

Water-based Immobilized Ag-doped TiO₂ Photocatalyst for Photocatalytic Degradation of RR4 Dye

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ABSTRACT

This study used water-based preparation of immobilised Ag-TiO₂ using the DSAT technique to avoid solvent interference of Ag-TiO₂ photocatalytic performance. The preparation of Ag-TiO₂ was conducted via the photodeposition method with silver nitrate (AgNO₃) as Ag precursor at various ratios of Ag dopant to TiO₂. The immobilisation of Ag-TiO₂ was prepared via water-based immobilisation using the DSAT method, and XRD and FESEM-EDX characterised the obtained photocatalyst. The photocatalytic performance of Ag-TiO₂ was measured by photocatalytic degradation of Reactive Red 4 (RR4) dye. The optimum photocatalytic performance of suspension mode Ag-TiO₂ was obtained at 3 % of Ag-TiO₂. Sample 3 % Ag-TiO₂ was applied under immobilisation mode with complete degradation of 30 mg/L RR4 dye achieved within 60 min under 55 W fluorescent lamp irradiation. It is 36 % faster compared to immobilised, unmodified TiO₂. The acquired results from FESEM-EDX indicated the presence of 0.6 % Ag on the Ag-TiO₂ photocatalyst sample. The photodegradation rate of immobilized 3 % Ag-TiO₂ sample under different solvents has shown the different values among all where it was $0.096 > 0.037 > 0.029 > 0.029 > 0.025 \text{ min}^{-1}$ for water-base, ethanol, methanol, dichloromethane and acetone respectively. Thus, the solvents can influence the photocatalytic performance of the immobilised 3 % Ag-TiO₂ photocatalyst by molecular interference between Ag-doped in TiO₂. The water-based immobilised 3 % Ag-TiO₂ sample also has a sustainable performance where the photocatalytic activities are comparable to 10 cycles.

Keywords: *Photocatalysis, Titanium dioxide, Silver, RR4 dye, Water-base immobilisation*

INTRODUCTION

Water is considered the most crucial element in our daily activities. However, the sources of clean water are gradually decreased due to high demand and rapid growth of the worldwide population. One of the main reasons for the decline of surface water quality in urban areas is the discharging of untreated industrial waste into the water bodies [1]. One of the main contributors to the pollution is the textile industries that release coloured untreated wastewater that may cause a severe hazard to the aqueous environment [2]. As anionic Reactive Red 4 dye is widely used in the industry, researchers have employed it as a model pollutant in wastewater treatment studies [3]. Technologies such as ozonation and chlorination are the conventional wastewater treatments that are commonly used. However, these treatment methods have limitations, such as ozone does not remain in the water for a long time. The application of chlorine to remove pollutants may lead to the formation of toxic side effects like cancer [4].

An advanced oxidation process may be a possible solution to overcome these drawbacks. Photocatalysis is one of the most favourable productive technologies under the advanced oxidation process because of its prevailing capability and potential to degrade major organic pollutants [5]. The synergy of comprehensive applicability and the absence of side effects benefit this novel technology. This method is commonly used to degrade organic pollutants such as dyes and is also a successful alternative in cost and accessibility [6]. Among the photocatalysts, titanium dioxide (TiO_2) is commonly used and widely known for its commercial availability, low cost and unique electronic structure [6, 7]. This semiconductor which has a vast bandgap energy (3.2 eV), can act as a catalyst by inducing ultraviolet light (UV) in the photo-oxidation of organic substrates [8]. The demonstration of outstanding photodegradation over heterogeneous pollutants is due to the high redox potential of hydroxyl and superoxide radicals [9]. These compounds and radicals are formed by photo-excitation in the existence of electron donors and acceptors, for instance, water and natural oxygen.

As TiO_2 is only active in the ultraviolet light region, the practicality of this photocatalyst under solar light water treatment is limited. Moreover, the photocatalytic activity of TiO_2 is decreased because of the fast recombination rate of the electron (e^-)/hole (h^+) pair. Therefore, modification of the photocatalyst is needed to extend the optical absorption into the visible range, reduce the bandgap energy, and lower the (e^-)/(h^+) pair recombination without minimising the photocatalytic activity. For this intent, modification with noble metals doping such as platinum (Pt), silver (Ag) and gold (Au) on TiO_2 photocatalyst is a promising solution to overcome the TiO_2 limitation, which the modifications have a significant impact on the photocatalytic activity of TiO_2 [10].

Photocatalyst recovery is another primary concern in the photocatalysis process. Most photocatalysis is in suspension mode and requires complete separation of the nanopowder catalyst from the treated wastewater after photocatalytic degradation of the pollutants. This separation process can cause secondary contamination and loss of photocatalyst [11]. The photocatalyst immobilisation technique is preferable since the filtration process can be discarded in the post-treatment process. Immobilisation is a method where a photocatalyst mixed with polymer binder in a solvent formulation is applied to a solid support material to hold them together [12-14]. Nevertheless, lower photocatalytic activity was observed when immobilisation mode was applied compared to under suspension mode by considering the equilibrium condition of surface area to volume ratio for both modes. This might be due to the chemical interaction

between solvent and modified TiO₂ photocatalyst, losing its actual photocatalytic performance during the immobilisation process.

