

Enhanced Photocatalytic Degradation of Methyl Orange using Ag-Doped TiO₂ Photocatalyst

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Abstract: In the present study, Ag-doped Titanium dioxide (Ag-TiO₂) photocatalyst was prepared by wet impregnation method. The effect of dopant concentration, incubation temperature and incubation time on the photocatalytic degradation of Methyl Orange (MO) in aqueous suspension under Ultra Violet (UV) light irradiation were studied systematically. The synthesized photocatalyst was characterized using XRD and SEM-EDX mapping. The characterization results confirmed that Ag was successfully doped into TiO₂ with anatase phase structure. The Ag-TiO₂ photocatalyst exhibited the highest dye removal of 85% efficiency with 5 wt.% dopant concentration when the incubation temperature and time were 70°C and 8 h, respectively. The kinetic study revealed that photocatalytic reaction follows Langmuir Hinshelwood (L-H) Model and pseudo-first order law with the highest regression coefficient of 0.992. Ag-TiO₂ was found to be an efficient photocatalyst showing enhanced photocatalytic activity for MO decolorization under UV irradiation.

Key words: Dye, titanium oxide, doping, photocatalyst, photodegradation, Ag-TiO₂

INTRODUCTION

Dyes are used primarily in the production of consumer products including paints, textiles, cosmetics, plastics and papers. Dye containing waste waters are usually recalcitrant to degradation by the conventional biological treatments due to its high toxicity as these compounds are often hardly biodegradable or even biocides (Oller *et al.*, 2011). The main issue is dyes contain a number of dangerous chemical substances such as dioxin, formaldehyde and heavy metals. These substances can potentially cause acute and chronic effects on the exposed living organisms and due to their stability, dyes remain in the environment for a long period of time. Besides, the presence of dyes on water surface prevents the sunlight from penetrating into the water and thus retards algae photosynthesis.

There are several decrement technologies including adsorption (Kyzas and Matis, 2015), microbial degradation (Casalatto *et al.*, 2011) and advanced oxidation processes (Zuorro and Lavecchia, 2014) which have been proposed for removal of azo dyes from textile discharges. Photocatalysis, however, offers better solutions compared

to the other technologies for the removal of azo dyes due to its ability to mineralize the pollutants completely. TiO₂ is feasible in terms of its inexpensiveness, non-toxicity and high redox potentials (Tan *et al.*, 2017). Nevertheless, pure unmodified TiO₂ has several drawbacks including its wide band gap energy level 3.0–3.2 eV resulting in poor absorbance of visible light (Hou *et al.*, 2009), low quantum efficiency derived from the high recombination rate of photo-induced electron-hole (e⁻/h⁺) pairs (Gou *et al.*, 2017), rapid recombination rate of photo-generated electron-hole pairs and inefficient utilization of UV light (Zhao *et al.*, 2016). In this regard, modification of TiO₂ surface by metal doping was proven to enhance its photocatalytic activity (Mohamed *et al.*, 2013) through electrons trapping which can greatly increase the efficiency of charge separation and also prevent recombination of electron-hole pairs. Behnajady and Eskandarloo (2013) showed that Ag-doped TiO₂ by liquid impregnation method improved the photocatalytic performance in the degradation of AR88. Zuas and Budiman (2013) used co-precipitation method to dope 3 wt.% of Cu with TiO₂. 90% of Congo Red dye was decolorized over Cu-TiO₂ photocatalyst, compared to

53% using pure TiO₂ (Lei *et al.*, 2016). Lei *et al.* (2016) also showed better photocatalytic performance for the impregnated Cu/TiO₂ in the degradation of both decabromodiphenyl ether (BDE209) and Tetrabromodiphenyl ether (BDE47) when exposed to UV irradiation in an anoxic atmosphere. Besides, Wang *et al.* (2016) reported the degradation of salicylic acid over iodine and nitrogen co-doped TiO₂ photocatalyst. Presence of iodine increased the rate constant of the acid removal and 78.3% of total organic carbon was eliminated upon 180 min under visible light irradiation. Although, these studies aimed to improve TiO₂ activity by metal doping, investigation of the process parameters during metal-doped TiO₂ experiments is still lacking. Therefore, this study was carried out with the aim to synthesize nanostructured Ag-doped titania at different dopant concentration, incubation time and temperature by the wet impregnation method. The synthesized Ag-doped TiO₂ photocatalysts were characterized for their phase structures and surface morphologies and subsequently investigated for their photocatalytic activity. The photocatalytic activity of the synthesized samples was investigated to decolorize MO dye as the model compound in aqueous solution under UV irradiation.

