



Faculty of Resource Science and Technology

The Multifunctionalised TiO_2/Ag /Cellulose Acetate Photocatalyst with enhanced Photodegradation and Antibacterial Activities

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The Multifunctionalised TiO₂/Ag/Cellulose Acetate Photocatalyst with enhanced Photodegradation and Antibacterial Activities

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.



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ABSTRACT

Titanium dioxide, TiO_2 photocatalyst has been greatly employed in the photocatalytic treatment of wastewater due to its excellent properties. The combined effects of doping and the inclusion of support material such as cellulose acetate (CA) can enhance the photocatalytic efficiency of TiO_2 photocatalysts. In this study, TiO_2 was synthesised via a green solvent template, ionic liquid, IL (1-butylimidazolium acetate) to produce high surface area photocatalyst and combined with silver (Ag) dopant to improve its photocatalytic performance in visible light. CA was added as support in the photocatalyst for the degradation of multiple dyes namely methylene blue (MB), methyl orange (MO) and rhodamine B (RhB). This study investigated the effect of different volumes of IL (0.5 mL – 5.0 mL) used in the synthesis of TiO_2 via the sol-gel method, the effect of different Ag concentrations (0.5 wt% - 5.0 wt%) and CA concentrations (0.5 wt% - 5 wt%) on the photocatalytic performance of TiO_2/Ag . The photocatalytic ability of TiO_2 -1/Ag 2 %/CA 0.5% photocatalyst under various operating parameters such as photocatalyst dosage, initial dye concentration, initial pH and effect of radical scavenger was investigated. The recyclability of TiO_2 -1/Ag 2 %/CA 0.5% was also determined. The characterisation of TiO_2 -1/Ag 2 %/CA 0.5% photocatalyst via X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Energy Dispersive X-Ray (EDX), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) analysis revealed the presence of Ag and CA on the surface of TiO_2 . Brunauer Emmett Teller (BET) surface area analysis has shown that the inclusion of IL in the synthesis greatly increased the surface area of TiO_2 from $130.9 \text{ m}^2/\text{g}$ to $174.8 \text{ m}^2/\text{g}$. Based on the preliminary experiments, 1.0 mL of IL, 0.5 wt% of Ag and 2.0 wt% of CA contributed to the highest photocatalytic degradation of $\text{TiO}_2/\text{Ag}/\text{CA}$ photocatalyst and were chosen for further studies. $\text{TiO}_2/\text{Ag}/\text{CA}$ (IL: 3 mL, Ag:

2 wt% & CA: 0.5%) showed the highest MB dye removal in individual and mixed dye conditions (MB, MO and RhB) after 120 min of treatment time upon UVA irradiation ($\lambda = 365$ nm) under solution with pH 7.4. The antibacterial activity of TiO₂-1/Ag 2 %/CA 0.5% investigated via disc diffusion method against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) bacteria demonstrated inhibition zones, indicating antibacterial effectiveness of TiO₂-1/Ag 2 %/CA 0.5%. As wastewater treatment requires the removal of chemical pollutants and unwanted biological components, TiO₂-1/Ag 2 %/CA 0.5% photocatalyst depicted in this study can be a promising degradative tool to meet this dual goal with high efficiency.

Keywords: Green materials, silver, photocatalysis, mixed dyes, wastewater

Fotopemangkin TiO₂/Ag/Selulosa Asetat Pelbagai Fungsi dengan Peningkatan Aktiviti Fotodegradasi dan Antibakteria

ABSTRAK

Fotopemangkin titanium dioksida, TiO₂ sering digunakan dalam rawatan air kumbahan disebabkan oleh ciri-cirinya yang sangat baik. Gabungan logam dengan semikonduktor dan bahan sokongan seperti selulosa asetat, CA menunjukkan peningkatan kecekapan yang ketara dalam fotopemangkin TiO₂. Dalam kajian ini, TiO₂ disintesis menggunakan pelarut hijau, cecair ionik (1-butylimidazolium acetate), untuk menghasilkan fotopemangkin yang berpermukaan luas dan digabungkan dengan perak (Ag) sebagai dopan untuk memperbaiki aktiviti fotodegradasi dalam cahaya tampak. CA telah ditambah sebagai sokongan dalam fotopemangkin untuk penyingkiran pelbagai pewarna fabrik iaitu metilena biru (MB), metil jingga (MO) dan rodamina B (RhB). Kajian ini menyiasat kesan isi padu cecair ionik yang berbeza (0.5 mL – 5.0 mL) dalam sintesis TiO₂ melalui kaedah sol-gel, kesan kepekatan Ag yang berbeza (0.5 wt% - 5.0 wt%) dan kesan kepekatan CA (0.5 wt% - 5 wt%) ke atas prestasi fotopemangkin TiO₂/Ag. Aktiviti fotodegradasi TiO₂/Ag/CA dalam pelbagai keadaan seperti dos fotopemangkin, kepekatan asal pewarna fabrik, pH asal dan kesan penggaut radikal telah dikaji. Kebolehkitaran semula TiO₂/Ag/CA juga telah ditentukan. Pencirian fotopemangkin TiO₂/Ag/CA melalui analisis XRD, FTIR, EDX, SEM dan TEM menunjukkan kehadiran Ag dan CA dalam TiO₂. BET menunjukkan bahawa penggunaan cecair ionik dalam sintesis fotopemangkin TiO₂ berjaya meningkatkan luas permukaannya daripada 130.9 m²/g kepada 174.8 m²/g. Berdasarkan kajian awal, TiO₂/Ag/CA dengan 1.0 mL cecair ionik, 0.5 wt% Ag dan 2.0 wt% CA menyumbang kepada aktiviti fotodegradasi tertinggi dan telah dipilih untuk kajian selanjutnya. TiO₂/Ag/CA (cecair ionik: 3 mL, Ag: 2% wt% dan CA: 0.5% wt%) menunjukkan penyingkiran MB adalah

tertinggi apabila wujud secara individu dan keadaan campuran (MB, MO dan RhB) dalam masa 120 minit di bawah penyinaran UVA ($\lambda = 365 \text{ nm}$) pada pH 7.4. Aktiviti antibakteria $\text{TiO}_2/\text{Ag}/\text{CA}$ yang dikaji melalui kaedah resapan cakera terhadap bakteria *E. coli* dan *S. Aureus* menunjukkan zon perencatan, membuktikan keberkesanan antibakteria $\text{TiO}_2/\text{Ag}/\text{CA}$. Fotopemangkin $\text{TiO}_2/\text{Ag}/\text{CA}$ yang digambarkan dalam kajian ini menunjukkan kecekapan yang tinggi dalam aktiviti fotodegradasi dan antibakteria. Hasil kajian ini menunjukkan kemampuan fotopemangkin $\text{TiO}_2/\text{Ag}/\text{CA}$ dalam memenuhi matlamat dwi rawatan air kumbahan iaitu penyingkiran bahan pencemar kimia dan komponen biologi yang tidak diingini.

Kata kunci: Bahan hijau, perak, pemfotomangkinan, campuran pewarna fabrik, air kumbahan

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LIST OF ABBREVIATIONS

Ag	Silver
BET	Brunauer Emmett Teller
CB	Conduction band
EDX	Energy Dispersive X-ray
FTIR	Fourier Transform Infrared Spectroscopy
MB	Methylene Blue
MO	Methyl orange
ROS	Reactive oxygen species
SEM	Scanning Electron Microscope
SPR	Surface plasmon resonance
TiO ₂	Titanium Dioxide
TEM	Transmission Electron Microscope
UV	Ultraviolet
UV-DRS	UV-Vis Diffuse Reflectance Spectroscopy
VB	Valence band
XPS	X-ray photoelectron spectroscopy
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Study Background

The aquatic ecosystem has been severely disrupted by the presence of organic contaminants in water, such as dyes and industrial chemicals. Titanium dioxide (TiO_2) photocatalysis has emerged as one of the most powerful tools for removing organic pollutants from aquatic environments among the various existing techniques. TiO_2 has been widely employed as a photocatalyst due to its important features including being non-toxic, inexpensive, resistant to photochemical corrosion, and having a high oxidizing power (Gopinath et al., 2019). However, there are nonetheless certain shortcomings that could lower the performance efficiency of TiO_2 . For instance, its high band gap such as 3.0-3.2 eV that is only excited by ultraviolet (UV) light results in poor adsorption capacity under visible light (Lin & Li, 2021). As a result, various attempts have been undertaken to circumvent these limitations, such as surface modification (Li et al., 2013), stabilization via support structures (Ju, 2019; Yang & Luo, 2021) and the inclusion of magnetic components to facilitate separation (Kanakaraju et al., 2018).

Numerous research studies have shown the improvement of TiO_2 photocatalytic performance by modifying its surface. Metal doping and embedment of support are two effective ways of modifying the surface of pure TiO_2 . Doping noble metals like gold (Au) and silver (Ag) onto TiO_2 has greatly enhanced TiO_2 's photocatalytic properties (Kochuveedu et al., 2012; Avciata et al., 2016). Ag, a noble metal candidate has been applied as a TiO_2 doping agent because of its benefits, particularly in enhancing TiO_2 's physicochemical properties (Wang et al., 2020; Nazhirah et al., 2021). Ag traps and captures

electrons from TiO₂'s conduction band, and then converts the electrons into superoxide radicals. Water molecules will react with holes generated in the TiO₂ valence band to produce hydroxyl radicals, which are required in photocatalytic oxidation (Din et al., 2018). The incorporation of Ag on the TiO₂ surface can achieve an obvious redshift as a result of the narrowing band gap and an improvement in photocatalytic activity (Park et al., 2020). Furthermore, the Ag⁺ ion could substitute the Ti⁴⁺ in the TiO₂ lattice, resulting in the deformation of the crystal lattice (Gao et al., 2015). Also, Ag has an important characteristic such as the surface plasmonic resonance (SPR) effect, that helps in extending light absorption to the visible light region (Khan et al., 2015; Furube & Hashimoto, 2017). Numerous studies have demonstrated that Ag dopant contributed to increased photocatalytic efficiency of TiO₂ (Petica et al., 2019; Zhou et al., 2019). Additionally, Ag is commonly used in antimicrobials since it works effectively against bacteria, fungi, and has shown promise in combating cancer cells (Gurunathan et al., 2015; Jatoi et al., 2019). Ag kills bacteria through its antibacterial action, which involves the breaking down of cell wall membranes, DNA denaturation and blockage of the bacteria's respiratory tracts (Abdelgawad et al., 2014; El-Naggar et al., 2016). TiO₂/Ag demonstrates high bacterial growth inhibition against *E. coli* and *S. aureus* (Bezir et al., 2018; Ghosh et al., 2020).

Despite the aforementioned positive characteristics of TiO₂/Ag, some prevalent issues of TiO₂/Ag are the particles may aggregate due to their large active surface area (Ahmad et al., 2016) and leaching out of the photocatalyst system (Wint et al., 2020). It is also recognised that excessive use of Ag can cause adverse effects on the human cells; examples of excessive Ag release are argyria and argyrosis (Jatoi et al., 2019). Therefore, supporting TiO₂/Ag on high surface area materials improves its mechanical strength while minimising the excess release of Ag and maintaining its antibacterial capabilities. Cellulose

acetate (CA) is greatly utilised due to its high specific surface area and porosity as well as interconnected pore structures, making it a suitable material to strengthen the mechanical capacity of TiO_2 (Gebbru & Das, 2017). CA is also well known for its excellent biocompatibility, biodegradability, hydrophilicity and high mechanical strength (Ashraf et al., 2020). In addition, CA is structurally rich in hydroxyl groups, allowing metal nanoparticles (NPs) to be immobilised on the surface (Yu et al., 2020). Immobilisation of TiO_2/Ag photocatalyst on cellulose-derived carbon beads with hollow network structure caused the homogeneous distribution of particles and increased availability of active sites (Yang & Luo, 2021). Past research has mainly used CA as a support to increase photocatalyst's surface area (Shalan et al., 2021) and for antibacterial applications (Jatoi et al., 2019). So far, however, there is very limited knowledge of the effects of CA concentration towards the photocatalytic efficiency of TiO_2/Ag . Our recent study revealed that adding CA in low concentration increases the photocatalyst's adsorption capacity and significantly aided the removal of MB (Kanakaraju et al., 2022).

This study aims to include a solvent template, IL in the synthesis of TiO_2 prior to the addition of Ag and CA. It is known that the application of ILs as a template solvent medium greatly influenced the catalytic activity, crystallinity and morphology of the photocatalyst (Mohaghegh et al., 2015). As compared to organic solvents, IL offers greater benefits such as thermal stability and chemical stability, low melting point, excellent electrochemical properties as well as the ability to dissolve various organic and inorganic materials (Ravishankar et al., 2015). Synthesis of TiO_2 with imidazolium ILs such as 1-butyl-3-methylimidazolium has resulted in excellent photocatalytic activity. TiO_2/Ag surface area increased 3 folds when it is synthesised with IL (1-Butyl-3-methylimidazolium trifluoromethanesulfonate) (Yoo & Pak, 2015).

Therefore, in this study, TiO_2 was synthesised via the sol-gel method with IL (1-Butyl-3-methylimidazolium acetate, Bmim[Ac]) to produce photocatalysts with high surface area. TiO_2 is then added to Ag via the wet-impregnation method to enhance its photocatalytic performance and introduce antibacterial properties to the photocatalyst. The photocatalyst was mixed with CA to further increase its adsorption capacity for the removal of dyes. Numerous types of dyes can be found in wastewater, and because their chemical structures differ, it is challenging to apply a single method to degrade them, especially when they are present in a mixture (Garba et al., 2020). To be in line with the idea, the performance of $\text{TiO}_2/\text{Ag}/\text{CA}$ photocatalyst on mixed dyes namely Rhodamine B (RhB), Methylene Blue (MB) and Methyl Orange (MO) was also investigated. The morphology, surface chemical properties and structural composition of $\text{TiO}_2/\text{Ag}/\text{CA}$ were determined and its photocatalytic activity under different operating conditions (photocatalyst dosage, initial dye concentration, and initial pH) was investigated. Antibacterial properties of $\text{TiO}_2/\text{Ag}/\text{CA}$ photocatalyst against gram-negative (*S. aureus*) and gram-positive (*E. coli*) bacteria, and strains were also investigated via disc diffusion method.

1.2 Problem Statement

There are many studies available on the fabrication of TiO_2 -based photocatalysts primarily aiming to produce photocatalysts with high photocatalytic performance. One of the commonly applied ways is via the addition of support materials to the photocatalyst. While previous studies are exclusively focused on the application of support materials in TiO_2/Ag to improve its surface area and antibacterial properties (Jatoi et al., 2019; Ashraf et al., 2020), there is very limited knowledge available on the effects of CA concentration in the photodegradation of dyes. A recent study has shown that 2 wt% CA in TiO_2/Ag contributed to the high adsorption of MB and significantly aided the removal of MB

(Kanakaraju et al., 2022). This showed that CA could enhance the efficiency of TiO₂/Ag in the degradation of dyes. However, to the best of our knowledge, there are no studies on TiO₂/Ag/CA which investigate the effects of the photocatalyst on mixed dyes. From the environmental perspective, studies on mixed dyes would be more relevant as pollutants occur in mixtures rather than as an individual component. Therefore, this signifies the importance of investigating the performance of the TiO₂/Ag/CA photocatalyst in the mixed dyes treatment system.

Besides that, the surface area of TiO₂ is equally important in the degradation of pollutants. The ability of ILs to synthesise morphology-controlled TiO₂-based photocatalysts has been elucidated in numerous studies (Łuczak et al., 2016; Kaur & Singh, 2017; Van Dao et al., 2018; Kuhn et al., 2019). There are studies available on TiO₂ synthesised with various types of IL as a solvent template via the sol-gel method, for instance, 1-Butyl-3-methylimidazolium hexafluorophosphate, (BmimPF₆) (Yan et al., 2018) and choline chloride–zinc chloride IL (Preethi et al., 2017). Imidazolium-based ILs are favourable for several reasons such as its wide range of air, water and electrochemical stability (Dai et al., 2014).

Previous works have shown that imidazolium ILs may oxidatively add to coordinatively unsaturated low-valent metal centres, which implies that it might stabilise metal nanoparticles not only electrostatically but also by coordination involving the cations (Wender et al., 2010). The low vapour pressure of imidazolium-based IL prevents the reduction of the photocatalyst's surface area (Dai et al., 2014). Another advantage of utilising imidazolium-based ILs is that the reaction medium can be removed easily by washing it with water and evaporating the solvent under a vacuum and reusing it for

subsequent reactions (Shirini et al., 2012). In addition, imidazolium-based ionic liquid is also less toxic and less volatile as compared to pyridine-based ionic liquid (Majumdar et al., 2014). Since the application of imidazolium-based IL such as 1-Butyl-3-methylimidazolium acetate, Bmim[Ac] has not been established, it is crucial to investigate the effect of Bmim[Ac] as a solvent template to compare its ability with other existing ILs established in the literature.

1.3 Objectives

The primary aim of this study was to investigate the photocatalytic performance of TiO₂/Ag/CA photocatalysts for the degradation of dyes. The following set of objectives was pursued to accomplish this aim:

- i. To synthesise TiO₂ photocatalysts via the sol-gel method with IL, 1-butyl-3-methylimidazolium acetate,
- ii. To determine the physicochemical properties of TiO₂/Ag/CA photocatalysts such as morphological, structural, crystallinity, compositional and surface chemical properties prepared via wet-impregnation method (TiO₂/Ag) and mechanical mixing (TiO₂/Ag/CA),
- iii. To investigate the photocatalytic activity of TiO₂/Ag/CA photocatalyst on dye degradation under various operating conditions (e.g. photocatalyst dosage, dye concentration and initial pH); and
- iv. To investigate the recyclability and antibacterial properties of TiO₂/Ag/CA photocatalyst

CHAPTER 2

LITERATURE REVIEW

2.1 Titanium Dioxide, TiO₂

Many organic contaminants released into water bodies are incredibly difficult to decompose or eliminate and may negatively affect aquatic systems and human health. Nanostructured semiconductors have shown great potential for wastewater remediation because of their high photocatalytic oxidation under ultraviolet (UV) radiation. Titanium dioxide, TiO₂ is recognised as a significant photocatalyst as compared to other semiconductors used in environmental remediation because of its excellent photocatalytic activity under UV irradiation, making it an efficient photocatalyst as its oxidation state can change without experiencing decomposition (Gopinath et al., 2020). The widespread application of TiO₂ in pollutant removal can be attributed to its inexpensiveness and properties such as high refractive index, chemical and photostability (Ferreira et al., 2021).

2.1.1 Crystalline Structure of TiO₂ Photocatalyst

TiO₂ is greatly utilised in various areas such as self-cleaning technology, cosmetics and water purification (Leong & Oh, 2018; Basavarajappa et al., 2020; Nazhirah, Ghoshal, Arifin, & Hamzah, 2021). The main reasons for its wide range of applications include having high oxidising power and chemical stability, non-toxic nature and inexpensive (Gopinath et al., 2020).

TiO₂ is also known as an n-type semiconductor and it exists in three crystalline phases, namely anatase, rutile, and brookite (Al-Mamun, Kader, Islam, & Khan, 2019). All three crystal phases have a TiO₆ octahedra structure whereby the titanium (Ti⁴⁺) atoms are

coordinated with six oxygen (O_2^-) atoms (Scarpelli et al., 2018). Anatase and rutile TiO_2 have a tetragonal geometry while brookite has an orthorhombic geometry (Scarpelli et al., 2018). Figure 2.1 shows the crystalline structures of TiO_2 while Table 2.1 summarises the properties of the crystalline phase of TiO_2 .

The anatase phase of TiO_2 is stable at low temperatures whereas the rutile phase of TiO_2 is stable at high temperatures. The brookite phase of TiO_2 is rare, unstable, uncommon, and ineffective option for photocatalytic applications (Al-Mamun et al., 2019). As a result, the application of brookite is greatly limited in comparison to the anatase and rutile phases of TiO_2 . Anatase and rutile have been extensively used in various applications because they are more stable as compared to brookite (Scarpelli et al., 2018). The photocatalytic efficiency of TiO_2 is influenced by its crystalline arrangement, with anatase exhibiting the highest activity due to its effective energy separation between the valence and conduction bands upon UV exposure (Ray, Lalman, & Biswas, 2009; Saravanan, Pakshirajan, & Saha, 2009). Additionally, anatase's chemical properties, like heightened electron mobility, low dielectric constant, and low density, further establish it as the favored phase of TiO_2 in the realm of photocatalysis (Gupta & Tripathi, 2011).

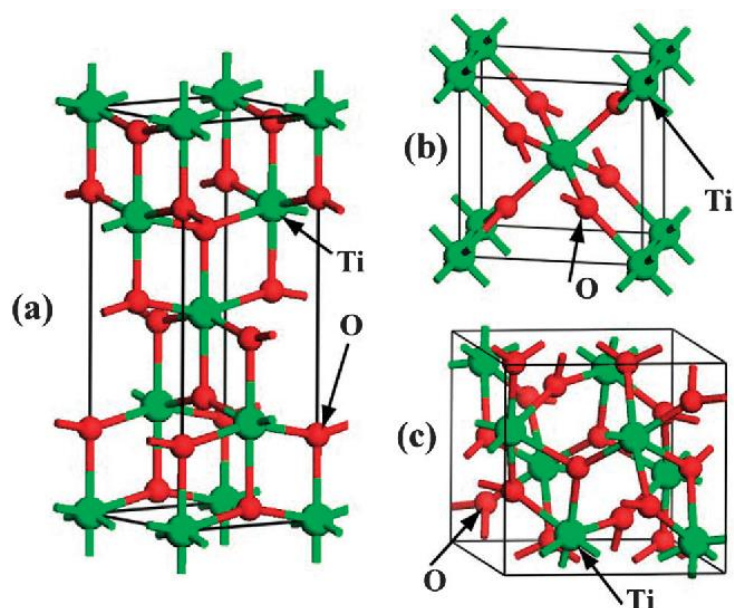


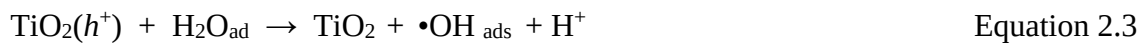
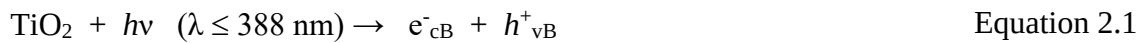
Figure 2.1: The schematic conventional cells for (a) Anatase, (b) Rutile (c) and Brookite TiO_2 (Source: (Zhang, Zhou, Liu, & Yu, 2014))

Table 2.1: Properties of different phases of TiO_2

Properties	Phases of TiO_2			Reference
	Anatase	Rutile	Brookite	
Crystal Structure	Tetragonal	tetragonal	orthorhombic	Scarpelli et al. (2018)
Atoms per unit cells	6	6	8	Gupta & Tripathi (2011)
Density, g/cm^3	3.79	4.13	3.99	Scarpelli et al. (2018)
Band gap, eV	3.2	3.0	3.4	Etacheri et al. (2015)
Refractive index	2.52	2.72	2.63	Khawam & Flanagan (2006)

2.1.2 Mechanism of TiO₂ Photocatalysis

Various relevant literature has established the mechanistic pathways of TiO₂ photocatalysis (Chakhtouna et al., 2019; Sharma et al., 2019). Typically, five main reactions occur on the surface of TiO₂ such as photoexcitation, diffusion, trapping, recombination and oxidation. As TiO₂ is exposed to UV irradiation (wavelength ≤ 388 nm), it excites the electrons across the band gap (3.2 eV anatase or 3.0 eV rutile crystalline phases) into the conduction band (CB), which leads to the formation of electron holes in the valence band (VB) (Equation 2.1). There are several oxidation reactions that occur as shown in Equation 2.2 and Equation 2.3. First, electrons transferred from adsorbed substrate RX (Equation 2.2), and second, electrons transferred from adsorbed solvent molecules (H₂O and HO[•]) (Equation 2.3). The second reaction plays a significantly larger role in the oxidation processes as a high concentration of H₂O and HO[•] adsorbed on the TiO₂'s surface. Primary oxidising species that contribute to the photooxidation of organic molecules into water and CO₂ are the •OH radicals (Equation 2.4). TiO₂ photocatalysis's mechanism is shown in Figure 2.2.



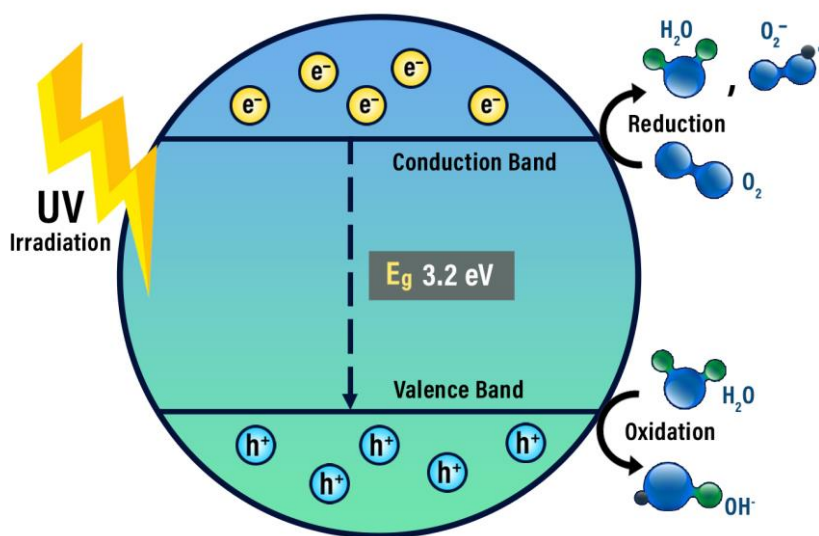


Figure 2.2: Schematic mechanism of TiO₂ photocatalysis
(Source: Kanakaraju et al. (2022))

2.1.3 Limitations of TiO₂ Photocatalyst

There are several drawbacks of TiO₂, which include: (1) a wide band gap (3.0–3.2 eV) that can only be activated by UV light with a wavelength lower than 388 nm (Daghrir et al., 2013), (2) performs poorly under irradiation of solar light irradiation because only a very small percentage of solar light can be absorbed (less than 5% of solar energy is emitted as UV irradiation), (3) fast electron and holes recombination, (4) retardation of charge carrier transfer, and (5) expensive recycling cost (Wu et al., 2014; Ge et al., 2015). These issues have been addressed via surface modifications, which included metals and non-metals doping, and coupling of TiO₂ with other semiconductors such as ZnO, SnO₂, CeO₂, and ZnO (Vinu & Madras, 2013; Hernández-Ramírez & Medina-Ramírez, 2016).

2.2 Surface Modification of TiO₂ via Doping

Surface modifications of TiO₂ such as doping have been greatly discussed in numerous literature. Doping is introducing impurities into a conventional photocatalyst in

order to alter the structure of the photocatalyst and its properties such as electrical and optical properties (Panigrahi & Devi, 2019). Doping affects the surface site distribution for nucleation and coarsening rate, then results in the modification of structural metastability and activation energy of fine crystalline materials (Schneider et al., 2014). Doping is also known to cause bathochromatic shifts such as reducing band gap or induction of intra-band gap, which contributes to higher absorption under visible light irradiation (Al-Mamun et al., 2019).

2.2.1 Doping of TiO₂ with Non-Metal

Non-metal elements are introduced into the crystal lattice of the catalyst via doping using non-metallic elements, these elements react with the oxygen atom and alter the electron cloud density of the oxygen atom (Qian et al., 2014; Liu et al., 2017; Nadeem & Idriss, 2018). This affects the oxygen's atomic energy level splitting and causes an intermediate band gap to arise in the catalyst's band gap (Wang et al., 2021). The catalyst's band gap is reduced by the intermediate band gap and extends the range of light wavelengths for absorption (Alansi et al., 2018; Fadillah et al., 2019; Saleh & Fadillah, 2019). Nitrogen (N), carbon (C), sulphur (S), chlorine (Cl), and fluorine are commonly used as non-metallic dopants to enhance the photocatalytic efficiencies of TiO₂ photocatalysts (Al-Mamun et al., 2019).

Among these non-metals, N is considered as the most promising dopant due to its stability and atom size, which is similar to the stability and atom size of oxygen in TiO₂ (Fang et al., 2007; Fujishima et al., 2008; Pelaez et al., 2012; Ananpattarachai et al., 2016). N dopant acts as a centre in trapping photogenerated electrons and retards the recombination rates of electrons and holes (Ansari et al., 2016). The addition of N in the TiO₂ lattice causes

the formation of a mid-gap energy flat near the valence band, which lowers the band gap of TiO_2 to 2.5 eV and thus enables light absorption of TiO_2 to visible light region (Basavarajappa et al., 2020). Doping of N with TiO_2 catalyst demonstrated strong absorption in the visible range and it is attributed to a reduced band gap from 3.23 eV to 2.89 eV (Selvaraj et al., 2013).

