Enhanced Photocatalytic Degradation of Methylene Blue Dye using Ag-Fe_2O_3 Core-shell Nanoparticles

Maheshwari Zirpe and Thakur Jyotsna*
C. K. Thakur A.C.S. College, New Panvel (W), Raigad, Maharashtra, 410206, INDIA
*thakurjyotsna@gmail.com

Abstract
This study aims to investigate the photocatalytic efficiency of Ag-Fe_2O_3 core-shell nanoparticles towards the degradation of methylene blue in the wastewater. Ag-Fe_2O_3 core-shell nanoparticles were synthesized by sol-gel auto combustion method and characterized by X-ray diffractometer, transmission electron microscopy, FTIR and BET technique etc.

Ag-Fe_2O_3 core-shell nanoparticles exhibited enhanced photocatalytic activity by degrading 96.33% of dye under sunlight. Neutral pH, 20 mg of catalyst loading, initial concentration of 10 mg/L and 30 min irradiation time are the optimized conditions. The degradation of MB fitted well with the Pseudo first-order kinetics.

Keywords: Ag-Fe_2O_3 core-shell nanoparticles, Methylene Blue, Photocatalytic degradation, Kinetics.

Introduction

Due to rapid industrialization, many organic pollutants are introduced to the environment. The voracious consumption of water by textile and leather industry for bleaching, dyeing, washing and finishing processes in turn, creates huge pollution of toxic dyes released into the water. Some of these dyes may be metabolized to carcinogenic substances[1]. Discharge and treatment of the effluent generated by the textile-processing industry are the biggest challenges towards sustainability. Various techniques have been tried to overcome these issues. such as oxidative degradation, adsorption, electrocoagulation, photocatalytic degradation etc.[2,3]

Photocatalytic degradation using nanomaterials is one of the viable options to decompose such organic pollutants[4]. There are many semiconductor nanomaterials such as TiO_2, Fe_2O_3 etc used regularly for photocatalytic activity due to their high specific surface area and high crystallinity. Hematite due to its narrow bandgap, with high chemical stability makes it act as a visible light photocatalyst[5]. The photocatalytic behaviour of Fe_2O_3 can be improved by coupling it with various metal oxides, inorganic nanoparticles, metal sulphides like SnS_2 etc.[6] Magnetic nanoparticles have been used to enhance the ability of the composite to separate from the solution.

Methylene blue is a thiazine dye widely used as an indicator, stain in bacteriology, used to dye the hemp, jute and flax, silk and wool[7,8]. In present work, Ag-Fe_2O_3 core-shell nanoparticles were used for photocatalytic degradation of methylene blue in aqueous solution. Incorporation of silver with Fe_2O_3 results in efficient antibacterial and photocatalytic capacity through the electron transfer process[9].

Material and Methods

Materials: Citric acid monohydrate (99%, Sigma Aldrich), Ferric nitrate nonahydrate (98%, Sigma Aldrich), Silver nitrate (Sigma Aldrich), Ammonia, Methylene blue were used without any purification. Deionised water was used for the preparation of solutions. All the reagents were A.R. grade.

Preparation of catalyst: The Ag-Fe_2O_3 was synthesised by facile sol-gel auto combustion method. Silver nitrate and Ferric nitrate nonahydrate were used as metal precursors and citric acid as a fuel. An aqueous solution containing a stoichiometric molar ratio of reactants was stirred for 10 mins, then NH_3 was added dropwise till the solution become alkaline. The solution was stirred for 1 hr at 60^0C, then the temperature is slowly raised to 100^0C till sol transforms into gel[10,11]. On further heating, gel undergoes auto combustion to form Ag-Fe_2O_3 nanoparticles.

Characterisation: Purity and morphology of the Ag-Fe_2O_3photocatalyst were characterized by X-ray diffractometer (X′pert PRO PANalytical). The average crystallite size was calculated by Scherer formula. Morphological features were determined by Transmission Electron Microscopy (JEOL 123 TEM fitted with a GATAN ORIUS CCD Camera). The specific surface area is determined by N_2 adsorption at 77K using the BET equation (SMART SORB 93). pHzpc value of catalyst was determined by the method described by Stumm.[12] Degradation profile of the dye was studied by recording Fourier transfer infrared (FT-IR) spectra on Shimadzu, IR Affinity-1 spectrophotometer before and after photodegradation.

Photocatalytic study: Photodegradation study was performed in sunlight by batch method by using a 50 mL solution of 10 mg/L of methylene blue dye. Before exposing to sunlight, the dye is equilibrated with the catalyst for 30 mins in dark. The pH of the solution was adjusted using 0.1M HCl and 0.1 M NaOH. After the reaction, the catalyst was separate by external magnet and absorbance of the dye was measured at 665nm using UV-Visible spectrophotometer (Shimadzu UV 1601, Japan).