MATERIALS AND METHODS

Chemicals and materials: Commercial TiO₂ (reported surface area 10 m²/g) was used as the starting material for the synthesis Ag-TiO₂ photocatalyst. Sodium hydroxide and silver nitrate were purchased from Merck all chemicals were used without further purification. Methyl Orange (MO) ((CH₃)₂NC₆H₄NNC₆H₄SO₃Na) with formula weight of 327 g/mol was obtained from Sigma Aldrich. All the reagents used were of analytical grade and solutions were prepared using distilled water.

Preparation of Ag-TiO₂ photocatalyst: The Ag-TiO₂ photocatalyst was prepared according to the procedures adopted by Lei *et al.* (2016) using wet impregnation method. The optimum concentration of Ag was firstly determined with varying Ag concentration between 5-20 wt.%. To prepare 5 wt.% Ag/TiO₂, 9.2126 g of TiO₂ was dispersed in 50 mL of distilled water. Under continuous stirring, 0.7874 g of silver nitrate was added to the diluted TiO₂ solution. The mixture was next incubated in a water bath for 2 h at 90°C. The product was then washed and calcined overnight in a furnace at 450°C. The aforesaid preparation steps were repeated by varying the incubation temperature between 25-70°C and incubation time of 1-24 h, respectively by using the optimum Ag

concentration obtained. For comparison purposes, TiO₂ without dopant was prepared through the same method and calcined at 450°C.

Characterization of Ag-TiO₂ photocatalyst: It is important to characterize the calcined photocatalysts in order to determine their chemical and physical properties and relate these properties to their photocatalytic performance. The morphology of selected samples were characterized using a Field Emission Electron Microscope (FESEM) (Carl Zeiss SUPRA 40VP) and an Energy Dispersive X-ray (EDX) (Carl Zeiss SUPRA 40 VP). Meanwhile, the X-Ray Diffraction (XRD) (X'Pert Pro-MPD, PAN alytical) system was operated at 40 kV and 30 mA with a scanning range of 2θ = 10-90° using Cu Kα (λ = 1.504Å) to determine the phases of the photocatalyst. The crystallite sizes were calculated with the Scherrer equation ($\Phi = K\lambda/\beta\cos\theta$) where Φ is the crystallite size, K is usually taken as 0.89, θ is the wavelength of the X-ray radiation (0.154 nm), β is the Full Width at Half-maximum Intensity (FWHM) and θ is the diffraction angle of the 101 peak for anatase at 2θ = 25.4°. Brunauer-Emmett-Teller (BET) was used to investigate the surface area of the photocatalyst. The sample was preheated at 200°C for 5 h and degassed under vacuum before measurements.

Control study: For adsorption study, the sample was conducted in the dark. In each test, 1 g of Ag-TiO₂ photocatalyst sample was added into a 200 mL of 10 ppm MO dye to form suspensions into a glass cell with dimension 150×100×100 mm (L×B×H) and aerated as shown in Fig. 1. An aquarium pump model NS 7200 was used as the aeration source. The degradation efficiency of MO was determined at specific time interval until saturation time was achieved (180 min). For photolysis study, similar experimental conditions with adsorption study were adopted under UV irradiation in the absence of TiO₂ photocatalyst. The absorbance was measured by using UV-Vis spectrometer (Shimadzu, UV-210A) at 476 nm to detect the changes in MO concentration. A linear calibration of absorption vs. concentration was obtained. Subsequently, degradation efficiency was determined using the following Eq. 1.

$$\xi = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Where:

ξ = MO degradation efficiency

C₀ = Initial concentration of MO

C_t = Final concentration of MO

Photocatalytic degradation of Methyl Orange (MO): The photocatalytic degradation of MO was carried out in a photoreactor equipped with 15 W UV lamp at the height of 5 cm from the surface of MO solution. The solution was magnetically stirred for 15 min in the dark to reach adsorption-desorption equilibrium with Ag-TiO₂ photocatalyst before the lamp was turned on to start the photo reaction. The 3 mL of sample solution was with drawn using syringe at a fixed time interval of 15 min and the collected sample was filtered through a 0.5 μ m filter to obtain clear solution prior to analysis. The photocatalytic degradation experiment was repeated using the bare TiO₂.