Heterogeneous photocatalysis has also extensively utilised dopants such as C (Ji et al., 2017; Payormhorm & Idem, 2020). TiO_2 -doped with C exhibited reduced recombination of charge with efficient charge transfer and greater storage capacity of electrons (Ji et al., 2017). Doping of C into TiO_2 lattice creates Ti-C or C-O-Ti bond by substituting the lattice of O or Ti atoms, forming a hybrid orbital above the valence band of TiO_2 which extends the absorption of photocatalyst in the visible region (Hua et al., 2020). C-doped TiO_2 nanorods demonstrated 90.2% of MB degradation within 10 min while undoped P25 TiO_2 showed 6.4% of MB degradation after 40 min of exposure to visible light (Shao et al., 2017).

Doping of TiO_2 with S has shown enhanced photocatalytic efficiency of the photocatalyst due to the excellent thermal stability of S dopant. The band gap of TiO_2 is narrowed with S dopant by altering the crystal and electronic structure of TiO_2 (Basavarajappa et al., 2020). S can be obtained using thiourea or sulfate and applied as a dopant (Ohno et al., 2004; Sano et al., 2012), S^{6+} act as a cation in substituting Ti^{4+} and showed favourable chemical reactions due to the differences in the ionic radius, which creates new states into the conduction band of TiO_2 from S-3s states just exceeding the valence states of O-2p (Ohno et al., 2004). In cationic substituted S-doped TiO_2 , S captures electrons, improves the electrical conductivity of TiO_2 and enhances electron-hole pairs

transfer, which increases the efficiency of photocatalyst under visible light exposure (Bakar & Ribeiro, 2016; Basavarajappa et al., 2020).

Although these studies clearly demonstrated the favourable impacts of non-metals on TiO_2 , there are still drawbacks to the application of non-metals as dopants in the fabrication of TiO_2 -based photocatalysts. For instance, aggregation and crystallisation of N-doped TiO_2 photocatalyst occurred upon annealing at 500 °C, which forms a catalyst with a larger particle size and reduces the number of active sites (Anas et al., 2016). In addition, oxygen vacancies are formed when non-metals are doped into the lattice of TiO_2 , which greatly increases the recombination centres of photo-induced electron-hole pairs (Dong et al., 2011).

2.2.2 Doping of TiO_2 with Metal

TiO_2 is commonly doped with three different types of metals, which are transition metal, noble metal and rare earth metal. Transition metals doped into TiO_2 photocatalyst produce a more efficient photocatalyst with a lower rate of photogenerated electron-hole pair and reduced band gap. The interaction of Ti (3d) with transition metal at d level produces a redshift on the band edge of TiO_2 , which changes the band gap efficiency and resulted overlapping of the conduction band. Transition metal-doped TiO_2 photocatalyst reduces band hole energy by creating a new conductive level between the valence band and conduction band (Aguilar et al., 2013).

Transition metal dopants like Fe, Mn, Cu, Zn, Ru, Co, V, Cr and W into TiO_2 affect the photocatalytic performance of as doping significantly influences TiO_2 's properties such as the energy of its band gap, thermal properties, particle size and surface area (Mogal et al., 2013; Saleem et al., 2018). Sol-gel synthesis of various dopant concentrations of Cr, V, and

Co with TiO₂ decreased the crystallinity of TiO₂ and resulted in a phase change from anatase to rutile phase (Koh et al., 2014). The physicochemical properties of photocatalysts are also directly affected by the concentration of transition metal dopants in the doping process (Al-Mamun et al., 2019).

Doping of noble metals like Pt, Pd, Ag and Au into TiO₂ also produces highly efficient photocatalysts upon irradiation of UV and visible light. When Ag is applied as a dopant, the SPR effect of Ag nanoparticles extends the light absorption of TiO₂ towards the visible light region (Liao et al., 2020). Previous work has shown 2.7 wt% (weight percentage) of Ag in Ag/TiO₂ showed high degradation (98.5%) of Orange II Dye under UV irradiation after 2 h while TiO₂ without Ag dopant showed 87.5% of dye degradation within 4 h (Petica et al., 2019). There are 17 elements under rare earth metals, and these elements include yttrium (Y), scandium (Sc), and 15 lanthanoid elements, which have shown promising results upon doping with TiO₂ photocatalyst (Al-Mamun et al., 2019). Doping of earth metals into TiO₂ photocatalyst is possible due to the presence of incomplete 4f and empty 5d orbitals in these rare earth metals (Teh & Mohamed, 2011). Reactive Blue 21 and Acid Red 114, two widely used textile dyes, degraded almost completely when treated with rare earth metals Pr³⁺ and Ce⁴⁺ doped TiO₂ (Goyal, 2013).

Despite the fact that metals significantly enhance TiO₂'s photocatalytic efficacy, there are still some drawbacks to their application as dopants. For instance, transition metal dopant in anatase TiO₂ not only causes the photocatalyst to be thermally unstable (Al-Mamun et al., 2019), but also contributes to reduced light capability and quantum efficiency of the photocatalyst (Wang et al., 2007). Meanwhile, TiO₂ doped with rare earth metals creates -O-Ti chemical bonds on the surface of TiO₂ and inhibits the growth of

nanocrystalline particles (Tong et al., 2007; Shi et al., 2009). Although the combination of TiO₂ with rare earth metals as photocatalysts has demonstrated promising results in the removal of organic persistent compounds, it is still very pricey to utilise rare earth metals in the doping process (Al-Mamun et al., 2019).

2.3 Silver, Ag as Dopant

Metals and non-metals dopants, as discussed previously, have advantages and limitations that make them appropriate dopants for TiO₂. Silver, Ag is known for its high stability, high thermal and electrical conductivity, inexpensive and non-toxic in comparison to other known metals. (Kakhki et al., 2017). Additionally, Ag is also preferred for general applications in the industry as compared to expensive noble metals like Pt, Pd, Rh, and Au (Guan et al., 2013). Past studies have demonstrated doping of Ag contributed to high photocatalytic efficiency since TiO₂/Ag photocatalyst possessed a large surface area, high stability and conductivity (Rostami-Vartooni et al., 2016). Other properties of Ag that make it a desirable dopant include its low resistance towards contact or high conductivity of electrons, which contributes to its role as an electron moderator in the Z-scheme photocatalyst structure (Nesfchi et al., 2021). The dual roles of Ag nanoparticles such as acting as an electron mediator and a photosensitizer, allow low-energy photons to generate stable electron-hole pairs (Adenuga et al., 2020).

One of the established methods for reducing the recombination of electron-hole pair recombination and extending the adsorption of TiO₂ towards visible light is adding Ag into the lattice of TiO₂ (Harikishore et al., 2014; Noreen et al., 2019). Ag enhances photocatalytic efficiency through two different mechanisms. First, it functions by trapping, capturing and transferring electrons from the TiO₂ conduction band to oxygen, where they are then

converted into superoxide radicals. Hydroxyl radicals are created when water molecules react with photogenerated holes in the TiO_2 's remaining valence band. These radicals are important for the photocatalytic oxidation of contaminants (Din et al., 2018). Second, it causes an SPR effect that simultaneously improves TiO_2 photocatalytic activity and extends light absorption to the visible light domain (Khan et al., 2015; Furube & Hashimoto, 2017).

Literature has established that the efficiency of TiO_2 is enhanced upon Ag doping through three major events, (1) TiO_2 's morphology is modified for the high affinity of dissolved oxygen (Suri et al., 2012; Murcia et al., 2017), (2) reduce charge carriers recombination (Cao et al., 2019; Ribao et al., 2019) and (3) plasmonic effect-electron injection (Dong et al., 2019; Xu et al., 2019). As photocatalytic performance is greatly influenced by the presence of reactive oxygen species (ROS) formed by photo-excited electrons of TiO_2 and adsorbed O_2 , higher oxygen species will be produced by increasing O_2 concentration on the surface of TiO_2 . Ag-doped TiO_2 improve its affinity for dissolved O_2 by providing it with a higher affinity of O_2 and increases its surface for O_2 adsorption. The presence of Ag in TiO_2 increases the ability of the photocatalyst to attract O_2 from the aqueous solution to the surface of TiO_2 (Torbina et al., 2018). When Ag's concentration in the photocatalyst increases from 0.0 wt% to 3.0 wt%, the adsorption of O_2 on Ag-doped TiO_2 photocatalyst increases as well (Xiong et al., 2011). Higher O_2 concentration on the photocatalyst's surface allows more O_2 and electrons to react, thus producing higher $\bullet\text{O}_2^-$ species to improve the separation of charge carriers (He et al., 2020).

The doping of Ag on TiO_2 forms the Schottky barrier at the interface of TiO_2/Ag interface (Liu et al., 2017). Ag acts as a centre in electron transfer whereby its Fermi energy level affects the separation of charge carriers at the interface of TiO_2 and Ag dopant (Shen

et al., 2010; Takai & Kamat, 2011). The Fermi level of Ag can be found at an energy level below TiO₂'s conduction band (Figure 2.2), and the Schottky barrier formed on the TiO₂/Ag junction caused the downward bending of the TiO₂ energy bands (He et al., 2021).

The formation of the Schottky barrier at heterojunction contributed to an excess of positively charged TiO₂ and negatively charged Ag. However, charge carrier separation is maintained because of the electron depletion layer between the opposing charges. Since Ag particles and TiO₂ have different Fermi levels, noble metal particles became negatively charged (He et al., 2021). The Fermi level gap encourages the movement of electrons from materials with a higher Fermi level to a lower Fermi level (Devi & Kavitha, 2016). Electron transmission can be enhanced, and charge carrier recombination can be retarded as the photo-generated electrons are trapped in Ag particles (He et al., 2021).

2.3.1 Synthesis of Ag-Doped TiO₂

There are several methods that can be applied to introduce Ag into the TiO₂ lattice. For instance, the sol-gel method (Sharma et al., 2018), hydrothermal method (Avciata et al., 2016; Hamed et al., 2020), solvothermal method (Yu et al., 2018; Zhou et al., 2019; Wei et al., 2020), photoreduction method (Díaz-Urbe et al., 2018; Zhang et al., 2020), electrochemical method (Petica et al., 2019), electrospinning method (Guan et al., 2013; Nalbandian et al., 2015), and wet impregnation method (Freire et al., 2020). Table 2.2 summarises a few of the frequently applied synthesis methods employed for the preparation of TiO₂/Ag single-doped and co-doped materials.

These techniques are frequently used in TiO₂/Ag fabrication due to several advantages. One of the frequently applied methods is sol-gel. Sol-gel is known to be an affordable and simple method which not only controls the purity and homogeneity of the

synthesised product but also controls the particle growth and size of the catalyst (Chakhtouna et al., 2021). It was found that doping a higher concentration of Ag into TiO₂ via the sol-gel method produced TiO₂/Ag with greater porous structures (Halin et al., 2018). Whereas hydrothermal synthesis contributed to better shape, size and crystalline phase of nanocomposite (Saharan et al., 2014; Singh et al., 2016). Although the solvothermal method and hydrothermal method are essentially identical, these two procedures differ in the type of solvent applied. While the hydrothermal method includes water in its reaction system, the solvothermal method includes organic solvents instead. The reaction system greatly affects the structure, crystallinity, morphology and shape distribution of TiO₂/Ag (Li et al., 2016). For instance, Hamed et al. (2020) reported the synthesis of TiO₂/Ag via hydrothermal method at 150 °C produced flowerlike morphology, which contributed to higher active sites. Additionally, it has been revealed that flower-like morphology's scattering effect helps to disperse photons through the rods and provides energy to excite electrons in the conduction band (Li et al., 2015).

TiO₂/Ag nanorods heterostructures fabricated by Zhou et al. (2019) using one-pot solvothermal in-situ synthesis formed a tight bond between Ag nanorods' core and TiO₂ nanoflakes. Results showed high degradation of MO (98.2%) under visible light, which is caused by the strong plasmonic resonance of Ag nanorods (Zhou et al., 2019). Wang et al. (2016) demonstrated similar results where TiO₂/Ag nanofibers synthesised via the solvothermal method exhibited high degradation of RhB after 3 cycles of photocatalytic degradation. High photocatalytic efficiency by TiO₂/Ag was attributed to its resistance towards electron transfer and crystallinity. The synthesis route utilised N, N-dimethylformamide (DMF) as solvent where Ag⁺ in DMF solution reacted with hydroxyl groups and oxygen on TiO₂ nanofibers' surface, causing nucleation of Ag atoms through a

homogeneous nucleation process on TiO₂ active growth sites and produce Ag particles with high crystallinity (Wang et al., 2016).

Synthesis of TiO₂/Ag via the wet impregnation method is also known to produce photocatalysts with high crystallinity (Zhou et al., 2014). TiO₂/Ag synthesised with the wet impregnation method demonstrated almost 80% of phenol degradation under visible light within 2 h, which was contributed by the presence of uniform Ag clusters on mesoporous TiO₂ (Zhou et al., 2014). Another study has synthesised TiO₂/Ag with high stability through the wet-impregnation method, which enabled Ag nanoparticles to be homogeneously dispersed on the surface of TiO₂. The synthesised photocatalyst showed almost 100% degradation of 2,4-dichlorophenol under visible light, with similar photocatalytic degradation performance even after 10 cycles of treatment (Jiang et al., 2012).

Electrospinning has become a universal and direct method in preparing nanofibers with rich porosity and large specific surface area (Li et al., 2021). TiO₂/Ag synthesised via the electrospinning method produced photocatalysts with both anatase and rutile phases, and the presence of Ag provided the photocatalyst with excellent crystallinity and surface morphology (Raffi et al., 2018). Ternary TiO₂/Ag/Cu₂O synthesised by Li et al. (2021) demonstrated 99.0% of MB degradation, increased by a factor of 1.5 times than that of TiO₂/Cu₂O nanofibers (65%) and by a factor of 3.5 than that of bare TiO₂ nanofibers (28%) in 150 min under visible light. This shows that the introduction of Cu₂O and Ag enhanced the visible light degradation ability of the composite material.

Table 2.2: Common methods utilised in the synthesis of TiO₂/Ag single-doped and co-doped materials

Synthesis method	Precursors	Characteristics			Pollutant & Percentage removal (%)	Reference
		Crystal structure, crystallite size (nm)	Morphology (SEM/FESEM)	XPS, TEM, EDX		
Single doping						
Hydrothermal	(Ti(Obu) ₄ , AgNO ₃)	Rutile, 86.00	Rods bundle and flower-like shape	Presence of Ti ³⁺ & Ti ²⁺ > Ti ⁴⁺ , rod size from 7.00 nm-10.00 nm)	MB, 75.00% within 5 h under Xenon lamp	Hamed et al. (2020)
Photoreduction	Ti(OC ₄ H ₉) ₄ , AgNO ₃	Anatase, N/A	Irregular block structure	Presence of Ag ⁰ & Ti ⁴⁺	Tetrabromobisphenol A, 100.00% in 10 min under UV-vis light, 20.00-27.00% in 2 h under visible light	Zhang et al. (2020)
Electrochemical	TiO ₂ nanopowder , Ag plates	Anatase, 15.60	Slight agglomeration of spherical-shaped particles	Presence of Ag ⁰ & Ti ⁴⁺	Orange II dye, 98.50% after 2 h under UV irradiation	Petica et al. (2019)

Table 2.2 continued

Electrospinning	$(\text{CH}_3\text{CH}_2\text{C}(\text{H}_2\text{O})_4\text{Ti}, \text{AgNO}_3$	Anatase, 110.00 – 134.00	Ag particles distributed uniformly on the surface of TiO_2 nanofiber	Presence of Ti, O, Ag and C	Phenol, 92.91 % under UV light	Norouzi et al. (2020)
Solvothermal	$\text{TiC}_{16}\text{H}_{40}\text{O}_4, \text{AgNO}_3$	Anatase, 200.00	TiO_2 nanoflakes, Ag nanorods	Presence Ag^0 & Ti^{4+} , 0.20 nm, presence of Ag, Ti & O	MO, 98.20% after 50 min under visible light irradiation	Zhou et al. (2019)
Sol gel	$\text{Ti}(\text{OCH}(\text{C}_2\text{H}_5)_2)_4, \text{AgC}_2\text{H}_3\text{O}_2$	Anatase, ~9.00	Dense agglomerates of spherical nanoparticles	Presence of Ag^0 , Ti^{3+} & Ti^{4+} , 4.00 nm - 6.00 nm, N/A	MO, 98.90% within 60 min under UV, and 99.30% within 80 min under solar irradiation	Saravanan et al. (2018)
Co-doping						
Hydrothermal	$\text{Ti}(\text{C}_4\text{H}_9\text{O})_4, \text{CH}_3\text{COOH}, \text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Anatase, 5.32-15.49	Spherical shaped particles	N/A, N/A, 2.16 wt% of Ag, 0.21 wt% of Fe, 51.36 wt% of Ti, 46.27 wt% O	4-Chlorophenol, 97.12% after 165 min under UV irradiation	Shojaie et al. (2017)
Photoreduction	$\text{TiC}_{16}\text{H}_{40}\text{O}_4, \text{AgNO}_3, (\text{C}_6\text{H}_{12}\text{O}_6)$	Mixture of anatase & brookite, 5.83	Presence of uniform black spots	Presence of Ag^0	MB, 97.82% in 180 min under visible light	Wang et al. (2021)

Table 2.2 continued

Electrospinning	Ti(OC ₄ H ₉) ₄ , AgNO ₃ , Cu(CH ₃ CO O) ₄ ·H ₂ O	Anatase, 200.00	Nanofibers becomes very rough, and with many particles grown on the surface.	Presence Ag ⁰ & Ti ⁴⁺ , 6.21 atomic% of Ti, 33.81 atomic% of O, 1.06 atomic % of Ag, 15.04 atomic% of Cu and 43.88% atomic of C	MB, 99.00% in 90 min under Visible light	Li et al. (2021)
Solvothermal	Ti(OCH(C H ₃) ₂) ₄ , AgNO ₃ , Er ₂ O ₃	Anatase, 20.00 – 300.00	Rough surfaced spheres	Presence Ag ⁰ , Ti ⁴⁺ , Ti ³⁺	RhB, 98.00% in 30 min under Visible light	Prakash et al. (2015)
Sol-gel	TiC ₁₂ H ₂₈ O ₄ , AgNO ₃ , CH ₄ N ₂ S	Anatase, 11.90	Primary NPs relatively uniform in size and approximately spherical and many pores were formed with their agglomeration	N/A, N/A, 36.35 atomic% of Ti, 57.67 atomic% of O, 4.44 atomic % of Ag and 2.53 atomic% of S	MB, ~100.00% degradation under visible light	Kunamared dy et al. (2018)

2.4 Modifications of Ag-Doped TiO₂ with Green Materials

TiO₂/Ag application is limited due to several reasons, such as recovery issues after treatment, Ag leached and released out of the system, reduced stability and high aggregation (Tóth et al., 2020). Secondary contamination may result due to the unsuccessful recovery of TiO₂ nanoparticles from the photocatalytic system. Irregular pore size reduced surface area, and the formation of colloidal suspension with water are linked to the challenges in recovering the photocatalyst after photocatalysis (Dong et al., 2015; Wang et al., 2015). In order to solve the issues above, polymers, activated carbon, silica, glass and zeolites have all been added to the photocatalyst as supporting materials (Dong et al., 2015; Kanakaraju et al., 2015; Bet-Moushoul et al., 2016).

Green materials, however, might be a superior choice because they can replace petroleum-based materials and have an abundant and sustainable supply in nature (Ma et al., 2011; Soheilmoghaddam et al., 2013). Sustainable methods can be used to produce TiO₂/Ag-based nanomaterials using green materials. The phrase “green chemistry” was first used in 1991 with the ultimate goal of reducing the negative impact on the environment and individuals, by eliminating or limiting the application of dangerous and harmful substances or chemicals (Kharissova et al., 2019). Green chemistry has several advantages, including lowering or avoiding the production of needless wastes, lower-risk chemical reactions, forming products that can be degraded and reaction products that don't linger in the environment (Kharissova et al., 2019).

Natural materials are excellent options for TiO₂'s support due to its low polar surface, high surface area and adsorption capacity for non-polar organic pollutants (Borges et al., 2016). Numerous green materials elements were explored as support materials to increase the mechanical strength, stability and reusability of TiO₂-based photocatalysts, including

biomass, biopolymers, plants, animals, and microbes. The properties of TiO_2/Ag photocatalysts have also been improved using green materials, like IL, plant-based materials, and ceramics. There are a few frequently used support materials, which include plant-based substances such as cellulose, its derivatives (such as cellulose acetate), alginate and chitosan. Chitosan acts as a stabilizer and reductant during the formation of Ag nanoparticles on the surface of TiO_2 (Grčić et al., 2020).

TiO_2/Ag photocatalysts have also been added with ceramic-based substances which include clay, kaolin, and bentonite. Natural clay minerals, like silica, alumina or ferrous materials, were greatly utilised in water purification applications as efficient absorbents and oxidants (Morotti et al., 2011; König et al., 2012). Several forms of naturally occurring clays, including bentonite, kaolinite, and montmorillonite (MT), have been investigated as cheaper alternatives, but can still be efficient adsorbents for eliminating textile dyes from wastewater (Wu et al., 2010; Khan et al., 2012).

Clay materials contribute to the high porosity, high surface area and increased active sites for TiO_2 photocatalyst (Yang et al., 2015; Pérez-Carvajal et al., 2016). This keeps TiO_2 from aggregating, increasing its reusability since it can be recovered after the photocatalytic treatment (Mishra et al., 2018). The interlayer cations of MT play a crucial part in its behaviour, it allows other cationic molecules to exchange easily through electrostatic contact or ion interchange (Abdel-Karim et al., 2021). Hence, the degradation of cationic pollutants such as trace metals in water and wastewater have been achieved using MT. Previous studies showed that minor modifications of MT contribute to a higher degradation of non-ionic and anionic pollutants (Liu et al., 2020; Yilmaz et al., 2020). The intercalation of TiO_2/Ag into or on the bentonite interlayers exhibited a photocatalyst with higher surface area and porosity, which improved its biological and electrochemical properties (Krishnan &

Mahalingam, 2017). Nevertheless, research on carbon, polymer, and ceramic-based nanocomposites is still in its infancy and needs additional investigations to be fully understood. (Yaqoob et al., 2018).

Apart from supports consisting of plant and ceramic materials, ILs, which are regarded as “green solvents” were used as an option instead of organic solvents due to their exceptional properties (Ren et al., 2020). According to the literature, green chemistry targets on minimising the amount of harmful organic solvents and/or reagents used in the analytical process, as well as reducing energy and waste production (Olives et al., 2017; Pacheco-Fernández & Pino, 2019). Excellent characteristics of ILs include a good solvent for a wide range of inorganic and organic materials, highly polar as a result of poorly coordinating ions, being immiscible with various organic solvents, and can contribute to a nonaqueous, polar alternative for two-phase systems (Vekariya, 2017).

ILs consist of organic cations with strongly induced anions and the synergistic effect of these ions contributes to their exceptional properties (Bielicka-Giełdoń et al., 2019). Additionally, ILs are widely applied as solvents, additives and templates due to high thermal and chemical stability as well as high polarity (Wei, et al., 2018). ILs have outstanding electrochemical characteristics, such as miscible with organic molecules, non-volatile, thermo-oxidative stable, do not react with air or water and have strong ionic conductivity (Singh et al., 2018). The polar and dispersive interactions of ILs can change depending on changes to its structure and properties (Gindri et al., 2014). These interactions between IL and TiO_2 affect the surface structure of TiO_2 and modify its photoactivity (Paszkievicz-Gawron et al., 2020). The inclusion of ILs in the TiO_2/Ag synthesis contributes to higher photocatalyst surface area and increases the photocatalytic efficiency towards contaminants removal (Dai et al., 2019), and also increases its stability and recyclability (Lin & Li, 2021).

2.4.1 Addition of Plant-Based Supports

A lot of interest has been given to cellulose, a linear polysaccharide with a wide range of chemical derivations and features like biodegradability and high mechanical strength with chemical stability (Zafar et al., 2016). Among the derivatives, CA is a biopolymer that has great applications in the biomedical industry, including tissue engineering and antibacterial applications. It has excellent biocompatibility, biodegradability, high mechanical strength, hydrophilic and excellent moisture management properties (Ashraf et al., 2020). Past studies have demonstrated that combinations of inert supports like cellulose with TiO_2 effectively maintain the stability of the TiO_2 photocatalyst and facilitate its recovery (Marinho et al., 2017).

A recent study by Yang and Luo (2021) studied the application of carbon beads made from cellulose as a charge carrier for TiO_2/Ag for ceftriaxone sodium removal. The hollow network structure of carbon beads synthesised from cellulose ensured uniform dispersion of TiO_2/Ag particles and provided greater active sites. Upon exposure to simulated sunlight, the $\text{TiO}_2/\text{Ag}/\text{C}$ beads demonstrated a highly stable photocatalyst with recyclability for up to five cycles for the removal of ceftriaxone sodium. After 270 min, $\text{TiO}_2/\text{Ag}/\text{C}$ displayed a marked degradation efficiency of 91.92% than pure TiO_2 (54.56%) and TiO_2/C (62.7%) (J. Yang & Luo, 2021).

Despite limited research on TiO_2/Ag modification with cellulose acetate as a support for the removal of contaminants, research on $\text{TiO}_2/\text{cellulose}$ or $\text{TiO}_2/\text{cellulose acetate}$ alone showed promising results. Recent research demonstrated that $\text{TiO}_2/\text{microcrystalline cellulose}$ under visible light irradiation removed over 90% of MB upon 4 h of exposure time (Virkutyte et al., 2012). Gebru and Das reported the first electrospun of $\text{TiO}_2/\text{cellulose acetate}$ composite with a smooth morphological structure, which possessed high porosity

and surface area for the removal of Pb (II) and Cu (II) ions in wastewater. The best Pb (II) (99.7%) and Cu (II) ion removal rates (98.9%) were achieved via TiO₂/cellulose acetate with the largest specific surface area (48.47 m²/g) (Gebbru & Das, 2017). A uniform network is produced when TiO₂ is added to the adsorbent matrix. The presence of TiO₂ also produced voids within the matrix by separating the cellulose acetate chains, improving the porosity of the adsorbent.

2.4.2 Addition of Ionic Liquids, IL

The presence of IL in photocatalyst preparation alters its morphology and structure via amphiphilicity, steric hindrance, electrostatic action and viscosity (Paszkievicz et al., 2016; Bender et al., 2018; Huang et al., 2020). Past studies have investigated the effect of room temperature IL on stabilizing the size of metal particle growth via one-pot synthesis of TiO₂/Ag powders (Zhang & Chen, 2009). According to the study, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF₆) helped to control the size of Ag and enable well dispersion of Ag on TiO₂ surface, which results in its excellent bactericidal properties (Zhang & Chen, 2009). From there onwards, numerous research has been carried out and supported ILs' ability to regulate the characteristics of TiO₂-based photocatalysts (Kaur & Singh, 2017; Van Dao et al., 2018; Kuhn et al., 2019).

Various ILs such as 1-Methyl-3-octyl-imidazolium-hexafluorophosphate, [Omim][PF₆], 1-Butyl-3-methylimidazolium trifluoromethanesulfonate, [Bmim][CF₃SO₃], 1-Methyl-3-octyl-imidazolium-tetrafluoroborate [Omim][BF₄], 1-Butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF₄], 1-Hexyl-3-methyl-imidazolium-hexafluorophosphate, [Hmim][PF₆], 1-Hexyl-3-methyl-imidazolium-tetrafluoroborate, [Hmim][BF₄], 1-Ethyl-3-methylimidazolium tetrafluoroborate, [Emim][BF₄], 1-Butyl-3-methylimidazolium hexafluorophosphate, [Bmim][PF₆] were used in the synthesis of

TiO₂/Ag (Behnajady & Eskandarloo, 2013). When TiO₂/Ag was synthesised with BCF₃-IL, TiO₂-IL/Ag samples reported a surface area of 147 m²/g, which was 3 times higher than TiO₂/Ag samples. Additionally, TiO₂/Ag with BCF₃-IL has a flower-like structure which with the highest electrocatalytic performance in comparison to TiO₂/Ag with BPF₆-IL, where rough aggregation of spherical particles was observed (Yoo & Pak, 2015).