Immobilisation via double-sided adhesive tape (DSAT) was introduced where it can work the best of others in replacing polymer binder in immobilisation system. DSAT shows a great potential to substitute polymer binders in the immobilised system. It has good criteria: waterproof, long-lasting, strong, intact with any support materials, and does not require solvent in preparing the system [13]. Therefore, this study proposed a water-based preparation of immobilised Ag-TiO₂ using the DSAT technique to avoid solvent interference of Ag-TiO₂ photocatalytic performance as this method uses distilled water as solvent. The photocatalytic degradation ability of water-base preparation immobilised Ag-TiO₂ will be tested under photodegradation of RR4 dye in comparison to the different solvents such as methanol dichloromethane, ethanol and acetone.

EXPERIMENTAL

Preparation of Immobilized Ag-TiO₂

The photodeposition of Ag-TiO₂ was prepared according to the method by Bhardwaj *et al.* with modifications [15]. Silver nitrate (AgNO₃) was used as an Ag precursor. This procedure added 3 g of TiO₂ to 40 mL of 50 % IPA and stirred until homogenised. 0.0478 g of AgNO₃ was added to the formulation to prepare 1 % of Ag in TiO₂. The mixture was then transferred into a Schlenk tube with N₂ gas condition to prevent oxidation by removing oxygen gas. Photo-deposition of Ag-TiO₂ was carried out by irradiating the mixture with a 250 W metal halide lamp (LIKO, Malaysia) for one hour. The irradiated solution was then centrifuged to separate the prepared Ag-TiO₂ catalyst and washed three times with distilled water. The prepared Ag-TiO₂ was dried at room temperature for 15 h, and the dried Ag-TiO₂ obtained with a light purple colour was kept in a screw cap bottle for the photocatalysis process. A similar procedure was repeated for preparing 3 and 5 % of Ag-TiO₂.

The photocatalysis process was used to determine the photoactivity of unmodified and Ag-TiO₂. A glass cell with dimensions 50 x 10 x 80 mm (L x W x H) was used as a container for the photodegradation test. RR4 dye (30 mg/L) is used as a model pollutant. Before the photodegradation, the mixture of 0.025 g of Ag-TiO₂ and 20 mL of RR4 dye is stirred in dark conditions for 5 min to homogenise and achieve adsorption-desorption equilibrium. Afterwards, the sample was irradiated via a 55 W fluorescent lamp to initiate the photocatalytic reaction. The aquarium pump (NS 7200) with a rate of 10 ml/min was used as the source of aeration. At every 5 min intervals, an aliquot was withdrawn from the suspension and filtered using a 0.45 µm membrane filter (Sartorius, Germany) to separate the photocatalyst from the treated dye. The absorbance reading of the treated dye is measured by a spectrophotometer (HACH DR 1900) at a wavelength of 517 nm. The photodegradation rate is calculated accordingly, and the optimum loading of Ag in TiO₂ was determined based on the highest photodegradation rate. The optimum modified Ag-TiO₂ sample will undergo a solvent preparation method to determine the effect of solvent on this modified TiO₂, as most immobilisation processes use solvent for the dissolution of the organic compound. Various solvents

such as acetone, methanol, ethanol and dichloromethane were used to replace distilled water during the preparation of Ag-TiO₂.

The immobilisation of Ag-TiO₂ was carried out using the DSAT method as previously studied by Wan Ismail *et al.* [12]. For the preparation of Ag-TiO₂ formulation, 0.5 g of photocatalyst is added to 10 mL of distilled water. 1 mL of 8 % PVA solution is added to the formulation as a binder. The mixture is mixed together under the sonication process for 30 minutes to produce a homogenised formulation. Using a brush coating technique, the Ag-TiO₂ was applied on a glass plate taped with double-sided adhesive tape and dried with a hot air blower. According to Nawi *et al.* [16], only 2-4 nm coating will allow light penetration through the sample. Thus the brush coating technique cannot be applied too thick as the photocatalytic performance can be reduced due to less light adsorption. The steps were repeated until the optimum weight of coating was achieved. The immobilised photocatalyst is washed with distilled water for 30 min to remove contaminants and residues. After that, the photodegradation of RR4 dye was determined by following the same procedure as photocatalysis evaluation under suspension mode. The reusability of the immobilised sample was determined by continuing the photodegradation of RR4 dye until the 10th cycle.

Characterisations

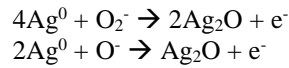
The morphology and the composition of the prepared photocatalyst were observed using FESEM-EDX (Hitachi SU8020). As for the preparation of the sample, the unmodified immobilised TiO₂ and Ag-TiO₂ sample was stuck in the carbon conductive adhesive tapes (CCAT) and coated with Au to prevent any accumulation of charge during the analysis. The crystallographic properties of prepared Ag-TiO₂ were determined by X-ray diffraction (PANalytical X'pert PRO, Netherlands) with Cu-K α at 1.5406 Å.

