

Studies on the Effect of Doped Titanium Dioxide Nanoparticles for the Photocatalytic Degradation of Methyl Orange Dye

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Abstract— The TiO₂ and Ag-TiO₂ nanoparticles were synthesized using sol gel method. The synthesized nanoparticles were characterized using analytical techniques such as XRD, SEM and EDAX. In our work the effect of TiO₂ photocatalyst with different dopant concentrations of 5 mole percent and 7 mole percent using silver as the dopant on the photocatalytic degradation was studied. Methyl orange dye was chosen as a model pollutant and was subjected to degradation under a UV light source. From the experimental results it was found that 5 mole percent Ag- TiO₂ showed higher percentage degradation when compared to 7 mole percent Ag- TiO₂ and pure TiO₂. Also the effect of temperature on the photocatalytic degradation was studied. The optimum condition was found to be 50 degree celcius as at this temperature the percentage degradation increased to 76.4 percent. Further the kinetic parameters for the obtained results were evaluated. The reaction followed pseudo first order kinetics and the rate constants of pure TiO₂, 5 mole percent Ag- TiO₂ and 7 mole percent Ag- TiO₂ catalysts were found to be 0.0403 per minute, 0.1595 per minute and 0.0942 per minute respectively

Keywords— Ag-TiO₂ nanoparticles, XRD, SEM, EDAX, Photocatalytic activity

I. INTRODUCTION

Water pollution is one of the most significant issues affecting human, aquatic life and the environment. The primary cause of water contamination is industrial effluent discharge, which primarily contains poisonous chemicals and poses a significant danger to living systems. It is well recognized that in nature these pollutants are mutagenic and carcinogenic, and it is a challenging job to eliminate them through traditional methods. Several methods have been used to remove organic compounds, such as coagulation, rainfall (heavy metal removal), flotation (oil separation), activated carbon adsorption, ion exchange, membrane processes, reverse osmosis and electro dialysis, but most of them are cumbersome

and not sufficiently effective to eliminate the contamination from the sewages.[1]

Photocatalytic degradation of such organic pollutants with nanoparticles is promising method for both drinking and industrial wastewater purification and treatment. Nanocatalysts based photocatalysis is a very promising method for the treatment of contaminated water. Photocatalytic systems fitted with artificial ultraviolet (UV) – light can be implemented at ambient temperature to degrade multiple chemical pollutants in water. A big range of chemical and physical methods used to synthesize different kinds of metal nanoparticles are currently accessible. In the photocatalytic responses, the nanocatalysts absorb light energy more or equal to energy gap that produces holes that further lead to efficient oxidation of the pollutants.[2]

The advanced oxidation processes (AOPs) involving heterogeneous semiconductor photocatalyst have attracted enormous attention owing to their compatibility as a pollution mediator. AOPs are described as procedures that generate extremely oxidizing species, such as hydroxyl radicals and other reactive oxidizing species, including radical anion superoxide, single oxygen and hydrogen peroxide that are capable of degrading target pollutants in wastewater. A semiconductor metal oxide is irradiated during photocatalysis with light energy higher than its band gap, leading in the photon absorption and excitation of an electron from the valence band to the conductive band, thus creating a positively charged hole in the valence band. This stage is referred as the ‘photo-excitation’ state. The energy difference between the valence band and the conduction band is known as the ‘Band Gap’. The positive-hole of the nanocomposite breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. This cycle continues when light is available. The most powerful advanced oxidation systems are based on the generation of hydroxyl radicals. These photoexcited charge carriers could participate in redox

reaction for degradation of pollutants by reacting with sorbed species. The electron-hole charge carriers may in turn undergo recombination which leads to decrease in the overall performance of the photocatalytic process. In order to solve the above mentioned problem, various techniques have been employed such as metal and non-metal ion doping, semiconductors coupling, noble metal deposition and dye sensitization.