According to Lin et al. (2021), TiO₂/Ag prepared via (BMIM)Cl contributed to the maximum removal of RhB (72.97%), whereas TiO₂, TiO₂/(BMIM)Cl, TiO₂/Ag⁺ showed only 2.71%, 41.11%, and 49.11% of removal, respectively. Ag/TiO₂(BMIM)Cl demonstrated improved efficiency due to the presence of AgCl, a photosensitive material (Daupor & Wongnawa, 2014). It was noted that the inclusion of (BMIM)Cl helped in increasing the stability and reusability of photocatalysts (Lin & Li, 2021). The inclusion of 1-butyl-3-methylimidazole group as ligands is credited with improving the stability of the photocatalyst, which is further substantiated by its high absolute value of Zeta potential (18.57 mV) in comparison to TiO₂ (−11.41 mV) and TiO₂/Ag⁺ (−6.60 mV) (Lin & Li, 2021).

Literature has the effectiveness of ILs at mediating the synthesis of certain structures, such as structures with high crystallinity and high stability, mesoporous structures and particles with homogenous size distribution. (Zhang et al., 2020). While ILs are thought of as "green" compounds, some ILs can be quite dangerous. (Bera & Belhaj, 2016). There have been some problems in utilising ILs. For example, ILs are toxic and nonbiodegradable according to life cycle assessments (Zhang et al., 2020). Preparation of ILs also requires chemicals and solvents, which can cause detrimental effects towards the environment and human beings (Singh & Savoy, 2020). Therefore, these factors should be considered when using ILs in the preparation of TiO₂-based photocatalysts.

2.5 Parameters Affecting The Performance of Ag-Doped TiO₂

The photocatalytic performance of TiO₂/Ag in the photocatalytic degradation of dyes is greatly influenced by various operational parameters. These parameters include photocatalyst dosage, initial concentration of pollutant and initial pH of solution.

2.5.1 Photocatalyst Dosage

The effect of photocatalyst dosage on dye degradation is crucial, in order to determine the ideal photocatalyst dosage which can maximise the photocatalytic degradation efficiency. Finding the optimum photocatalytic dosage is important to prevent an excessive amount of catalysts that can reduce the photocatalytic degradation rate and make the process more cost-effective (Shet & Shetty K, 2016). Typically, photocatalytic efficiency increases as the photocatalyst dosage increases because of a greater concentration of active sites. As there are more active sites, more hydroxyl radicals are produced, which then contributes to higher photocatalytic performance (Binjhade et al., 2022).

Effective pollutant removal by photocatalyst increased first with increasing photocatalyst dosage and subsequently declined (Ge et al., 2021). Several factors might cause reduced photocatalytic efficiency of TiO₂. The factors include, (1) high photocatalyst dosage resulting in the excessive catalyst in the system which may reduce light scattering and the number of photons that reach the catalyst surface (Golshan et al., 2018; Li et al., 2019) and (2) high photocatalyst dosage can cause catalyst particles to aggregate and self-bind, hence reducing the concentration of active sites for degradation (Golshan et al., 2018; Babaei et al., 2021).

Previous studies have shown that photocatalytic performance is greatly affected by photocatalyst dosage in treatment systems. Shet and Shetty (2016) reported that 0.5 g/L and

1.0 g/L of Ag@TiO₂ contributed to complete phenol degradation, but the degradation efficiency decreased to around 37% when 1.5 g/L of catalyst was applied. Similarly, another study also revealed that Fe₃O₄/SiO₂/TiO₂-Ag photocatalyst contributed to 98.1% of phenol degradation with 0.1 g/L of photocatalyst dosage but it declined to 80.0% when the dosage was increased to 0.5 g/L (Ghasemy-Piranloo et al., 2019). These studies imply that photocatalytic efficiency would decline after it reaches the optimum dosage (Shet & Shetty, 2016).

2.5.2 Initial Concentration of Pollutant

The degradation performance of TiO₂ is also affected by the initial concentration of pollutants. In general, there are several factors influencing the effect of dye concentration such as (1) the concentration of dyes, (2) the presence of sites on the photocatalyst surface and (3) the surface of dye molecules (Hasanpour et al., 2021). It is known that the photocatalytic performance of TiO₂ is reduced with a higher concentration of the initial pollutant. As the concentration of pollutants increases, the concentration of reactive oxidation species to be consumed increases as well (Golshan et al., 2018). The available active sites on the photocatalyst surface become limited as the active sites compete with photons on the photocatalyst's surface, resulting in lower degradation rates (Khasawneh & Palaniandy, 2021). At high pollutant concentrations, light penetration onto the surface of the photocatalyst is also restricted, reducing the interaction between light and the catalyst to produce ROS (Golshan et al., 2018).

The photocatalytic degradation of reactive blue 255 azo dye by TiO₂/Ag reported a great decrease from 99.99% removal to 27.01% when the initial concentration of dye increased from 100 ppm to 300 ppm (Fard & Fazaeli, 2018). Another study on the photocatalytic degradation of disperse dye Violet-26 using TiO₂ showed a similar trend,

whereby the degradation efficiency decreased from 75% to 55% as the initial dye concentration increased from 50 ppm to 150 ppm (Jamil et al., 2020). These studies have shown that the degradation of dyes at higher initial concentrations became more difficult due to higher concentrations of dye molecules. At lower dye concentrations, a higher probability of reaction can be observed between dye molecules and hydroxyl radicals. However, as the concentration of dye molecules increases, the competition between hydroxyl radicals and dye molecules becomes greater. Furthermore, at high concentrations of dye, most of the active sites on the photocatalyst have been occupied by dye molecules and this limited the presence of available active sites. As a consequence, the degradation efficiency of dye molecules is reduced, especially at a high initial concentration of dyes.

2.5.3 Initial pH

The pH of the reaction solution can greatly influence the degradation of dye pollutants. The pH of an aqueous medium affects several surface properties of the photocatalyst, such as the photocatalyst molecule's ionisation, surface charges and band edge position (Hasanpour et al., 2021). These changes on the photocatalyst's surface affect its photocatalytic oxidation and adsorption properties on pollutants as well as its degradation efficiency (Kumar & Pandey, 2017). TiO₂ has pHPzc (point zero charge) of approximately 6.3, therefore when the pH of the solution is below 6.3, TiO₂ photocatalyst will be positively charged (Equation 2.5) and become negatively charged as the pH increases from 6.3 (Equation 2.6) (Ge et al., 2021).



The adsorption of anionic dyes is favoured by positively charged TiO_2 , which act as a strong Lewis acid and attracts anionic dyes, which are strong Lewis base. However, the adsorption of cationic dyes is reduced in acidic conditions as positively charged TiO_2 repels positively charged cationic dyes (Kumar & Pandey, 2017). Meanwhile, the adsorption of cationic dyes is favoured under the basic condition as the negatively charged TiO_2 attracts positively charged cationic dyes (Dariani et al., 2016).

Literature has shown that the photocatalytic degradation rate of dyes is affected by the pH of the solution. Removal of MB increased in basic pH due to the presence of higher hydroxide ions (OH^-) concentration, which are important oxidizing species required in MB degradation (Kumar et al., 2015). Cationic dyes such as MB and RhB can be adsorbed easily by electronegative clusters due to the electrostatic attraction, whereas anionic dyes such as MO are not able to be adsorbed easily due to their strong electrostatic repulsion (Bootharaju & Pradeep, 2013).

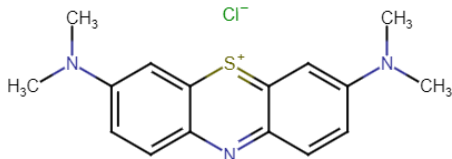
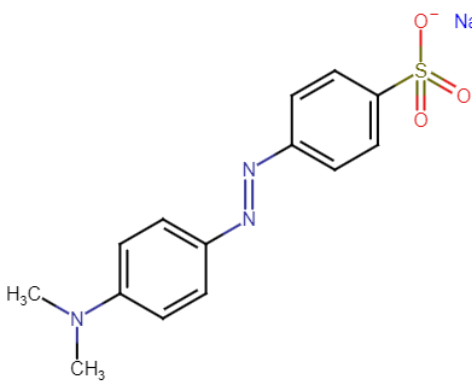
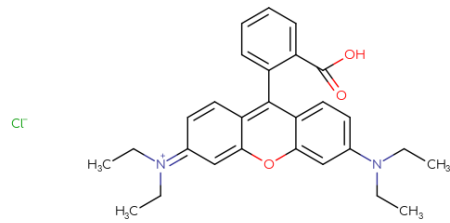
2.6 Dyes

Dyes are substances that are used to add colours to other substances that lack those specific colours and are commonly applied to improve the attractiveness of the product (Gopinath et al., 2020). Dyes have been greatly utilised in various industries such as textiles, paper, food, and cosmetics. It has been estimated that about 15% of the dyes are still present in the industrial effluent before being released into the water bodies (Bonetto et al., 2015). Additionally, it is stated that approximately 20% of the total dye generated worldwide is wasted during the dying process and released into water bodies without additional treatment, resulting in significant environmental damage. These dye pollutants are all comparatively highly toxic, carcinogenic, and perhaps mutagenic (Narayan et al., 2018). Recent estimates show that there are around 100,000 commercially coloured items, totalling 7×10^5 tonnes of

dyestuff produced annually (about 10% of dyes used in industry) have been discharged into aquatic environment (Eshaq & ElMetwally, 2019; Mosbah et al., 2019; Ihsanullah et al., 2020).

Dyes are organic compounds with colours and are grouped into three categories such as non-ionic (disperse dyes), anionic (acidic dyes) and cationic (basic dyes) (Pooresmaeil & Namazi, 2020). The most widely utilised dyes in textile industries are cationic and anionic, owing to their properties such as high solubility in water (Vickers, 2017). Among these dyes, the cationic and anionic dyes that are common and have been extensively applied in various industrial applications include MB, MO and RhB. Table 2.3 summarises the properties of MB, MO and RhB dyes.

Table 2.3: The properties of MB, MO and RhB Dyes (Selvam & Sarkar, 2017; Singh et al., 2018; Wu et al., 2021; Yusuf et al., 2022)

Dye/Properties	MB	MO	RhB
Physical form	Dark green crystalline powder or crystal	Orange-yellow powder or crystals	Green crystals or reddish-violet powder
Molecular formula	$C_{16}H_{18}N_3SCl$	$C_{14}H_{14}N_3NaO_3S$	$C_{28}H_{31}ClN_2O_3$
Molecular weight (g/mol)	319.85	327.33	479.02
Chemical Structure			
Absorption (λ_{max}), nm	664	465	554
Water solubility	Soluble in water	Slightly soluble in water, insoluble in ethanol	Very soluble in water
Safety/toxicity	Carcinogenicity	Carcinogenicity, genotoxicity, mutagenicity	Carcinogenicity

Potential effects and risks	Can cause oesophagal irritation, nausea, gastrointestinal pain, headache, diarrhoea, vomiting, fever, dizziness, and elevated blood pressure	Can cause vomiting, and diarrhea	Can damage the eyes, cause irritation and severe oral noxiousness in humans
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2.6.2 Methylene Blue, MB

MB is a common blue, cationic and thiazine dye that has a chemical formula of $C_{16}H_{18}N_3SCl$ and a molecular weight of 319.85 g/mol. MB is greatly used in textile industries as a colorant and is also widely used in the medical field as a staining agent, as well as for preventive and therapeutic measures (Selvam & Sarkar, 2017). MB is predominantly used in the garment and textile sectors to dye various fabrics (Liu et al., 2021). Additionally, MB dye is utilised in medicine, microbiology, and diagnostics as a sensitizer in the photo-oxidation of organic compounds (Rahman et al., 2012) as well as in aquaculture to cure a variety of fish diseases (Sharma et al., 2022). MB has also been commonly selected as a model pollutant in degradation studies due to several reasons such as (1) it is an active species with a characteristic peak in the UV-vis spectrum, (2) its presence in any medium could be easily detected as it exhibits blue colour in an oxidised state, and (3) have been greatly used in textiles industry so its removal is highly desirable (Din et al., 2021).

Literature has shown that MB is a very useful dye. However, manufacturing industries that use MB dyes in their manufacturing processes may discharge the residues into the environment. MB has been discovered to possess significant toxicity at high concentrations due to the unique stability of the aromatic ring in the MB molecular structure. MB is known to be both carcinogenic and non-biodegradable (Contreras et al., 2019). It can be extremely dangerous to human health if ingested and is known to damage the nervous system and eyes (Din et al., 2021). The negative effects of this dye usually include oesophageal irritation, nausea, gastrointestinal pain, headache, diarrhoea, vomiting, fever, dizziness, and elevated blood pressure (Alharby et al., 2021). Untreated waste discharge containing dyes can have detrimental consequences on the ecosystem, including raising the

chemical oxygen demand (COD) of water bodies and increasing toxicity (Owamah et al., 2013).

2.6.3 Methyl Orange, MO

MO dye has been greatly applied in the textile industries (Bazrafshan et al., 2014). It has a molecular weight of 327.33 g/mol, molecular formula of $C_{14}H_{14}N_3NaO_3S$ and a characteristic peak at 465 nm (Hanafi & Sapawe, 2020). It is also known as a typical azo anionic dye with high solubility in water (Wu et al., 2021). MO dye is frequently applied as a colorant in the leather and textile industries (Znad et al., 2018). It finds extensive usage in printing, paper-making, medicine, and food processing enterprises (Sejie & Nadiye-Tabbiruka, 2016; Bhowmik et al., 2018). According to Znad et al. (2018), MO has been applied as an indicator in the pharmaceutical industry's kinetic assay method for cyproheptadine analysis and in the coulometric method for measuring fenoterol in the presence of other anti-asthmatic drugs

Despite the extensive and various applications of MO, there are a few setbacks of MO towards the environment. MO is an azo dye with water solubility and is known to cause cancer as well as being an acidic or anionic colour, which can result in vomiting and diarrhea (Hanafi & Sapawe, 2020). Due to its stability, poor biodegradability, and water solubility, it is not easy to remove MO in aqueous solutions using conventional purification of water or treatment techniques (Sejie & Nadiye-Tabbiruka, 2016). Literature has shown that MO is a major environmental pollutant since it dissolves in water and has been greatly discharged from industrial wastewater (Narayan et al., 2018; Wu et al., 2021). MO has aromatic and -N=N- groups in its molecules that are very toxic, and can be harmful to the environment and living organisms (Bai et al., 2020).

2.6.4 Rhodamine B, RhB

RhB is a typical water-soluble dye used frequently in the textile industry for dyeing wool materials. It has been frequently used as a colouring agent, photosensitizer, water tracer, fluorescent dye, and other functions in other industries, including those in the paper, plastic, printing, biomedical, and leather sectors (Merouani et al., 2010; Chen et al., 2012; Tuzen et al., 2018). RhB is an amphoteric dye under the large class of xanthene dyes and is known as one of the least harmful xanthene basic dyes (Yusuf et al., 2022). The chemical formula of RhB is $C_{28}H_{31}ClN_2O_3$ with a molecular weight of 479.02 g/mol. It has an absorption spectrum characteristic of 554 nm (Üner et al., 2017). It is also showing high water solubility properties with high chemical stability and non-biodegradability (Yan et al., 2019).

Although RhB is considered the least benign dye but there are several environmental issues associated with RhB. (Yusuf et al., 2022). The extensive use of RhB in numerous sectors leads to the partial discharge of wastewater containing RhB dyes into the environment. Water contamination caused by RhB has been linked to numerous environmental problems and health issues for both people and animals. Literature has shown that RhB dyes contributed to detrimental effects on humans, such as skin irritation, dermatitis, allergies and cancer (Singh et al., 2018). In addition, studies have shown that ingesting RhB may damage the central nervous system and other vital organs in humans such as the kidney, brain and liver (Gao et al., 2011). Furthermore, RhB significantly reduces light penetration to algae and other aquatic plants, impeding the process of photosynthesis, which can negatively impact aquatic life (Kooh et al., 2016).

2.7 Antibacterial Properties of TiO₂-based Materials

Wastewater containing pathogenic bacteria such as *E. coli* may cause waterborne infections, which can be dangerous to humans and wildlife (He et al., 2021). Various strategies were employed to remove these microorganisms from wastewater such as chlorination, ozonation and UV irradiation (Reddy et al., 2017). These conventional disinfection techniques, however, have a few disadvantages which include either being chemically or energetically intensive and producing harmful chemical compounds (Khadgi et al., 2017; Wang et al., 2018).

Photocatalysis has been applied to replace the conventional disinfection method and gained popularity for its environmental friendliness, effectiveness, and ability to produce green energy (Wang et al., 2017). In recent years, TiO₂ has been used as self-cleaning and disinfectant material for coating clinical tools and food packaging. As a result, much emphasis has been given to photocatalytic disinfection of TiO₂. It is one of the most researched photocatalysts that can effectively inactivate viruses and degrade organic pollutants because of its chemical stability, abundance, nontoxicity, and cost-effectiveness (Coto et al., 2017).

There are several processes known to be involved in TiO₂ microorganism disinfection (Hajipour et al., 2012; Pelaez et al., 2012; Zhukova, 2015). Firstly, when exposed to equal energy of light or higher than the band gap energy of TiO₂, electron-hole pairs are created and eventually move to TiO₂'s surface. Then, the holes and their surrounding OH or H₂O react and produce highly reactive •OH radicals, while the electrons and oxygen vacancies nearby react to produce superoxide ions. Finally, bacteria cells on the surface of TiO₂ are destroyed by the generated ROS which results in the death of the bacteria. The oxidative species such as h⁺, •OH radical and •O₂⁻ are very reactive and involved in the

breaking down of microorganism cells (Zhao & Drlica, 2014). Figure 2.3 depicts a potential mechanism for TiO₂-based photocatalyst's photocatalytic disinfection of microorganisms. Literature has shown that factors involved in the photocatalytic disinfection include characteristics of water (e.g. turbidity, ions, dissolved organic matter, pH, dissolved oxygen, temperature), presence of ROS and interaction between bacteria and photocatalyst (He et al., 2021).

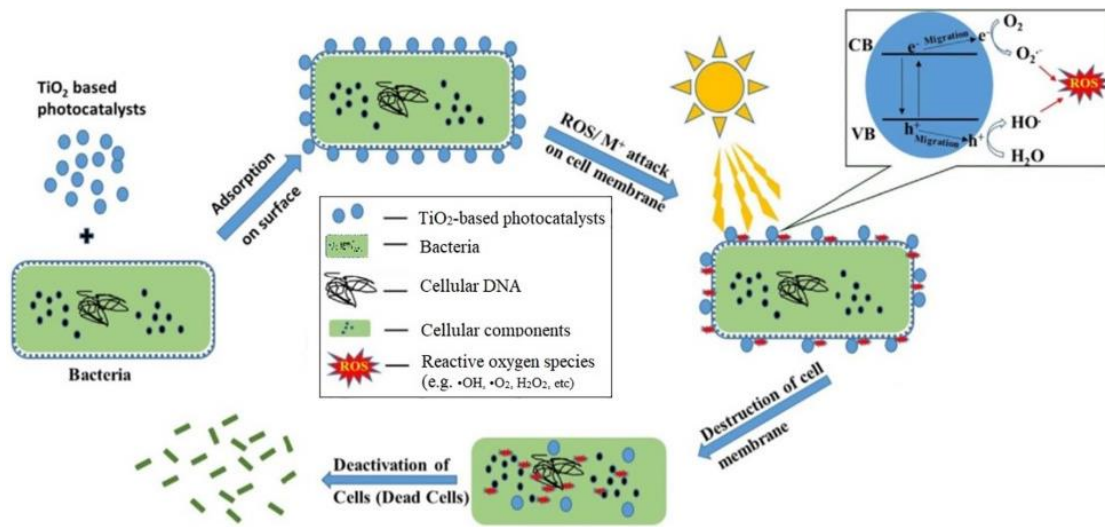


Figure 2.3: Photocatalytic disinfection mechanism of bacteria by TiO₂-based photocatalysts (Source: Reddy et al., (2017))

TiO₂ coatings were tested for their antibacterial activity on a range of bacteria and results revealed the inactivation of all bacteria strains under UVA irradiation (Nakano et al., 2013). Recently, cotton fabric with super hydrophobicity was prepared using a mixture of TiO₂ and perfluorodecyltriethoxysilane (PFDTs) demonstrated reliable antibacterial activity when tested against *E.coli* (Zhang et al., 2019). Higher antibacterial activity against Gram-positive bacteria (*S. aureus*) can be seen in TiO₂ anatase, in comparison to Gram-negative bacteria (*P. aeruginosa*) whereby the presence of UV irradiation also improves the antibacterial performance of TiO₂ by producing highly reactive species such as H₂O₂ and •O₂⁻ (Tao et al., 2019). The envelope of Gram-negative bacteria has three layers whereby the

outer membrane (OM), is a protective and distinctive characteristic that separates Gram-negative bacteria from gram-positive bacteria (Breijyeh et al., 2020). Due to the presence of this protective layer, gram-negative bacteria showed higher resistance and cannot be killed, unlike gram-positive bacteria (Miller, 2016; Exner et al., 2017; Gupta & Datta, 2019).

Literature has also shown that TiO₂ coupled with other metals like Cu (Liu et al., 2021) and Ag (Ghosh et al., 2020) exhibited greater antibacterial as compared to TiO₂ alone. Ag nanoparticles have been widely utilised for various applications including in healthcare, medical, food, and industrial applications. Past studies reported cytotoxicity of Ag nanoparticles toward microorganisms, viruses, and cancer cells can be enhanced when it is incorporated into TiO₂/Ag nanocomposite, as a result of the synergic effect between TiO₂ and Ag nanoparticles (Wang et al., 2012). Although the actual anti-(bacterial, viral, and cancer) mechanisms of TiO₂/Ag photocatalysts are still unclear, numerous studies have linked their potent cytotoxicity to the simultaneous synergistic actions of silver ions and ROS, particularly hydroxyl free radicals produced during the photocatalytic process (Ma et al., 2011; Kiwi et al., 2014).

TiO₂/Ag photocatalysts demonstrate high efficiency in killing bacteria belonging to both Gram-positive and Gram-negative groups such as *E. coli* (Liu et al., 2012), *S. aureus* (Zawadzka et al., 2016) and many others. TiO₂/Ag incorporated into CA nanofiber matrix demonstrated excellent antibacterial performances against *E. coli* and *S. aureus* for 36 h and substantial bacterial growth inhibition for 72 h (Jatoi et al., 2019). It was found that modified TiO₂ with 1 wt% of Ag exhibited the highest antibacterial effectiveness compared to pure TiO₂ where more than 99.99% of *E. coli* bacteria were inhibited after 60 min of UVA irradiation, due to increased ROS generated by TiO₂/Ag photocatalyst (Moongraksathum et al., 2019).

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials and Reagents

The starting materials, titanium (IV) butoxide, $\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$ (97% reagent grade) and 2-propanol, $(\text{CH}_3)_2\text{CHOH}$ were purchased from Sigma-Aldrich and Merck. The IL, 1-butyl-3-methylimidazolium acetate, [Bmim-Ac] $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_2$ ($\geq 95\%$), silver nitrate, AgNO_3 (ACS reagent, $\geq 99.0\%$), CA, MB (dye content 82%), MO (dye content 85%) and RhB (dye content 80%) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl), Sodium hydroxide (NaOH) and ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$, $\geq 99.5\%$) were obtained from Merck. Sodium chloride, NaCl was obtained from UNI-CHEM Chemical Reagents. Sodium phosphate dibasic (Na_2HPO_4), Potassium phosphate monobasic (KH_2PO_4) and L-ascorbic acid, $\text{C}_6\text{H}_8\text{O}_6$ (99.7%) were purchased from R&M Chemicals. Mueller Hinton agar was purchased from Sigma Aldrich. All of the solutions were prepared with distilled water and the chemicals involved were used without additional purification.

3.2 Synthesis of TiO_2 Photocatalyst

The synthesis procedures of TiO_2 -IL were adapted from Kowsari et al. (2020) and all syntheses were conducted in the Environmental Sustainability Laboratory at the Faculty of Resource Science and Technology (FRST), Universiti Malaysia Sarawak (UNIMAS). The TiO_2 -IL was synthesised using the sol-gel method in the presence of IL, Bmim[Ac] (Figure 3.1). Figure 3.2 illustrates the synthesis of TiO_2 using IL. Titanium (IV) butoxide and 2-propanol were used as precursors to synthesise TiO_2 . Titanium (IV) butoxide and 2-propanol were stirred for 20 min (Solution A) while Bmim[Ac] was varied (0.0 mL, 0.5 mL, 1.0 mL, 3.0 mL and 5.0 mL) and mixed into 100 mL of volumetric flask containing distilled water

(Solution B). TiO₂ synthesised with 0 mL, 0.5 mL, 1 mL, 3 mL and 5 mL of IL was denoted as TiO₂-0, TiO₂-0.5, TiO₂-1, TiO₂-3 and TiO₂-5, respectively. After 20 min of continuous stirring of solution A, solution B was added dropwise into solution A and left under constant stirring for 2 h. Then, the solution was filtered and rinsed with distilled water several times to remove IL and impurities. It was oven-dried for 2 h at 100 °C and subsequently calcined in the furnace for 5 h at 300 °C to obtain the anatase phase of TiO₂. The obtained white powders were kept in vials and stored in the desiccator. The photocatalytic efficiency of all synthesised TiO₂ photocatalysts in the presence of ILs was investigated using a 5 ppm MB solution and their dosages were varied from 0.1 g/L to 10.0 g/L and exposed to UVA ($\lambda = 365$ nm) irradiation for 120 min. TiO₂-1 was chosen for the TiO₂/Ag synthesis because it demonstrated maximum performance efficiency.

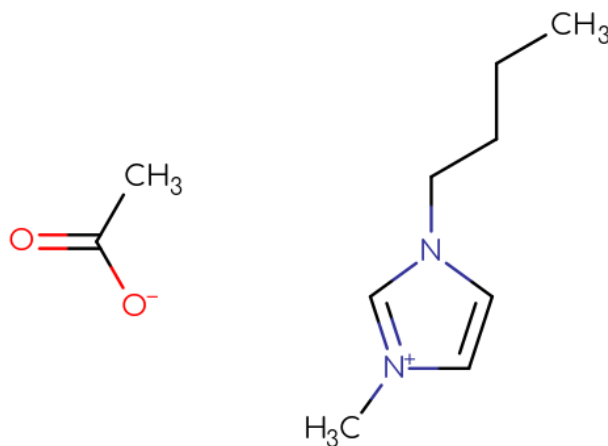


Figure 3.1: Chemical structure of Bmim[Ac]

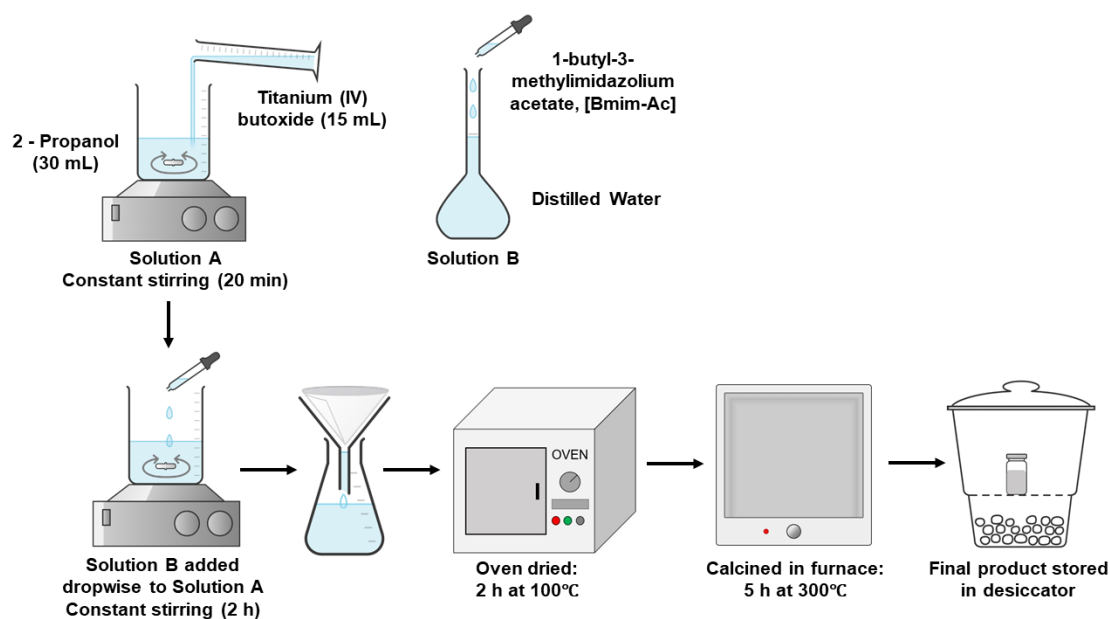


Figure 3.2: Synthesis of TiO_2 using IL

3.3 Synthesis of TiO_2/Ag Photocatalyst

TiO_2/Ag photocatalyst synthesis methods were obtained from Kanakaraju et al. (2022). The weight percentage of Ag was varied from 0.5 wt% to 5 wt% to investigate the effect of its concentration on TiO_2 doping. To prepare 1 g of 2 wt% of TiO_2/Ag photocatalyst, 0.9685 g of TiO_2 -1 and 0.0315 g of Ag precursor (AgNO_3) were mixed in a 100 mL beaker containing distilled water. Then, it was incubated in a water bath at 90°C for 3 h. The resulting TiO_2/Ag was dried in the oven at 105°C for 2 h to remove excess moisture in the photocatalyst. TiO_2/Ag photocatalyst was calcined in the furnace for 5 h at 300°C to increase its crystallinity. The TiO_2/Ag photocatalyst was left to cool down at room temperature before being stored in a desiccator. Similar processes were used in the preparation of other TiO_2/Ag photocatalyst samples, i.e., 0.5 wt%, 1 wt%, 4 wt% and 5 wt% of TiO_2/Ag . All synthesised TiO_2/Ag photocatalysts (1.0 g/L) were assessed for their photocatalytic efficiency using similar experimental conditions as TiO_2 . TiO_2/Ag with 2 wt% of Ag which demonstrated the highest degradation of MB was subsequently mixed with CA.