The degradation percentage (D %) of dye was calculated using the following equations:

$$D\% = \frac{(C_o - C_e)\times 100}{C_o} = \frac{(A_o - Ai)\times 100}{Ao} \quad (1)$$

where C_o is the initial concentration of dye in mg/L, C_e is equilibrium concentration of dye in mg/L, V is the volume of solution in L, m is weight in grams, A_o is the initial absorbance and A_i is the absorbance at time t.

The effect of irradiation time, pH, catalyst loading and initial concentration was studied for optimization of the photodegradation process.

Results and Discussion

X-Ray Diffractometer analysis: The XRD pattern of prepared powder in figure 1 clearly shows the separate diffraction peaks corresponding to the cubic spinel phase of Ag and Fe_2O_3. Strong reflections can be seen which correspond to (111), (200) and (311) of Ag and (220), (310), (411), (421) and (520) of Fe_2O_3 according to JCPDS crystallographic table. (JCPDS 65-2871) and (JCPDS 39-1346). Low strength of Fe_2O_3 peaks in spectra indicates Ag coating on Fe_2O_3 particles. There were no additional peaks in XRD which indicates the formation of high purity nanohybrid. The average crystalline particle size was estimated to be 84.25 nm using Debye Scherer's formula (eq. 2):

$$d = k\lambda/\beta cos\theta \quad (2)$$

where d, k, λ, ß, θ are the crystal size, Scherrer's constant (0.89), X-ray wavelength (0.154nm), the peak (FWHM) full width at half maximum and Bragg's diffraction angle respectively.

Transmission Electron Microscopy analysis: TEM image (Figure 2a) depicts the formation of core-shell Ag-Fe_2O_3 nanocubes. Selected area electron diffraction pattern (SAED) image confirms the formation of a crystalline composite of Ag and Fe_2O_3.

pH of the zero point of charge (pHzpc): The photocatalysis is greatly influenced by the pH of the solution. The pH of zero charge Ag-Fe_2O_3 was found to be 6. It means at pH 6 and above, the catalyst surface gets deprotonated which results into increase in its binding capacity toward dye.