In the present work the TiO_2 and Ag- TiO_2 nanoparticles were synthesized using sol gel method. The synthesized nanoparticles were characterized using analytical techniques like XRD, SEM and EDAX. The effect of TiO_2 photocatalyst with different dopant concentrations of 5 mol% and 7 mol% using silver as the dopant on the photocatalytic degradation was studied. Methyl orange dye was chosen as a model pollutant and was subjected to degradation under a UV light source. From the experimental results it was found that 5 mol% Ag- TiO_2 showed highest degradation. Also the effect of temperature on the photocatalytic degradation was studied. The optimum condition was found to be 50°C. Further the kinetic parameters for the obtained results were evaluated. The reaction followed pseudo first order kinetics and the rate constants of pure TiO_2 , 5 mol% Ag- TiO_2 and 7 mol% Ag- TiO_2 catalysts were found to be 0.0403 min^{-1} , 0.1595 min^{-1} and 0.0942 min^{-1} respectively.

II. EXPERIMENTAL

2.1 Material and Methods

A. Materials

For experimental process titanium tetra butoxide (Sigma Aldrich, Purity: 97%), silver nitrate (Bangalore Fine Chemicals, Purity: 99.9%), methanol (Spectrum Chemicals, Purity: 99%) and ammonia solution (Spectrum Chemicals) of analytical grade were procured and used without further purification.

B. Synthesis of TiO_2 and Ag- TiO_2 nanoparticles:

Sol-gel method was followed to synthesize TiO_2 and Ag- TiO_2 nanoparticles which is similar to the method followed by Pereumal et al.[3] For the synthesis of TiO_2 , Titanium tetra butoxide and methanol were used as precursors with molar ratio of 1:4. The temperature was maintained at 60°C with constant stirring. Distilled water was added drop wise to this mixture by maintaining 1:1 ratio with methanol for hydrolysis reaction to take place. The pH of the solution mixture was maintained in the range of 9-10 by dropwise addition of aqueous ammonia solution. The mixture was stirred continuously for 2 hours and was aged for 24 hours for gel development. The gel was washed several times with methanol and distilled water to remove the impurities and unreacted reactants. The gel was dried in an oven at 80°C to expel the dampness content and calcined in muffle furnace at 500°C for 2 hours to acquire crystalline nanoparticles.

For the synthesis of Ag- TiO_2 , Titanium tetra butoxide, methanol and silver nitrate were used as precursors. The temperature was maintained at 60°C with constant stirring to synthesize nanoparticles of smaller particle size. Silver nitrate solutions of concentrations 5 mol% and 7 mol% was added drop wise to this mixture by maintaining 1:1 ratio with

methanol for doping purpose. The pH of the solution mixture was maintained in the range of 9-10 by dropwise addition of aqueous ammonia solution. The blend was mixed continuously for 2 hours and was aged for 24 hours for gel development. This gel was washed with methanol and distilled water for a few times to expel the pollutants and unreacted reactants. The gel was dried in a hot air oven at 80°C to expel the dampness content and calcined in muffle furnace at 500°C for 2 hours to acquire crystalline nanoparticles.

2.2 Characterization of TiO_2 and Ag- TiO_2 nanoparticles

The X-ray diffraction (XRD) analysis was carried out for the calcined TiO_2 and Ag- TiO_2 nanoparticles using X'Pert3 Powder X-ray Diffractometer with CuK-alpha radiation operating at current and voltage of 30 mA and 45 kV. In order to visualize the morphology and purity of the samples scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) were performed using VEGA3 TESCAN microscope.

