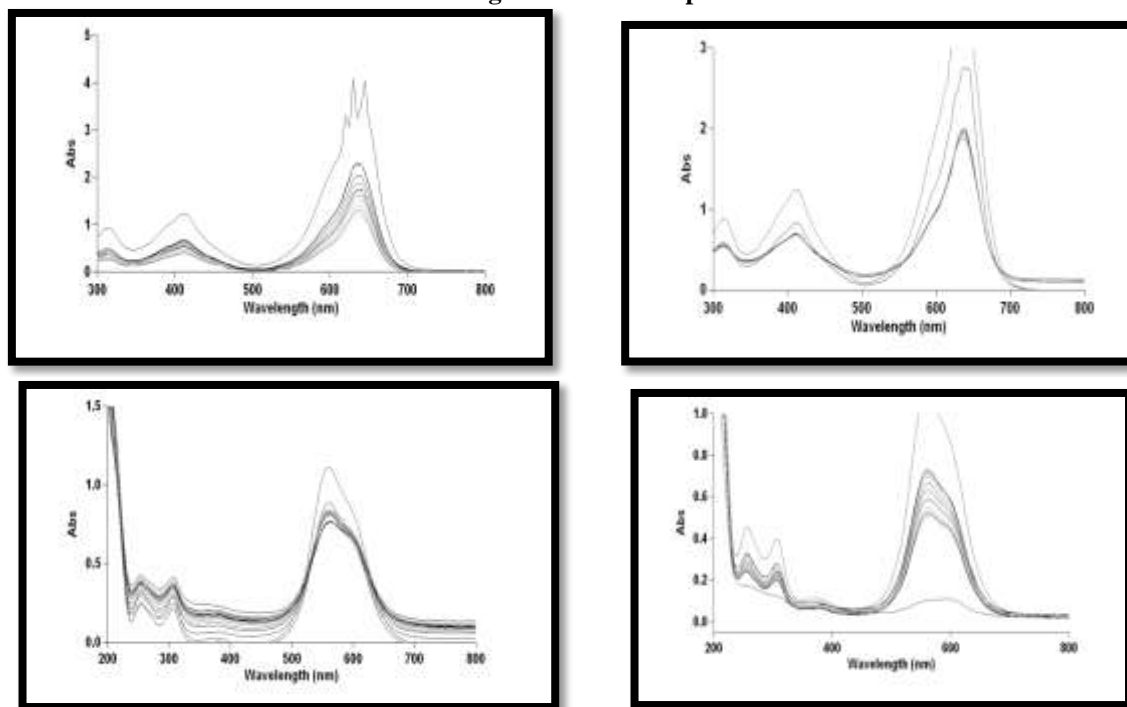


Figure-3
Time dependent UV-spectra for the organic dyes

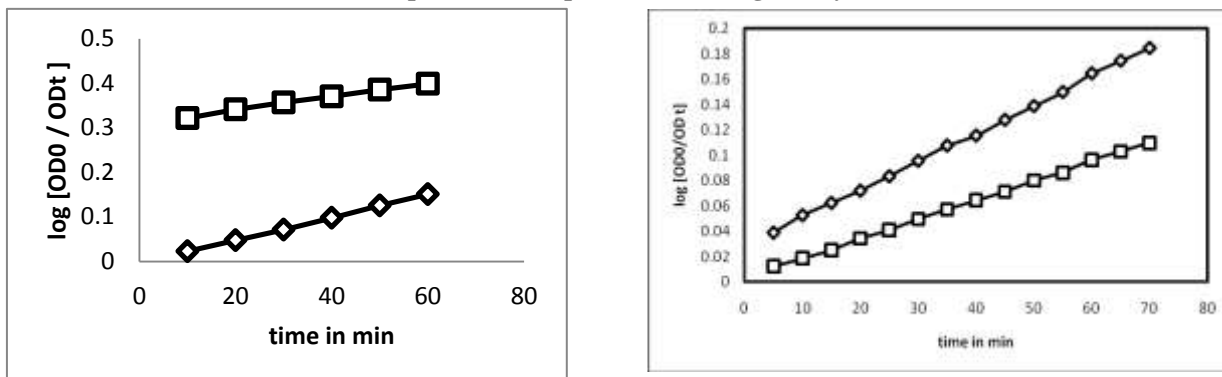


Figure 4
Kinetic plots of organic dyes AG and BFA

References

1. Robinson T., McMullan G., Marchant R. and Nigam, *Bioresour. Technol.*, **77**, 247-255 (2001)
2. Thou-Jen Whang, Hsien-Yu-Huang, Mu-Tao Hsieh and Jyun-Jen Chen, October (2009)
3. Jose Ruben Morones and Jose Luis Elechiguerra, *Nano technology*, 10(October), **16**, (2005)
4. Daniel M.C. and Struc D.A., *Chem. Rev.*, **104**, 293-346 (2004)
5. Pradeep T., Nano the essentials, Tata McGraw-Hill Publishing Company Limited, Edition (2007)
6. Maribel G., Guzman Jean Dille, Stephan Godet, World academy of science, *Engineering and technology*, **43**, (2008)
7. Jose Luis Elechiguerra, Justin L Burt and Jose R. Morones, *Journal of nano biotechnology*, **29**, (2005)
8. Jun Ping Zhang, Li Qi Sheng and Ping Chen, *Technical institute of physics and chemistry*, **4(6)**, 645-648 (2003)
9. Demberelnyamba Dorjnamjin, Maamaa Ariunaa and Young Key Shim, *International Journal of Molecular sciences*, **9(5)**, 807-820 (2008)
10. Das R., Nath S.S., Chakdar D., Gope G., Bhattacharjee R., *Journal of nano Technology*, (2009)
11. Valentine Rupa A., Manikandan D., Divakar D., Sivakumar T., 237(1998), 25, available online 30 January (2007)
12. Beltran F.J., Encinar J.M. and Alonso M.A., *Ind.Eng. Chem.Res.*, **37**, 25 (1988)
13. Stefan M. and Bolton J., *Environ. Sci. Technol.* **32**, 1588 (1998)
14. Shen Y.S., Ku Y. and Lee K.C., *water Res.* **29**, 907 (1995)
15. Kalayil Manian manesh, Anantha Iyengar gopalan, Kwang-pill lee, and shanmuga sundaram, komathi. Aug 6 (2009)
16. Badr Y. and Mahmoud M.A., *Journal of physics and Chemistry of solids*, **68(3)**, 413-419 (2007)
17. Nikhi R. Jana, Tapan K. sau, and Tarasankar pal., *The Journal of Physical Chemistry*, **10**, 115-121 (1998)
18. Jun-Hond liu, Ai-Qin wang, yu-shan clui, Hong-ping lin, andclung-yuan mou, *Journal of physical chemistry*, **8**, 40-43 (2004)
19. Yukihide Shiraishi and Naoki Toshima, *Journal of molecular catalysis A: Chemical*, **141(1-3)**, 187-192 (1999)
20. Lorreaine Mulfinger, sally D.solomon, Mozghan Bahadory, AravindanV. Jeyarajasingam, Susan a. Rutkowsky and Charles Boritz, *Journal of chemical education*, **1**, (2007)
21. Ales Panaek, Libor Kvitek, Robert prucek, Milon kolar, Reneta veerova, Nadezda pizurova, virendar k. sharma, Tat Jananaveena and Radek zboril, *The journal of physical chemistry*, (2006)