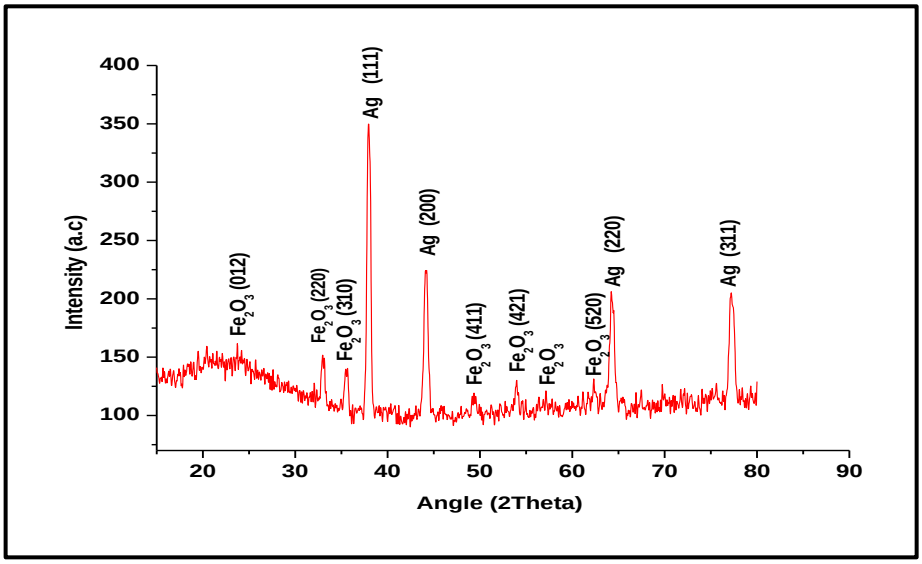


Figure 1: The XRD pattern of Ag-Fe_2O_3

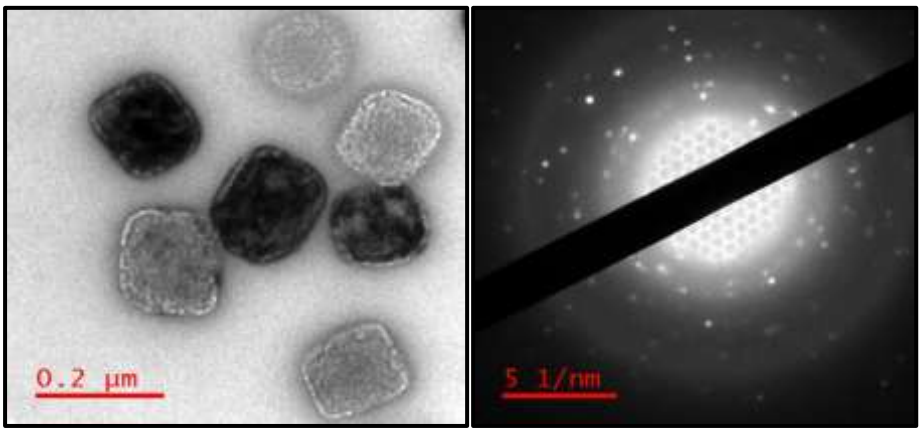


Figure 2: a) TEM image of cubic Ag-Fe_2O_3 nanohybrid b) SAED image of Ag-Fe_2O_3

Photocatalytic degradation of methylene blue: Ag-Fe_2O_3 core-shell nanoparticles were found to show enhanced catalytic behaviour towards methylene blue dye. Degradation of dye was confirmed from FTIR analysis. The efficiency of Ag-Fe_2O_3 core-shell nanoparticles as photo-catalyst was determined at various conditions to optimize parameters for efficient photo-degradation.

FTIR Analysis: Photo-degradation of methylene blue dye was evaluated by FTIR analysis of methylene blue before degradation and after 30 min photo-catalytic degradation. The spectra are represented in figure 3a and 3b respectively. Methylene blue which is 3,7-bis(dimethylamino) phenothiazine-5-ium chloride shows a broad peak at 3459.59 cm^{-1} ascribed to the hydroxyl free radicals of water molecule [13]. The peaks at 2941.29 cm^{-1} and 2847.47 cm^{-1} represent stretching vibration of $–CH_3$ and –CH– aromatic groups, the peak at 1633.78 cm^{-1} is attributed to N-H bending vibrations of primary amines.

The absorption band in fig. 3a at 623.26 cm^{-1} belongs to C-S-C framework vibration which disappeared in fig. 3b; it indicates the breaking of C-S-C- framework. The appearance of absorption peaks at 1151.28 cm^{-1} and 1035.45 cm^{-1} after photodegradation characterizes S=O bond and C-O bending vibrations[14]. It describes the destruction of the conjugate structure of N-S heterocyclic compound and aromatic ring during photocatalytic oxidation.

Effect of Contact time: Fig. 4 shows the strong absorption band at λ = 665 nm decreasing with time and found negligible after irradiation for 30 min. It was found that 96.33% of the dye degraded in 30 min (fig. 5). Further, increase in time results in the gradual degradation of dye. Thus, the irradiation time was optimized as 30 min. However, equilibration in dark for 1h showed a negligible change in the absorbance; it supports that dye removal resulted due to photdegradation in sunlight.

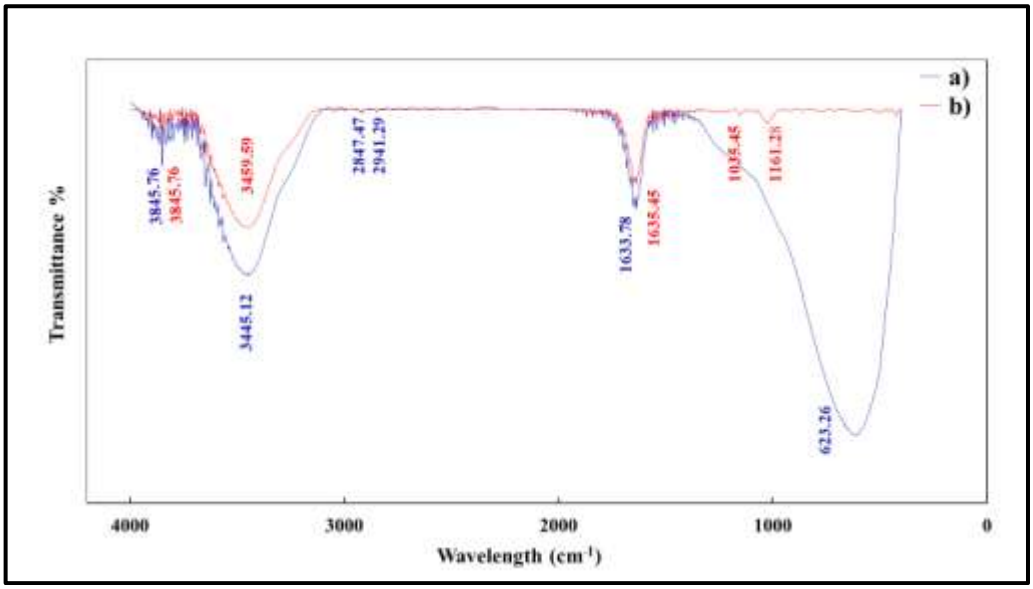


Figure 3: FTIR spectra before and after photodegradation of methylene blue by Ag-Fe_2O_3 catalyst

