Photo-Catalytic Degradation of Toxic Dyes by Silver Nano Particles Synthesized From Peels Extracts of *Citrus medic a*t Through Green Method.

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Abstract-Dyes are chemical compounds which are used to convey colour to various materials, but during the processing and operation it produces toxics and hazardous side product which is very harmful to ecosystem and biodiversity. Researchers are developing various methods to degrade such toxic dyes and use of noble metal nano particle as a catalyst is emerging field of interest among scientific community. In this research article we had scanned our previously synthesized silver nanoparticle from *Citrus medica*peels extracts; Synthesis and characterization were previously reported by authors.SynthesizedAgNPs has excellent photo-catalytic potential against various toxic dyes like Methylene blue, Rose bengal, Acridine Orange, Methyl Orange. Our nano-catalyst methylene blue nearly 52.15% in 5 hours while in absence of nano-catalyst dye degrades nearly32.85%. It is also capable of degrading acridine orange study shows it degrade Acridine orange dye 58.74% in just 4 hours and rose bengal dye 59.57 % followed by 4 hours of Continuous UV absorption. It also degrades methyl orange dye nearly 52% in 10 hours of solar irradiation. Synthesized AgNPs can be used as photo-catalyst for degrading toxic dyes.

Keywords- Photo-catalyst, Methylene Blue, Acridine Orange, Methyl Orange, Rose Bengal

Introduction

Water resources are limited and water requirement is increasing at very high rate in developing countries like India so there is great need of water recycling and water purification so it can be used for various propose like in agriculture and industry. Solar energy is quite suitable source for photo-catalytic detoxification of waste water[1-4]

Non bio-degradable and hazardous nature of organic toxic dyes is one of the major concerns for scientific community. Waste water generated during the processing and operation of dyes is one of the remarkable sources of water pollution which is harmful to aquatic creatures and human health[5, 6]. Most of the organic dyes are non bio-degradable by standard biological methods. Methods including adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation, ion exchange and oxidation with peroxide are usually applied efficiently. Nevertheless, they do not destruct the pollutant molecule[7–9].

Among Nobal metal nanoparticle, silver nanoparticle (AgNPs) receiving a lot of consideration because of their non-toxic nature and a variety of reimbursement, including as antibacterial agents, Optical property and excellent photo-catalytic activity[10-11].Several research has revealed that silver nano-particle can degrade 95% of methylene blue dye in within 72 hours and AgNPs are capable of degrading 90% of methylene orange dye within 6 hours, at pH 2[12]

In this research article we had scanned our previously synthesized silver nanoparticle from *Citrus medica*peels extracts, Synthesis and characterization were previously reported by authors.SynthesizedAgNPs has excellent photo-catalytic potential against various toxic dyes like Methylene blue, rose bengal , Acradin Orange, Methyl Orange.

Material and Methods

We had synthesized silver nanoparticle from *Citrus Medica* Peels extract by green method.

Characterization of synthesized AgNPs was done by different spectroscopic technique like UV-Visible spectroscopy, X-ray diffraction method followed by SEM, EDAX and HR-TEM studies. The results of UV-Vis absorption study show a strong absorption bandof silver nanoparticles (AgNPs) at λ_{max}440 nm. The X-ray diffraction analysis confirmed that the synthesized AgNPs are cubic crystal solid. The SEM analysis of AgNPs shows average sizeof 1.35 μm, while the EDAX analysis confirmed the significant presence of silver with carbon, oxygen, chlorine and Iron as other contaminants. This

analysis is followed by TEM which shows that the water-soluble AgNPs, have approximate size 53nm, previously communicated by authors[13].

Assessment of photo-catalytic activity

The photo-catalytic activity of AgNPs was investigated using different dyes like Methylene blue, rose bengal, Acridin orange and Methyl orange. Before exposing the suspension to sunlight it was kept in dark condition until adsorption-desorption equilibrium was established. [14].

The experiment was performed with or without Ag NPs in solar irradiation and dark condition. The concentrations of the dyes for each prepared sample were analyzed by using UV–Vis spectroscopy technique, and the absorptions peaks of the dyes at characteristic wavelength were observed in all prepared sample. Calibration curves were used to calculate the concentrations of the dyes. The decolourization efficiencies of the dyes were estimated using the following relation.