RESULTS AND DISCUSSION

Characterization of Ag-TiO₂ Photocatalyst: Figure 1 and 2 shows the XRD pattern of bare TiO₂ and Ag-TiO₂

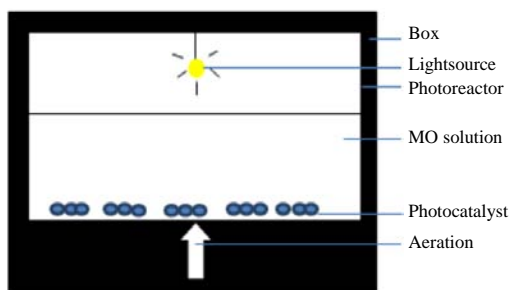


Fig. 1: Schematic diagram of photocatalytic degradation of MO

photocatalyst. Bare TiO₂ matches JCPDS 00-021-1272 which indicates the anatase structure. There is no trace of rutile and brookite phases which is favorable as anatase has better photocatalytic activity than other phases. The XRD result revealed at $2\theta = 25.28, 37.8, 48.05, 53.89, 55.06$ and 62.69° corresponding to crystal planes of (101), (004), (200), (105), (211) and (204) (JCPDS 21-1272). Mogal *et al.* (2014) also obtained the anatase structure of TiO₂ at the same peaks corresponding to crystal planes of (200) and (220) (JCPDS 01-1164) (Mogal *et al.*, 2014). After the addition of Ag, it can be seen that most of the 2θ peak positions of the major diffraction pattern in all samples show no shifting, having similar values of bare TiO₂. The diffraction peak at 44.1° of metallic Ag was detected in Fig. 2, however, at 10 wt.% Ag and above. It could be probably Ag is situated in the bulk (inside the TiO₂ crystals) at lower concentrations. The result is in agreement with the research work by Melian *et al.* (2012), Mohamed and Al-Sharif (2013). In addition, another additional peak was also spotted at 64.2° . The intensity of the Ag peaks increases gradually as the weight percentage of Ag increases. The presence of Ag phase does not change the crystalline structure of the TiO₂ substrate. This may indicate that Ag is formed on the crystal borders and on the surface of the TiO₂.

The crystallite size for Ag-TiO₂ prepared at various Ag loading was estimated from Scherrer equation and is tabulated in Table 1. From Table 1, the crystallite size for bare TiO₂ is approximately 94 nm and the size generally

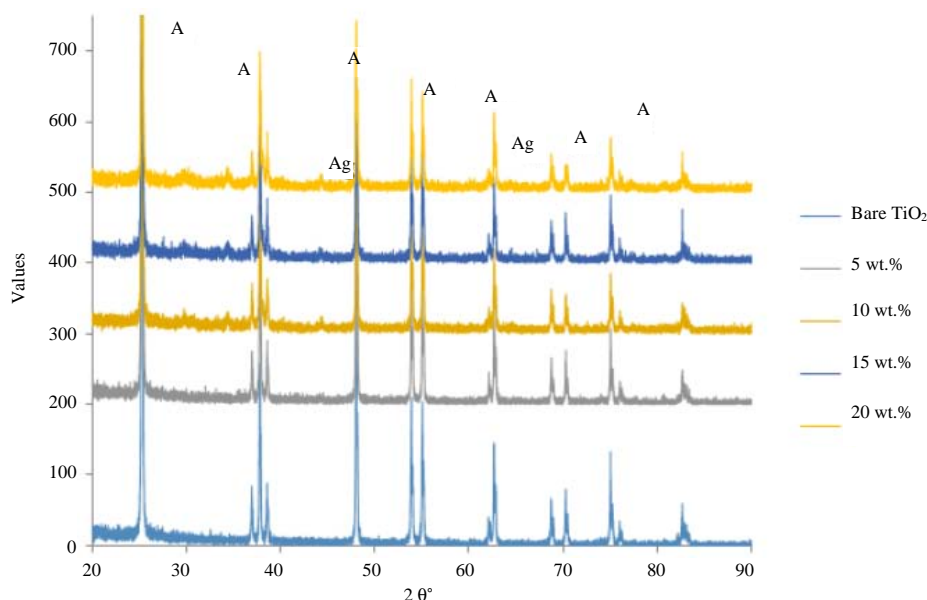


Fig. 2: XRD pattern of Ag/TiO₂ at different Ag concentration (Ag = Silver, A = Anatase)

Table 1: Crystallite size for TiO₂ and AgTiO₂ prepared at various concentrations

Sample	Crystallite size (nm)
Bare TiO ₂	93.9
5 wt.% AgTiO ₂	57.4
10 wt.% AgTiO ₂	66.8
15 wt.% AgTiO ₂	86.1
20 wt.% AgTiO ₂	73.8

decreases to 57-86 nm upon incorporation of Ag particles. However, the crystallite size for AgTiO₂ increases with increasing Ag concentration from 5-20 wt.%.