RESULTS AND DISCUSSION

Physical Observation

Figure 1(a-d) shows the photocatalyst's colour changes from white to shades of purple with the increasing percentage of Ag, which indicates the significant incorporation of Ag onto TiO₂. Indeed, the use of AgNO₃ as a silver precursor will lead to the colouration of the final prepared catalyst with certain shades of purple [17]. According to Dong *et al.*, the specific charge transfer transitions between Ag and TiO₂ contribute to the changes in the colour of the photocatalysts [18]. Wenderich and Mul reported that the irradiation of TiO₂ and Ag precursor mixture in an aqueous solution for a fixed time is adequate to reduce silver ion (Ag⁺) to silver metal (Ag⁰) and ensure their deposition on the TiO₂ surface [19].

However, after being exposed to open air, the prepared Ag-TiO₂ samples' colour changed from pale to dark purple. This phenomenon could attribute to the formation of Ag₂O. Priya *et al.* mentioned that the formation of Ag₂O on TiO₂ is due to oxygen ion reverse-spill as the dominant oxidation mechanism of deposited Ag⁰ [20]. Thus, the mechanism can be expressed as in Equation 1 and Equation 2:



Equation 1

Equation 2



Figure 1: Colour intensity of photocatalyst of a) control, b) 1, c) 3, and d) 5 % Ag-TiO₂

Structural and Elemental Properties

Figure 2 shows the XRD pattern of unmodified and modified Ag-TiO₂ samples. XRD results showed that all the modified Ag-TiO₂ samples are in single anatase form with no phase transformation. The Ag-TiO₂ samples showed several diffraction peaks at $2\theta = 25.355^\circ$, 37.842° , 48.141° , 53.945° , 55.183° , 62.810° , and 68.872° were indexed as (101), (004), (200), (105), (211), (204), and (116) respectively. Figure 3 (a) and (b) exhibit the FESEM micrographs of unmodified TiO₂ and 3 % Ag-TiO₂. The FESEM images with 100×10^3 magnifications reveal that both unmodified TiO₂ and modified 3 % Ag-TiO₂ display nearly

similar morphologies, which consist of almost spherical nanoparticles clump together to form microstructures.

Furthermore, the modified 3 % Ag-TiO₂ has more dark-spot compared to the unmodified TiO₂. This occurrence may demonstrate the deposition of Ag nanoparticles on the TiO₂ nanostructure's surface. However, the nanoparticles are too small; thus, the FESEM resolution is insufficient to detect the particles. The elemental analysis of the modified 3 % Ag-TiO₂ and unmodified TiO₂ was carried out by EDX. The EDX result of the photocatalysts is shown in Figures 3 (c) and (d). The EDX pattern in Figure 3 (d) exhibits a weak peak of Ag at 3 KeV, which is typical for absorption of metallic silver nanoparticles, in addition to a strong peak of Ti and O. EDX image of unmodified TiO₂ (Figure 3 (c)) shows the detection peaks of Ti and O with no Ag peak. For 3% Ag-TiO₂, the wt% detected was 0.6, different from the calculation (3 %). This might be due to the formation of Ag₂O during the photodeposition of Ag-TiO₂, as Ag₂O can be produced when metallic Ag reacts with oxygen at a temperature below 195° C. Nevertheless, the data confirms the presence of Ag in the photocatalyst, indicating successful loading of Ag onto TiO₂.