3.4 Synthesis of TiO₂/Ag/CA Photocatalyst

Different CA wt% (0.5, 1, 2, 3, 4, and 5 wt%) was mixed with TiO₂/Ag 2% photocatalyst to synthesise TiO₂/Ag/CA (Kanakaraju et al., 2022). For example, to prepare TiO₂/Ag with 0.5 wt% of CA, 0.005 g of CA was added into a beaker with 100 mL distilled water containing 0.995 g of TiO₂/Ag. Then, the mixture was stirred continuously for 2 h, filtered and dried in the oven for 2 h at 100 °C to remove moisture. Fine powder of TiO₂/Ag/CA photocatalysts was obtained by grinding with a pestle and mortar. Then, the photocatalyst was stored in glass vials. The same steps were used in the preparation of other TiO₂/Ag/CA photocatalyst samples, i.e., 1 wt%, 2 wt%, 3 wt%, 4% and 5 wt% of TiO₂/Ag/CA photocatalyst.

3.5 Characterisation of Photocatalysts

The TiO₂, TiO₂/Ag and TiO₂/Ag/CA photocatalysts were analysed using X-ray diffraction spectrometer (XRD) to observe their crystallinity and crystal structure. The valence states of the surface elements present in TiO₂/Ag/CA photocatalyst were identified using X-ray photoelectron spectroscopy (XPS) (Quantera II, ULVAC-PHI) with an Al K α X-ray source (25W) operating at 15kV. The spectra were measured using pass energy of 112 eV and dwell time of 20 ms. The energy of C 1s at 284.8 eV was used as a reference for charge correction to estimate the binding energy values. Fourier Transform Infrared (FTIR) spectroscopy was used to investigate the chemical bonds and functional groups present in the photocatalyst. The spectra of the synthesised TiO₂/Ag/CA photocatalysts were recorded using potassium bromide, KBr in the range of wavenumber between 400-4000 cm⁻¹. Energy-dispersive X-ray (EDX) spectrometer coupled with SEM (Jeol Model JSM-5300LV) was used to determine the elemental composition of TiO₂/Ag/CA photocatalyst. The microstructure and particle size of TiO₂/Ag/CA photocatalyst were observed using

Transmission electron microscope (TEM, JEOL Model JEM 1230). The band gap of the samples was analysed using the UV-DRS (Cary 5000) with the excitation wavelength scanned from 200 nm to 800 nm. Brunauer–Emmett–Teller (BET) analyzer with N₂ adsorption at 77 K was used to measure the specific surface area of TiO₂, TiO₂/Ag and TiO₂/Ag/CA photocatalysts.

3.6 Determination of Point Zero Charge of TiO₂/Ag/CA

The method for the determination of the point zero charges (pH_{pzc}) was taken from Kanakaraju et al. (2018). Approximately 50 mL of 0.01 M of NaCl solution was added into Erlenmeyer flask and the NaCl solution was boiled to remove dissolved CO₂ and cooled at room temperature (Khandaker et al., 2017). The pH of the mixtures was adjusted to 2.00, 4.00, 6.00, 7.00, 8.00, 10.00, and 12.00 using NaOH (0.1 M) or/and HCl (0.1 M). A similar amount of TiO₂/Ag/CA photocatalyst was added to each flask containing NaCl solution and agitated for 24 h. The final pH solution (pH_{final}) in each flask was measured after 24 h. The pH_{pzc} of TiO₂/Ag/CA photocatalyst is the point where pH_{final}=pH_{initial}.

3.7 Photocatalytic Degradation Experiments

The photocatalytic performance efficiency of TiO₂-IL, TiO₂/Ag and TiO₂/Ag/CA photocatalysts were investigated based on individual MB dye removal. Figure 3.3 illustrates the set-up of the photocatalytic degradation experiment. Preliminary experiments were performed using 0.1 g/L of TiO₂-IL (0.0 mL-5.0 mL), TiO₂/Ag (0.5% - 5.0%) and TiO₂/Ag/CA (0.5% - 5.0%) for the removal of 5 ppm MB. Typically, a required amount of the photocatalyst and 100 mL of MB solution were stirred constantly in dark conditions for 30 min to achieve an adsorption equilibrium between the dye solution and photocatalyst. The first sample (t₃₀) was collected after 30 min of equilibrium. Then, the reaction suspension was exposed to a UVA light source (150 W, 240 V) for 2 h under continuous

stirring. Throughout the 2 h of treatment, 10 mL of sample was taken every 30 min. All samples were centrifuged at 6000 rpm to retrieve supernatant and MB concentration was determined via UV–Vis spectrophotometer. MB concentration was analysed by measuring the absorbance at the wavelength, $\lambda = 664$ nm. The percentage of MB removal was calculated using Equation 3.1:

$$\text{Removal Percentage (\%)} = \frac{C_0 - C_f}{C_0} \times 100 \quad \text{Equation 3.1}$$

C_0 = MB initial concentration

C_f = MB final concentration

The best performing $\text{TiO}_2/\text{Ag}/\text{CA}$ was further investigated for MB removal by varying the photocatalyst dosage (0.1 g/L – 2.0 g/L), initial concentration (5 ppm – 20 ppm) and pH (3 – 12). The best experimental condition obtained to achieve the maximum MB removal was further applied for the degradation of other individual dyes namely MO and RhB. All dyes were mixed as equimolar for the degradation of the mixed dye solution. All details of photocatalytic procedures were similar to those previously mentioned. Control experiments were conducted using undoped TiO_2 , $\text{TiO}_2\text{-IL}$, TiO_2/Ag and $\text{TiO}_2/\text{Ag}/\text{CA}$. The contribution of dark adsorption, UV and visible light effect, and the extent of MB molecules adsorption on different photocatalysts were studied. The control experiments were performed with 3 g/L photocatalyst dosage, 5 ppm initial MB concentration, unadjusted pH 7.4 and irradiation time of 2 h.

Radical scavenger experiments were carried out to identify the contribution of holes, hydroxyl radicals and superoxide radicals on the photocatalytic degradation of MB. The method for the radical scavenger experiments was adapted from Li et al. (2021). The radical scavenger reagents used to identify the contribution of hole, hydroxyl radical and superoxide

radical were ethylene glycol, 2-propanol and ascorbic acid, respectively. The concentration of the radical scavenger reagents were fixed at 0.01 M and were added into MB solution. Then, the experiments were conducted under optimised conditions (3 g/L photocatalyst dosage, 5 ppm initial MB concentration, unadjusted pH 7.4 and irradiation time of 2 h). The percentage of MB removal was calculated using Equation 3.1, as mentioned previously.

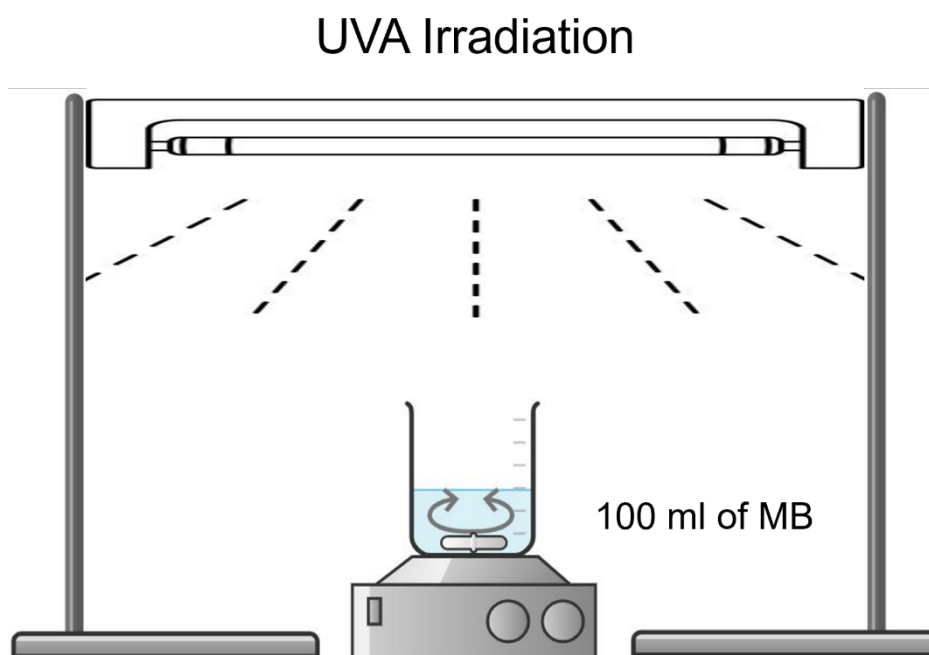


Figure 3.3: Schematic diagram illustrating the photocatalytic degradation of MB dye under UVA irradiation

3.8 Recyclability Study

The recyclability study was conducted to investigate the efficiency of $\text{TiO}_2/\text{Ag}/\text{CA}$ photocatalyst on dye removal. $\text{TiO}_2/\text{Ag}/\text{CA}$ photocatalyst was obtained after photocatalyst treatment using filter paper. The photocatalyst was filtered, rinsed many times with distilled water and oven-dried for 2 h at 100 °C. A similar step was repeated after each photocatalytic treatment and reused for the next photocatalytic treatment. The photocatalytic treatment was repeated two times using recovered $\text{TiO}_2/\text{Ag}/\text{CA}$ photocatalyst and the dye solution was freshly prepared for each photocatalytic treatment.

3.9 Antibacterial Study

The antibacterial study was performed via disc diffusion method to determine TiO₂/Ag/CA's effectiveness against both Gram-negative and Gram-positive bacteria as represented by *E. coli* and *S. aureus*, respectively. Prior to the antibacterial study, cultures of *E. coli* and *S. aureus* were obtained from the Microbiology Laboratory 2, Faculty of Resource Science and Technology, UNIMAS. The bacterial stock cultures were revived in nutrient broth (NB), followed by glycerol stock preparations for storage. To prepare the working bacterial cultures, 200 uL of bacterial glycerol stock cultures were pipetted into 4 mL of NB and placed onto an orbital shaker at 150 rpm overnight. TiO₂-1/Ag 2%/CA 0.5% photocatalyst was made at 5 concentrations (denoted as S1-S5): 1, 2, 3, 4 and 5 g/L, using PBS solution in test tubes. Five sterile filter papers were dipped into each of the test tubes. Next, the overnight grown *E. coli* and *S. aureus* cultures were swabbed onto six Mueller-Hinton (MH) agar plates using sterile cotton buds. The treated filter papers were then placed onto the agar surface as shown in Figure 3.4, followed by an incubation period of 24 h at 37 °C. The diameter of the inhibition zones was measured after 24 h. TiO₂-1/Ag 2%/CA 0.5% concentration with the highest inhibition diameter obtained was used in comparing the effects of TiO₂-0, TiO₂-1, TiO₂-1/Ag 2% and TiO₂-1/Ag 2%/CA 0.5% (denoted as C1-C4) on *E. coli* and *S. aureus*. The procedures were repeated to analyse the impact of different photocatalysts on *E. coli* and *S. aureus*.

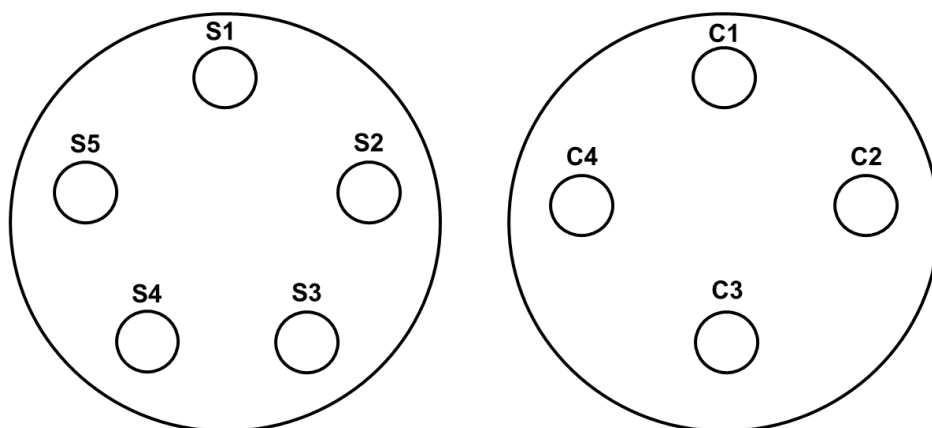


Figure 3.4: Disc diffusion method for the antibacterial study

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterisation of TiO₂/Ag/CA Photocatalyst

4.1.1 XPS Analysis

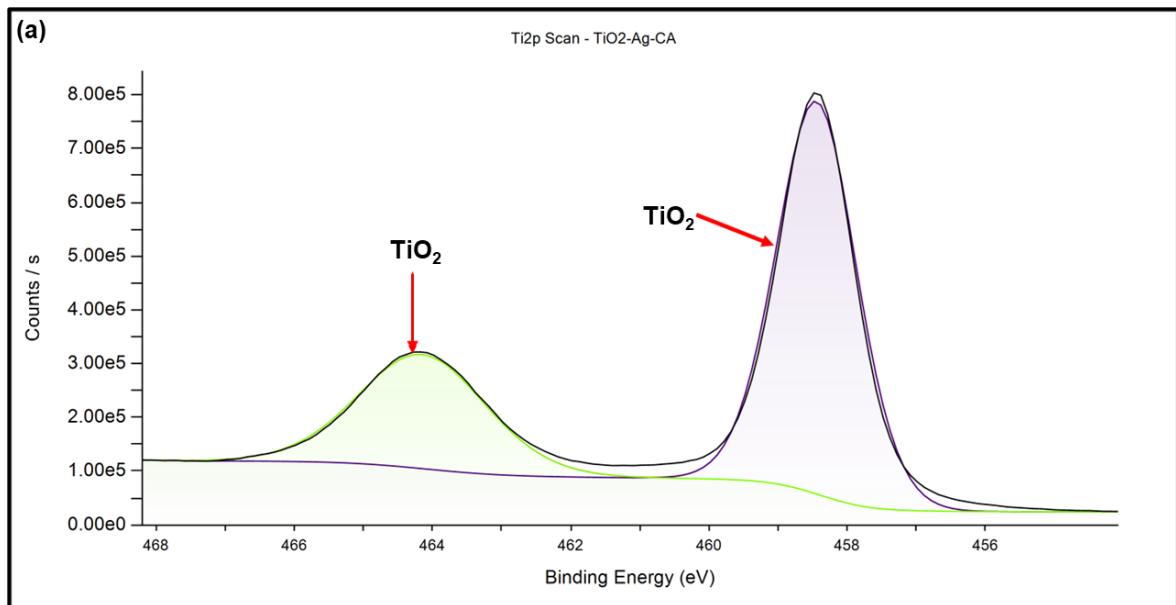
TiO₂-Ag 2 wt%/CA 0.5 wt% photocatalyst was chosen for the XPS analysis due to its ability to demonstrate the highest MB removal among other TiO₂/Ag/CA photocatalysts. Figure 4.1 shows the high-resolution spectra of Ti 2p, O 1s, Ag 3d and C 1s. The two main peaks located at 458.44 eV and 464.23 eV were ascribed to Ti 2p_{3/2} and Ti 2p_{1/2} in TiO₂ (Figure 4.1a). Past studies have also reported similar findings (Pawar et al., 2016). The splitting energy between the Ti 2p_{3/2} and Ti 2p_{1/2} is 5.7 eV confirmed the presence of the Ti⁴⁺ state in the photocatalyst (Zhang, Wang, Zhou, Wang, & Zhang, 2017).

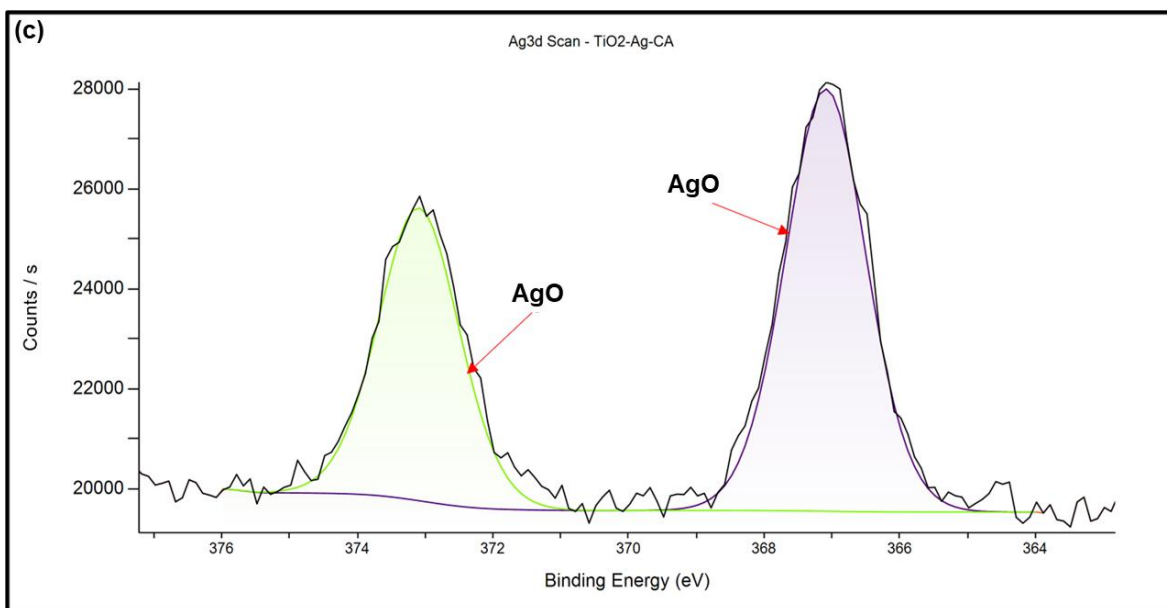
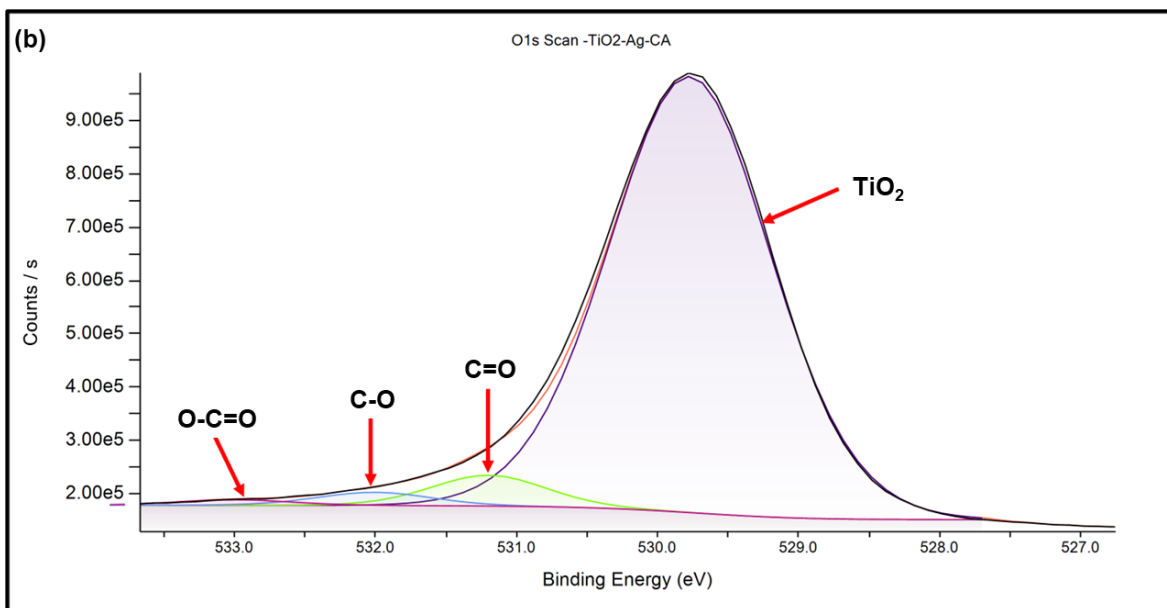
The peak of O could be divided into four isolated peaks after fitting (Figure 4.1b). The peak at 529.77 eV was ascribed to the presence of O₂⁻ within the lattice of TiO₂. Previous works have shown that the O 1s spectrum of 1% Ag-TiO₂ was divided into two peaks at 529.32 eV and 531.82 eV, which corresponded to lattice oxygen (Ti-O bond) and hydroxyl (-OH groups), respectively (Zhang et al., 2017). Meanwhile, the peaks at 531.20 eV, 532.01 eV and 533.0 eV were ascribed to C=O, C-O and O-C=O, respectively. The main contribution for peaks at about 530 eV is due to the presence of Ti-O of titania and C=O moieties (Lopez et al., 2018).

Ag 3d spectrum (Figure 4.1c) had two peaks at 367.09 eV and 373.09 eV, which were assigned to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively (Saikia, Das, & Saikia, 2022). According to the literature, when the difference between two peaks is 6 eV, the Ag is present in the metallic zerovalent [Ag(0)] oxidation state in the composite (Karimi-Maleh et al.,

2020; Xu et al., 2019). However, there are studies which have also validated the presence of Ag^{2+} (AgO) in Ag -doped TiO_2 , which was associated with Ag 3d5/2 XPS signal at 367.0 eV (Taing, Cheng, & Hemminger, 2011; Xin, Jing, Ren, Wang, & Fu, 2005). As such, the Ag 3d5/2 XPS signal at 367.09 eV in Figure 4.1c can be attributed to a chemical state of Ag^{2+} . Furthermore, there are no diffraction lines corresponding to Ag_0 were observed in XRD experiments, indicating that Ag exists in Ag^{2+} state instead of Ag_0 .

The peak of C could be divided into four isolated peaks after fitting (Figure 4.1d). The peaks at 284.89 eV, 286.8 eV, 288.38 eV and 289.23 eV were ascribed to the presence of C-C, C-O, O-C=O and C=O, respectively. Previous studies have demonstrated similar results, whereby the binding energy detected at 284.6, 285.8, 287.1, and 289.8 eV were assigned to (C-C-OH bonding), (O-C-O or C=O bonding), (O-C-O bonding), and (O-C-O or C=O bonding), respectively, revealing that the carbon atoms came from cellulose molecules (Mahato, Prasad, & Mathur, 2009; J. Zhang et al., 2009).





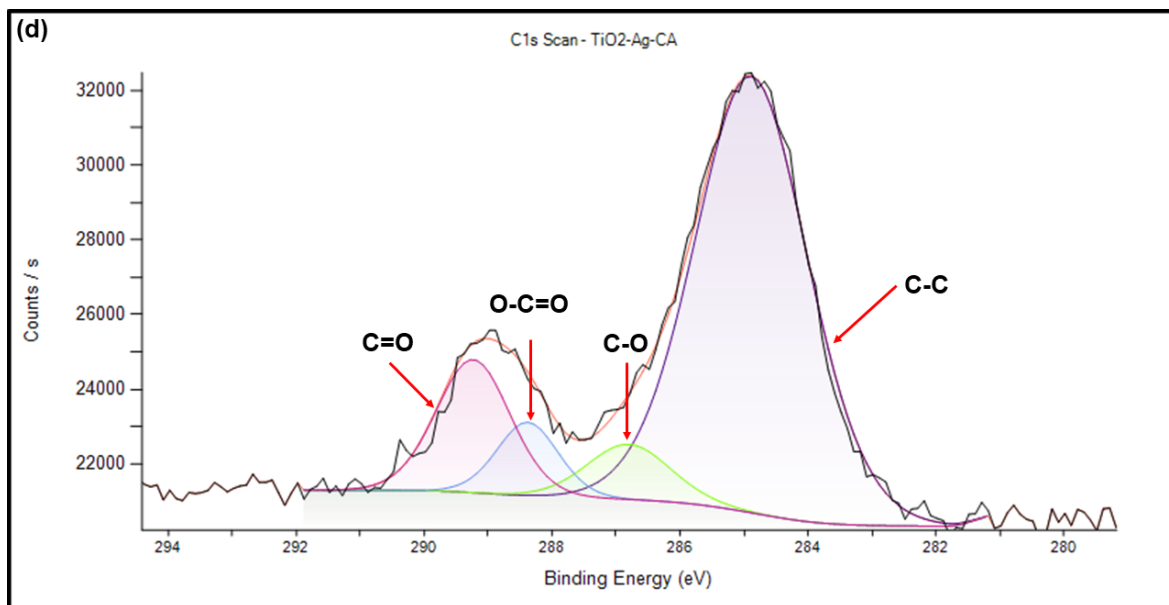


Figure 4.1: XPS Spectra of (a) Ti 2p, (b) O 1s, (c) Ag 3d and (d) C 1s

4.1.2 XRD Analysis

The X-ray diffraction patterns for TiO₂-0, TiO₂-1, TiO₂-1/Ag 2% and TiO₂-1/Ag 2%/CA 0.5% showed typical anatase diffraction peaks at $2\theta = 25.6^\circ, 38.5^\circ, 48.2^\circ, 53.9^\circ, 55.1^\circ, 62.9^\circ, 68.9^\circ, 70.4^\circ, 75.2^\circ$ and 82.6° , according to JCPDS 021-1272 (Figure 4.2). The photocatalysts were dominated by the anatase crystal structure of TiO₂. The diffraction peak at $2\theta = 44.4^\circ$ in the TiO₂-0 sample is ascribed to the presence of carbon (JCPDS = 01-080-0017). The low presence of carbon in the sample may be caused by contamination of the sample (Ungan & Tekin, 2019).

The intensity of the anatase peak for TiO₂-0 (Figure 4.2d) is slightly higher as compared to TiO₂-1 (Figure 4.2c). However, the diffraction peak at $2\theta = 44.4^\circ$ for TiO₂-1 corresponds to carbon disappearing. Upon addition of Ag, a new peak appears at $2\theta = 31.3^\circ$ which corresponds to the presence of Ag₂O₃ (JCPDS 01-072-0607) (Figure 4.2b), indicating successful doping of Ag into TiO₂ photocatalyst. The diffraction peak at $2\theta = 44.4^\circ$ in TiO₂-1/Ag 2% which corresponds to Ag cubic (JCPDS 040783) overlapped with the carbon peak.

As a result, the addition of Ag increases the peak's intensity. The diffraction peak of Ag (111) at $2\theta = 38.5^\circ$ also overlaps with the anatase peak of TiO_2 . The addition of CA does not contribute to any new peaks (Figure 4.2a), indicating that no peaks were detected which could signify the presence of CA in the photocatalyst. This could be attributed to the lower concentration of CA in the photocatalyst. Literature has reported that there could be a few reasons, for instance, the dopants are highly dispersed and in low concentration (Zhou & He, 2012) or below the detection limit of XRD (Wu et al., 2011).