On the other hand, the correlation between elemental composition and morphological changes of particles can be identified by EDX, since, the composition is very sensitive for the application. Figure 3 shows the EDX spectra of bare TiO₂ and Ag-TiO₂ photocatalyst. From Figure 3a, Ti peaks were observed at 0.45 and 4.51 keV while the O peak was detected at 0.52 V. These peaks were originated from TiO₂. Meanwhile, the Ag peak was successfully identified at 2.9 and 3.15 keV as shown in Fig. 3b. Even though, the peaks of Ag are insignificant owing to its content in TiO₂ matrix, they indicate the Ag present in the photocatalyst and thus, support XRD findings. The presence of Ag originated from the Ag precursor (AgNO₃) used in the preparation of Ag-TiO₂ photocatalyst. The atomic percentage of Ti, O and Ag in Ag-TiO₂ were 33.07, 66.58 and 0.34 wt.%, respectively. Mapping analysis was performed to observe the dispersion of Ag on TiO₂ surface. From Fig. 4, the EDX mappings show the uniform dispersion of Ag onto the surface of TiO₂ and present in the form of metal oxides (Ag oxides).

FESEM analysis was performed in order to observe the changes of the TiO₂ morphological structure when Ag was incorporated. Figure 5 shows the FESEM images of bare TiO₂ and Ag-TiO₂. Bare TiO₂ comprises of spherical and square-like shape with irregular sizes. It can be seen that slightly agglomeration occurred in the certain spot. There were no distinct changes on the shape of TiO₂ after Ag was impregnated. However, it can be observed that the color changed from white to grey upon impregnation. The changes in the color proved that Ag was successfully impregnated on TiO₂ surface in agreement with the existence of Ag peaks in EDX spectra. TEM analysis was performed to observe the Ag-TiO₂ particles at higher magnification (50 kX) and the TEM micrograph is shown in Fig. 6. Apparently, spherical-like shaped TiO₂ particles could be seen and this observation is tally with the one observed using FESEM. However, a close inspection of the TEM image showed that tiny round particles was observed to deposit on the surface of the