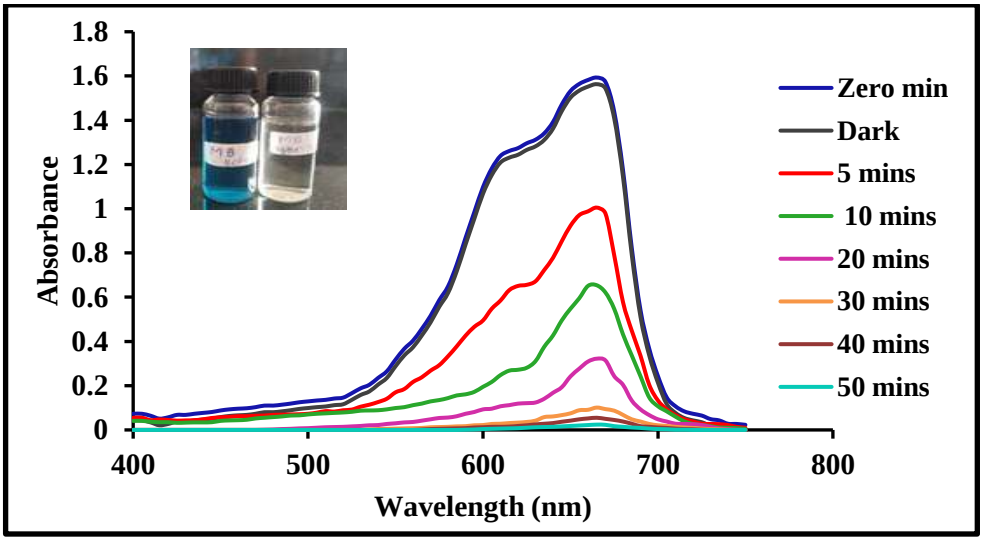


Figure 4: The UV-visible spectra of photodegradation of methylene blue solution using Ag-Fe_2O_3 catalyst under solar light in a neutral suspension with time

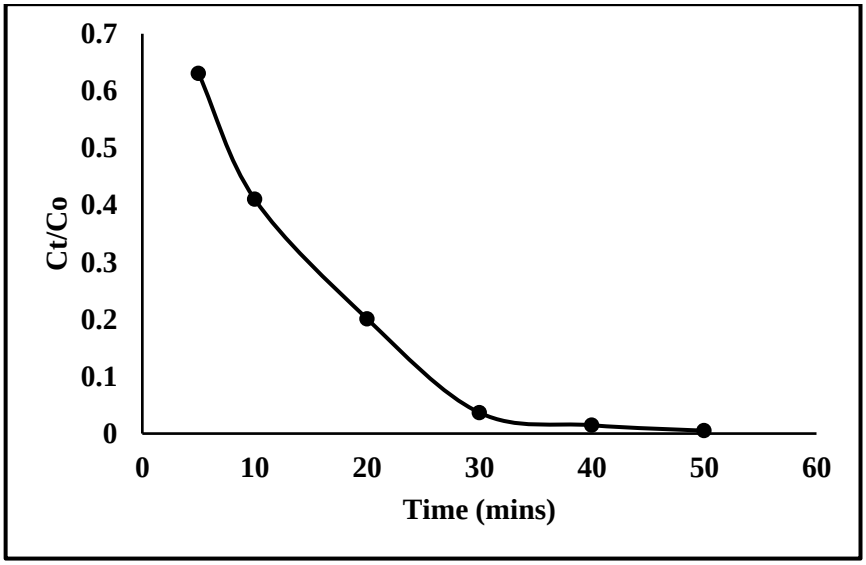


Figure 5: Effect of time on degradation efficiency of methylene blue using Ag-Fe_2O_3 photocatalyst