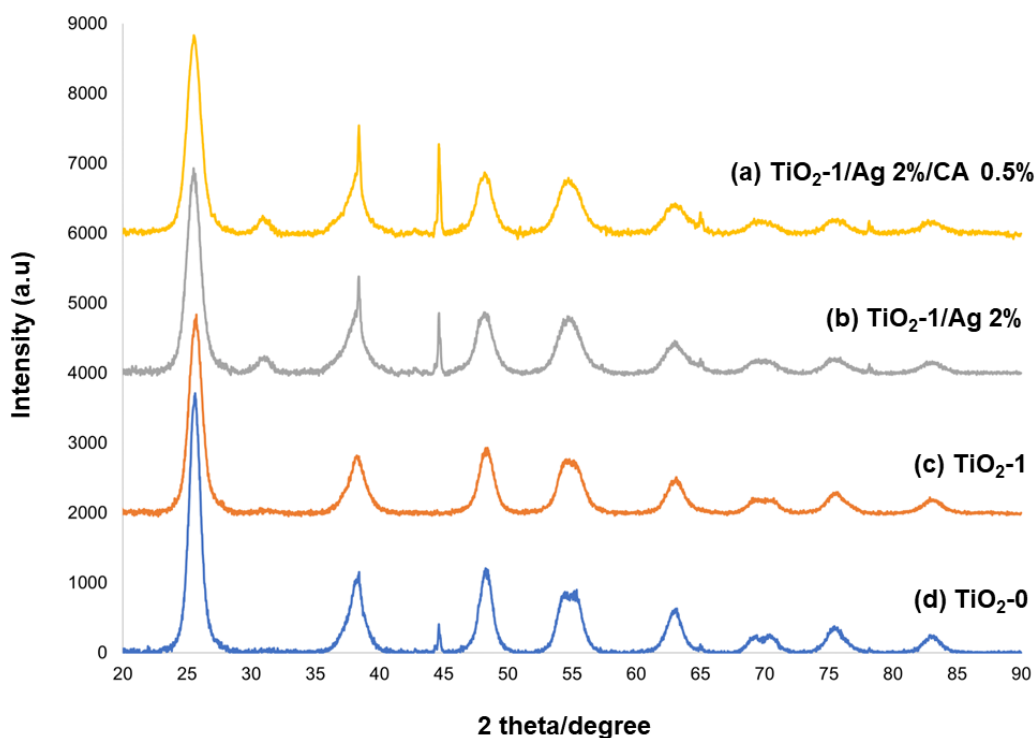


Figure 4.2: XRD patterns of (a) TiO_2 -1/Ag 2%/CA, (b) TiO_2 -1/Ag 2%, (c) TiO_2 -1 and (d) TiO_2 -0

4.1.3 FTIR Analysis

The FTIR spectra show the comparison between different photocatalysts in the range of 4000 cm^{-1} to 400 cm^{-1} (Figure 4.3b). The vibration of the Ti–O–Ti bond is observed at

the absorption bands around 500 cm^{-1} to 700 cm^{-1} for TiO_2 -1, TiO_2 -1/Ag 2% and TiO_2 -1/Ag 2%/CA 0.5% (Figure 4.3). The strong absorption bands at $750\text{--}500\text{ cm}^{-1}$ are assigned to the vibration stretching of the Ti–O–Ti bond in the TiO_2 lattice (Oladipo et al., 2019). Besides that, the band that appeared at 3421 cm^{-1} in the FTIR spectrum of TiO_2 /Ag and the absorption band that appears near 1600 cm^{-1} was attributed to the bending and vibrational modes of OH and C=O which are attributed to the presence of water and CO_2 in the environment (Kanakaraju et al., 2022).

Meanwhile, the absorption band around 497 cm^{-1} is associated with the framework of Ag (Ghosh et al., 2020), indicating the presence of Ag in the photocatalyst. Vakhrushev and Boitsova (2021) reported similar findings where a band ranging from 400 to 670 cm^{-1} was also observed in the FTIR spectra of all the TiO_2 /Ag composites, which is assigned to the overlapping peak between the Ti–O–Ti bond and Ag–O bonds. The spectra for TiO_2 /Ag/CA (Figure 4.3b) appeared to be similar to TiO_2 /Ag (Figure 4.3c). The incorporation of CA resulted in sharp peaks around 1600 cm^{-1} and 1100 cm^{-1} indicating the formation of CA bonding in the composite.

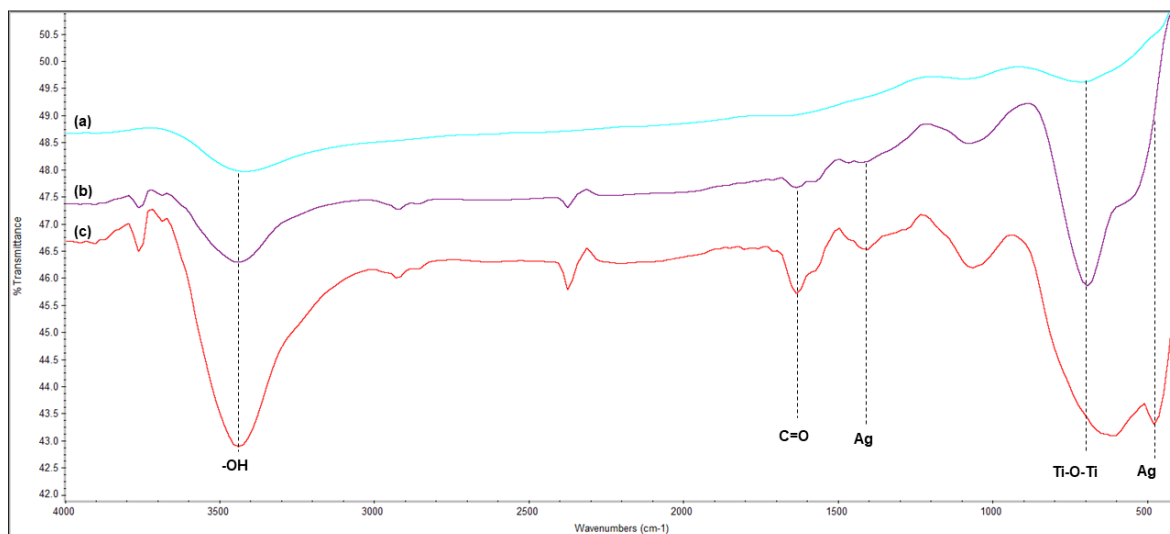


Figure 4.3: FTIR spectra of (a) TiO_2 -1, (b) TiO_2 -1/Ag 2% and (c) TiO_2 -1/Ag 2%/CA 0.5%

4.1.4 SEM and TEM Analysis

SEM images of Figure 4.4a-b illustrated the morphology of TiO_2 synthesised with and without IL, which consisted of circular-shaped agglomerated particles with irregular sizes. This indicates that there is no distinct difference in the shape of the photocatalyst, demonstrating that the presence of the IL in the synthesis does not alter the shape of TiO_2 (Huang et al., 2020). In contrast to TiO_2 -0, however, TiO_2 -1 (Figure 4.4b) particles exhibit smaller circular-shaped agglomerated particles with lesser agglomeration. It was reported that IL can help in the growth of the particles and prevent agglomeration, by structuring and building a protective coating on the surface of growing structures (Paszkievicz et al., 2016). Hence, the addition of IL in the synthesis assisted in creating smaller-sized particles and reducing the agglomeration of particles.

Figure 4.4c shows the morphology of TiO_2 -1/Ag 2%. Similar to TiO_2 , TiO_2/Ag displayed circular-shaped particles with irregular sizes. Although the presence of Ag was not visible, the EDX results confirmed the presence of Ag. The morphology of CA alone can

be observed under 3 different magnifications namely $\times 1000$ (Figure 4.4e), $\times 5000$ (Figure 4.4f) and $\times 10000$ (Figure 4.4g). The observation revealed that CA exhibits particles with a cylindrical shape and a smooth surface. This observation is depicted in Figure 4.4d, where the presence of a cylindrical-shaped particle confirms the incorporation of CA within the TiO_2/Ag photocatalyst. Circular-shaped particles found on the rod-shaped particles suggest that TiO_2 particles are attached to the surface of the rod-shaped particles.

TEM image of $\text{TiO}_2\text{-1}/\text{Ag}$ 2%/CA 0.5% consisted of spherical shapes particles with diameters ~ 6.9 nm. Although Ag was not observed on the photocatalyst surface based on the TEM image of $\text{TiO}_2\text{-1}/\text{Ag}$ 2%/CA 0.5% (Figure 4.4h), the XRD results (Figure 4.2), SEM (Figure 4.4) and EDX (Figure 4.5) confirmed Ag's presence in $\text{TiO}_2\text{-1}$ photocatalyst.

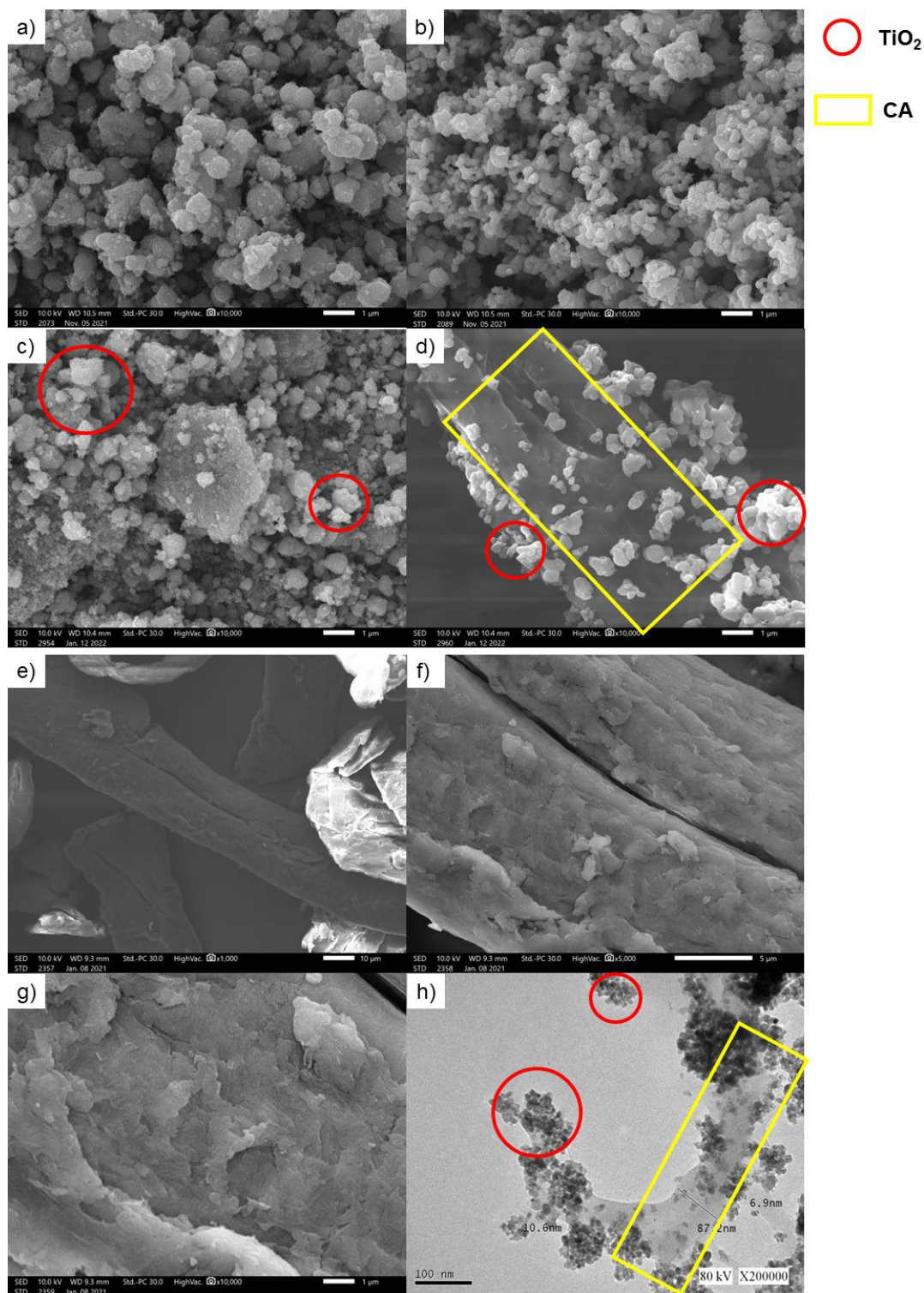


Figure 4.4: SEM images of (a) TiO_2 -0, (b) TiO_2 -1, (c) TiO_2 -1/Ag 2%, and (d) TiO_2 -1/Ag 2%/CA 0.5%, CA alone (e) $\times 1000$, (f) $\times 5000$ and (g) $\times 10000$, (h) TEM image of TiO_2 -1/Ag 2%/CA 0.5%

4.1.5 EDX Analysis

The EDX analysis of TiO₂-1/Ag 2% showed the elemental composition of Ti, O and Ag elements as 59.93%, 38.52%, and 1.55%, respectively (Table 4.1, Figure 4.5), indicating that TiO₂-1 was successfully doped with Ag. In addition, intense peaks of C (37.86%) observed in the EDX spectrum of TiO₂-1/Ag 2%/CA 0.5% (Figure 4.5d) further supported the existence of C, which is attributed to the presence of CA.

Table 4.1: Elemental Composition of TiO₂ Photocatalysts

Samples	Weight % of Elements			
	Ti	O	Ag	C
TiO ₂ -0	58.37±0.19	41.63±0.10	N.D.	N.D.
TiO ₂ -1	60.87±0.18	39.13±0.09	N.D.	N.D.
TiO ₂ -1/Ag 2%	59.93±0.2	38.52±0.10	1.55±0.05	N.D.
TiO ₂ -1/Ag 2%/CA 0.5%	32.18±0.16	28.56±0.09	1.40±0.04	37.86±0.04

*ND: Not Detected

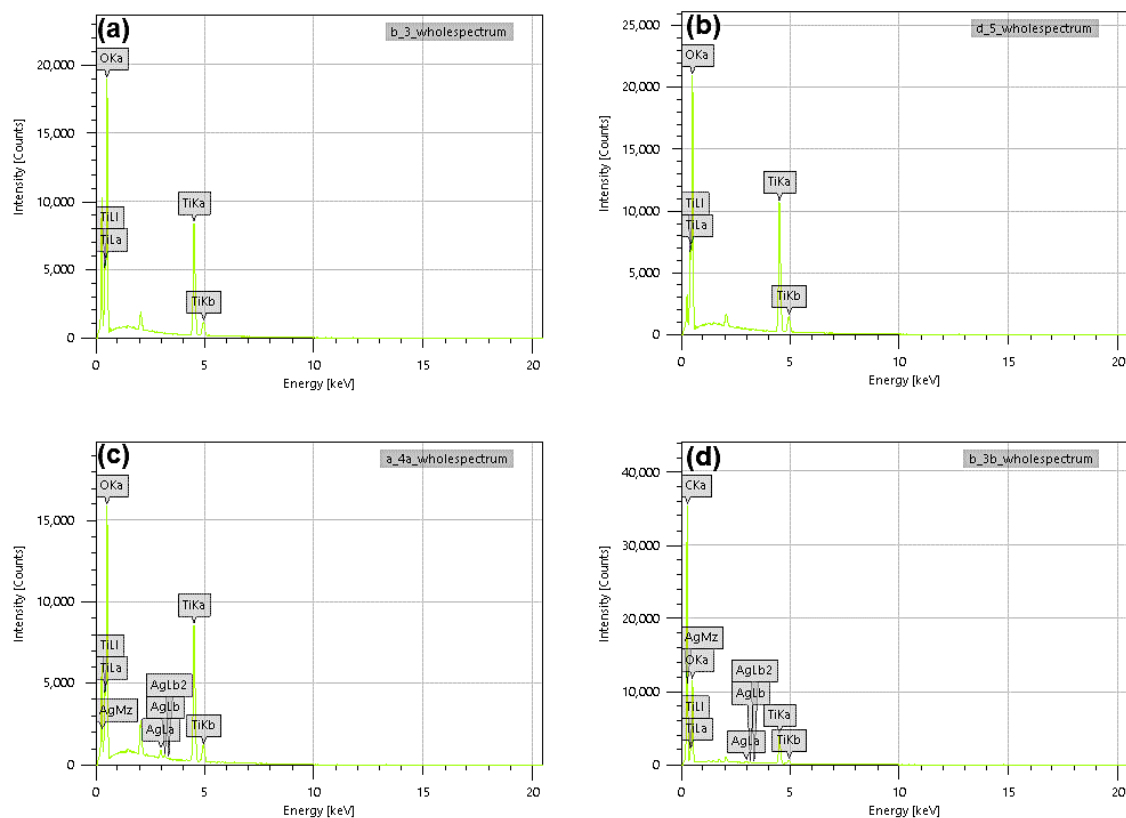


Figure 4.5: EDX spectra of (a) TiO₂-0, (b) TiO₂-1, (c) TiO₂-1/Ag 2% and (d) TiO₂-1/Ag2%/CA 0.5%

4.1.6 UV-DRS Analysis

The UV-Vis DRS of TiO₂, TiO₂/Ag and TiO₂/Ag/CA were compared (Figure 4.6). The Kubelka-Munk function allows the absorption curve or band gap of the photocatalyst to be approximated from its reflectance (Wang et al., 2013). The diffuse reflectance spectra of materials were transformed into the Kubelka-Munk function (KM) using the equation below:

$$KM = \frac{(1 - R)^2}{2R}$$

Where R is the reflectance

There is no significant difference in the band gap energy (3.65 eV, cutoff wavelength at 340 nm) that can be observed between the UV-Vis DRS spectra of TiO₂-1, TiO₂-1/Ag 2% and TiO₂-1/Ag 2%/CA 0.5% (Figure 4.6). It is observed that the presence of CA and Ag did

not contribute significantly to the UV-Vis adsorption since there is no significant difference in the band gap energy. This indicates that the presence of UV light is important to activate the catalyst for the photocatalytic activity of TiO_2/Ag and improvement in visible light region during degradation can be attributed to physical properties of TiO_2/Ag such as surface area and crystalline form of TiO_2 . In addition, consistent band gap energy upon the addition of Ag can be attributed to a lower concentration of Ag, similar to the study reported by Ratshiedana et al. (2021).

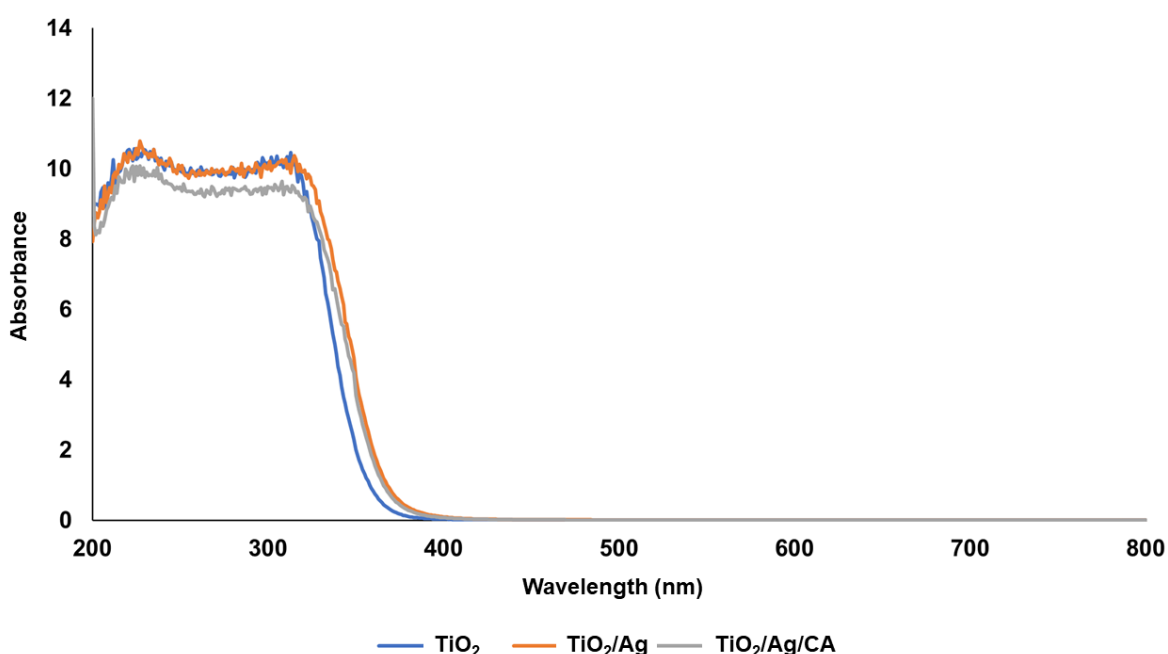


Figure 4.6: UV-DRS Spectra of TiO_2 -1, TiO_2 -1/Ag 2% and TiO_2 -1/Ag 2%/CA 0.5%

4.1.7 BET Analysis

The BET analysis using nitrogen adsorption-desorption isotherm showed that all photocatalysts shared a similar type of adsorption isotherm. All photocatalysts samples namely TiO_2 -0, TiO_2 -1, TiO_2 -1/Ag 2%, and TiO_2 -1/Ag 2%/CA 0.5% exhibited adsorption type IV adsorption isotherm (Figure 4.7). It was also revealed that the surface area of TiO_2 -0, TiO_2 -1, TiO_2 -1/Ag 2%, and TiO_2 -1/Ag 2%/CA 0.5% photocatalysts were $130.9 \text{ m}^2/\text{g}$,

174.8 m²/g, 178.6 m²/g, and 186.5 m²/g, respectively (Table 4.2). The addition of IL increased the specific surface area of TiO₂ from 130.9 m²/g to 174.8 m²/g. When compared to TiO₂-0, TiO₂-1 showed a 33.5% higher surface area, which may be the result of controlled titania aggregation. (Preethi et al., 2017).

A similar finding was obtained by Yoo et al. (2015), whereby the surface area of the TiO₂/Ag synthesised with IL increased up to 3 folds compared to only 147 m²/g in the TiO₂/Ag synthesised without IL. Another study has also reported that the surface area of TiO₂ synthesised with IL increased significantly from 160 m²/g (in the absence of IL) to 283 m²/g (Verma et al., 2019). Furthermore, the surface area of TiO₂/Ag is slightly increased with the introduction of Ag. Increased surface area and average pore size of the catalyst can be associated with the addition of Ag dopant into the TiO₂ lattice (Oladipo et al., 2019). The incorporation of CA into the photocatalyst, as observed in TiO₂/Ag/CA, did not lead to a significant increase in the surface area. This finding suggests that the presence of CA does not play a substantial role in increasing the surface area of the photocatalyst.

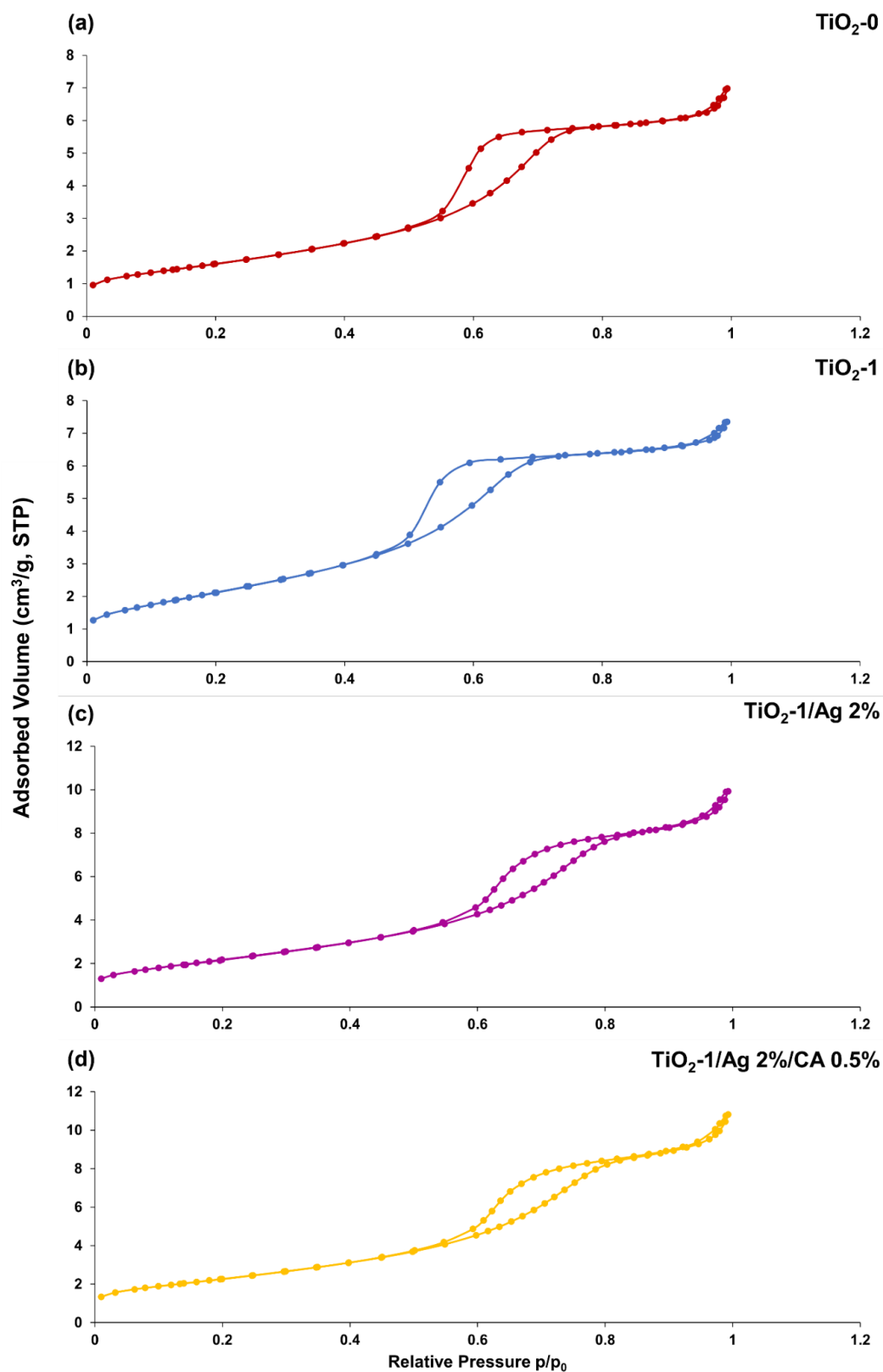


Figure 4.7: BET adsorption-desorption isotherm (a) $\text{TiO}_2\text{-0}$, (b) $\text{TiO}_2\text{-1}$, (c) $\text{TiO}_2\text{-1/Ag 2\%}$, and (d) $\text{TiO}_2\text{-1/Ag 2\%/CA 0.5\%}$

Table 4.2: BET Specific Surface Area of TiO₂ Photocatalysts

Samples	BET Surface Area, m ² /g	Pore Volume, cm ³ /g	Pore size, cm ² /g
TiO ₂ -0	130.90	0.24	71.96
TiO ₂ -1	174.80	0.25	57.29
TiO ₂ /Ag 2%	178.63	0.34	75.61
TiO ₂ /Ag 2%/CA 0.5%	186.50	0.37	78.81

4.1.8 The pH Value at the Point Zero Charge of (pH_{pzc}) of TiO₂/Ag/CA

The pH_{pzc} is the pH of the adsorbent which takes a zero value, where the positively charged site equals the negatively charged sites (Sobhanardakani & Zandipak, 2017). The pH_{pzc} of TiO₂-1/Ag 2%/CA 0.5% photocatalyst was determined to be 7 (Figure 4.8). The surface of TiO₂-1/Ag 2%/CA 0.5% is positively charged in acidic conditions (pH < 7) and negatively charged in basic conditions (pH > 7). TiO₂ reacts with H⁺ to form positively charged TiOH₂⁺ in acidic conditions but reacts with OH⁻ to form negatively charged TiO⁻ and water in basic conditions (Kumar & Pandey, 2017).