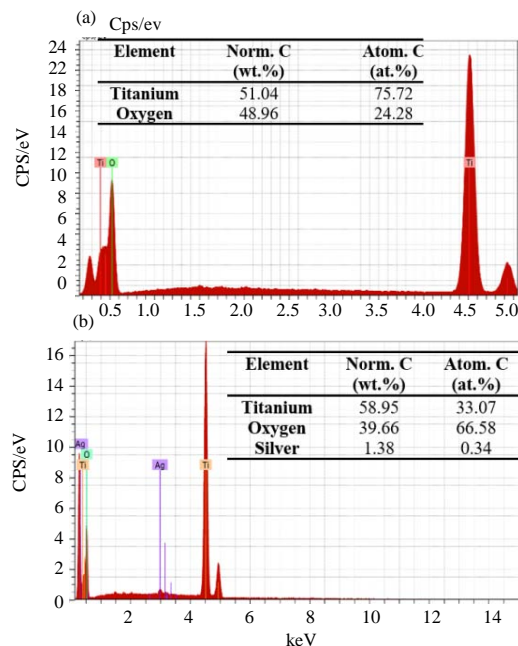


Fig. 3: EDX spectra of: a) Bare TiO₂ and b) Ag-TiO₂ with 2 h of incubation time

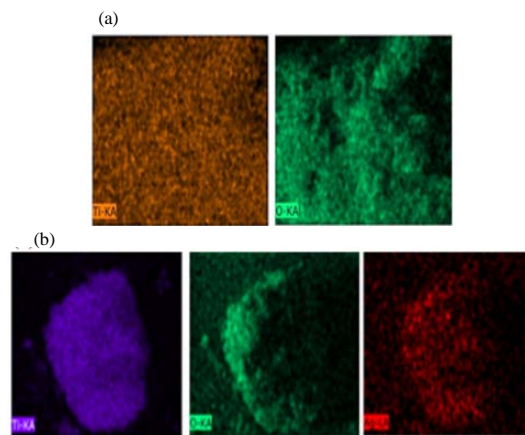


Fig. 4: EDX mappings of: a) Bare TiO₂ and b) Ag-TiO₂

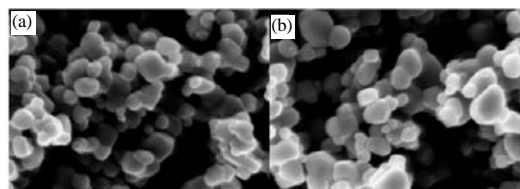
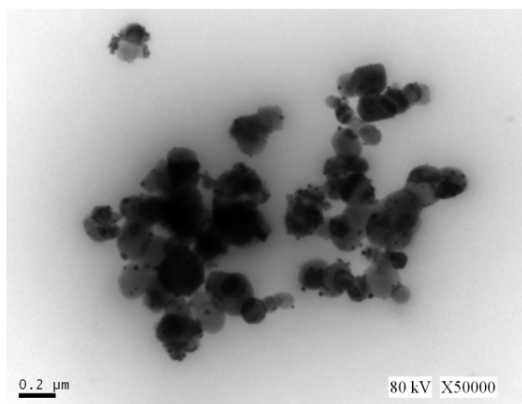


Fig. 5: FESEM images of: a) Bare TiO₂ and b) Ag-TiO₂ photocatalyst

TiO₂ particles and it is presumably to be the Ag particles. Nevertheless, the tiny particles were not distributed homogeneously on the surface of TiO₂

Fig. 6: TEM images of Ag-TiO₂ photocatalyst

In order to get better photocatalytic activity, high surface area of the catalyst is often desired. The BET surface area of bare TiO₂ was found to be 9.71 m²/g which is close to the value reported in the technical datasheet (10 m²/g). It was observed that when Ag was introduced, the surface area decreased slightly to 9.32 m²/g. Surface area decreased with the increasing Ag loading in Ag-TiO₂ photocatalyst. This could be due to partial pore obstruction caused by the deposition of Ag aggregates on the TiO₂ surface (Sakthivel *et al.*, 2004, Zhao *et al.*, 2011).

Photocatalytic performance of Ag-TiO₂ photocatalyst:

The photocatalytic performance of Ag-TiO₂ photocatalyst for the removal of MO was studied based on the reaction kinetics at different parameters.

Effect of Ag concentration: From Fig. 7, it can be clearly seen that the optimum metal loading of Ag-TiO₂ is at 5 wt.% with MO removal efficiency of 68.2%. Compare to bare TiO₂, Ag-TiO₂ photocatalyst show higher removal efficiency up to Ag loading of 15 wt.% and then decreases. At 5 wt.% Ag, the metallic Ag particles deposited on TiO₂ surfaces acted as electron scavengers and contributed to the decrease of electron-hole recombination in TiO₂. In contrast in high Ag content, it has been reported that the probability for the hole capture is increased by a large number of negatively charged Ag particles on TiO₂ which reduces the efficiency of charge separation (Hosseini *et al.*, 2011). Moreover, the dopants could behave as electron/hole recombination center thus lowering the performance of photocatalytic activity. Melian *et al.* (2012) also found that excess in Ag loaded into TiO₂ leads to low photocatalytic activity. A similar finding was also reported by Vamathevan *et al.* (2002) who used sucrose as model compound in his study.

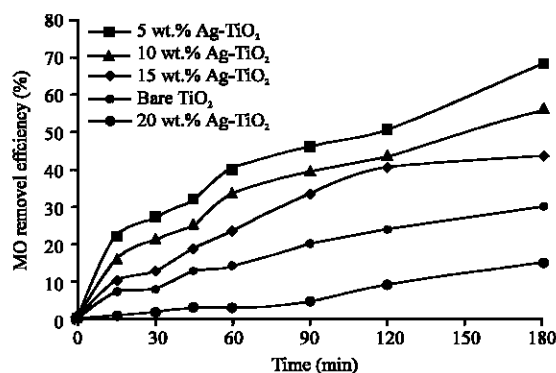


Fig. 7: MO removal efficiency with different Ag concentration

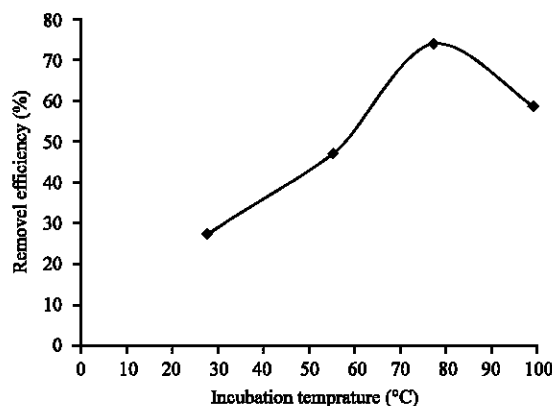


Fig. 8: Comparison of removal efficiency of MO at different incubation temperature