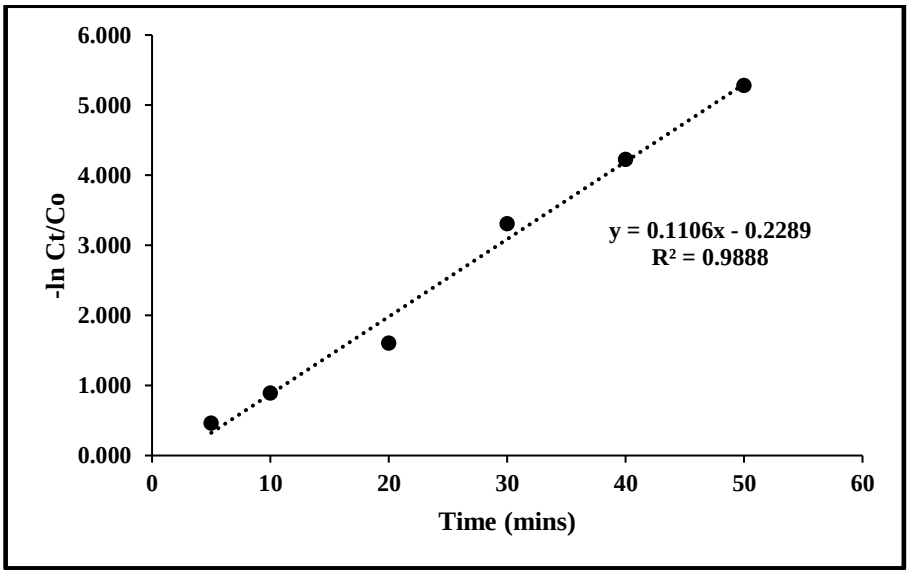


Figure 6: Apparent Langmuir-Hinshelwood First-order kinetics in the presence of Ag-Fe_2O_3

Kinetic modelling: The photocatalytic degradation of the dye was found to follow Langmuir-Hinslewood pseudo-first-order reaction[15] which describes degradation by the Photo-Fenton catalysis process.

$$-ln\frac{Ct}{Co} = Kt \quad (3)$$

where C_o is the original concentration of dye (mg/L), C_t is the residual concentration at time t min, K is the pseudo-first-order rate constant in min^{-1}. The linear plot of ln (C_o/C_t) against time in fig. 6 implies that the photodegradation process follows pseudo-first-order reaction. The rate constant calculated was 0.1106 $min.^{-1}$

Effect of pH: The effect of pH on the degradation efficiency of the catalyst was assessed at pH 2 to 9. As shown in fig. 7, the degradation of dye increases with the increase in pH. Maximum decomposition of about 96 % was observed at pH 7 and then it increased gradually. Thus, pH 7 was fixed for the study. The results clearly indicate that the degradation favours at higher pH. It may be due to the formation of hydroxyl radicals (●OH) at the surface of the catalyst which acts as an oxidative species and reacts unselectively and instantaneously with the dye[16].

Effect of catalyst loading: The effect of catalyst loading on the photocatalytic degradation of methylene blue dye was also evaluated by using dose increments from 5 mg to 40 mg. Increase in catalyst loading resulted into increase in percentage degradation as shown in fig. 8. Maximum degradation of about 96 % was found to obtain using 20 mg of catalyst.

Effect of the initial concentration of dye: Fig. 9 clearly shows that the degradation efficiency decreases with increase in the initial concentration of dye which may be attributed to the amount of hydroxyl radical generated by the photocatalyst due to increase in the concentration of dye.