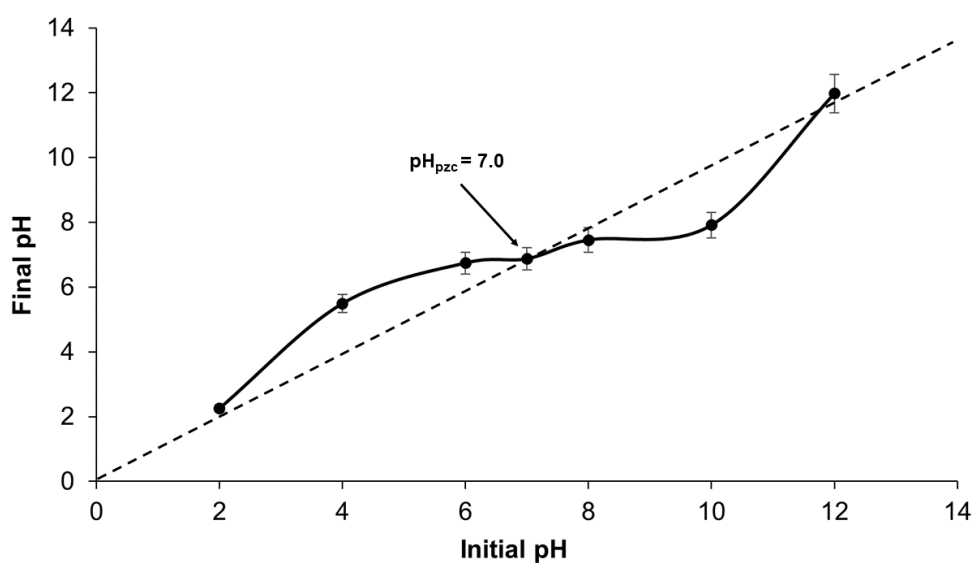


Figure 4.8: The pHpzc plot for TiO₂-1/Ag 2%/CA 0.5% photocatalyst using 0.1 M NaCl solution

4.2 Preliminary Experiments

4.2.1 Effect of Ionic Liquid and Dosage

Figure 4.9 depicts the effect of varying the volume of Bmim[Ac] (0.0 - 5.0 mL) and dosage of TiO₂-IL (0.1 g/L - 5.0 g/L) on the MB removal. This preliminary experiment focused on determining the best volume of IL needed in the synthesis of sol-gel TiO₂ to achieve high photocatalytic performance. The MB removal ranged from 30.7% to 94.7%, with the overall pattern indicating that MB removal increases with the increasing IL volume. However, it is noticeable that MB removal is low at 0 mL and 5 mL of IL when compared to other volumes of IL. It can be observed that the efficiency of TiO₂ synthesised with 1 mL of Bmim[Ac] continuously showed the highest removal of MB for all photocatalyst dosages, except at 5 g/L (Figure 4.9). This implies that the degradation efficiency of TiO₂ increases from 0 mL of IL to 1 mL of IL, with decreased efficiency as the volume of IL increases.

Another observation was the photocatalytic performance of TiO₂ improved when IL was included in the synthesis. Controlled growth of TiO₂ particles during the synthesis is

mainly due to the interactions of Lewis acid-base and intermolecular hydrogen bonding between IL and titania (Preethi et al., 2017). The BET results (Table 4.2) also demonstrated that with the application of IL in the synthesis, the specific surface area of TiO₂ increases and thus enhances the efficiency of the photocatalyst. A review of selected studies that used IL in the synthesis of TiO₂ revealed that employing IL produces TiO₂ with a high surface area and crystallinity (Table 4.3). TiO₂-1 synthesised in this study demonstrates higher surface area as compared to previous works (Table 4.3) that applied the sol-gel method in the synthesis. Upon the addition of IL, the specific surface area of the TiO₂ photocatalyst increased and provided more active sites for the adsorption of MB. However, using a higher volume of IL in the synthesis resulted in a lower photocatalytic performance of TiO₂ (Paszkievicz et al., 2016). A high concentration of IL may contribute to the high concentration of TiO₂ particles on its surface, which prevents the formation of spherical microparticles with a developed surface area (Liu et al., 2009).

Figure 4.9 also depicts the effect of dosage on the photocatalytic performance of TiO₂ for MB removal. A photocatalytic dosage of 0.1 g/L contributed to lower MB removal, ranging from 33.7% to 56.6%, and increasing MB removal from 26.7% to 74.9% for 0.5 g/L. There are no obvious changes in MB removal as the photocatalyst dosage increases from 1.0 g/L to 5.0 g/L, suggesting that 1.0 g/L is sufficient to attain high MB removal. The photocatalyst has reached saturation, and increasing the photocatalyst dosage does not improve the removal of MB any further. Although the concentration of active sites rises with increasing photocatalyst dosage, there is a saturation point when light penetration is hindered due to the presence of excess free TiO₂ particles (Shet & Shetty, 2016). Hence, it can be concluded that 1 mL of IL provided the highest MB removal and as such, TiO₂-1 photocatalyst was chosen for further photocatalytic experiments.

Table 4.3: Properties of TiO₂-based Photocatalysts synthesised through IL-assisted methods

Precursors	IL	Synthesis method	Phase composition	Structure properties	BET (m ² /g)	Reference
Titanium tetraisopropoxide, isopropyl alcohol	[ChCl][ZnCl ₂] ₂	Sol-gel	Anatase	Mesoporous structure	75.1	Preethi et al. (2017)
Titanium tetraisopropoxide, acetic acid	[Bmim][PF ₆]	Sol-gel	Anatase, rutile	Mesoporous structure	50-110	Yan et al. (2018)
Titanium tetraisopropoxide, water	[Emim][Ac]	Hydrothermal	Anatase	Flowerlike particles	51.8-147.8	Zhang et al. (2015)
Tetrabutyl titanate, absolute ethanol	[Bmim]PF ₆	Hydrothermal	Anatase	Mesoporous structure	116.9	Huang et al. (2020)
Ti(IV) n-butoxide, absolute ethanol	[ODmim]Cl, [TDmim]Cl	Solvothermal	Anatase	Microspheres	119-211.0	Gołębiewska et al. (2018)
TiO ₂ particles, titanium (IV) n-butoxide, absolute ethanol	[Bmim]Br, [Bmim]PF ₆ , [Bmim][OctS O ₄]	Solvothermal	Anatase	Microspheres	76.0-271.0	Łuczak et al. (2017)
Titanium (IV) butoxide, 2-propanol	Bmim[Ac]	Sol-gel	Anatase	Spherical structures	174.8	This work

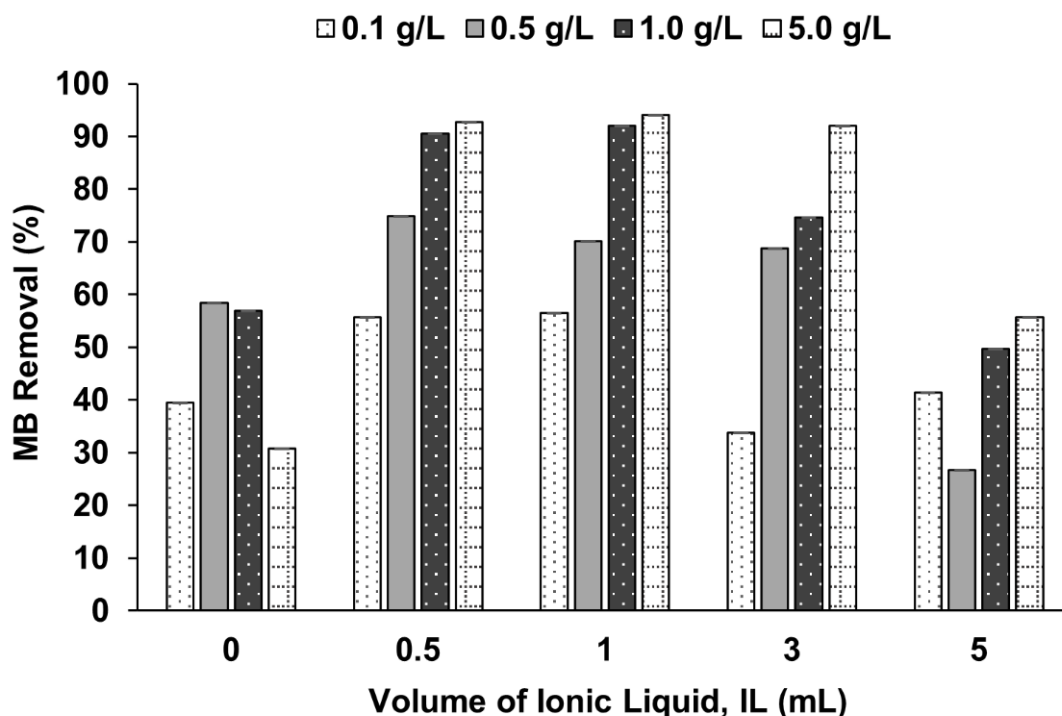


Figure 4.9: Photocatalytic degradation of MB using TiO_2 synthesised with IL (0.0 – 5.0 mL), photocatalyst dosage (0.1 g/L – 5.0 g/L), initial MB concentration (5 ppm) and unadjusted pH (7.4)

4.2.2 Effect of Ag Concentration

The effect of Ag concentration on the removal of MB is investigated by using 1 g/L of $\text{TiO}_2\text{-Ag}$ in 5 ppm of MB at varying Ag concentrations (0.5 wt% – 5 wt%). Based on Figure 4.10a, the dark adsorption of MB by TiO_2/Ag photocatalysts ranged from 1.7% (TiO_2/Ag 0.5%) to 20.3% (TiO_2/Ag 2%) and then decreased with the increasing Ag concentration. The improved adsorption capacity of TiO_2/Ag is attributed to the formation of a Lewis acid-base on the surface of the catalyst (Yunhai Zhang et al., 2020). In addition, it was found that TiO_2 's surface acidity increases with Ag concentration, which contributes to a high concentration of adsorbed active sites on the modified surface of TiO_2 (Dong et al., 2015). It is also discovered that MB removal increases with UV irradiation time and Ag

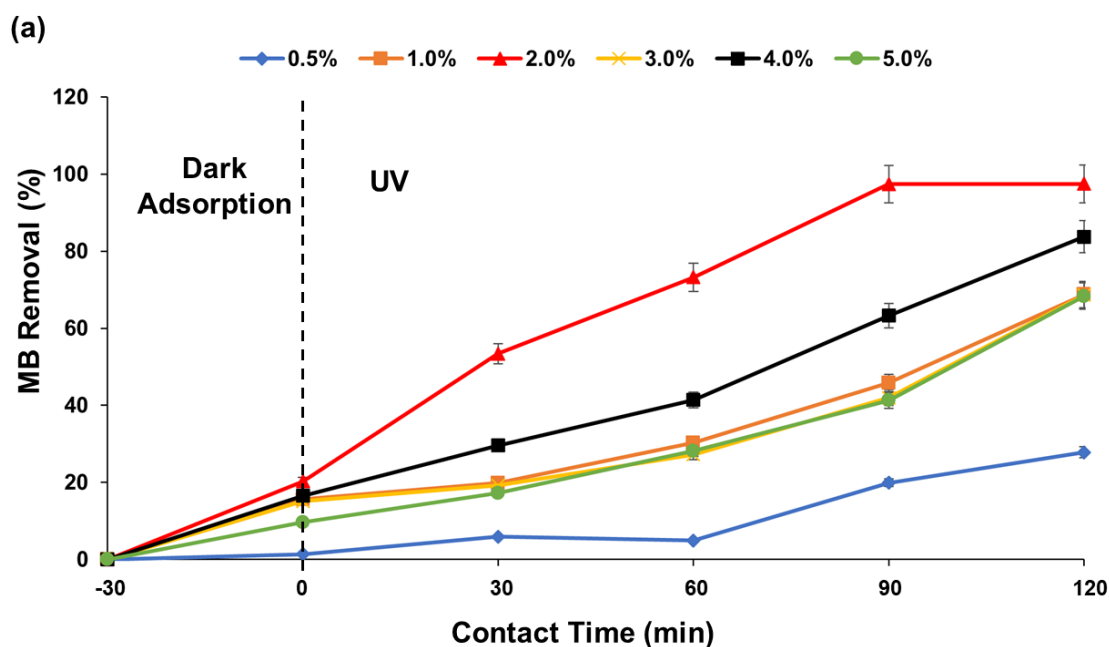
concentration. Among all these samples, TiO₂/Ag 2% displayed a degradation efficiency of 97.4% within 120 min. Photocatalytic performance improves at higher Ag concentrations from 0.5% to 2%, reaching a maximum removal at 2%, and decreases thereafter.

When Ag is introduced into the photocatalyst, it acts as an electron acceptor and forms the Schottky barrier with TiO₂, reducing the recombination rate and thus improving the photocatalytic performance (Zhao et al., 2020). However, higher Ag concentration may cause Ag to agglomerate and increase the interface between Ag and TiO₂ (Hamed et al., 2020). A high concentration of negatively charged Ag particles increases hole capture and lowers charge separation, subsequently contributing to lower degradation efficiency (Hosseini et al., 2011). Studies have reported that the concentration of Ag typically ranged from 1 wt% to 5 wt% (Wang et al., 2015; Shojaie et al., 2017). Based on the photocatalytic performance, 2 wt% of TiO₂/Ag was selected as the most suitable Ag concentration to be combined with CA.

4.2.3 Effect of CA Concentration

The effect of CA on TiO₂-1/Ag photocatalyst was investigated by varying the wt% of CA from 0.5 to 5%. The adsorption of MB in the dark ranged from 17.3% (TiO₂-1/Ag 2%/CA 4%) to 26.8% (TiO₂-1/Ag 2%/CA 2%), implying that the addition of CA slightly increases the adsorption of MB in the dark (Figure 4.10b). Besides that, it was also observed that all six TiO₂-1/Ag 2%/CA photocatalysts contributed to almost similar photocatalytic performance upon UV irradiation. After 30 min of UV irradiation, all samples demonstrated increasing MB removal before reaching a near plateau. However, it was noticeable that TiO₂-1/Ag 2% with 0.5 wt% of CA exhibited a rapid increase in MB removal (61.9%) after 30 min of UV irradiation as compared to other samples. A lower concentration of CA results in higher MB removal within 60 min of UV irradiation in comparison to a higher CA

concentration in the photocatalyst. An increase in the concentration of CA has been reported to cause agglomeration in the photocatalyst and contribute to lower active sites of the TiO_2/Ag (Kanakaraju et al., 2022). TiO_2 particles form agglomerates easily because of its extremely large surface area, and this provides a tremendous driving force for particle bonding (Zhang et al., 2013). Based on the photocatalytic performance, 0.5 wt% of CA was chosen as the best concentration due to its consistency and high photocatalytic efficiency under UV irradiation.



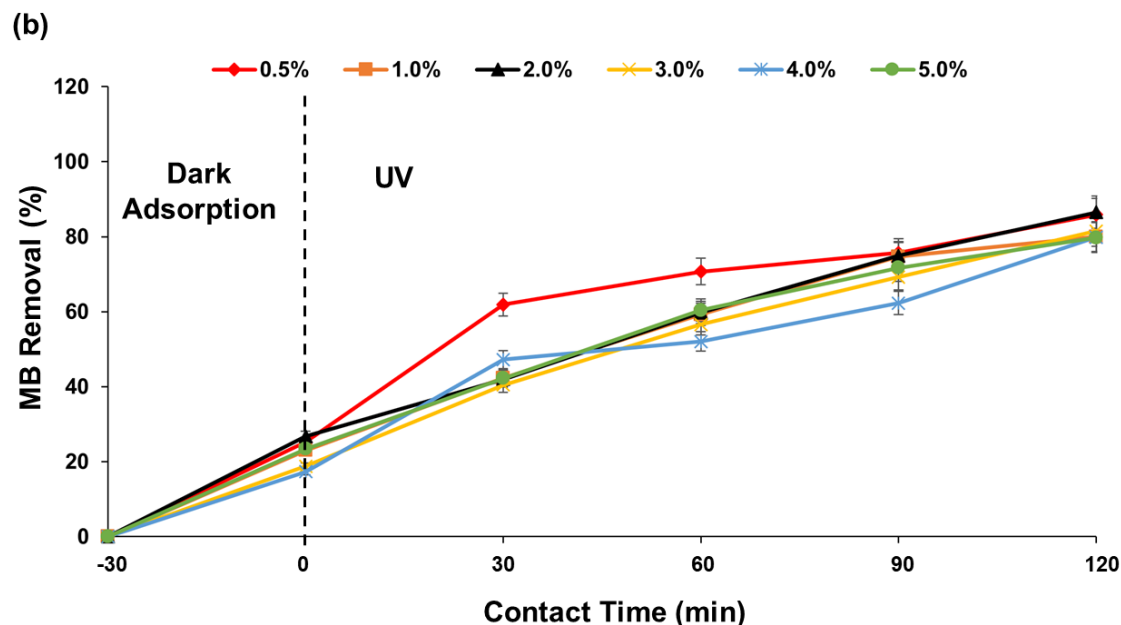


Figure 4.10: (a) Photocatalytic degradation of MB by TiO_2 -1/Ag with different Ag concentrations (0.5 wt% - 5.0 wt%) and (b) TiO_2 -1/Ag 2%/CA with different CA concentrations (0.5 wt% - 5.0 wt%) under UV irradiation

4.3 Control Experiments

Control experiments under dark conditions, visible light and UV irradiation were performed using TiO_2 -0, TiO_2 -1, TiO_2 -1/Ag 2% and TiO_2 -1/Ag 2%/CA 0.5% to compare the role of adsorption on MB removal. Dark adsorption for all samples varied from 6.5% (TiO_2 -1) to 38.7% (TiO_2 -1/Ag 2%/CA 0.5%) (Figure 4.11). In general, the photocatalysts demonstrated low MB removal in the dark as all samples were inactive in the presence of UV irradiation (Kanakaraju et al., 2022). TiO_2 -1/Ag 2%/CA 0.5% has the highest adsorption in the dark condition (Figure 4.11) as compared to other samples, possibly due to the presence of CA in the photocatalyst. The adsorption of MB molecules on CA's hydrophobic can be due to the dual action of Van der Waals force and hydrophobicity between CA and MB molecules (Shalan et al., 2021).

Under visible light irradiation, MB removal by TiO₂ samples was only 13.8% (TiO₂-1) and 22.0% (TiO₂-0) within 120 min (Figure 4.11). Literature has established that TiO₂ only exhibit absorption in the UV light region (Khan et al., 2014; Ding et al., 2015). The poor performance of TiO₂ samples under visible light degradation is due to their wide band gap energy. When Ag was introduced into the photocatalyst system, TiO₂'s degradation under visible light increased dramatically from 13.8% to 95.0%. (Figure 4.11) ascribed to the surface plasmon absorption of Ag particles in the visible region (Liu et al., 2014). Past works have shown the effective separation of electrons and holes in TiO₂ by Ag (Ding et al., 2015; Basumatary et al., 2022). It was observed that when CA was added to the photocatalyst, 100% of MB removal was achieved within 120 min (Figure 4.11). TiO₂-1/Ag 2%/CA 0.5% demonstrated a slight increment in MB removal as compared to TiO₂-1/Ag 2%.

MB removal ranged from 41.1% (TiO₂-0) to 100% (TiO₂-1/Ag 2%/CA 0.5%) under UV irradiation, suggesting that UV irradiation increases MB removal. It is noticeable that there is a great increase in MB removal under UV irradiation by TiO₂-1 compared to visible irradiation, which may be attributed to the high surface area that allows more MB molecules to be adsorbed on the photocatalysts. TiO₂-1/Ag 2% also exhibited rapid MB removal upon UV irradiation, followed by complete MB removal after 60 min of UV exposure (Figure 4.11), indicating the charge transfers occur more efficiently under UV irradiation as compared to visible light for TiO₂-1/Ag 2% photocatalyst. Meanwhile, TiO₂-1/Ag 2%/CA 0.5% showed increasing MB removal upon UV irradiation and reached complete removal within 120 min as well. TiO₂-1/Ag 2% and TiO₂-1/Ag 2%/CA 0.5% exhibit comparable UV and visible irradiation performance. It was also observed that the dark adsorption by TiO₂-1/Ag 2%/CA 0.5% has contributed to 41.1% in the overall performance. Based on these

results, there is no significant difference in the photocatalytic performance between TiO_2 -1/Ag 2% and TiO_2 -1/Ag 2%/CA 0.5%. This may imply that the presence of CA may not contribute to adsorption or photocatalytic activity greatly, but rather function as a support. Previous research has shown that inert supports are functionalised with active nanoparticles, which helped in maintaining the stability of the TiO_2 photocatalyst and easy recovery of the photocatalyst after photocatalytic treatment (Marinho et al., 2017).

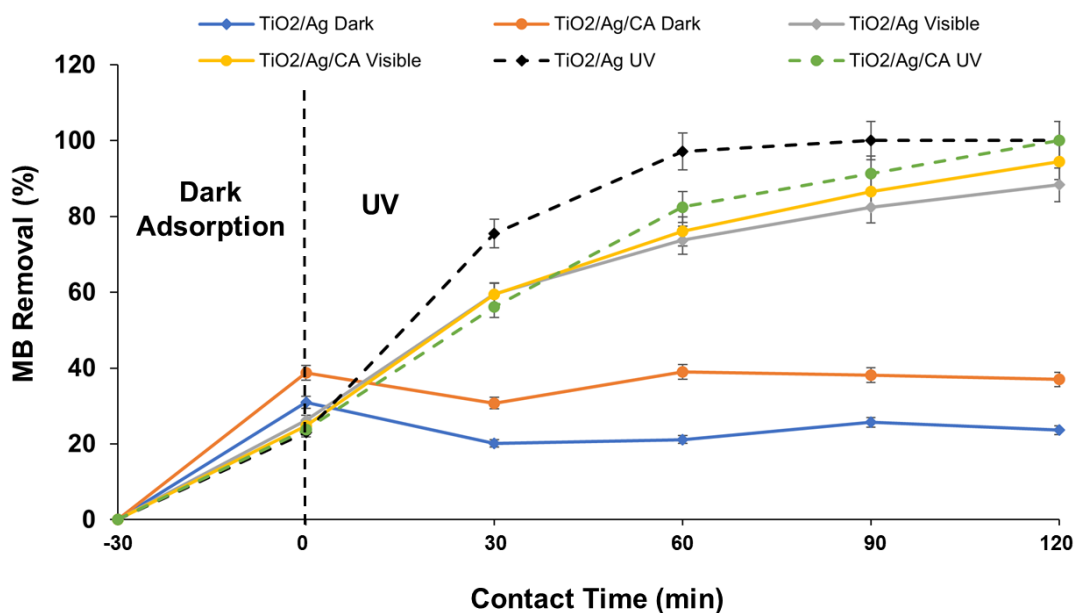


Figure 4.11: Photocatalytic degradation of MB under dark condition, visible light and UV light (Experimental conditions: 1.0 g/L photocatalyst dosage, 5 ppm MB dye and unadjusted pH 7.4)

4.4 Parameters Affecting the Photocatalytic Performance of TiO_2 -1/Ag 2%/CA 0.5%

4.4.1 Effect of Dosage

Figure 4.12a illustrates the removal of MB using the best-performing TiO_2 -1/Ag 2%/CA 0.5% photocatalysts at varying dosages (0.1–20.0 g/L). The MB removal increases with the increasing photocatalyst dosage from 35.5% at 0.1 g/L) to complete removal at 3 g/L. Higher removal of MB can be associated with increased active sites as the photocatalyst

dosage increases. Since there is a higher number of active sites, more organic pollutants are absorbed on the TiO_2 surface resulting in a higher MB removal (Khaki et al., 2017). A further increase of dosage beyond 3 g/L did not result in any positive increase in removal suggesting that 3 g/L is sufficient to achieve complete MB removal within 120 min. Aggregation of free TiO_2/Ag particles at a higher photocatalyst dosage (20.0 g/L) can lead to decreased photocatalytic efficiency by reducing the concentration of active sites and surface area available for light absorption. In addition, the overloading of TiO_2/Ag particles resulted in greater opacity, screening and scattering effect, which prevented light penetration to the reaction medium (Shet & Shetty, 2016).

4.4.2 Effect of MB Concentration

The performance of 3 g/L of TiO_2 -1/Ag 2%/CA 0.5% on the removal of MB at varying concentrations (5 – 25 ppm) is illustrated in Figure 4.12b. When the initial MB concentration increases from 5 ppm to 25 ppm, the MB removal declines from 100% to 39.5%. At low MB concentration, complete MB removal is achieved since there is a lesser amount of MB to be adsorbed on the active sites of the photocatalyst. However, as the concentration of MB increases, the amount of MB molecules increases as well and the active sites of the photocatalyst are insufficient for the degradation of a high amount of MB molecules. As a result, lower MB removal can be observed at higher MB concentrations. In addition, the density of the solution also increases with increasing MB concentration, which restricts the penetration of light into the solution (Kumar et al., 2015). Hence, the reduced energy or photons contributed to the poor photocatalytic efficiency of $\text{TiO}_2/\text{Ag}/\text{CA}$ photocatalysts at higher MB concentrations (Mozia et al., 2009). Thus, 5 ppm of MB concentration was determined to be the most suitable initial concentration for TiO_2 -1/Ag 2%/CA 0.5% to perform at its maximum efficiency.

4.4.3 Effect of pH

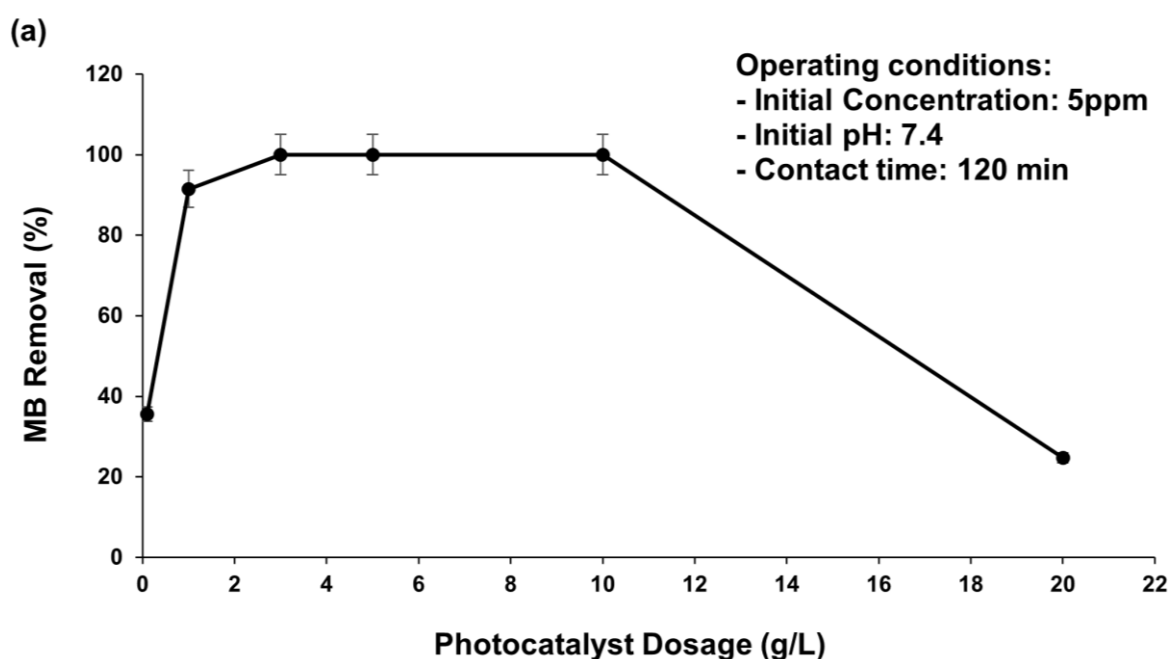
The removal of MB at different pH values, namely pH 3, 6.5, and 12, was investigated using 3 g/L of TiO₂-1/Ag 2%/CA 0.5% and 5 ppm of MB solution. Figure 4.12c revealed that when the pH value was adjusted to 3, dye removal was the lowest compared to other pHs. Reduced MB adsorption at lower pH is caused by the competition for potential adsorption sites between excess H⁺ ions and MB molecules (Jawad et al., 2017). Lower pH causes H⁺ ions to react with the hydroxyl group, which restrains the hydrogen bond between MB and TiO₂/Ag/CA photocatalyst (Qin et al., 2017).

The MB removal increases from 23.4% to 86.9% when the pH value increases from pH 3.0 to 6.5. MB removal of 88.7% was obtained at a basic pH of 12 and this indicates that as the pH increases, the MB removal increases as well. Higher degradation of MB was also reported at higher pH ranging from pH 9 to 13 when using TiO₂/Ag photocatalyst (Kumar et al., 2015; Sahoo et al. 2012). In basic pH, the high concentration of hydroxide ions (OH⁻) resulted in a higher concentration of free radicals which are important oxidizing species for MB degradation (Kumar et al., 2015). The results revealed that TiO₂-1/Ag 2%/CA 0.5% photocatalyst attained the highest efficiency at an unadjusted pH, with the highest MB removal of 95.64% being obtained at an unadjusted pH of 7.4.

