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

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

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A thesis submitted

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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 m^2/g to 174.8 m^2/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 TiO_2/Ag/CA photocatalyst and were chosen for further studies. TiO_2/Ag/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 (λ = 365 nm) under solution with pH 7.4. The antibacterial activity of TiO_2-1/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 TiO_2-1/Ag 2 %/CA 0.5%. As wastewater treatment requires the removal of chemical pollutants and unwanted biological components, TiO_2-1/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 TiO_2/Ag/Selulosa Asetat Pelbagai Fungsi dengan Peningkatan Aktiviti Fotodegradasi dan Antibakteria

ABSTRAK

Fotopemangkin titanium dioksida, TiO_2 *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* TiO_2*. Dalam kajian ini,* TiO_2 *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* TiO_2 *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* TiO_2*/Ag. Aktiviti fotodegradasi* TiO_2*/Ag/CA dalam pelbagai keadaan seperti dos fotopemangkin, kepekatan asal pewarna fabrik, pH asal dan kesan penggaut radikal telah dikaji. Kebolehkitaran semula* TiO_2*/Ag/CA juga telah ditentukan. Pencirian fotopemangkin* TiO_2*/Ag/CA melalui analisis XRD, FTIR, EDX, SEM dan TEM menunjukkan kehadiran Ag dan CA dalam* TiO_2*. BET menunjukkan bahawa penggunaan cecair ionik dalam sintesis fotopemangkin* TiO_2 *berjaya meningkatkan luas permukaannya daripada 130.9* m^2/g *kepada 174.8* m^2/g*. Berdasarkan kajian awal,* TiO_2*/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.* TiO_2*/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 (λ = 365 nm) pada pH 7.4. Aktiviti antibakteria* TiO_2*/Ag/CA yang dikaji melalui kaedah resapan cakera terhadap bakteria E. coli dan S. Aureus menunjukkan zon perencatan, membuktikan keberkesanan antibakteria* TiO_2*/Ag/CA. Fotopemangkin* TiO_2*/Ag/CA yang digambarkan dalam kajian ini menunjukkan kecekapan yang tinggi dalam aktiviti fotodegradasi dan antibakteria. Hasil kajian ini menunjukkan kemampuan fotopemangkin* TiO_2*/Ag/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 TiO_2's conduction band, and then converts the electrons into superoxide radicals. Water molecules will react with holes generated in the TiO_2 valence band to produce hydroxyl radicals, which are required in photocatalytic oxidation (Din et al., 2018). The incorporation of Ag on the TiO_2 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 Ti^{4+} in the TiO_2 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 TiO_2 (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). TiO_2/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 TiO_2/Ag, some prevalent issues of TiO_2/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 TiO_2/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 (Gebru & 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 TiO_2/Ag/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 TiO_2/Ag/CA were determined and its photocatalytic activity under different operating conditions (photocatalyst dosage, initial dye concentration, and initial pH) was investigated. Antibacterial properties of TiO_2/Ag/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 TiO_2/Ag in the degradation of dyes. However, to the best of our knowledge, there are no studies on TiO_2/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 TiO_2/Ag/CA photocatalyst in the mixed dyes treatment system.

Besides that, the surface area of TiO_2 is equally important in the degradation of pollutants. The ability of ILs to synthesise morphology-controlled TiO_2-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 TiO_2 synthesised with various types of IL as a solvent template via the sol-gel method, for instance, 1-Butyl-3-methylimidazolium hexafluorophosphate, ($BmimPF_6$) (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 TiO_2/Ag/CA photocatalysts for the degradation of dyes. The following set of objectives was pursued to accomplish this aim:

i. To synthesise TiO_2 photocatalysts via the sol-gel method with IL, 1-butyl-3-methylimidazolium acetate,

ii. To determine the physicochemical properties of TiO_2/Ag/CA photocatalysts such as morphological, structural, crystallinity, compositional and surface chemical properties prepared via wet-impregnation method (TiO_2/Ag) and mechanical mixing (TiO_2/Ag/CA),

iii. To investigate the photocatalytic activity of TiO_2/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 TiO_2/Ag/CA photocatalyst

CHAPTER 2

LITERATURE REVIEW

2.1 Titanium Dioxide, TiO_2

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, TiO_2 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 TiO_2 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 TiO_2 Photocatalyst

TiO_2 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).

TiO_2 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 TiO_6 octahedra structure whereby the titanium (Ti^{4+}) 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).