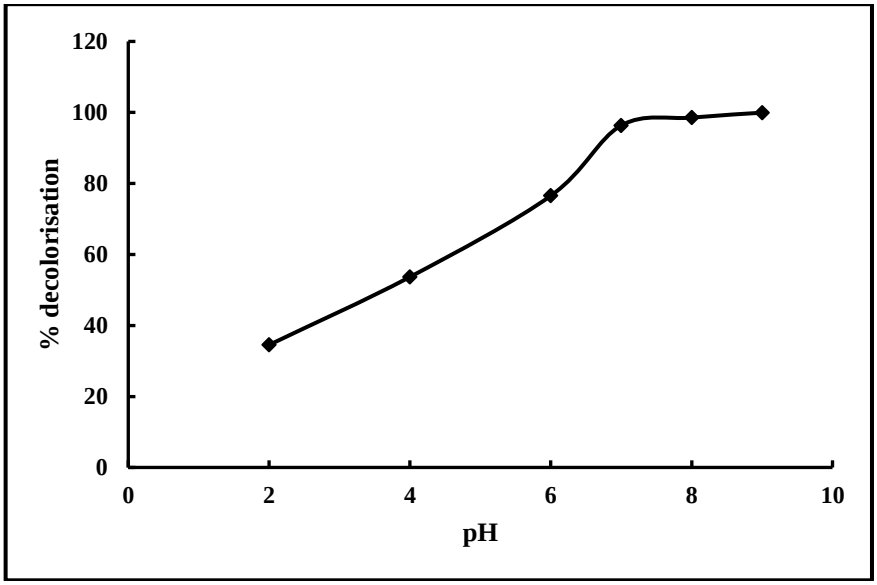


Figure 7: Effect of pH on photocatalytic degradation of methylene blue dye

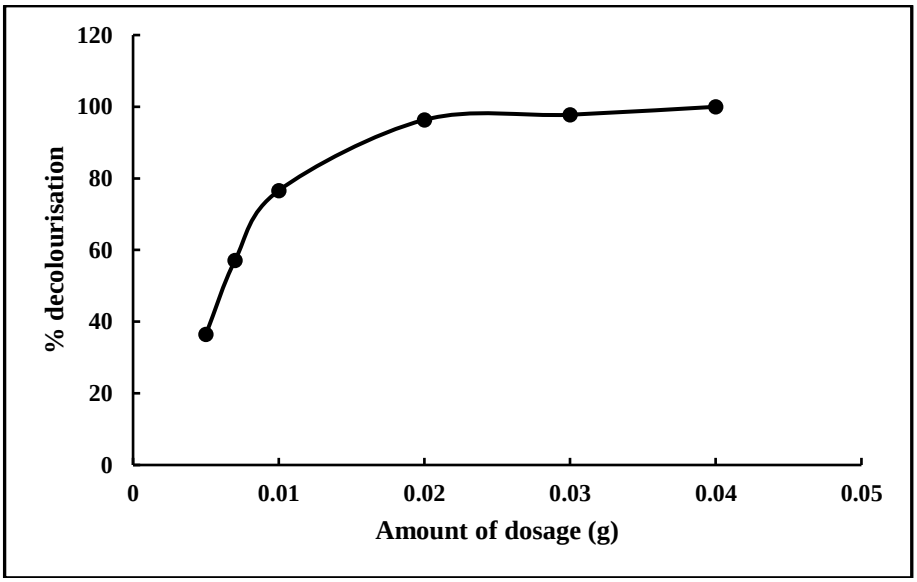


Figure 8: Effect of the catalytic loading on the degradation of methylene blue dye

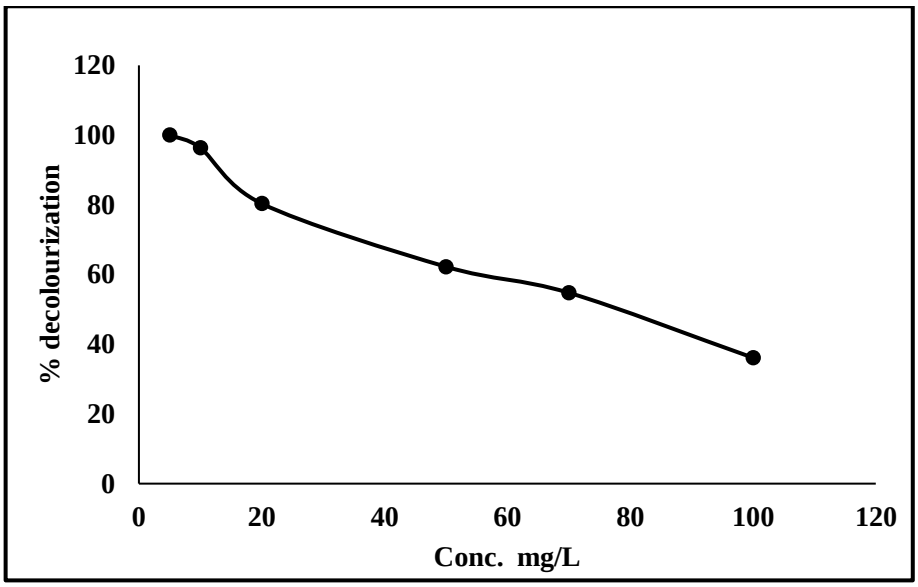


Figure 9: Effect of initial concentration on photodegradation of methylene blue dye

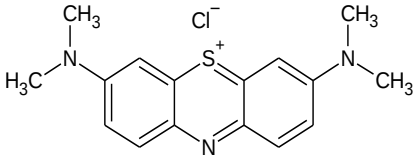
Photocatalytic Process: In the presence of air or oxygen, the irradiated semiconductor nanoparticles are capable of destroying many organic contaminants. The activation of Ag and Fe_2O_3 by sunlight (hυ) produces electron (e^-) – hole (h^+) pairs which act as strong oxidising agent.