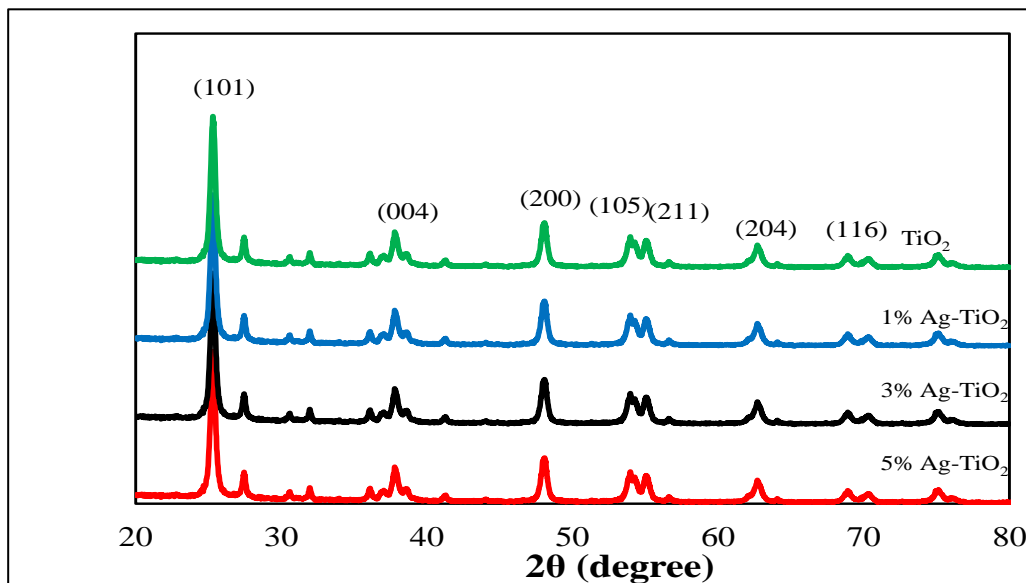


Figure 2: XRD pattern of unmodified and modified Ag-TiO₂ samples

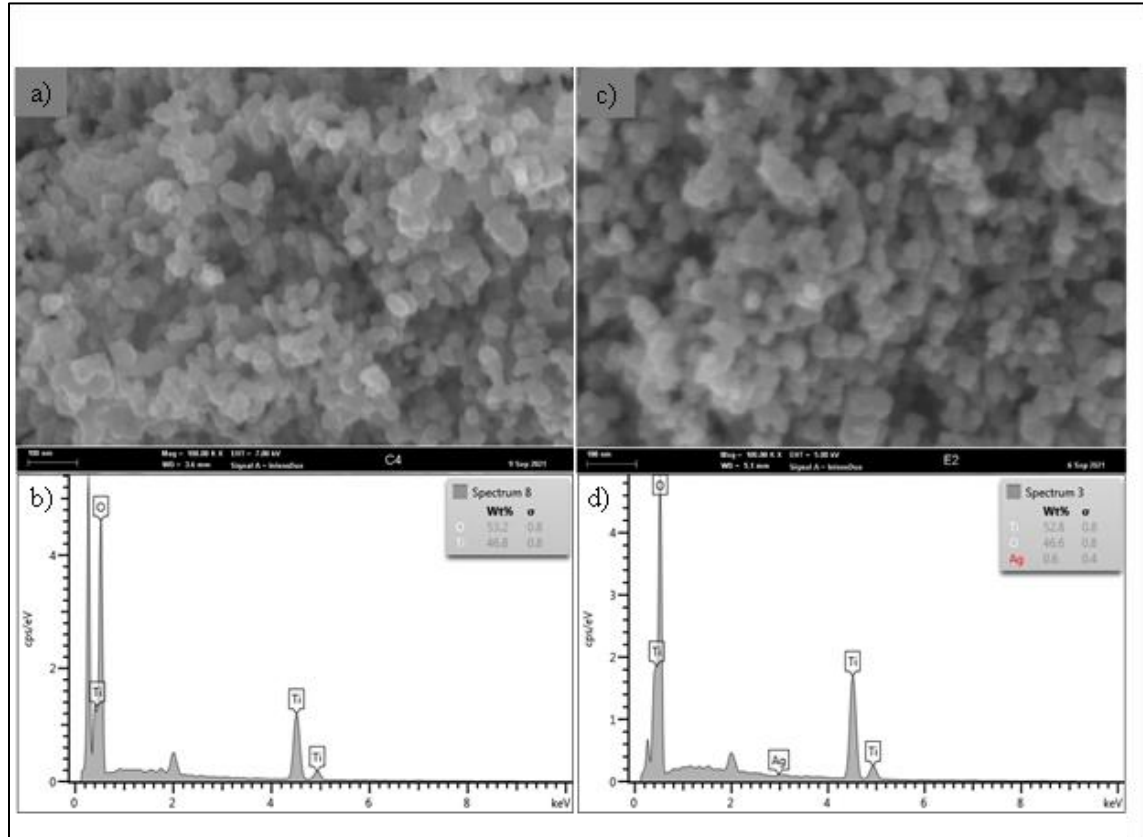


Figure 3: FESEM and EDX images of (a-b) TiO₂, and (c-d) 3 % Ag-TiO₂

Photodegradation Study

The photocatalytic performance of unmodified TiO₂ and modified Ag-TiO₂ was determined by photodegradation of RR4 dye (30 mg/L) as a model pollutant under light irradiation (55 W lamp). The photocatalytic activity was determined based on C/C₀ over time irradiation displayed in Figure 4 (a). The Langmuir-Hinshelwood model describes the degradation kinetics of pollutants in the aqueous phase of heterogeneous catalytic reaction [21]. The reaction rate of the photodegradation follows pseudo-first-order kinetics, which can be expressed as in Equation 3:

$$\ln \frac{C}{C_0} = -k_{app}t \quad \text{Equation 3}$$

Where C₀ represents the initial dye concentrations, C represents the time-varying dye concentrations (both in mg/L), K_{app} represents the apparent kinetic constant (min⁻¹), and t represents irradiation time (min). Figure 4 (b) shows the photodegradation rate of unmodified and modified Ag-TiO₂.