2.3 Photocatalytic activity assessment

The photocatalytic efficiency of as prepared catalysts has been investigated by measuring the degradation of methyl orange as a model pollutant under ultraviolet light irradiation. The light used for photocatalytic activity was supplied by a 15W UV lamp, which was placed horizontally inside the photoreactor as shown in the Fig. 1. For each test, reaction suspensions were prepared by adding 1g/L of catalysts into a glass beaker containing 300mL of 3000 mg/L methyl orange aqueous solution. The glass beaker was placed inside the experimental chamber under constant stirring with a magnetic stirrer. At given time intervals, 25 ml of aliquot was withdrawn and filtered it to remove the photocatalysts. The photocatalytic degradation of methyl orange has been estimated from the reduction in absorption intensity of methyl orange at the characteristic lambda max 463 nm by employing UV-visible spectrophotometer (T80-UV/Vis spectrometer). The photocatalytic efficiency was estimated using the following expression



Fig 1: Photocatalytic reactor setup

$$\% \text{ Degradation} = (C_0 - C)/C_0 \times 100 \quad (1)$$

Where C_0 is the initial concentration of methyl orange, obtained before illumination and C is the concentration after irradiation time, respectively.

III. RESULTS AND DISCUSSION

3.1 X-ray diffraction (XRD) analysis

To investigate the crystal structure of pure TiO₂, 5 mol% and 7 mol% Ag-TiO₂ nanoparticles, XRD analysis have been

carried out as shown in Fig. 2(a), (b) and (c). The diffraction peaks of synthesized TiO₂ are corresponding to the anatase phase of TiO₂ (JCPDS Card: 21-1272) (Peak Values: 25.3, 37.9, 47.9, 55, 62.5, 70.2 and 75.1 corresponding to 101, 004, 200, 105, 204, 220 and 215 peaks respectively).

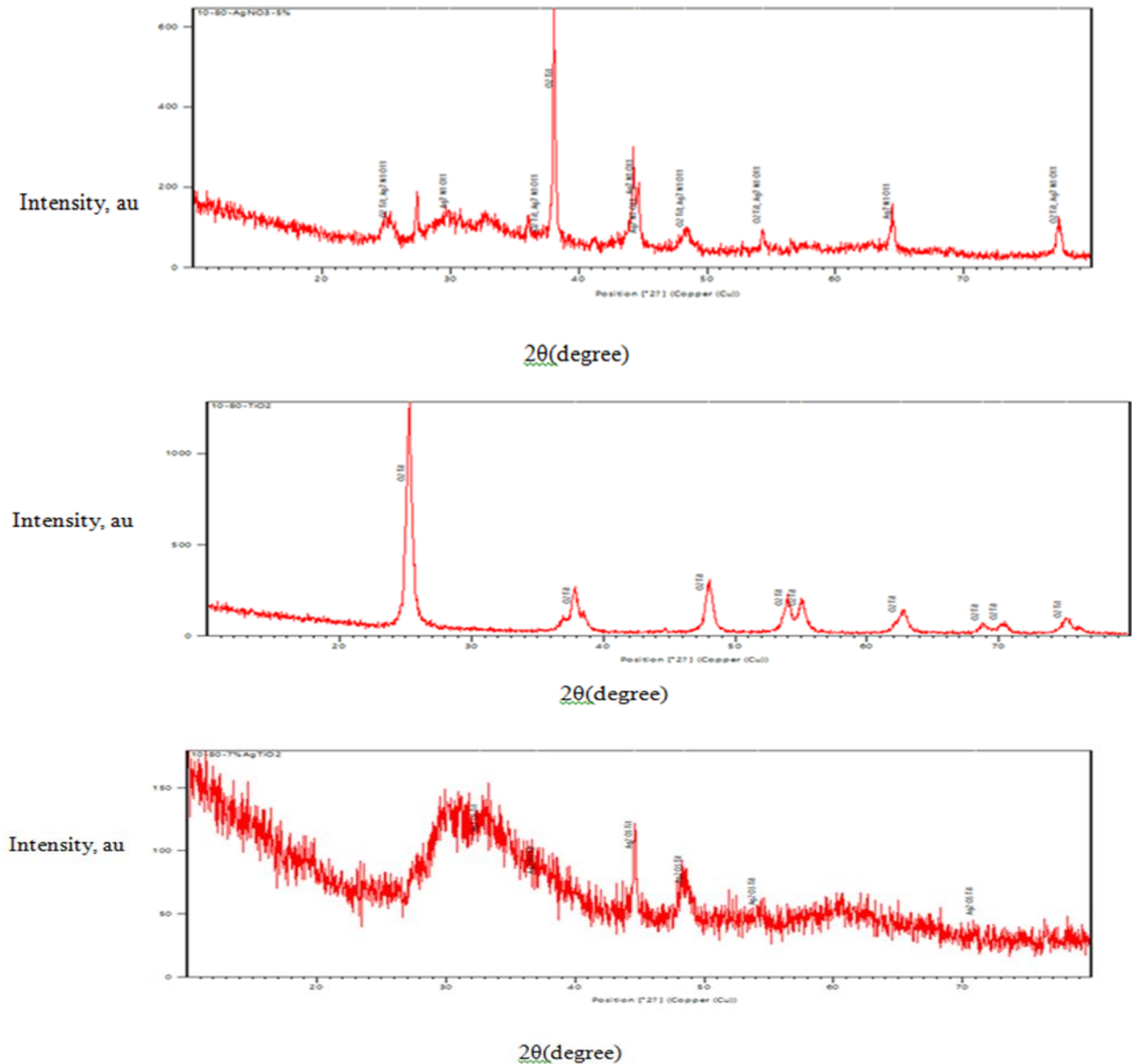
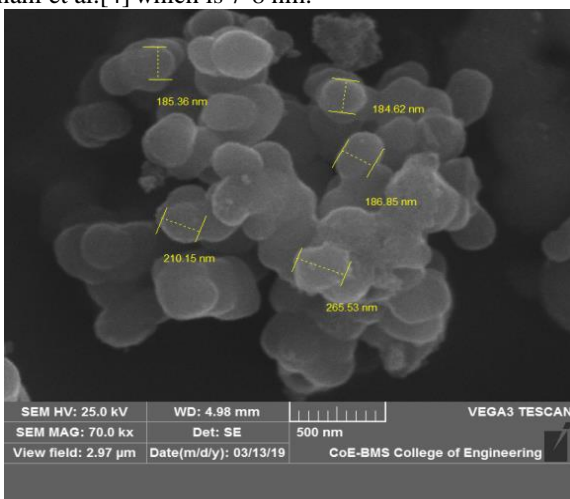