$Ag + h\upsilon \rightarrow h^+ + e^-$
$Fe_2O_3 + h\upsilon \rightarrow h^+ + e^-$

The oxidative and reductive reactions further may take place as:

H_2O or $OH^- + h^+ \rightarrow OH\bullet$
$O_2 + e^- \rightarrow O_2^-$

The hydroxyl radicals thus, formed are responsible for the degradation of methylene blue into degradation products like SO_4^{2-} and phenols[17].



Methylene Blue

+ OH• → Degradation Products
($CO_2 + H_2O + NH_4^+ + NO_3^- + Cl^- + SO_4^{2-}$)

Table 1
Comparison between Ag-Fe_2O_3 and previously used photocatalysts

Nano-photocatalyst	% Degradation	Time	pH	K min^{-1}	Reference
MgO	97.6	2 hrs	11	1.8×10^{-3}	18
Silver	95.3	72 hrs	6	-	19
ZnS:CdS	73	6 hrs	10	3.61×10^{-3}	20
SnS_2-SiO_2@α-Fe_2O_3	96	100 min		1.96×10^{-2}	21
TiO_2	97	180 min	10	1.8×10^{-3}	17
MoS_2-ZnO	97	20 mins	11	1.63×10^{-1}	22
Fe_2O_3	65	90 mins	3	1.74×10^{-1}	23
Ag-Fe_2O_3	96.33	30 mins	7	1.11×10^{-1}	Present Study

Comparison with other photocatalysts: Photocatalytic efficiency of Ag-Fe_2O_3 was compared with the few of previously used photocatalysts for degradation of methylene blue. The data presented in table 1 shows that Ag-Fe_2O_3 is efficient in the degradation of methylene blue dye as compared to other photocatalysts.

Conclusion

Ag-Fe_2O_3 core-shell nanoparticles showed a remarkable potential for photodegradation of methylene blue dye. 20 mg of nanoparticles exceptionally decomposed 96.33% dye within 30 min at neutral pH. Also, the catalyst can be easily separated by an external magnet from the reaction mixture which makes the catalyst eco-friendly.

Simple sol–gel preparation route using less hazardous chemicals is the additional benefit of this catalyst. This study provides Ag-Fe_2O_3 as a promising candidate for practical applications in the field of photocatalysis.

Acknowledgement

Authors would like to acknowledge SAIF, IIT Mumbai for providing the facility of FTIR analysis, National Centre for Nanosciences and Nanotechnology, University of Mumbai, for XRD analysis and CIF, Gwalior for providing TEM facility for this research work.

References

1. Bruno L., Cíntia Z., Fávaro-P., João A.P. and Julio C.P., Effects of textile dyes on health and the environment and bioremediation potential of living organisms, *Biotechnology Research and Innovation*, **3(2)**, 275-290 **(2019)**

2. Kansedo J., Katheresan V. and Sie Yon J.L., Efficiency of various Recent Wastewater Dye Removal Methods: A review, *Journal of Environmental Chemical Engineering*, **6(4),** 4676-4697 **(2018)**

3. Lubis S., Nika S.S., Putra V.P. and Sheilatina, Preparation and Characterization of Titania/Bentonite Composite Application on the Degradation of Naphthol Blue Black Dye, *Res. J. Chem. Environ*., **22(2),** 48-53 **(2018)**

4. Dung N.Q., H.N., Duy C.N., Hai N.Q., Hang T.T.N., Loan T.T.N., Long G.B. and Nhuong C.M., A Facile synthesis, Characterization and photocatalytic activity of Magnesium Ferrite Nanoparticle Via the solution combustion, *Journal of Chemistry*, **2019,** 1-8 **(2019)**

5. Benhamouda K., Djebbar and Sehili T., Fast and Efficient Methylene Blue Photodegradation Process Using Natural Iron Oxide as Catalyst in the Dark and Under Irradiation, *J. Mater. Environ. Sci*., **9(3),** 1043-1050 **(2018)**

6. Guan-Ting P., Kasimayan U., Sayee K.R., Sridharan B. and Yang T.C.K., Degradation of Methylene Blue in the presence of

visible light using SiO2@α-Fe2O3 Nanocomposites deposited on SnS2 Flowers, *Materials (Basel)*, **11(6),** 1030 **(2018)**

7. Gupta A.K., Indu M., Pillai S. and Sahoo C., Photocatalytic degradation of methylene blue dye from aqueous solution using silver ion-doped TiO2 and its application to the degradation of real textile wastewater, *Journal of Environmental Science and Health, A*, **47(10),** 1428-1438 **(2012)**

8. Ashraf A.M., Abukhadral M.R. and Shaban M., TiO2 Nanoribbons/Carbon Nanotubes Composite with Enhanced Photocatalytic Activity; Fabrication, Characterization and Application, *Scientific Reports*, **8(781),** 1-17 **(2018)**