Based on the graph obtained in Figure 4 (a), all samples show photocatalytic degradation under RR4 dye, which degrades almost 50 % in 10 min. 3 % Ag-TiO₂ was able to degrade RR4 dye faster than other samples. It degrades almost 80 % under 10 min irradiation. It is clearly shown that 3 % Ag-TiO₂ is the optimum modified sample considering its higher photocatalytic degradation of RR4 dye.

The degradation rate has shown a similar observation where the k value of 3 % Ag-TiO₂ was ca. 0.12 min⁻¹. This is due to the significant presence of Ag in TiO₂, which increases the photocatalytic performance. Jang et al. [22] stated that the efficient separation of e⁻/h⁺ pairs and minimum recombination assisted the fast photocatalytic reaction. According to Ohtani et al. [23], the fast performance of the catalyst is due to the improvement of the charge carrier separation initiated by the Ag nanoparticles that trap the excited electrons from titanium dioxide and leave the holes for the degradation reaction of organic pollutants. Due to localised surface plasmon resonance, the Ag nanoparticles can extend their wavelength response toward the visible region and assist in visible light absorption [24].

Another factor that may contribute to the high performance of the 3 % Ag-TiO₂ is the successful formation of heterojunction. Lyu et al. [25] reported that the formation of heterojunctions in the Ag-based TiO₂ sample led to the remarkable removal of the bacterial cells [25]. Concerning the formation of the Ag₂O on the catalyst, it has been stated that the photo-excitation of Ag₂O rather than Ag⁰ acts as active sites responsible for the enhanced photocatalytic activity, whereas Ag⁰ might contribute to the stability [26]. While Jiang et al. [27] mentioned that the high surface area and numerous crystal boundaries provided by the aggregation of Ag₂O nanoparticles efficiently increased the escape probability of photogenerated electrons and the contact probability of photogenerated holes with exterior materials, promising outstanding photocatalytic activity and excellent stability of as-prepared Ag₂O samples.

In addition, the synthesised heterostructure type Ag-Ag₂O/TiO₂ by a simple electrochemical method resulted in a highly active and stable photocatalyst under visible light, following a Z-scheme charge transfer mechanism [28]. Contradictory to the statement mentioned above, Ziashahabi et al. [29] reported that silver oxidation in the heterostructure changed the metal-semiconductor interface and suppressed the plasmonic enhancement and silver oxidation only affected the catalytic activity in the dark. Akel et al. [30] also agreed that Ag₂O could act as an electron acceptor in the light-induced reaction of cationic dye and is transformed by reducing Ag⁺, yielding Ag⁰. They mentioned that Ag/Ag₂O is not stable under the experimental conditions; thus, to address Ag/Ag₂O as a photocatalytically active material would be impractical.

However, when the Ag loading is increased to 5 % Ag-TiO₂, the photocatalytic activity decreases by 15.66 %, as shown in Figure 4 (b). The decrement is due to the excessive amount of Ag incorporated with TiO₂. At higher Ag loading beyond the optimum, recombination centres are formed for the charge carrier. Therefore the probability of the e⁻/h⁺ pair is increased in the photocatalyst [31].