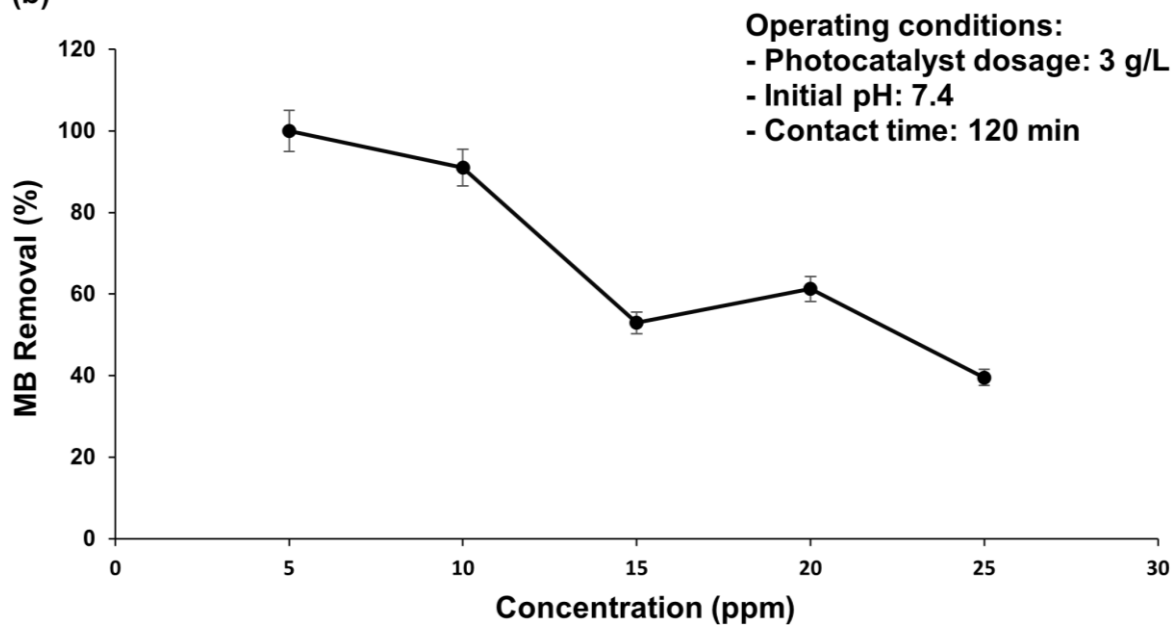
4.4.4 Effect of Radical Scavenger

MB removal using different radical scavengers (e.g. ethylene glycol, 2-propanol, and ascorbic acid) was investigated using 3 g/L of TiO₂-1/Ag 2%/CA 0.5% and 5 ppm of MB solution (Figure 4.12d). The introduction of 2-propanol and ascorbic acid led to the complete elimination of MB. According to Figure 4.12d, the presence of ethylene glycol in the system resulted in a reduction of MB removal compared to the scenario where scavengers were not added. This demonstrates that photocatalytic degradation of MB by TiO₂-1/Ag 2%/CA 0.5%

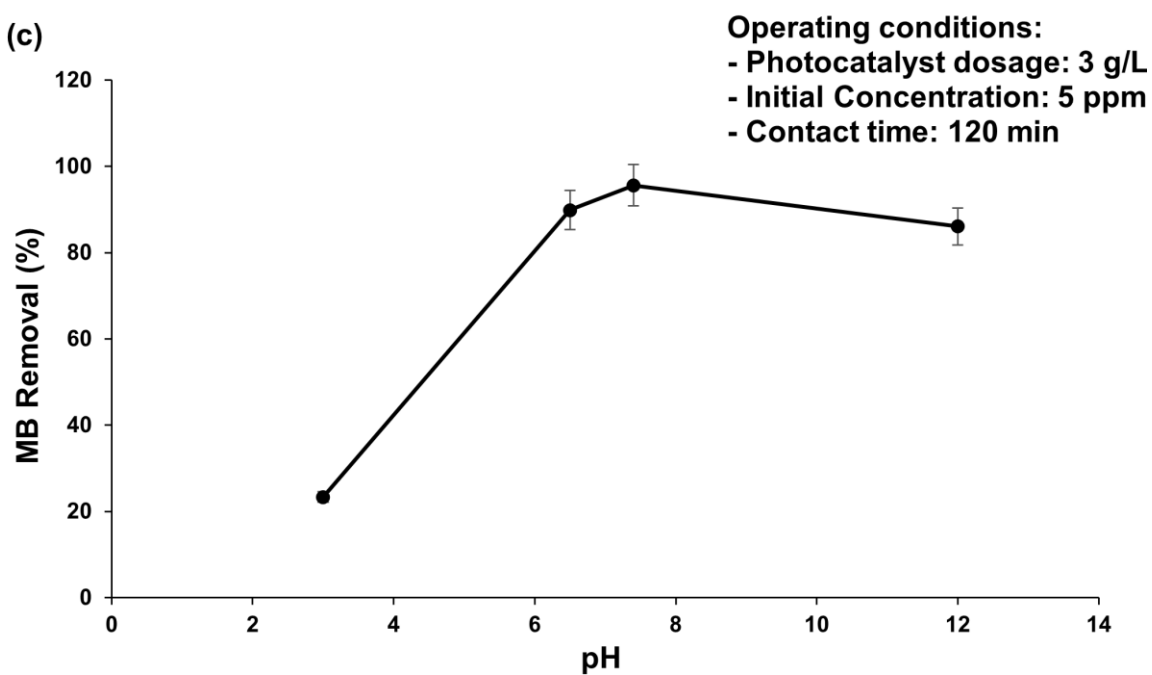
is dependent on the reactive species h^+ . A similar observation can be drawn from a study conducted by Rajput et al. (2018), in which the introduction of h^+ scavengers resulted in a decline in the photocatalytic efficacy of Ag-doped graphene TiO_2 for pentachlorophenol degradation. Similarly, Raza et al. (2020) exhibited that the presence of ethylene diamine tetraacetic acid (EDTA) as a h^+ scavenger considerably reduced the degradation of MB. This underscores the substantial scavenging of photogenerated holes, leading to the inhibition of the overall photodegradation process of MB. Based on Figure 4.12d, it is evident that h^+ scavenger is the main oxidative species involved in the degradation of MB by TiO_2 -1/Ag 2%/CA 0.5% photocatalyst.



(b)



(c)



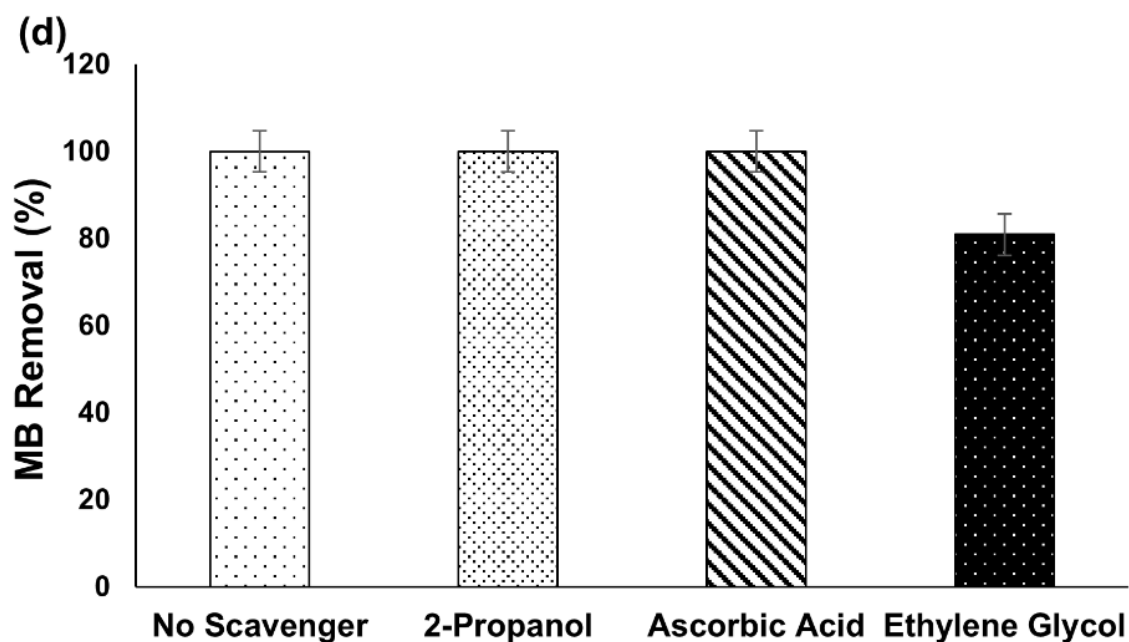


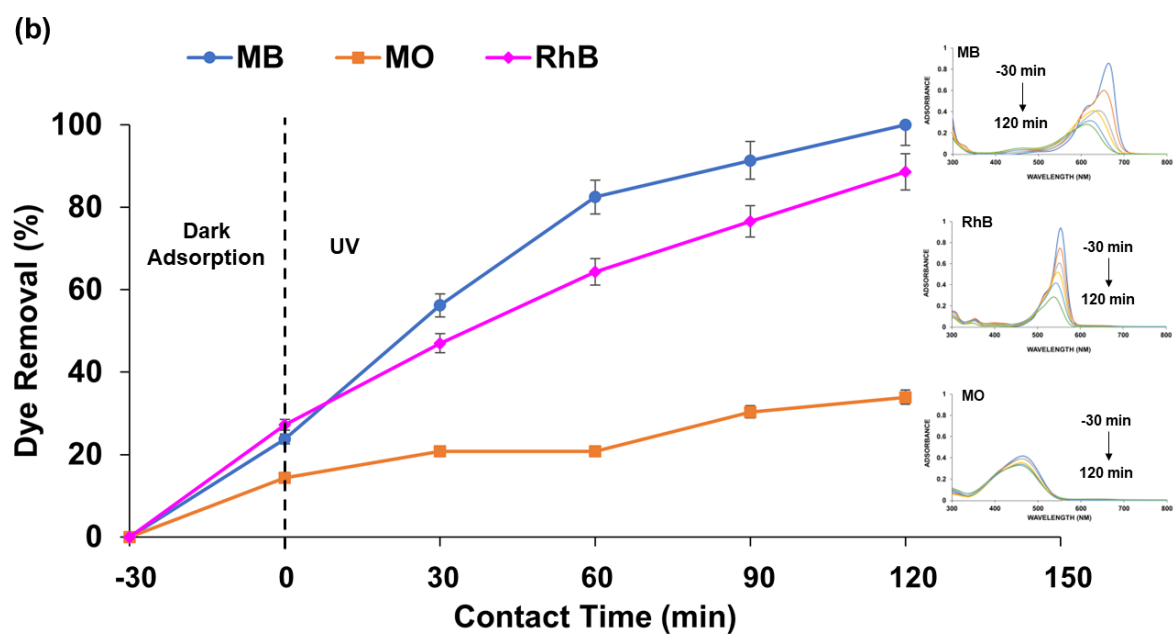
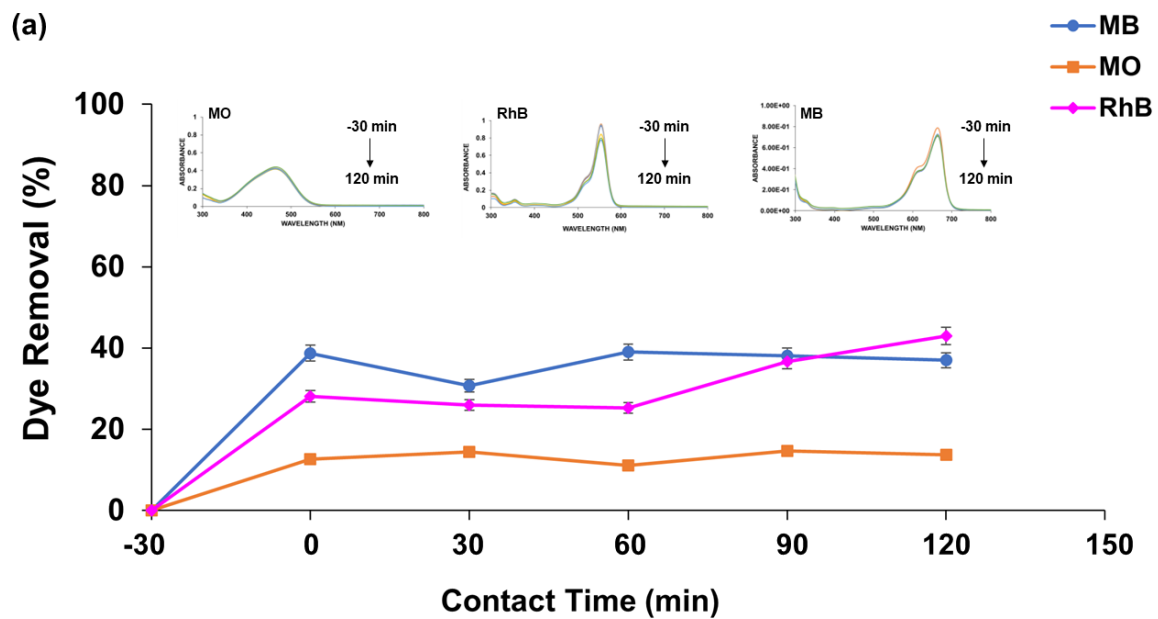
Figure 4.12: (a) Photocatalytic degradation of TiO_2 -1/Ag 2%/CA 0.5% at different photocatalyst dosages (0.1 – 20.0 g/L), (b) different initial concentrations of MB (5 – 25 ppm), (c) different pHs of MB (pH 3- pH 12), and (d) presence of radical scavengers

4.4.5 Effect of Individual and Mixed Dyes

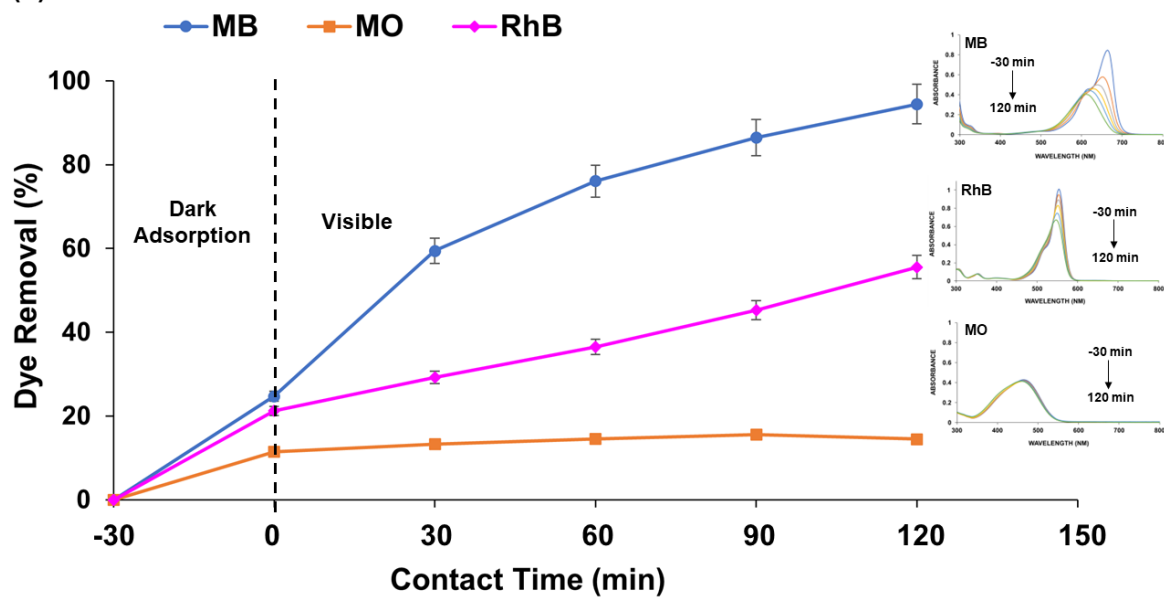
The photocatalytic performance of TiO_2 -1/Ag 2%/CA 0.5% photocatalyst was compared using individual dyes, MB, MO and RhB and mixed dye solutions containing equimolar of MO, RhB and MB. From Figure 4.13, it can be seen that TiO_2 -1/Ag 2%/CA 0.5% photocatalyst consistently exhibits the highest degradation efficiency of MB in both individual and mixed dyes under all conditions. MO appeared to be the least removed individual dye in all conditions (Figure 4.13a-c). Meanwhile, RhB demonstrated 66.0% under visible light irradiation and complete removal under UV irradiation, in contrast, to complete MB removal under both visible and UV irradiations. The difference in the photocatalytic performance of TiO_2 -1/Ag 2%/CA 0.5% towards these dyes is caused by the electrostatic interaction between dyes and the photocatalyst surface (Duan et al., 2018). Cationic dyes such as MB and RhB can be adsorbed easily by electronegative clusters due

to the electrostatic attraction, whereas anionic dyes such as MO are not able to due to their strong electrostatic repulsion (Bootharaju & Pradeep, 2013). The poor adsorption of MO on $\text{TiO}_2\text{-1/Ag 2\%/CA 0.5\%}$ photocatalyst resulted in lower photocatalytic degradation as compared to the other cationic dyes.

There have not been many reports on mixed dyes degradation for mixed basic and acidic dyes, as the reactions of the photoelectron-basic dyes and photo-hole-acidic dye may not be able to be controlled simultaneously (Lebedev et al., 2019). However, there has been a report on the ZnFe_2O_4 nanophotocatalyst for mixed dyes removal of MB and RhB, whereby ~99.0% of removal were achieved under both individual and mixed dye conditions (Patil et al., 2018). Similarly, $\text{TiO}_2\text{-1/Ag 2\%/CA 0.5\%}$ photocatalyst also exhibited higher photocatalytic degradation of dyes, especially MO under mixed dye conditions. As can be observed in Figure 4.13d, the adsorption of MO under mixed dye increased significantly as compared to that of the individual dyes (Figure 4.13a-c). It can also be noted that the adsorption process played a significant role in the overall elimination of the co-existing dyes, in contrast to their individual presence. The contribution of adsorption to the removal of mixed dyes ranged from 81.8% to 93.6%, suggesting that the role of adsorption appears superior to the photocatalysis process under mixed dyes conditions (Figure 4.13d). Similar performance of mixed dyes removal by $\text{TiO}_2\text{-1/Ag 2\%/CA 0.5\%}$ was observed in the UV-Vis absorption spectra (Figure 4.13d) under all conditions (dark condition, visible and UV light irradiation). $\text{TiO}_2\text{-1/Ag 2\%/CA 0.5\%}$ photocatalyst can be considered an efficient photocatalyst under mixed dye conditions as it can degrade multiple dyes simultaneously and enhance dye removal as compared to individual dye degradation. $\text{TiO}_2\text{-1/Ag 2\%/CA 0.5\%}$ has shown high adsorption of dyes, which may be due to having a higher surface area (Table 4.2).



(c)



(d)

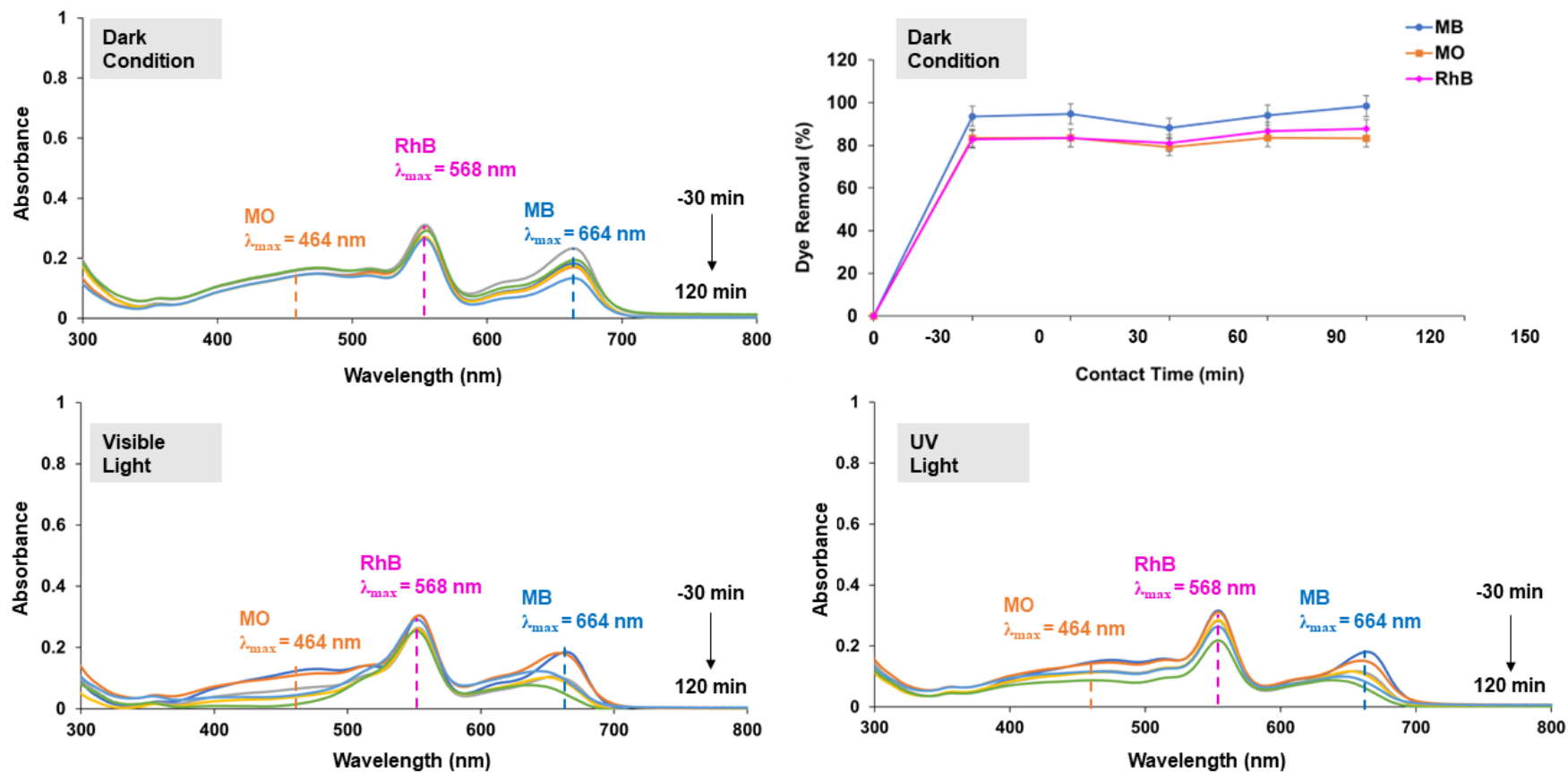


Figure 4.13: Photocatalytic degradation of individual dyes under (a) dark condition, (b) visible light irradiation, (c) UV light irradiation and (d) mixed dyes under dark condition and UV-Vis adsorption spectra for dye degradations under all conditions (Experimental conditions; photocatalyst dosage: 3.0 g/L, initial dye concentration: 5 ppm and pH: unadjusted pH 7.4)

4.5 Recyclability Study

The recycling potential of the TiO_2 -1/Ag 2%/CA 0.5% photocatalyst for the degradation of MB dye was assessed to determine its stability. The performance of TiO_2 -1/Ag 2%/CA 0.5% photocatalyst on MB removal greatly declined from 100.0% in the first cycle to 23.5% in the third cycle (Figure 4.14). The loss of photocatalysts during the recycling process can contribute to reduced MB removal after each photocatalytic cycle (Kanakaraju et al., 2018). As the photocatalyst dosage decreases, the number of active sites decreases resulting in reduced photocatalytic efficiency. In addition, the remaining MB molecules from previous cycles might have occupied the active sites of TiO_2 (Liao et al., 2019) leading to the saturation of the active sites. SEM images (Figure 4.15) revealed that the morphology of the photocatalyst has changed slightly from the first cycle to the third cycle while the EDX results (Table 4.4) showed the absence of Ag and CA in the photocatalyst after the first cycle.

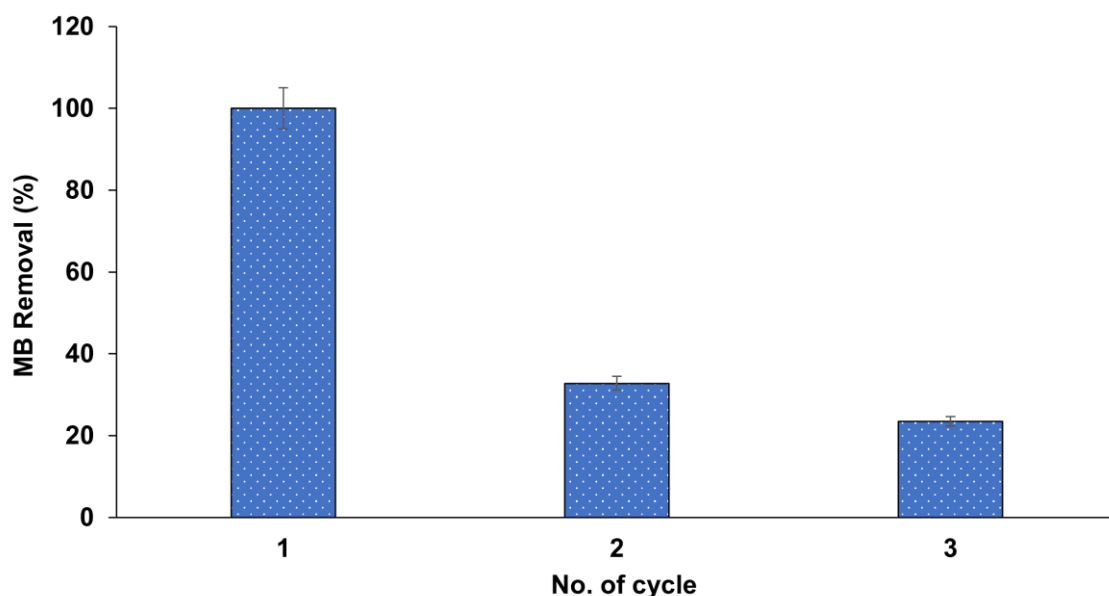


Figure 4.14: Photocatalytic Degradation of MB at different cycles

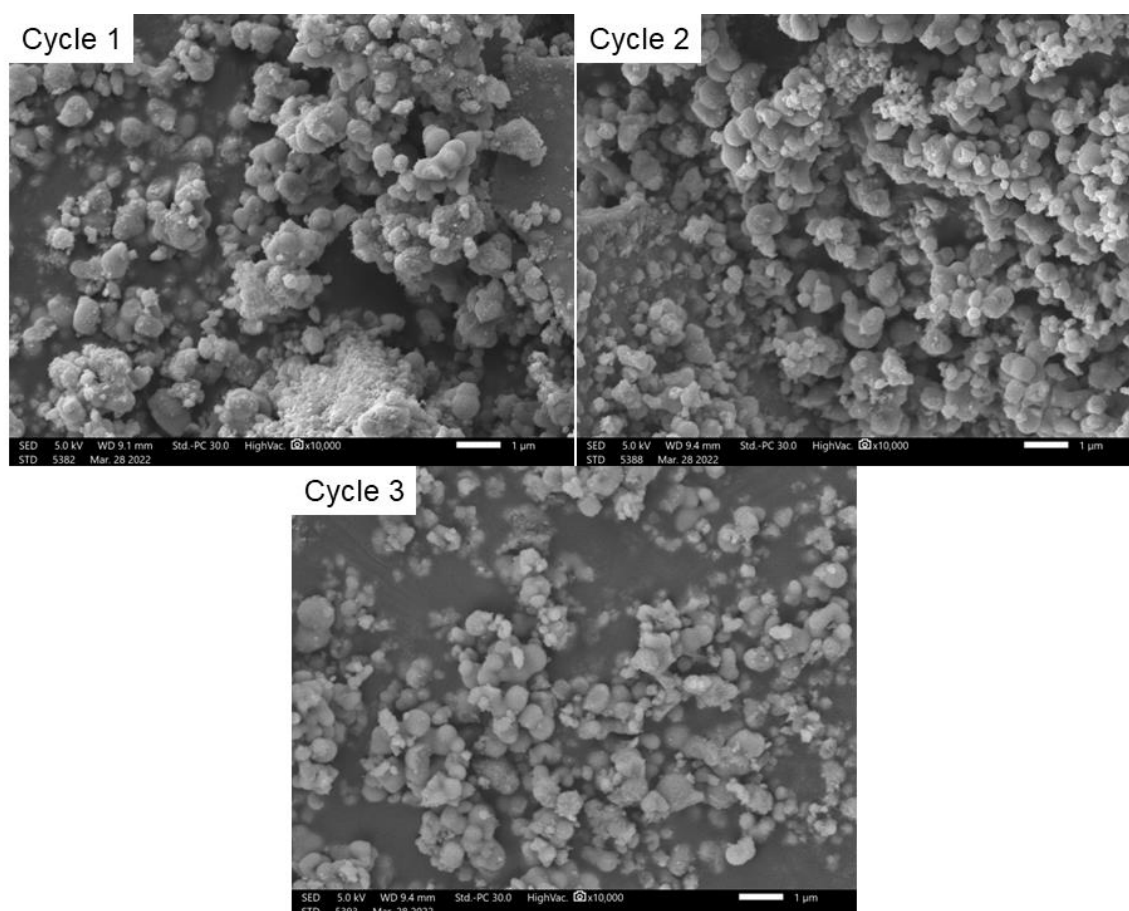


Figure 4.15: SEM images of TiO₂-1/Ag 2%/CA 0.5% Photocatalyst at different cycles of photocatalytic treatment