Fig 2: The XRD patterns of the (a) pure TiO₂ (b) 5 mol% TiO₂ and (c) 7 mol% TiO₂

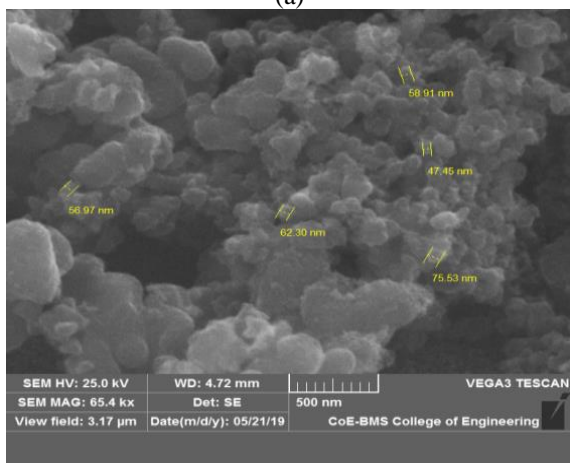
The diffraction peaks obtained for Ag-TiO₂ indicated that the incorporation of silver lead to change in the crystal structure of TiO₂. It was found that the diffraction peaks shifted towards the higher 2θ value with increasing dopant concentration which is due to the lattice strain present in the samples.