Effect of incubation temperature: The condition of preparation of Ag-TiO₂ also influences the reaction of the catalyst. Figure 8 illustrates the percentage removal of MO solution at different incubation temperature. After 3 h of degradation process, the incubation temperature at 25°C showed the lowest removal efficiency of MO which was 27.4% while the highest MO removal efficiency was at 70°C with 73.5%. The incubation temperature of 70°C could have changed the surface properties of the Ag-TiO₂ photocatalyst which is in agreement with BET surface area analyses. Ag-TiO₂ at 5 wt.% Ag loading has the largest BET surface area among all modified TiO₂ samples (9.53 m²/g). The larger surface area as well as the increase in pore volumes provides a more interfacial area for the reaction to occur, thus, increasing the photo-degradation activity of MO.

Effect of incubation time: Based on Fig. 9, the degradation rate of MO was improved with increasing incubation time between 1-8 h and then decreased thereafter. The highest MO removal obtained was 84.9% at 8 h of incubation time.

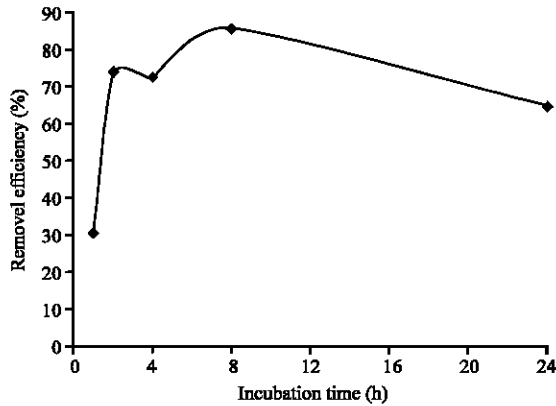


Fig. 9: Removal efficiency of MO at different incubation time

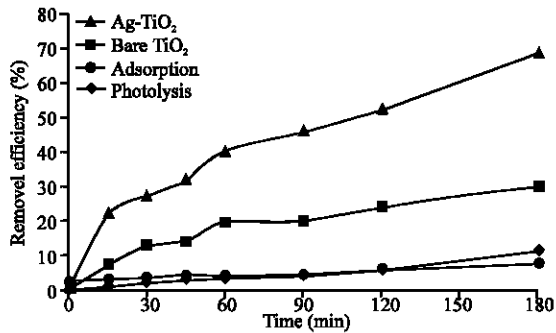


Fig. 10: Comparison of MO removal efficiency between Ag-TiO₂ and control tests

Prolonging the incubation time promoted the growth of photocatalyst particles, thus, lead to agglomeration (Reli *et al.*, 2002). As a result, this would reduce the surface area of photocatalyst as well as its photocatalytic activity due to weakening interaction between Ag-TiO₂ photocatalyst (Cheng *et al.*, 2007).

Figure 10 compares the optimum performance of Ag-TiO₂ photocatalyst on the removal of MO with control experiments. The control experiments were conducted under the same conditions for MO photo-degradation test except for photolysis which was carried out without the presence of catalyst and without the presence of UV light source for adsorption. The order of degradation of MO was as follows, Ag-TiO₂ (UV)>bare TiO₂ (UV)>photolysis>adsorption. Photolysis and adsorption led to the little removal of MO. Thus, it can be established that the photocatalytic performance can be enhanced by reacting the photocatalyst samples under UV light irradiation as it can excite more electrons and holes in TiO₂.

Kinetics study of photodegradation of MO: The photocatalytic degradation of MO fitted well with the

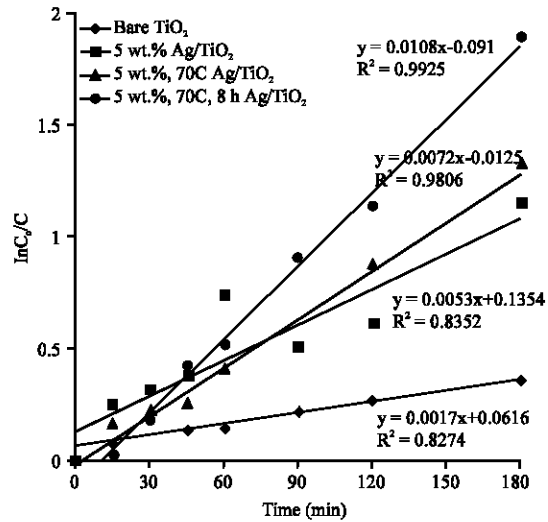


Fig. 11: Kinetics of photodegradation of MO at optimum parameters

pseudo-first-order kinetic model for both bare TiO₂ and Ag-TiO₂. The reaction rate is written in the form of:

$$r = \frac{-dc}{dt} = kC \quad (2)$$

Where:

k = The pseudo-first order reaction rate coefficient

C = The concentration of MO

The integration of the expression with $C = C_0$ at $t = 0$ gives:

$$\int_{C_0}^C \frac{-dC}{C} = k \int dt \quad (3)$$

$$-(\ln C - \ln C_0) = kt \quad (4)$$

$$\ln \frac{C_0}{C} = kt \quad (5)$$

The half-life of Ag-TiO₂ photocatalyst which was described as the time taken for the amount of photocatalyst to decrease by half can be obtained from the reaction rate coefficients. It was calculated using the following Eq. 6:

$$t_{1/2} = \frac{\ln 2}{k} \quad (6)$$

Plotting the natural logarithm of the ratio of MO initial concentration and the concentration after photocatalytic degradation ($\ln C_0/C$) versus irradiation time (min.) yields a linear relationship as shown in Fig. 11. The rate constants, k are obtained from the slope of the graphs.

Table 2: Rate coefficients, R² values and half-lives at different parameter

Parameters	k (min ⁻¹)	R ²	Half-life (min)
Concentration (ppm)	5.3×10 ⁻³	0.835	130.77
Incubation temperature (°C)	7.2×10 ⁻³	0.981	96.25
Incubation time (h)	1.08×10 ⁻²	0.992	64.29

Table 2 summarizes the reaction rate coefficients obtained from the slope of the graphs with its respective R-squared values (R²) and the half-lives of the photocatalyst. From Table 2, the degradation of MO using Ag-TiO₂ photocatalyst prepared at 5 wt.% of Ag, 70°C of incubation temperature and 8 h of incubation time demonstrated the highest rate constant of 1.08×10⁻² min⁻¹ and R² value of 0.992. The half-life was 64.29 min.

CONCLUSION

The objectives of the study were to prepare hybrid Ag-TiO₂ photocatalyst by wet impregnation method using different Ag concentration, incubation temperature and incubation time as well as to investigate the photocatalytic activity on the degradation of MO. The prepared photocatalyst was characterized using XRD, BET, EDX and FESEM analyses. The XRD analysis illustrated the anatase structure of TiO₂. The EDX spectra showed the composition of Ag on TiO₂ surface while the mappings showed the presence of Ag with uniform distribution on TiO₂ surface. The FESEM images showed the spherical and square-like shape of TiO₂. The colour also changed from grey to white when Ag was incorporated. This study also proved that Ag-TiO₂ photocatalyst has better photocatalytic performance over bare TiO₂, photolysis and also adsorption in the removal of MO dye. The photocatalyst prepared using 5 wt.% of Ag at 70°C and 8 h of incubation temperature and time showed an optimum result in which the photocatalyst was able to remove 84.94% of MO with in 3 h. The reaction kinetics also showed that the rate coefficient of Ag-TiO₂ was 1.08×10⁻² min⁻¹ and the half-life obtained was 64.29 min. The study suggested that Ag-TiO₂ is a promising photocatalyst for the degradation of organic pollutants under UV irradiation.