9. Huan X., Jia T., Ligeng X., Liangzhu F., Liang C., Rui P., Shuai Z. and Zhuang L., Graphene Oxide–Silver Nanocomposite as a Highly Effective Antibacterial Agent with Species-Specific Mechanisms, *ACS Applied Materials and Interfaces*, **5(9),** 3867-3874 **(2013)**

10. Huang J., Rongiun Z., Sun Z., Yang W. and Zhao J., Sol-Gel Auto Combustion synthesis of Zinc Ferrite for moderate Temperature Desulfurization, *Energy and Fuels*, **21**, 2682-2687 **(2007)**

11. Linfeng Z. and Yuanxin W., Sol-Gel synthesized magnetic MnFe2O3 spinel ferrite Nanoparticles as Novel Catalyst for Oxidative Degradation of Methyl Orange, *Journal of Nanomaterials*, **2013**, 1-6 **(2013)**

12. Stumm W., Chemistry of the Soild-Water Interface, Wiley/Interscience, NewYork **(1992)**

13. Cardenas-Peña Arlette M., Ibanez Jorge G. and Vasquez-Medrano R., Determination of the Point of Zero Charge for Electrocoagulation Precipitates from an Iron Anode, *Int. J. Electrochem. Sci*., **7,** 6142 – 6153 **(2012)**

14. Gaoxuan X., Jainfeng H., Liyun C., Yujan Z., Zongquan B. and Zhiping Z., Microscale flower-like magnesium oxide for highly efficient photocatalytic degradation of oganic dyes in aqueous solution, *RSC Adv.*, **9,** 7338 **(2019)**

15. Juan G., Junwang T., Maofa G., Ritchie R.O., Sujun W., Wang F., Xiaolin Y. and Xiao W., Facile self-assembly synthesis of Fe_2O_3/graphene oxide for enhanced photo-Fenton reaction, *Environmental Pollution*, **248**, 229-237 **(2019)**

16. Al-Rayyani A.M., Baeissa E.S., Mohamed R.M. and Mkhalid I.A., Photocatalytic Degradation of Methylene Blue by Fe/ZnO/SiO2 Nanoparticle under Visible Light, *Journal of Nanotechnology*, **2012**, 1-5 **(2012)**

17. Abdelmonem Y., Al-Hetlani E., Amin Mohd. O., Arafa M., Azeez F., Madkour M. and Nazeer A.A., The effect of surface charge on photocatalytic degradation of methylene blue dye using chargeable titania nanoparticles, *Scientific Reports*, **8,** 1-9 **(2018)**

18. Aziz B.K. and Karim M.A.H., Efficient catalytic photodegradation of methylene blue from medical lab wastewater using MgO nanoparticles synthesized by direct precipitation method, *Reaction Kinetics, Mechanisms and Catalysis*, **128(2)**, 1127-1139 **(2019)**

19. Annadurai G., Baburaja M., Gnanajobitha G., Malarkodi C., Paulkumar K., Rajeshkumar S., Sivakavinesan M. and Vanaja M., Degradation of Methylene Blue Using Biologically Synthesized Silver Nanoparticles, *Bioinorganic Chemistry and Applications*, **2014**, 1-8 **(2014)**

20. Abedini A., Bahmanrokh G., Erfani M., Hussein Mohd. Z., Navasery M., Soltani N., Saion E. and Vaziri P., Visible Light-Induced Degradation of Methylene Blue in the Presence of Photocatalytic ZnS and CdS Nanoparticles, *Int. J. Mol. Sci.*, **13,** 12243-12258 **(2012)**

21. Guan-Ting P., Kasimayan U., Savee K.R., Sridharan B., Thomas C.K. and Yang, Degradation of Methylene Blue Dye in the Presence of Visible Light Using SiO2@α-Fe2O3 Nanocomposites Deposited on SnS2 Flowers, *Materials*, **11**, 2-17 **(2018)**

22. Alothman O., Fouad Y., Kaur H., Kansal M., Mehta S.K., Ratika S., Singh S. and Umar A., Rapid Solar-Light Driven Superior Photocatalytic Degradation of Methylene Blue Using MoS2-ZnO Heterostructure Nanorods Photocatalyst, *Materials*, **11**, 2-16 **(2018)**

23. Benhamouda K., Djebbar K. and Sehili T., Fast and Efficient Methylene Blue Photodegradation Process Using Natural Iron Oxide as Catalyst in the Dark and Under Irradiation, *J. Mater. Environ. Sci.*, **9**, 1043-1050 **(2018)**.

(Received 20th June 2020, accepted 25th August 2020)