3.2 Scanning Electron Microscopy (SEM)

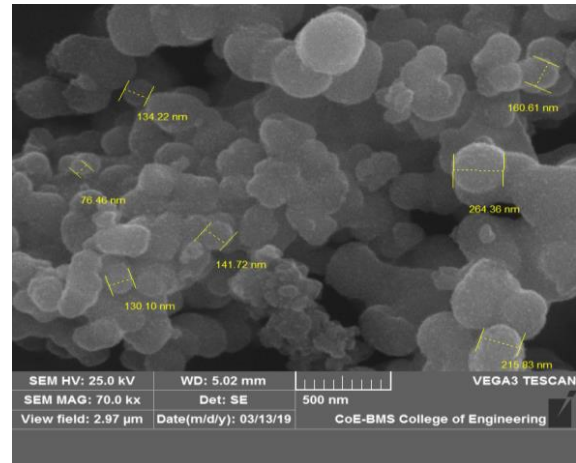
The SEM micrographs of pure TiO₂, 5 mol% and 7 mol% Ag-TiO₂ nanoparticles are displayed in Fig. 3(a), (b) and (c) respectively. Figures show that the shape of TiO₂ nanoparticles are more spherical with aggregation of tiny crystals when compared to that of 5 mol% and 7 mol% TiO₂ nanoparticles. The agglomerated and also individual particles were found in the structure. The average particle size of 5 mol% Ag-TiO₂ was found to be 60.23nm which is very less when compared to the average particle size of pure TiO₂ and 7 mol% Ag-TiO₂ which was observed to be 190nm for both. The particle size of TiO₂ attained in the present work is more when compared to the particle size of TiO₂ estimated by Nainani et al.[4] which is 7-8 nm.



(a)



(b)

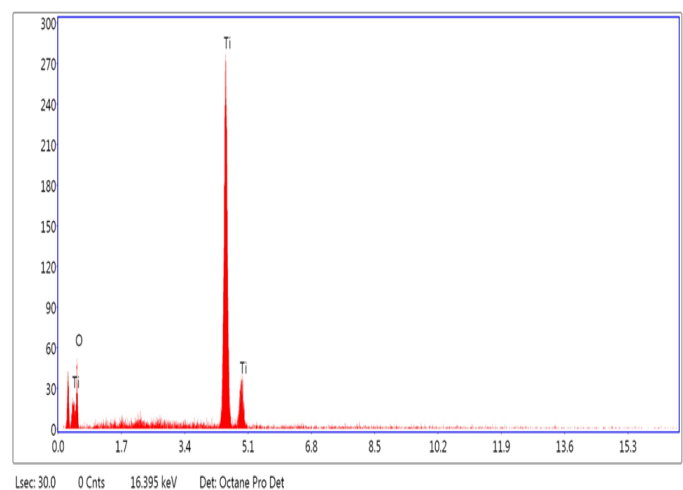


(c)

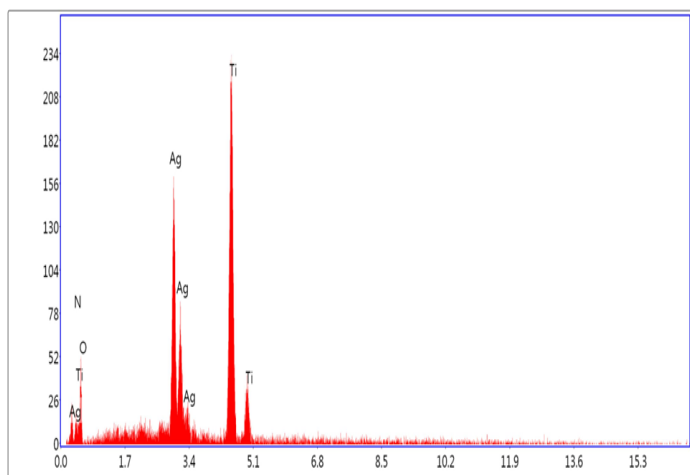
Fig 3: SEM micrographs of (a) TiO₂ with 70kx magnification (b) 5 mol% Ag-TiO₂ with 65kx magnification and (c) 7 mol% Ag-TiO₂ with 70kx magnification