Degradation (%) = $(C_o–C_t)/C_o×100$

where C_o and C_t represents the concentration of dye before illumination and dye after a certain irradiation at time *t* respectively.

Results and discussion

Photo-catalytic degradation of methylene blue dye by using synthesized AgNPs

Photo catalytic degradation of MB dye with the help of synthesized AgNPs was verified by UV-Visible spectrometer. The UV-Visible spectroscopy result shown decrease in the peak of MB at different interval of time. Initially, the absorption peak of MB was found at 664nm and at a high absorption value which decreased rapidly on exposing to sunlight, see **Figure-1(a).** The completion of the photo catalytic degradation of dye was confirmed when absorbance value for MB peak reach near to baseline. Amount of degradation of dye in percentage (%) of AgNPs was calculated 52.15% in 5 hrs, **Figure-1(b)** shows degradation on Methylene blue dye without nano catalyst amount of degradation of dye in percentage (%) was found32.85% in 5 hrs and UV-Visible spectroscopy results clearly reveals that dye degrade faster with synthesizednano-catalyst **Figure-1(c)** shows comparative study of dye degradation in different condition, our results also match with previous study[15]

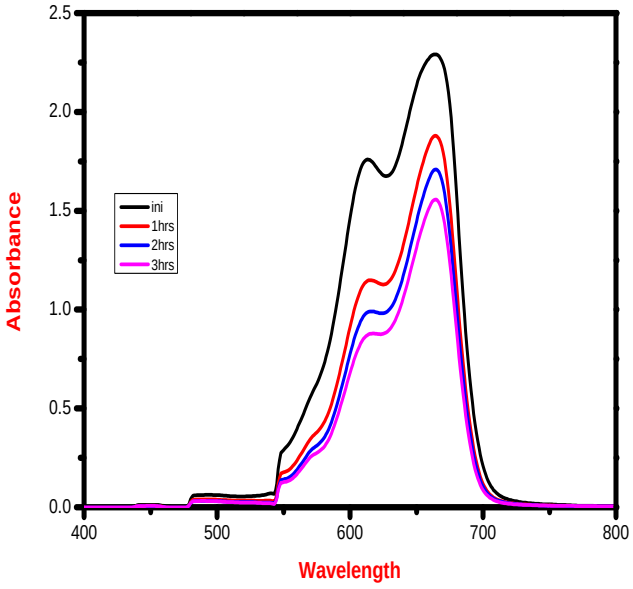