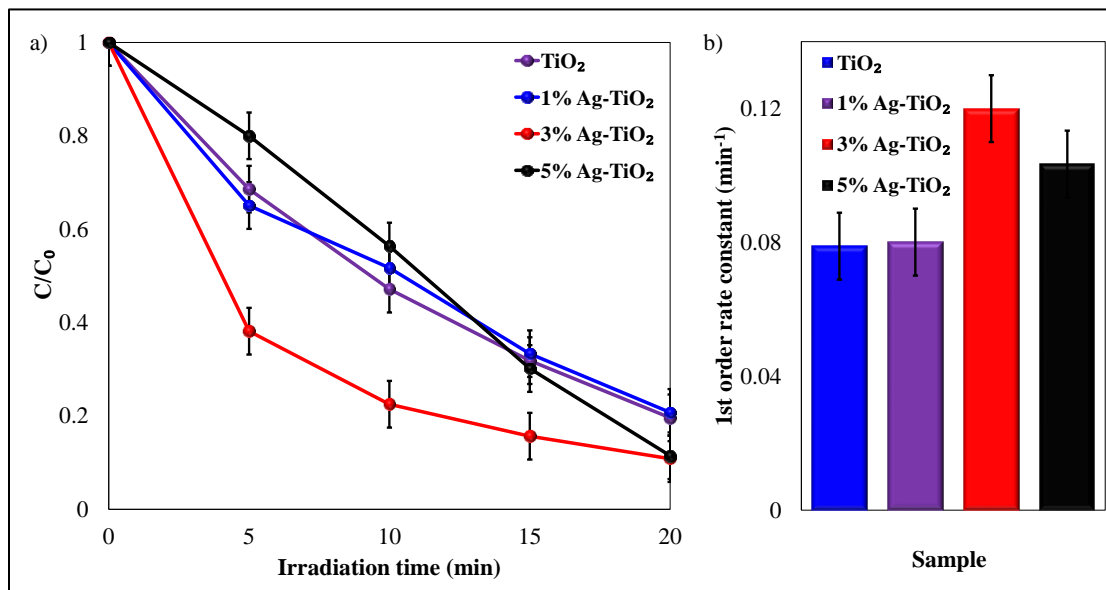


Figure 4: Photocatalytic performance of TiO_2 and 1-5 % Ag- TiO_2

The photocatalytic performance of 3 % Ag- TiO_2 under different solvent effects under suspension and immobilised modes is shown in Figures 5 (a) and (b). It is observed in Figure 5 (a) that the methanol-prepared photocatalyst has the highest percentage of decrement in suspension mode compared to the other solvent-prepared with a water-based photocatalyst preparation shows the highest photocatalytic degradation rate. It shows that the solvents (acetone, methanol, ethanol and dichloromethane) can influence the photocatalytic performance of the immobilised 3 % Ag- TiO_2 photocatalyst. This solvent effect may be significant in preparing immobilised Ag- TiO_2 .

As shown in Figure 5 (b), when the immobilisation mode is applied, the photocatalytic performance under water-based was reduced by 22 % compared to the suspension mode. Ismail et al. [12] reported that the low photocatalytic performance might be due to less surface contact than in suspension mode. It can be considered the lowest % reduction compared with the immobilised Ag- TiO_2 under solvent effect, where it is ca. 80, 76, 70 and 77 % reduction under acetone, methanol, ethanol and dichloromethane, respectively.

Bregadze et al. [32] mentioned that the solvent interference lowered the photocatalytic performance of the modified TiO_2 samples. This could attribute to intermolecular interference of the solvent molecule between TiO_2 and co-catalyst [15]. Partial corrosion of Ag NPs also may affect the photocatalytic performance, as mentioned by Ma et al. [33]. In contrast, Janus et al. [34] reported that the presents of carbon in the photocatalyst had influenced the absorption capacity of the materials. The comparative C/C_0 of the samples with the control experiments are shown in Figure 6. The control experiments are applied in this study to discard the effect of photolysis and adsorption, thereby proving the efficiency of Ag- TiO_2 samples in photocatalytic enhancement.

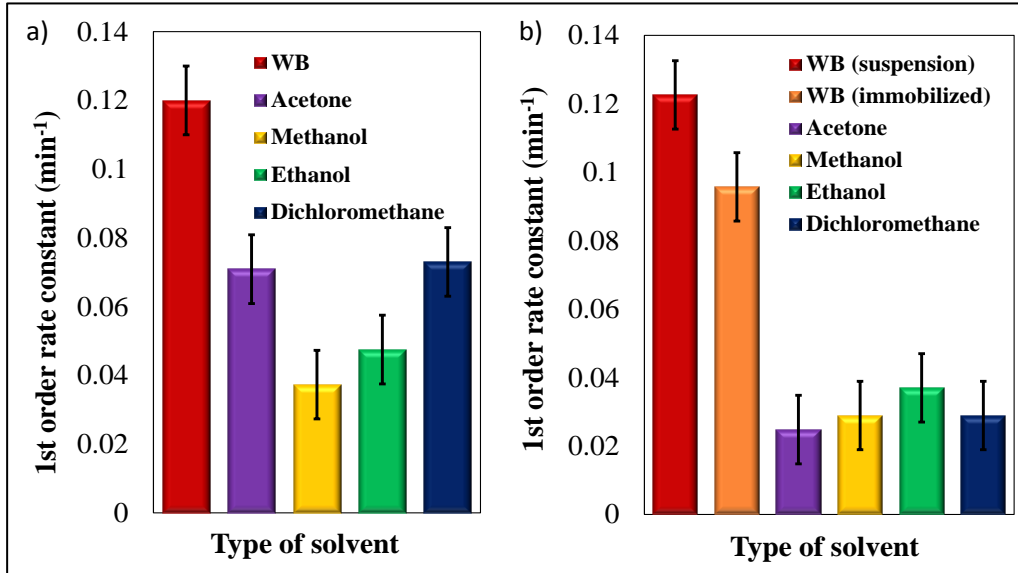


Figure 5: Percentage decrement of 3 % Ag-TiO₂ sample by a solvent preparation under a) suspension mode and b) immobilised mode