3.3 Energy dispersive X-ray spectroscopy (EDAX) analysis

The EDAX spectrum of pure TiO₂, 5 mol% and 7 mol% Ag-TiO₂ nanoparticles are shown in Fig. 4(a), (b) and (c). From the Fig. 3(d) the atomic% of Ti and O were estimated to be 28.66 and 71.34 respectively. From the Fig. 3(e) the atomic% of Ti, O and Ag were estimated to be 24.43, 67.33 and 5.04 respectively. From the Fig. 3(f) the atomic% of Ti, O and Ag were estimated to be 19.61, 69.73 and 7.36 respectively. The results obtained by this analysis indicated that the synthesized nanoparticles were in stoichiometric proportion when compared to the EDAX results obtained by Avciata et al.[5] The analysis carried out by EDAX shows the presence of Ag in the doped sample along with the main constituent Ti and O. The existence of independent peaks of these elements suggested that Ag particle is effectively assimilated into the TiO₂ structure.

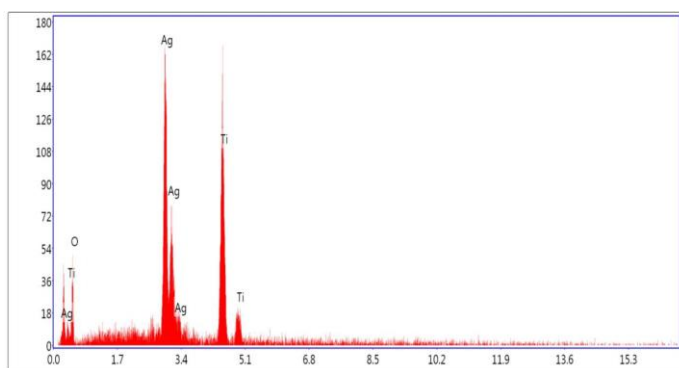


(a)



Lsec: 30.0 0 Cnts 0.000 keV Det: Octane Pro Det

(b)



Lsec: 30.0 4 Cnts 2.630 keV Det: Octane Pro Det

(c)

Fig 4: (a) EDAX spectrum of TiO₂ (b) EDAX spectrum of 5 mol% Ag-TiO₂ and (c) EDAX spectrum of 7mol% Ag- TiO₂

3.4 Photocatalytic Activity Evaluation

The photocatalytic activities of Ag-doped TiO₂ nanoparticles with 5 mol % and 7 mol% of Ag were investigated by degrading methyl orange as a model pollutant under ultraviolet light illumination of 15W capacity. The resultant solution was tested for absorbance in UV-VIS spectrophotometer at definite interval of time [10, 20, 30, 40, 50 and 60 min]. Fig 5 shows that the 5 mol% Ag - TiO₂ exhibited highest degradation of 65% of the model pollutant after irradiation time of 60 min when compared to 7 mol% Ag-TiO₂ and pure TiO₂ photocatalysts. Even 7 mol% Ag-TiO₂ showed a significant increase in the photocatalytic activity when compared to pure TiO₂. But the percentage degradation attained in the present work is less when compared to the results obtained by Sowmya et al.[6] where more than 90% degradation was obtained in 60 minutes and 100% degradation in 80 minutes using 0.1 wt% Ag-TiO₂ as the photocatalyst to degrade congo red dye as the model pollutant. However, the studies reported by Nainani et al.[4] on the effect of dopant concentration on the photocatalytic degradation of methyl orange dye indicated that the optimized doping concentration of Ag content in Ag-TiO₂ was found to be 1.5 mol% as it degraded 99% of methyl orange dye after irradiation time of 3 hours which is a longer duration when compared to 60 min at which the highest degradation of 65% was achieved in present work.