Figure-1(a) Degradation of MB in presence of AgNPs,

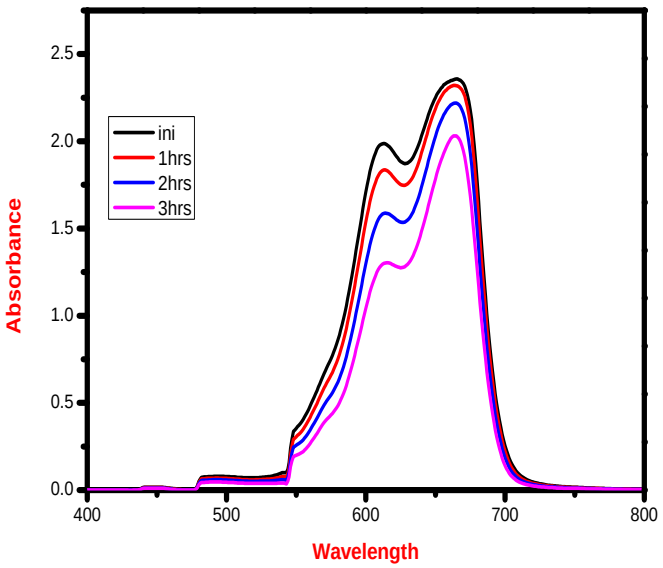

Figure-1(b) Degradation of MB without catalyst

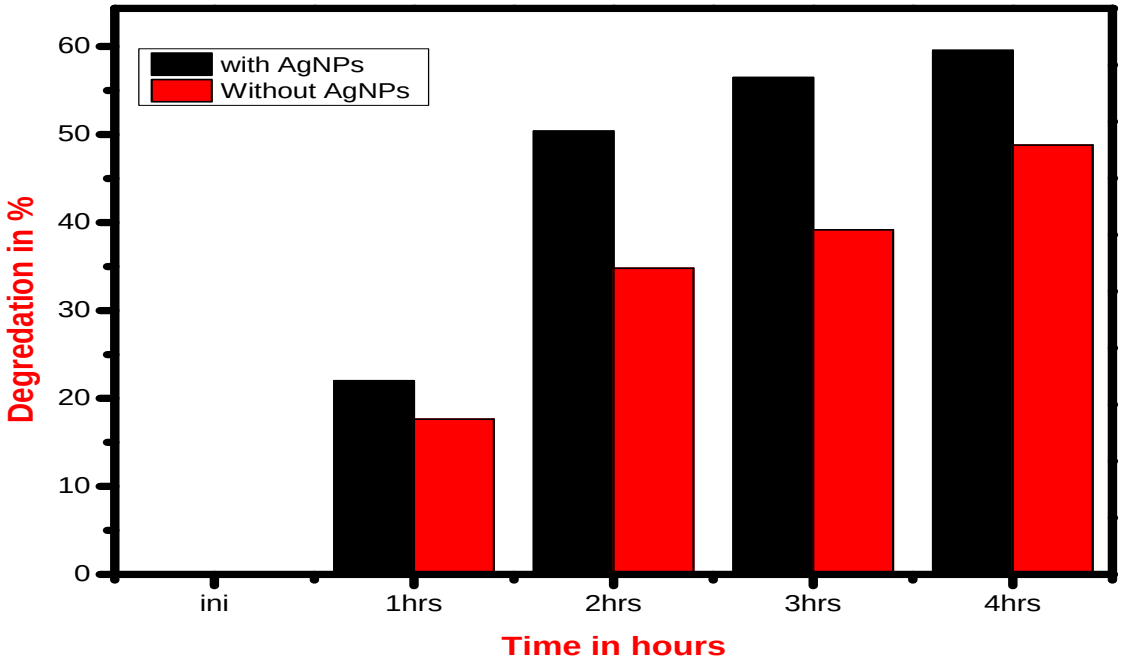

Figure 1(c) Comparative study of dye degradation

Photo-catalytic degradation of rose bengaldye by using synthesized AgNPs

Photo catalytic degradation of RB dye with the help of synthesized AgNPs was verified by UV-Visible spectrometer. The UV-Visible spectroscopy result shown decrease in the peak of RB at different interval of time. Initially, the absorption peak of RB was found at 543 nm and at a high absorption value which decreased rapidly on exposing to sunlight, see **Figure-2(a)**. The completion of the photocatalytic degradation of dye was confirmed when absorbance value for RB peak reach near to baseline. Amount of degradation of dye in percentage (%) of AgNPs was calculated 59.57% in 4 hrs, **Figure**-2(b) shows degradation on rose bengal dye without nano catalyst amount of degradation of dye in percentage (%) was found 48.88% in 4 hrs and UV-Visible spectroscopy results clearly reveals that dye degrade faster with synthesized nano-catalyst **Figure**-2(c) shows comparative study of dye degradation in different condition, our results also match with previous study[16] .