Table 4.4: Elemental Compositions of TiO₂-1/Ag 2%/CA 0.5% Photocatalyst at different cycles of photocatalytic treatment

Samples	Weight Percentage of Elements (wt%)				
	Ti	O	Ag	C	Total
Cycle 1	54.87±0.20	43.13±0.11	2.00±0.05	ND	100.00
Cycle 2	53.93±0.19	45.07±0.10	ND	ND	100.00
Cycle 3	52.50±0.25	47.50±0.14	ND	ND	100.00

*ND: Not Detected

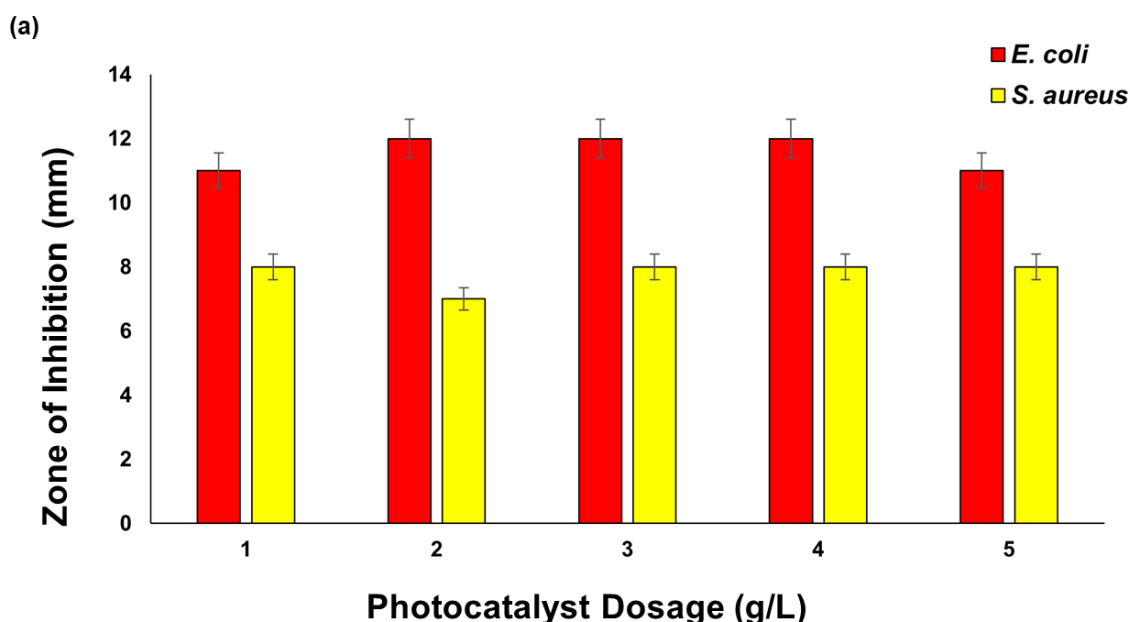
4.6 Antibacterial Study

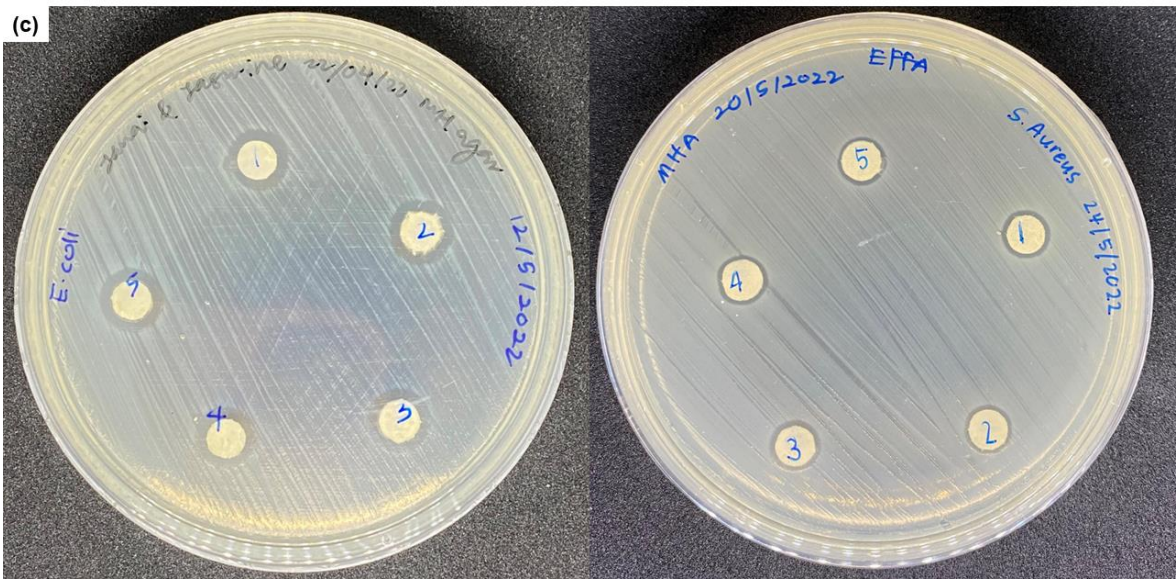
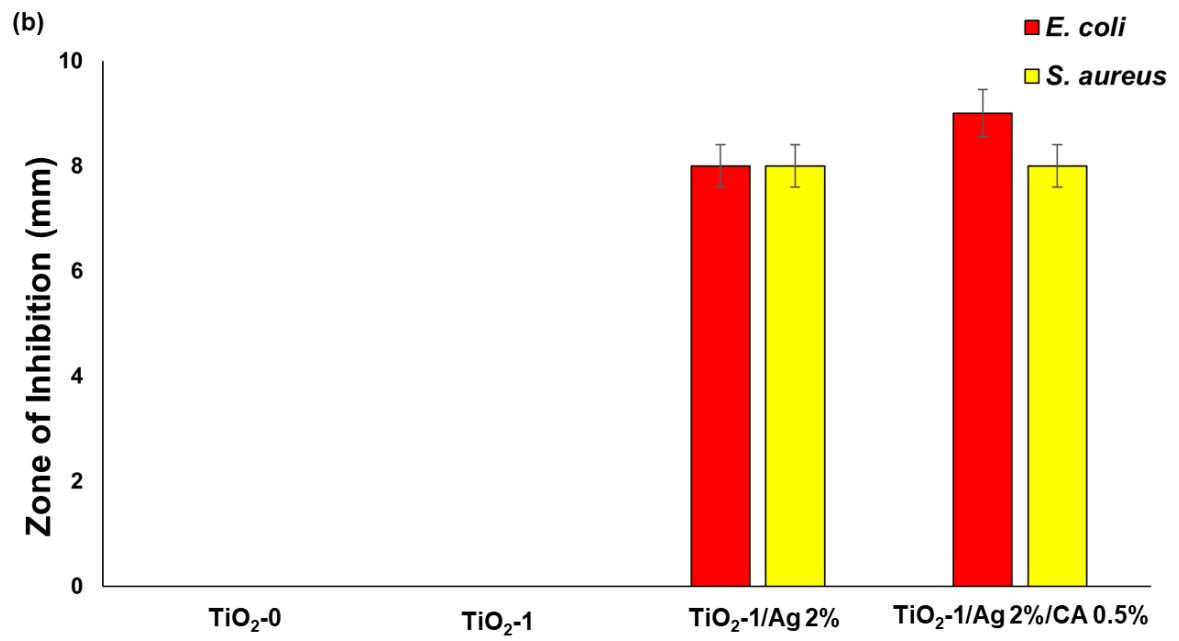
The antibacterial activity of the TiO_2 -1/Ag 2%/CA 0.5% photocatalyst was determined against the Gram-positive *S. aureus* and Gram-negative *E. coli*. The antibacterial properties of different TiO_2 -1/Ag 2%/CA 0.5% photocatalyst dosages (1, 2, 3, 4 and 5 g/L) on *E. coli* and *S. aureus* were also studied. Inhibition zones seen in Figure 4.16a and Figure 4.16b, demonstrated the antibacterial activity of TiO_2 -1/Ag 2%/CA 0.5% photocatalyst against both bacterial species. However, the results revealed that varying the concentrations does not contribute to a significant difference in the inhibition zone for both bacteria. In general, higher antibacterial activities were observed against *E. coli* compared to *S. aureus*. A similar observation was reported in a previous study when multifunctional cellulose/ TiO_2 /Ag composite nanofibers were tested against *E. coli* and *S. aureus* (Ashraf et al., 2020).

Based on Figure 4.16a, a photocatalyst dosage of 4 g/L was chosen to observe the antibacterial activity of undoped TiO_2 , TiO_2 -1/Ag 2% and TiO_2 -1/Ag 2%/CA 0.5% against *E. coli* and *S. aureus*. Figure 4.16d shows that bacterial colonies were present around the disc with TiO_2 -0 (1) and TiO_2 -1 (2), indicating that undoped TiO_2 does not possess any antibacterial activity against both bacteria tested. However, a clear zone of inhibition was formed around discs with TiO_2 -1/Ag 2% (3) and TiO_2 -1/Ag 2%/CA 0.5% (4). The formation of inhibition zones exhibited the antibacterial effect of TiO_2 -1/Ag 2%/CA 0.5% on both bacteria, with a higher inhibition zone against *E. coli* as compared to *S. aureus*. Literature has established that the structures of gram-positive and gram-negative cells have different compositions, whereby the layer of peptidoglycan in gram-positive bacteria is thicker as compared to gram-negative bacteria. As a result, it is more difficult for the nanoparticles to penetrate the cell wall of gram-positive bacteria (Dhanalekshmi et al., 2013). Hence, since

S. aureus is a gram-positive bacteria, it has lower inhibition zones as compared to *E. coli*, a gram-negative bacteria.

The gradual diffusion of Ag ions from the TiO₂-1/Ag 2% and TiO₂-1/Ag 2%/CA 0.5% photocatalyst discs into the MH agar during the incubation period demonstrated the antibacterial activity of the photocatalyst. Ag ions that diffused into the MH agar were directly involved in the killing of the bacterial cells, interactions with protein thiol groups or via damage to the bacterial DNA (Jia et al., 2012; Song et al., 2013). The interaction of Ag ions with protein thiol groups is known to inactivate respiratory enzymes that will result in the formation of ROS (Matsumura et al., 2003; Guo et al., 2005). Ag ions behave as photo-generated electron trapping sites and improve the photocatalytic activity by increasing the concentration of hydroxyl radicals, which is important for the photocatalyst in the antibacterial study (Bahadur et al., 2016).





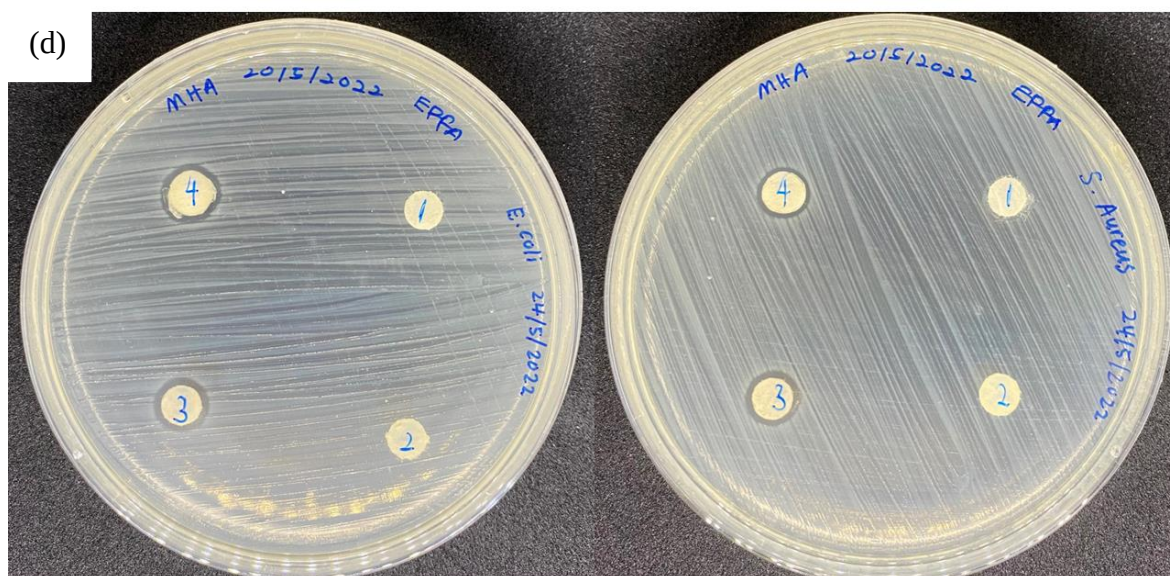


Figure 4.16: Antibacterial activity of (a) different TiO_2 -1/Ag 2%/CA 0.5% Photocatalyst concentrations, (b) TiO_2 , TiO_2 /Ag 2% and TiO_2 /Ag 2%/CA 0.5%, (c) Inhibition zones (mm) by different TiO_2 /Ag 2%/CA 0.5% concentrations and (d) Inhibition zones (mm) by TiO_2 , TiO_2 -1/Ag 2% and TiO_2 /Ag 2%/CA 0.5%, against *E. coli* and *S. aureus* on MH agar

4.7 Proposed Mechanism of Degradation

Figure 4.17 illustrates the proposed mechanism of TiO_2 -1/Ag 2%/CA 0.5% photocatalyst for the degradation of dyes. According to the findings, the adsorption of dyes in dark conditions increased upon the addition of CA in the photocatalyst system. Therefore, it suggests that dye molecules are first adsorbed onto the photocatalyst, and photocatalytic degradation occurs upon the irradiation of UV or visible light. The proposed mechanism has been adapted from previous works (Gogoi et al., 2020; He et al., 2021). Upon light irradiation, the photon ($h\nu$) energy is absorbed by the photocatalyst and excites the electrons (e^-) and positive holes (h^+) at the conduction band and the valence band, respectively. Then, h^+ undergoes photo-oxidation and produces $\bullet\text{OH}$ radicals whereas e^- undergoes photo reduction by reacting with oxygen, O_2 to form superoxide anion radical ($\bullet\text{O}_2^-$). The $\bullet\text{O}_2^-$

reacts with water molecules, H_2O and produces more $\bullet\text{OH}$ radicals. As a result, the $\bullet\text{OH}$ radicals react with degraded dye molecules to form intermediate products and continue to react with the intermediate products. Subsequently, the intermediate products such as R-NH_3^+ , phenol, aniline and aldehydic/carboxylate species are degraded by the $\bullet\text{OH}$ radicals form H_2O and CO_2 .

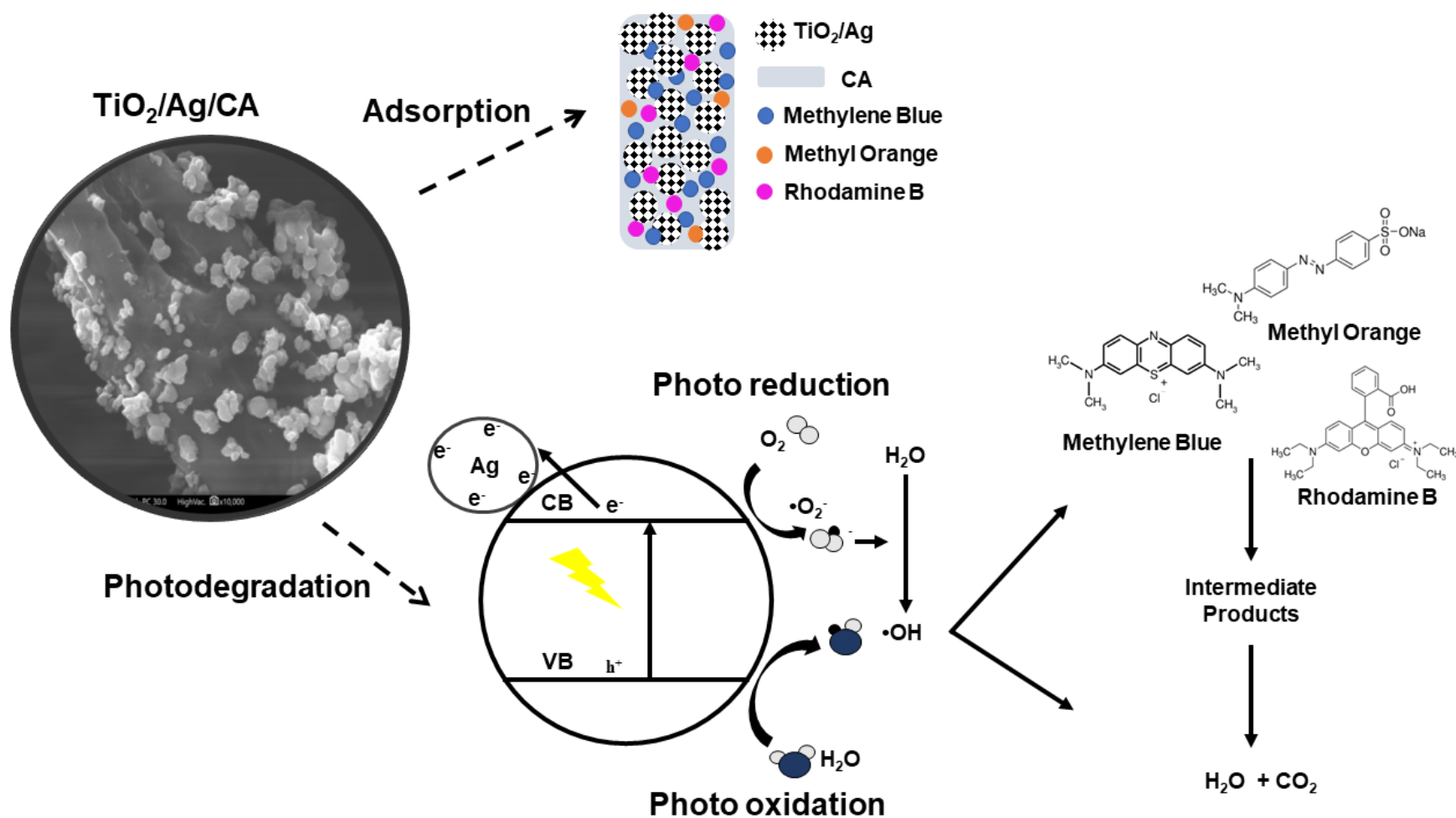


Figure 4.17: Proposed schematic diagram of the degradation of dyes by $\text{TiO}_2\text{-1/Ag 2\%/CA 0.5\%}$ Photocatalyst

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

TiO₂-1/Ag 2 %/CA 0.5% photocatalyst was successfully prepared by utilising IL, Bmim[Ac] as a solvent template for TiO₂ synthesis. The surface area of TiO₂ increased by 34% when Bmim[Ac] was used in the synthesis compared to TiO₂ without the inclusion of IL. The increased specific surface area of TiO₂ contributed to high MB removal under UV irradiation but MB removal remained low under visible light irradiation and dark condition. With the introduction of Ag into TiO₂ via the wet impregnation method, the photocatalytic performance of TiO₂ has significantly increased under visible light and UV light irradiation. This is attributed to the presence of Ag which facilitates efficient charge transfers in visible light and UV light irradiation. The addition of CA into the TiO₂/Ag photocatalyst via mechanical mixing acts as a support for the photocatalyst to ease recovery after photocatalytic treatment. The results revealed that TiO₂-1/Ag 2 %/CA 0.5% consistently exhibited high adsorption under all conditions, such as MB adsorption as high as 41% to the overall dye removal and complete removal of MB dyes within 120 min under the irradiation of UV and visible light. The investigated parameters, such as dosage, pH, initial concentration of MB and the presence of radical scavenger greatly influenced MB removal. One of the major findings included that the degradation of dyes greatly increased when all dyes, MB, MO, and RhB co-exist in the solution. This study has found that MO dye can be removed at least 80% more efficiently under mixed dyes conditions than it could be removed individually, which was only around 8.2% under dark conditions, signifying that adsorption contributed greatly to the removal of dyes under mixed conditions. TiO₂-1/Ag 2 %/CA 0.5%

photocatalyst exhibits high adsorption capacity under mixed dye conditions, which is crucial in photocatalytic treatment as textiles discharged in wastewater frequently contain mixtures. Furthermore, the antibacterial study of TiO₂-1/Ag 2 %/CA 0.5% photocatalysts on *E. coli* and *S. aureus* indicates the antibacterial properties of TiO₂-1/Ag 2 %/CA 0.5% photocatalysts. The use of this material in wastewaters containing dyes and bacteria will be highly sought after due to its possession of adsorption, photocatalysis, and antibacterial functionalities.

5.2 Recommendations

Future investigation into the synthesis of TiO₂ warrants exploration through the utilization of alternative ionic liquids (ILs). This would enable a comprehensive comparison of the efficacy of diverse ILs in generating high surface area photocatalysts. Additionally, the potential reusability of the selected IL for synthesis could be probed by collecting, distilling, and reusing the IL. Notably, this facet was not addressed in the current study due to the primary objective of initially synthesizing TiO₂ using the Bmim-Ac IL, a novel approach in contrast to prior research endeavours. Furthermore, the toxicity level of the IL applied in synthesis procedures should also be tested to explore its potentially harmful effects, especially towards the environment.

Studies on the leaching of Ag from the photocatalyst system could also be investigated to determine the amount of Ag that has leached out from the treatment system. The reason for not conducting a leaching study was that it wasn't included as one of the focal points of this study. Given that previous literature has highlighted potential negative consequences of Ag presence in aquatic environments, the analysis of Ag concentration after photocatalytic treatment becomes exceedingly pivotal and could be incorporated into forthcoming research endeavours. Further study should also be done on incorporating CA in

membrane form instead of powder form. This may help in increasing the mechanical stability and its recyclability for photocatalytic removal of dyes and bacteria.

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APPENDICES

Appendix 1: MB removal using different dosage of TiO₂ prepared by IL

Dosage	MB Removal $\pm$ SD (%)				
	TiO ₂ -IL				
	0.0 mL	0.5 mL	1.0 mL	3.0 mL	5.0 mL
0.1 g/L	39.461 $\pm$ 0.002	55.645 $\pm$ 0.005	56.524 $\pm$ 0.001	33.748 $\pm$ 0.005	41.437 $\pm$ 0.003
0.5 g/L	58.435 $\pm$ 0.008	74.913 $\pm$ 0.006	70.175 $\pm$ 0.001	68.817 $\pm$ 0.001	26.728 $\pm$ 0.004
1.0 g/L	56.864 $\pm$ 0.002	90.530 $\pm$ 0.004	92.031 $\pm$ 0.003	74.625 $\pm$ 0.001	49.487 $\pm$ 0.001
5.0 g/L	30.769 $\pm$ 0.002	92.031 $\pm$ 0.004	94.025 $\pm$ 0.002	92.043 $\pm$ 0.002	55.636 $\pm$ 0.004

Appendix 2: MB removal by TiO₂/Ag with varying Ag concentration

Ag Concentration (wt%)	MB Removal $\pm$ SD (%)
	TiO ₂ /Ag
0.5	27.81 $\pm$ 0.005
1.0	68.754 $\pm$ 0.001
2.0	97.432 $\pm$ 0.001
3.0	68.628 $\pm$ 0.001
4.0	83.749 $\pm$ 0.001
5.0	68.291 $\pm$ 0.001

Appendix 3: MB removal by TiO₂-1/Ag 2 %/CA 0.5% with varying CA concentration

CA Concentration (wt%)	MB Removal $\pm$ SD (%)
	TiO ₂ /Ag
0.5	91.498 $\pm$ 0.001
1.0	87.834 $\pm$ 0.001
2.0	96.550 $\pm$ 0.001
3.0	98.451 $\pm$ 0.001
4.0	97.379 $\pm$ 0.001
5.0	97.468 $\pm$ 0.002

Appendix 4: MB removal under different conditions

Condition	MB Removal $\pm$ SD (%)			
	TiO ₂ -0	TiO ₂ -1	TiO ₂ -1/Ag 2%	TiO ₂ /Ag 2%/CA 0.5%
Dark	25.540 $\pm$ 0.0041	10.183 $\pm$ 0.0011	23.598 $\pm$ 0.0021	36.987 $\pm$ 0.0023
Visible Light	18.025 $\pm$ 0.0004	14.706 $\pm$ 0.0021	88.346 $\pm$ 0.0040	94.433 $\pm$ 0.0012
UV Light	41.726 $\pm$ 0.0008	72.809 $\pm$ 0.0003	100.00 $\pm$ 0.0002	100.00 $\pm$ 0.004

Appendix 5: MB Removal by TiO₂-1/Ag 2 %/CA 0.5% photocatalyst at different: a) photocatalyst dosage (0.1 g/L – 20.0 g/L), b) initial concentration of MB (5 ppm - 25 ppm), c) pH of MB solution (pH 3 – pH 12)

Photocatalyst Dosage (g/L)	MB Removal $\pm$ SD (%)
0.1	35.582 $\pm$ 0.001
1.0	91.498 $\pm$ 0.003
3.0	100.00 $\pm$ 0.001
5.0	100.00 $\pm$ 0.001
10.0	100.00 $\pm$ 0.001
20.0	24.688 $\pm$ 0.001
MB Concentration (ppm)	MB Removal $\pm$ SD (%)
5	100.00 $\pm$ 0.003
10	91.003 $\pm$ 0.001
15	52.954 $\pm$ 0.009
20	61.230 $\pm$ 0.005
25	39.493 $\pm$ 0.005
pH	MB Removal $\pm$ SD (%)
3	100.00 $\pm$ 0.005
6.5	89.896 $\pm$ 0.001
7.4	95.640 $\pm$ 0.003
12	86.076 $\pm$ 0.005

Appendix 6: Photocatalytic Degradation of MB using different radical scavengers (ethylene glycol, 2-propanol and ascorbic acid)

Scavenger	MB Removal $\pm$ SD (%)
No scavenger	100.00 $\pm$ 0.004
2-Propanol	100.00 $\pm$ 0.005
Ascorbic Acid	100.00 $\pm$ 0.002
Ethylene Glycol	80.93 $\pm$ 0.002

Appendix 7: Dye removal under individual and mixed conditions

Condition	Individual Dye Removal $\pm$ SD (%)		
	MO	MB	RhB
Dark	8.21 $\pm$ 0.001	38.69 $\pm$ 0.002	39.17 $\pm$ 0.001
Visible Light	15.95 $\pm$ 0.001	100.00 $\pm$ 0.002	66.00 $\pm$ 0.001
UV Light	37.33 $\pm$ 0.001	100.00 $\pm$ 0.001	100.00 $\pm$ 0.001
Condition	Mixed Dyes Removal $\pm$ SD (%)		
	MO	MB	RhB
Dark	78.26 $\pm$ 0.001	92.11 $\pm$ 0.001	83.19 $\pm$ 0.002
Visible Light	100.00 $\pm$ 0.001	100.00 $\pm$ 0.001	90.19 $\pm$ 0.001
UV Light	98.37 $\pm$ 0.001	100.00 $\pm$ 0.001	91.07 $\pm$ 0.001

Appendix 8: MB removal at different number of cycles using TiO₂-1/Ag 2 %/CA 0.5% Photocatalyst

Cycle	MB Removal $\pm$ SD (%)
1st	100.00 $\pm$ 0.004
2nd	32.812 $\pm$ 0.070
3rd	23.508 $\pm$ 0.025

Appendix 9: Antibacterial Study on *E.coli* and *S. aureus* by TiO₂ Photocatalysts

Photocatalyst	Zone of inhibition (mm)	
	<i>E.coli</i>	<i>S.aureus</i>
TiO ₂ -0	0.00 $\pm$ 0.00	0.00 $\pm$ 0.00
TiO ₂ -1	0.00 $\pm$ 0.00	0.00 $\pm$ 0.00
TiO ₂ -1/Ag 2%	8.00 $\pm$ 0.00	8.00 $\pm$ 0.00
TiO ₂ -1/Ag 2%/CA 0.5%	9.00 $\pm$ 0.00	8.00 $\pm$ 0.00