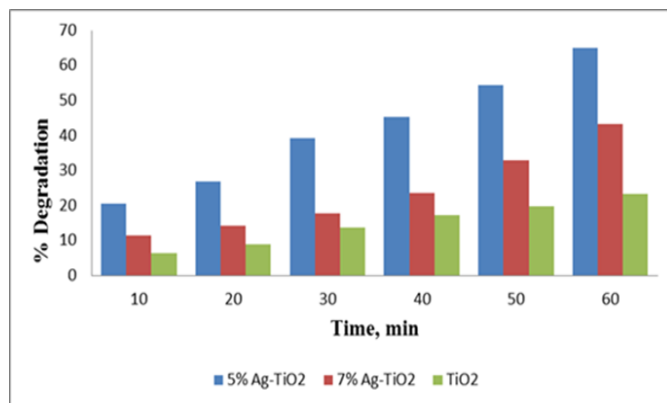


Fig 5: Comparison between efficiencies of 5 mol% Ag-TiO₂, 7 mol% Ag-TiO₂ and TiO₂ photocatalysts

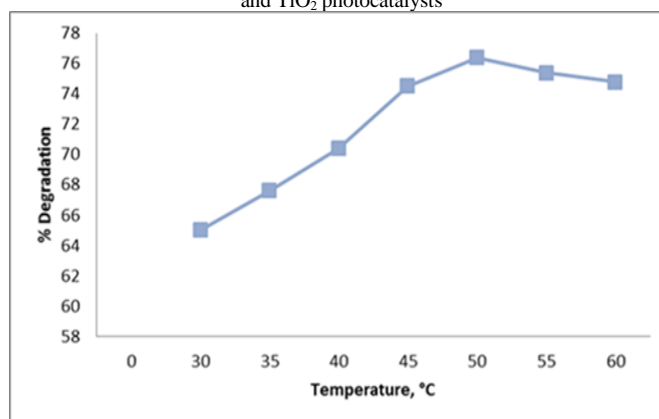


Fig 6: Effect of temperature

3.5 Effect of Temperature

In order to study the effect of temperature on the photodegradation of methyl orange, experiments were carried out and plot of % degradation versus temperature in the temperature range of 30 to 60 °C is shown in Fig 6. From the figure it can be inferred that the highest degradation of 76.4% was acquired at 50°C. But further increase in temperature to 55°C and 60°C temperature lead to slight decrease in the degradation which is similar to the results reported by C. C. Chen et al.[7] This is because at higher temperature exothermic reactions take place which reduces the photocatalytic activity of the photocatalyst.

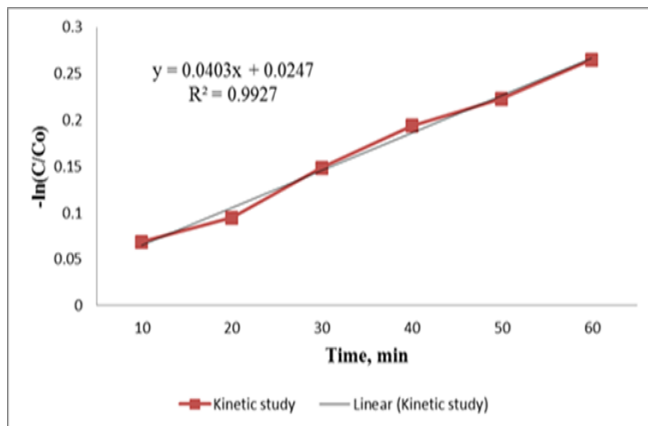
3.6 Kinetic Study

Kinetics of degradation of methyl orange was studied under UV light irradiation at initial dye concentration of 3000 mg/L, and pH of 7. The catalyst loading of 1 g/L was used. The effect of dye concentration on the rate of degradation is given in the form of Eq. 2.