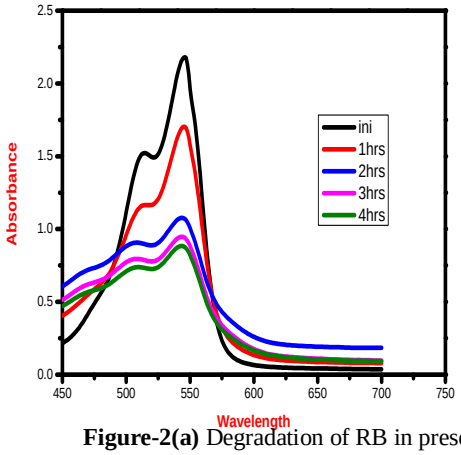

Figure-2(a) Degradation of RB in presence of AgNPs,

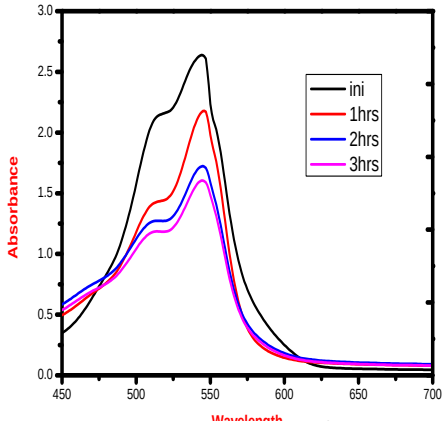

Figure-2 (b) Degradation of rose bangle without catalyst

Photo-catalytic degradation of acridin orange dye by using synthesized AgNPs

Photo catalytic degradation of AO dye with the help of synthesized AgNPs was verified by UV-Visible spectrometer. The UV-Visible spectroscopy result shown decrease in the peak of AO at different interval of time. Initially, the absorption peak of AO was found at 491nm and at a high absorption value which decreased rapidly on exposing to sunlight, see **Figure-3(a).** The completion of the photo catalytic degradation of dye was confirmed when absorbance value for AO peak reach near to baseline. Amount of degradation of dye in percentage (%) of AgNPs was calculated 58.74% in 4 hrs, **Figure-3(b)** shows degradation on acridinorange dye without nano catalyst amount of degradation of dye in percentage (%) was found 46.75% in 4 hrs and UV-Visible spectroscopy results clearly reveals that dye degrade faster with synthesized nano-catalyst **Figure -3(c)** shows comparative study of dye degradation in different condition, our results also match with previous study[17]