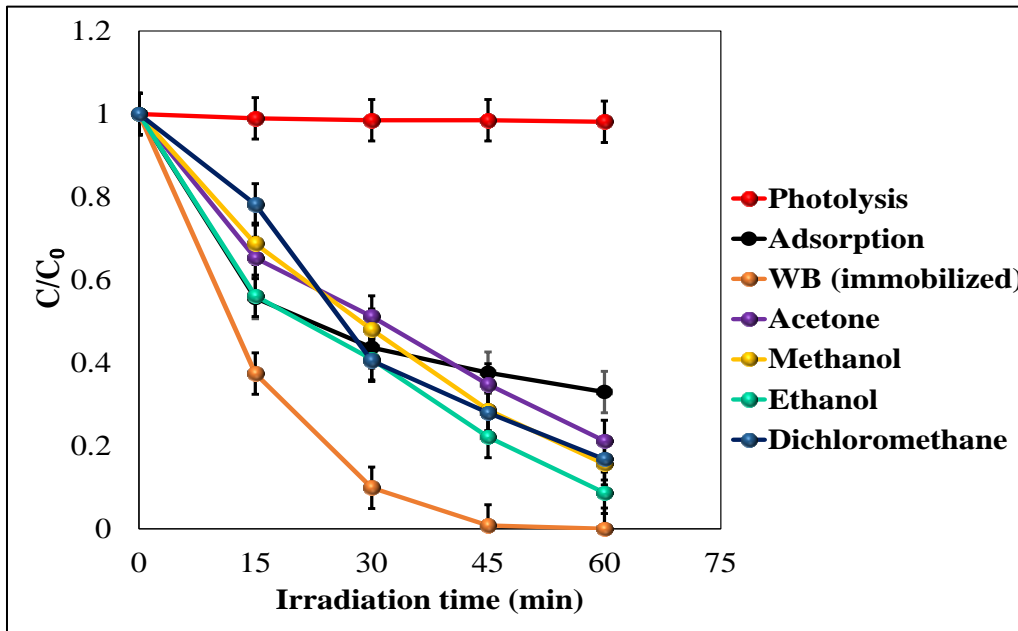


Figure 6: Comparative C/C_0 with time for different solvent preparation of 3 % Ag-TiO₂

Immobilised 3 % Ag-TiO₂ has also been tested upon multiple usages to observe its adhesiveness and photocatalytic sustainability. Figure 7 shows the photocatalytic activity of RR4 dye upon multiple usages where the stable photocatalytic activity of immobilised 3 % Ag-TiO₂ was obtained upon the 10th cycle. The sustainability is due to the intact of this 3 % Ag-TiO₂ onto glass support material without any leaching effect. The sustainable result for each cycle also gives a significant theory where sustained photoactivity could be attributed to the solid intermolecular attraction between Ag and TiO₂ where it does not easily split apart.

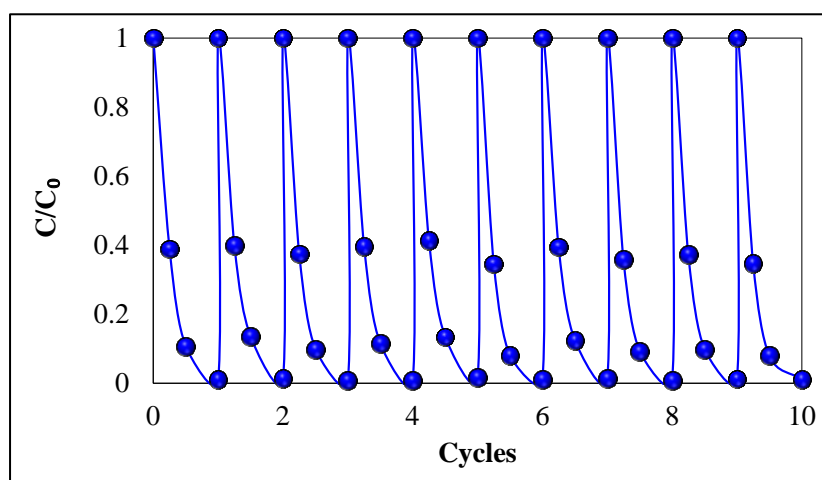


Figure 7: Effect of photocatalytic degradation of RR4 dye upon cycle

Possible Mechanism of Photodegradation

The reaction mechanism was proposed based on the obtained experimental results and analysis (Figure 8). Upon visible light irradiation, the photogenerated electrons are excited to the conduction band of Ag while the holes are left behind with positive charges. In the visible light reaction of Ag-TiO₂ photocatalyst, Ag can sensitise TiO₂ due to its strong localised surface plasmon resonance (SPR). It can generate electrons with higher kinetic energy because of the low heat capacity [35]. Thereby, Ag can act as a light harvester to initiate the photocatalytic reaction of Ag-TiO₂. Due to TiO₂'s more positive potential value, the excited electrons of Ag are transferred to the conduction band of TiO₂. This electrons jump can reduce the recombination rate of electrons and holes, resulting in the enhanced photocatalytic performance of Ag-TiO₂.

It is assumed that because of the efficient separation of the charge carriers instead of recombination, the electrons at the conduction band of TiO₂ contributed to the formation of •O₂⁻. In contrast, the generated holes at the valence band reacted with H₂O to produce •OH. During photocatalytic degradation, these reactive radicals, •O₂⁻, •OH, and h⁺, can oxidise the ionic RR4 dye into a harmless substance (Figure 8 (a)).