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REFERENCES

- Behnajady, M.A. and H. Eskandarloo, 2013. Characterization and photocatalytic activity of Ag-Cu/TiO₂ nanoparticles prepared by sol-gel method. *J. Nanosci. Nanotechnol.*, 13: 548-553.
- Caselatto, A.M.F., J.F. Ferreira, E.B. Tambourgi, R. Moraes and E. Silveira, 2011. Biodegradation of textile azo dyes by *Shewanella putrefaciens* (CCT 1967). *Chem. Eng.*, 24: 871-876.
- Cheng, Y., S.U.N. Hongqi, J. Wanqin and X.U. Nanping, 2007. Effect of preparation conditions on visible photocatalytic activity of titania synthesized by solution combustion method. *Chin. J. Chem. Eng.*, 15: 178-183.
- Gou, J., Q. Ma, X. Deng, Y. Cui and H. Zhang *et al.*, 2017. Fabrication of Ag₂O/TiO₂-Zeolite composite and its enhanced solar light photocatalytic performance and mechanism for degradation of norfloxacin. *Chem. Eng. J.*, 308: 818-826.
- Hosseini, M.G., M. Shokri, M. Khosravi, R. Najjar and M. Darbandi, 2011. Photodegradation of an azo dye by silver-doped nano-particulate titanium dioxide. *Toxicol. Environ. Chem.*, 93: 1591-1601.
- Hou, X.G., M.D. Huang, X.L. Wu and A.D. Liu, 2009. Preparation and studies of photocatalytic silver-loaded TiO₂ films by hybrid sol-gel method. *Chem. Eng. J.*, 146: 42-48.
- Kyzas, G.Z. and K.A. Matis, 2015. Nano-adsorbents for pollutants removal: A review. *J. Mol. Liquids*, 203: 159-168.
- Lei, M., N. Wang, L. Zhu, Q. Zhou and G. Nie *et al.*, 2016. Photocatalytic reductive degradation of polybrominated diphenyl ethers on CuO/TiO₂ nanocomposites: A mechanism based on the switching of photocatalytic reduction potential being controlled by the valence state of copper. *Appl. Catal. B Environ.*, 182: 414-423.
- Melian, E.P., O.G. Diaz, J.D. Rodriguez, G. Colon and J.A. Navio *et al.*, 2012. Effect of deposition of silver on structural characteristics and photoactivity of TiO₂-based photocatalysts. *Appl. Catal. B Environ.*, 127: 112-120.
- Mogal, S.I., V.G. Gandhi, M. Mishra, S. Tripathi and T. Shripathi *et al.*, 2014. Single-step synthesis of silver-doped titanium dioxide: Influence of silver on structural, textural and photocatalytic properties. *Ind. Eng. Chem. Res.*, 53: 5749-5758.
- Mohamed, M.M. and M.S. Al-Sharif, 2013. Visible light assisted reduction of 4-nitrophenol to 4-aminophenol on Ag/TiO₂ photocatalysts synthesized by hybrid templates. *Appl. Catal. B Environ.*, 142: 432-441.

- Oller, I., S. Malato and J.A. Sanchez-Perez, 2011. Combination of advanced oxidation processes and biological treatments for wastewater decontamination-a review. *Sci. Total Environ.*, 409: 4141-4166.
- Reli, M., K. Koci, V. Matejka, P. Kovar and L. Obalova, 2012. Effect of calcination temperature and calcination time on the kaolinite/TiO₂ composite for photocatalytic reduction of CO₂/Vliv kalcinacni teploty a doby kalcinace na kompozit kaolinit/TiO₂ pro fotokatalytickou redukcii CO₂. *GeoSci. Eng.*, 58: 10-22.
- Sakthivel, S., M.V. Shankar, M. Palanichamy, B. Arabindoo and D.W. Bahnemann *et al.*, 2004. Enhancement of photocatalytic activity by metal deposition: Characterisation and photonic efficiency of Pt, Au and Pd deposited on TiO₂ catalyst. *Water Res.*, 38: 3001-3008.
- Tan, L.L., W.J. Ong, S.P. Chai and A.R. Mohamed, 2017. Photocatalytic reduction of CO₂ with H₂O over graphene oxide-supported oxygen-rich TiO₂ hybrid photocatalyst under visible light irradiation: Process and kinetic studies. *Chem. Eng. J.*, 308: 248-255.
- Vamathevan, V., R. Amal, D. Beydoun, G. Low and S. McEvoy, 2002. Photocatalytic oxidation of organics in water using pure and silver-modified titanium dioxide particles. *J. Photochem. Photobiol. A Chem.*, 148: 233-245.
- Wang, X., J. Song, J. Huang, J. Zhang and X. Wang *et al.*, 2016. Activated carbon-based magnetic TiO₂ photocatalyst codoped with iodine and nitrogen for organic pollution degradation. *Appl. Surf. Sci.*, 390: 190-201.
- Zhao, W., L. Feng, R. Yang, J. Zheng and X. Li, 2011. Synthesis, characterization and photocatalytic properties of Ag modified hollow SiO₂/TiO₂ hybrid microspheres. *Appl. Catal. B Environ.*, 103: 181-189.
- Zhao, W., Z. Zhang, J. Zhang, H. Wu and L. Xi *et al.*, 2016. Synthesis of Ag/TiO₂/graphene and its photocatalytic properties under visible light. *Mater. Lett.*, 171: 182-186.
- Zuas, O. and H. Budiman, 2013. Synthesis of nanostructured copper-doped titania and its properties. *NanoMicro Lett.*, 5: 26-33.
- Zuorro, A. and R. Lavecchia, 2014. Evaluation of UV/H₂O₂ advanced oxidation process (AOP) for the degradation of diazo dye Reactive Green 19 in aqueous solution. *Desalin. Water Treat.*, 52: 1571-1577.