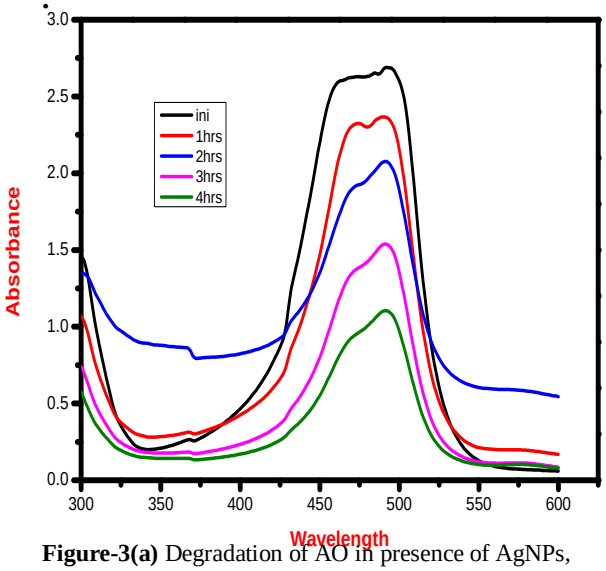

Figure-3(a) Degradation of AO in presence of AgNPs,

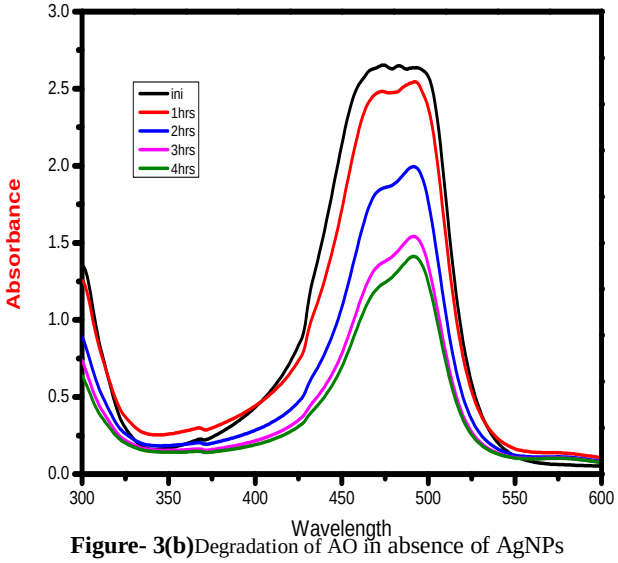

Figure- 3(b) Degradation of AO in absence of AgNPs

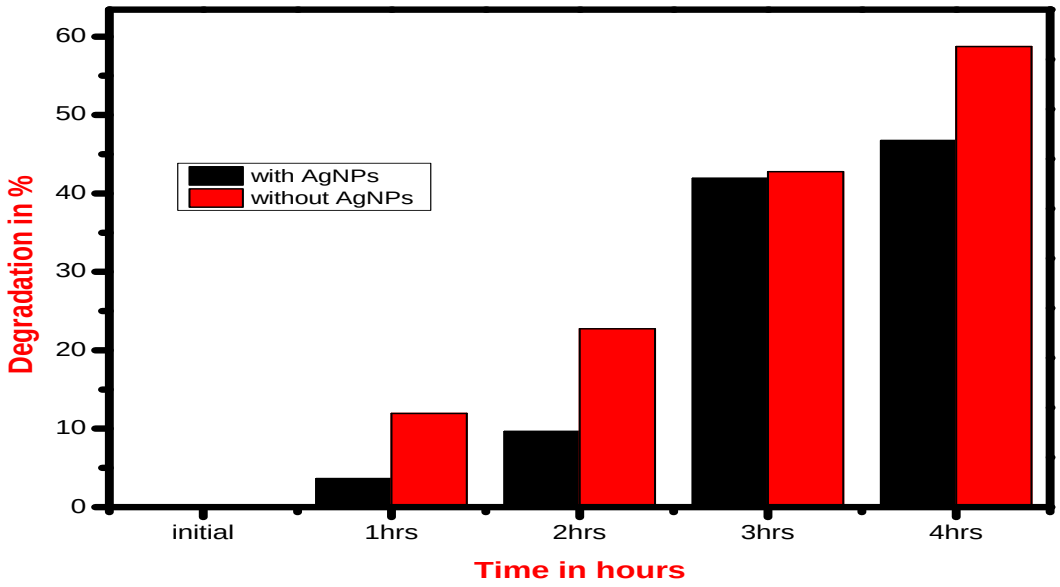

Figure- 3(c) comparative study of dye degradation

Photo-catalytic degradation of Methyl Orange dye by using synthesized AgNPs

Photo catalytic degradation of MO dye with the help of synthesized AgNPs was verified by UV-Visible spectrometer. The UV-Visible spectroscopy result shown decrease in the peak of MO at different interval of time. Initially, the absorption peak of MO was found at 507 nm and at a high absorption value which decreased rapidly on exposing to sunlight, see **Figure**-4(a). The completion of the photo catalytic degradation of dye was confirmed when absorbance value for MO peak reach near to baseline. Amount of degradation of dye in percentage (%) of AgNPs was calculated 52% in 10 hrs, **Figure**-4(b) shows degradation on methyl orange dye without nano catalyst amount of degradation of dye in percentage (%) was found35% in 10 hrs and UV-Visible spectroscopy results clearly reveals that dye degrade faster with synthesized nano-catalyst **. Figure**-4(c) shows comparative study of dye degradation in differentcondition, our results also match with previous study[18].