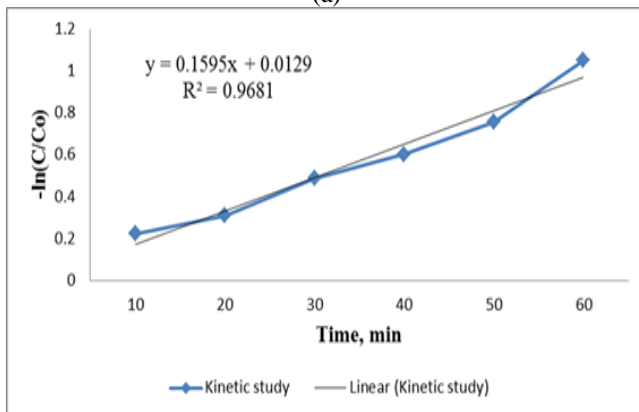
$$-\ln(C/C_0) = k * t \quad (2)$$

where C is the concentration of the dye after irradiation at time 't', C₀ is the initial dye concentration before irradiation and k is the reaction rate constant. To estimate the parameters in the Eq. 2, the graphs of $-\ln(C/C_0)$ versus time were plotted for the photodegradation of methyl orange dye by pure TiO₂, 5 mol% and 7 mol% Ag-TiO₂ nanoparticles as shown in Fig 6(a), (b) and (c). From the plots, the rate constants were estimated as 0.0403 min⁻¹, 0.1595 min⁻¹ and 0.0942 min⁻¹ for pure TiO₂, 5 mol% and 7 mol% Ag-TiO₂ respectively and the regression coefficient were estimated as 0.9927, 0.9681 and

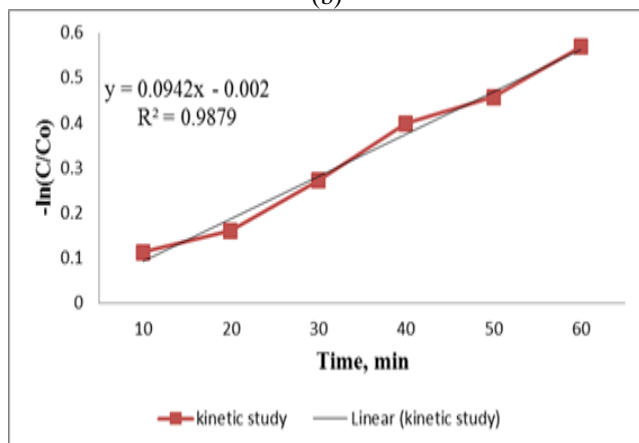
0.9879 for pure TiO₂, 5 mol% and 7 mol% Ag-TiO₂ respectively which is more when compared to the rate constant of 0.014 min⁻¹ and regression coefficient of 0.98 obtained by Sowmya et al.[6] From the kinetic study, the photocatalytic degradation of methyl orange organic pollutants follow a pseudo first-order kinetic law which is similar to the results reported by Rupa et al.[8] which indicated that the photocatalytic degradation of reactive yellow-17 dye using 1 wt% Ag deposited TiO₂ photocatalysts followed pseudo first order kinetic law.



(a)



(b)



(c)

Fig 6: Kinetic study curve of methyl orange degradation by (a) pure TiO₂, (b) 5 mol% TiO₂ and (c) 7 mol% TiO₂

IV. CONCLUSIONS

The pure TiO₂, 5 mol% and 7 mol% Ag-TiO₂ nanoparticles were synthesized by sol gel method and were used as photocatalyst for the photocatalytic degradation of methyl orange dye under UV light. The synthesized nanomaterials were characterized using XRD, SEM and EDAX analytical techniques. Percentage degradation was found to be highest for 5 mol% Ag-TiO₂ photocatalyst. Doping TiO₂ with Ag enhanced its photocatalytic activity. The optimum value of temperature was found to be 50°C as at this temperature the percentage degradation increased to 76.4%. The reaction followed pseudo first order kinetics for degradation of dye using various dopant concentrations of the synthesized photocatalysts.

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