However, when there is the presence of a solvent, the photocatalytic performance of Ag-TiO₂ becomes lowered. This is possible because of the solvent intermolecular interference within the Ag and TiO₂ reaction. Consequently, the electrons from Ag cannot be transferred to TiO₂, causing a decline in photocatalytic performance as summarized in Figure 8 (b).

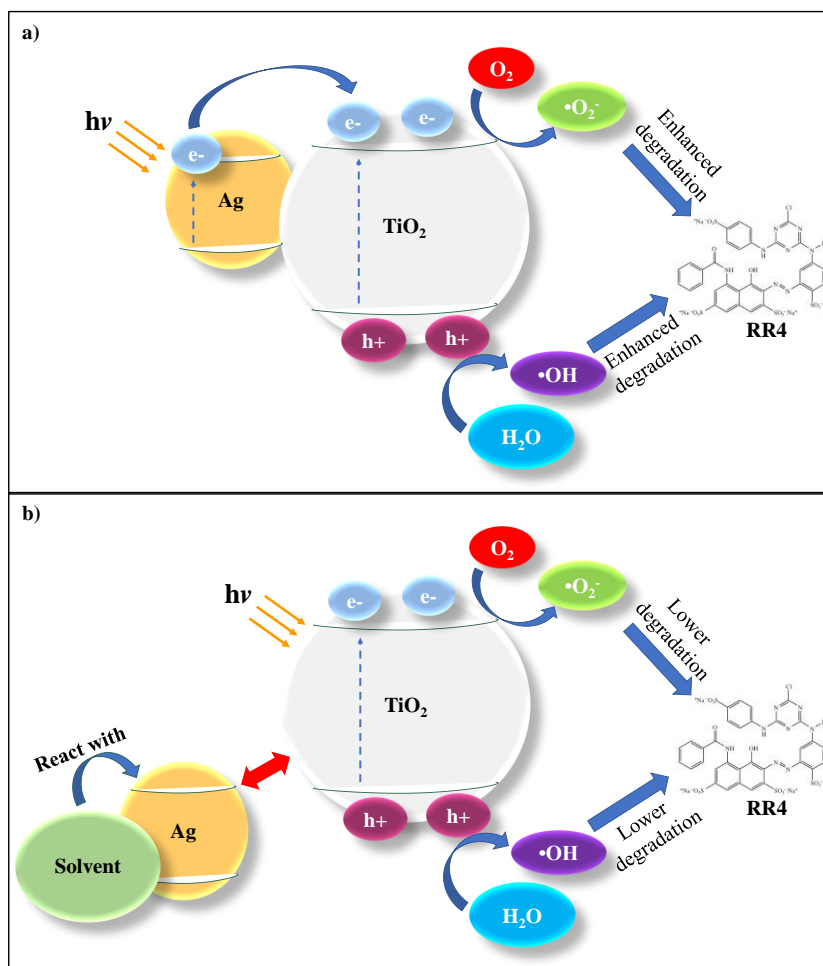


Figure 8: Schematic illustration of the possible mechanism of Ag-TiO₂ a) without solvent interference and b) with solvent interference

CONCLUSION

This work presented the TiO₂ modification with various amounts of Ag using a photodeposition method. Ag-TiO₂ with a 3 % doping amount containing 0.6 wt% Ag was identified as the optimum Ag-doped TiO₂ with the fastest photodegradation rate under RR4 dye. The 3 % Ag-TiO₂ sample undergoes the solvent effect study upon preparation, and it is proven that few solvents like acetone, ethanol, methanol and dichloromethane lowered the photocatalytic performance of Ag-TiO₂. This observation is significant since a regular TiO₂ preparation may use one of these solvents. Water-based preparation shows a higher photocatalytic performance as compared with solvent preparation. Thus, a water base is the best method for immobilised TiO₂ preparation. DSAT immobilisation method was chosen for the water-based TiO₂ immobilisation. It shows that a photocatalytic performance under RR4 dye degradation has a 22 % decrement compared to solvent prepared immobilised Ag-TiO₂, where the decrement was 70 to 80 %. Water-based immobilised Ag-TiO₂ was also durable upon the 10th cycle with sustained photocatalytic degradation. This photocatalytic sustainability proved a strong interaction between Ag and TiO₂, which might be one of the reasons to state that Ag is doped on a TiO₂ lattice.

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AUTHOR'S CONTRIBUTION

Nureel Imanina Abdul Ghani: Carried out the research, wrote and revised the article. Muhammad Afiq Rosli; Siti Raihan Hamzah: Performed the analysis and provided the theoretical framework. Nadiah Sabihah Natar; Mohammad Saifulddin Mohd Azami: Contributed data or analysis tools and conceptualised the central research idea. Syahirul Ikhwan Ab Aziz; Nur Syazana Nazeri; Nur Hidayatul Syazwani Suhaimi; Nur Syamimi Mohamad Abdul Adzis: Collected the data. Wan Izhan Nawawi Wan Ismail; Sarina Mohamad: Designed the research, supervised research progress, anchored the review and revisions and approved the article submission.

CONFLICT OF INTEREST STATEMENT

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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