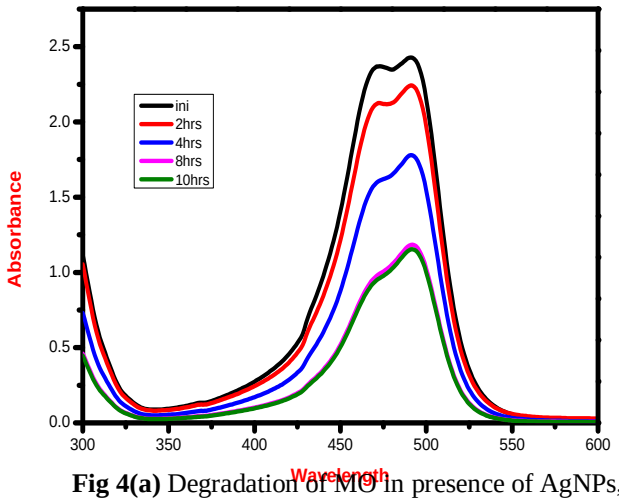

Fig 4(a) Degradation of MO in presence of AgNPs, AgNPs

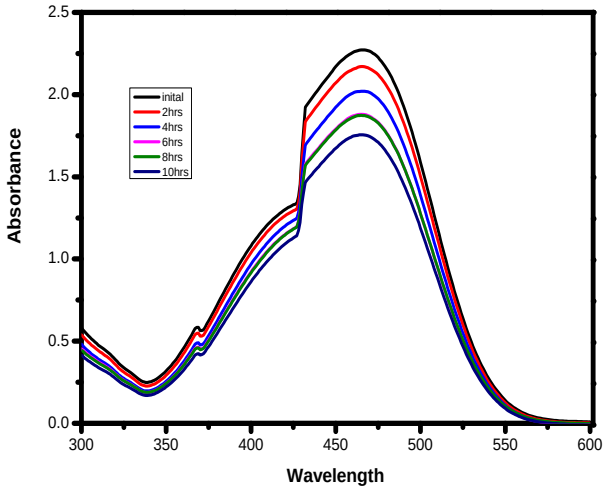

Figure-4(b) Degradation of MO in absence of

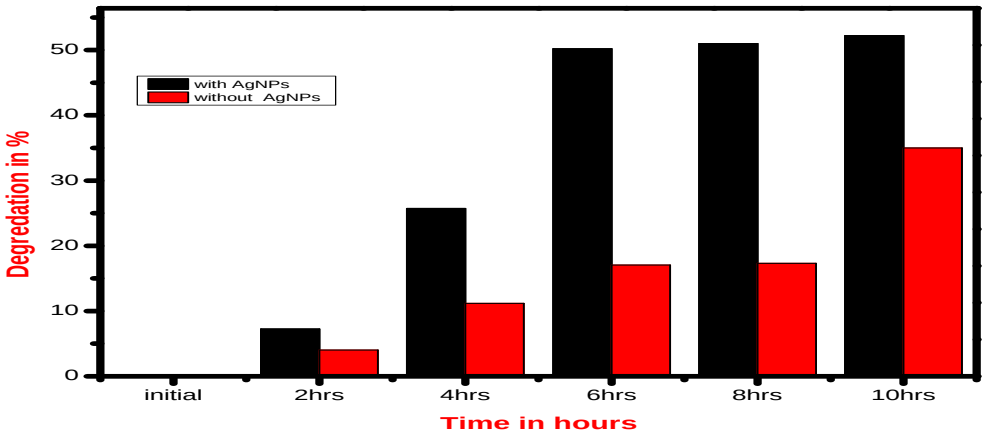

Figure- 4(c) Comparative study of dye degradation

Conclusion

Dyes are chemical compounds which are used to convey colour to various materials, but during the processing and operation it produces toxics and hazardous side products which is very harmful to ecosystem and biodiversity. Researchers are developing various methods to degrade such toxic dyes

and use of noble metal nano particle as a catalyst is emerging field of interest among scientific community. Synthesized AgNPs has excellent photo-catalytic potential against various toxic dyes like Methylene blue, Rose bengal, Acridin Orange, Methyl orange. Our nano-catalyst depredates methylene blue nearly 52.15% in 5 hours while in absence of nano-catalyst dye degrades nearly32.85%. It is also capable of degrading acridine orange. Study shows that it degrades acridine orange dye 58.74% in just 4 hours and rose bengal dye 59.57 % followed by 4 hours of continuous UV absorption. It also degrades methyl orange dye nearly 52% in 10 hours of solar irradiation. Synthesized AgNPs can be used as photo-catalyst for degrading toxic dyes.

References

1. Tributsch, H. Feasibility of toxic chemical waste processing in large scale solar installations. *Solar energy*, 1989,*43*(3): 139-143.
2. Tyner, C. E. Application of solar thermal technology to the destruction of hazardous wastes. *Solar energy materials*, 1990, *21*(2-3): 113-129.
3. Liu, C.; Liu, H.; Wang, X. and Han, L. Preparation of Novel TiO_2/TiPhotoelectrode and Photoelectrocatalytic Degradation of Rhodamine B. In *2008 2nd International Conference on Bioinformatics and Biomedical Engineering* 2008,(May). $P_{p.}$ 4709-4712, IEEE.
4. Freudenhammer, H.D.; Bahnemann, L.; Bousselmi, S-V.; Geissen, A.; Ghrabi, F.; Saleh, A.; Si-Salah, V.; Siemon and A. Vogelpohln. "Detoxification and recycling of wastewater by solar-catalytic treatment." *Water Science and Technology*, 1997, 35, (4) : 149-156.
5. Galindo, C.; Jacques, P. and Kalt, A. Photooxidation of the phenylazonaphthol AO_20 on TiO_2: kinetic and mechanistic investigations. *Chemosphere*, 2001, *45*(6-7): 997-1005.
6. Herrmann, J. M. Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catalysis today*, 1999, *53*(1): 115-129.
7. Pagga, U. and Taeger, K. Development of a method for adsorption of dyestuffs on activated sludge. *Water Research*, 1994, *28*(5): 1051-1057.
8. Krik, O. Encyclopedia of Chemical Technology. 4th ed., 8 (1993) 753.
9. Gouvea, C.A.; Wypych, F.; Moraes, S.G.; Duran, N.; Nagata, N. and Peralta-Zamora, P. Semiconductor-assisted photocatalytic degradation of reactive dyes in aqueous solution. *Chemosphere*, 2000, 40(4): 433-440.
10. Kim, D.; Jeong, S. and Moon, J. Synthesis of silver nanoparticles using the polyol processandtheinfluence of precursorinjection. *Nanotechnology*
11. , 2006,*17*(16): 4019.
12. Vanaja, M.; Paulkumar, K.; Baburaja, M.; Rajeshkumar, S.; Gnanajobitha, G.; Malarkodi, C.; Sivakavinesan, M. and Annadurai, G.*Bioinorg.Chem. Appl.*, 2014 (1).
13. Suprihatin, I.E.; Lestari, G.A.D.; Mardhani, R. and Edoway, V. Silver nanoparticles (AgNPs) as photocatalyst in the photodegradation of rhemazol brilliant blue. In *IOP Conference Series: Materials Science and Engineering* (Vol. 959, No. 1, $P_{p.}$ 012018). IOP Publishing,October,2020.
14. *Sati, S.C.; Ankit S. Bartwal, and Alok Kumar Agarwal. "Green synthesis of silver nanoparticles from Citrus medicapeels and determination of its antioxidant activity." (2020).
15. Zhao, W.; Bai, Z.; Ren, A.; Guo, B. and Wu, C. Sunlight photocatalytic activity of CdS modified TiO_2 loaded on activated carbon fibers. *Applied Surface Science*, 2010, *256*(11): 3493-3498..
16. Bogireddy, N.K.R.; Kumar, H.A.K. and Mandal, B.K. Biofabricated silver nanoparticles as green catalyst in the degradation of different textile dyes. *Journal of environmental chemical engineering*, 2016, *4*(1): 56-64.
17. Murugadoss, G.; Kumar, D.D.; Kumar, M.R.; Venkatesh, N. and Sakthivel, P.

Silver decorated CeO_2 nanoparticles for rapid photocatalytic degradation of textile rose bengal dye. *Scientific Reports*, 2021, *11*(1): 1-13.

18. Qamar, M. Photodegradation of acridine orange catalyzed by nanostructured titanium dioxide modified with platinum and silver metals. *Desalination*, 2010, *254*(1-3): 108-113.
19. Selvam, G.G. and Sivakumar, K. Phycosynthesis of silver nanoparticles and photocatalytic degradation of methyl orange dye using silver (Ag) nanoparticles synthesized from Hypneamusciformis (Wulfen) J.V. Lamouroux. *Applied Nanoscience*, 2015,*5*(5): 617-622.