SYNTHESIS OF TITANIUM DIOXIDE SUPPORTED ON MESOSTRUCTURED SILICA NANOPARTICLES FOR PHOTOCATALYTIC DECOLOURIZATION OF CONGO RED

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Specially dedicated to my husband, Mohamed Izal and

my princess, Aisyah Humaira,

'Thank you for always standing next to me and wait for me patiently'

&

To Ma, Aboh and late father,

Che Zaleha Che Endek, Razak Kadir and Abdul Rahman

To my beloved siblings, family and family-in-laws

'Thank you for your endless love and encouragement during my hard time'

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ABSTRACT

Various dyes that had been widely used in industries may produce harmful effects to the living organisms and the environment if not treated properly before being discharged into water bodies. Photocatalytic decolourization is one of the promising techniques to degrade dyes due to its mild operating conditions and green technology process. In this study, the effects of titanium dioxide (TiO_2) supported on mesostructured silica nanoparticles (MSN) under different preparation methods were investigated for photocatalytic decolourization of congo red (CR). The microwave-synthesized mesoporous titania nanoparticles (MTN) supported on MSN were prepared by impregnation method (MTN/MSN), while electrogenerated TiO_2 was supported on MSN by in-situ electrochemical (TiO_2/MSN-E) and impregnation (TiO_2/MSN-I) methods, respectively. The properties of the catalysts were characterized using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Nitrogen adsorption-desorption, electron spin resonance (ESR) analysis and ^{29}Si magic angle spin nuclear magnetic resonance (^{29}Si MAS NMR). The results indicated that the introduction of MTN and TiO_2 did not change the lattice structure of MSN but decreased the surface area and pore volume of the catalysts as a consequence of pore blockage. The photocatalytic activity of the catalysts towards decolourization of 10 mg L^{-1} CR at pH 5 with 1.0 gL^{-1} catalyst after 5 h was in the following order: TiO_2/MSN-E > MTN/MSN > TiO_2/MSN-I. The TiO_2/MSN-E (94 %) showed the best performance compared to other catalysts, probably due to the presence of abundant Si-O-Ti bonds oxygen vacancies and titanium site defect in MSN frameworks. The kinetics study of the catalysts indicated that decolourization of CR followed the pseudo first order Langmuir-Hinshelwood model. The response surface methodology study for TiO_2/MSN-E catalyst demonstrated good significance of model with a high coefficient of determination (R^2 = 0.9698) and a regenerated study showed that the catalysts were still stable after 5 cycles. The employment of the catalyst on decolourization of simulated dyes revealed remarkable performance, suggesting the potential use of the catalysts for textile wastewater treatment.

ABSTRAK

Pelbagai pencelup yang telah digunakan secara meluas dalam industri mungkin mendatangkan kesan berbahaya kepada organisma hidup dan persekitaran jika tidak dirawat dengan betul sebelum dilepaskan ke dalam sumber air. Penyahwarna fotopemangkinan adalah salah satu teknik yang meyakinkan untuk mengurai pencelup kerana keadaan operasi yang sederhana dan proses teknologi hijau. Dalam kajian ini, kesan titanium dioksida (TiO_2) disokong pada mesostruktur silika zarahnano (MSN) terhadap kaedah penyediaan yang berbeza telah dikaji terhadap penyahwarna fotopemangkinan merah kongo (CR). Sintesis-ketuhar gelombang mikro liang meso titania zarahnano (MTN) telah disokong pada MSN dengan menggunakan teknik pengisitepuan (MTN/MSN), manakala penjana elektron TiO_2 telah disokong pada MSN dengan *in-situ* elektrokimia (TiO_2/MSN-E) dan pengisitepuan (TiO_2/MSN-I). Sifat-sifat pemangkin telah dicirikan dengan menggunakan pembelauan sinar-X (XRD), spektroskopi inframerah transformasi Fourier (FTIR), penjerapan-penyahjerapan nitrogen, analisis resonans putaran elektron (ESR) dan ^{29}Si putaran sudut ajaib resonans magnet nukleus (^{29}Si MAS NMR). Hasil kajian menunjukkan bahawa pengenalan MTN dan TiO_2 tidak mengubah struktur kekisi MSN tetapi mengurangkan luas permukaan dan isipadu liang mangkin disebabkan liang tersumbat. Aktiviti fotopemangkinan pemangkin terhadap penyahwarnaan 10 mg L^{-1} CR pada pH 5 apabila menggunakan 1.0 g L^{-1} pemangkin selepas 5 jam adalah dalam turutan berikut: TiO_2/MSN-E > MTN/MSN > TiO_2/MSN-I. TiO_2/MSN-E (94 %) menunjukkan prestasi yang terbaik berbanding pemangkin yang lain, mungkin disebabkan oleh kehadiran ikatan Si-O-Ti yang banyak, kekosongan oksigen dan kecacatan tapak titanium dalam kerangka MSN. Kajian kinetik pemangkin menunjukkan bahawa penyahwarnaan CR mengikut tertib model pertama pseudo Langmuir-Hinshelwood. Kajian kaedah gerak balas permukaan untuk pemangkin TiO_2/MSN-E menunjukkan model penemuan baik dengan pekali penentu yang tinggi (R^2 = 0.9698) dan kajian kebolehgunaan semula menunjukkan pemangkin masih stabil selepas 5 kitaran. Penggunaan pemangkin terhadap penyahwarnaan pencelup simulasi menunjukkan prestasi luar biasa, mencadangkan potensi penggunaan pemangkin untuk rawatan air sisa tekstil.

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LIST OF ABBREVIATIONS

AOP	-	Advance oxidation process
APTES	-	3-aminopropyltriethoxysilane
BET	-	Brunauer Emmet and Teller
C	-	Concentration
CR	-	Congo red
CTAB	-	Cetyltrimethylammonium bromide
EG	-	Ethylene glycol
ESR	-	Electron Spin Resonance
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier Transform Infrared
MB	-	Methylene blue
MO	-	Methyl orange
MTN	-	Mesoporous TiO_2 Nanoparticles
MSN	-	Mesostructured Silica Nanoparticles
NH_4OH	-	Ammonium solution
RhB	-	Rhodamine B
RSM	-	Response surface methodology
^{29}Si MAS NMR		^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance
TEAP	-	Tetraethylammonium perchlorate
TEOS	-	Tetraethyl orthosilicate
TiO_2	-	Titanium dioxide
TTIP	-	Titanium (IV) isopropoxide
UV-Vis	-	Ultraviolet Visible
XRD	-	X-Ray Diffraction

LIST OF SYMBOLS

%	-	Percentage
θ	-	Theta
λ	-	Wavelength
°C	-	Degree Celcies
Cm	-	Centimeter
eV	-	Electron volt
g	-	Gram
g L^{-1}	-	Gram per liter
h	-	Hour
K	-	Kelvin
Min	-	Minute
mg L^{-1}	-	Miligram per liter
mM	-	Milimolar
mL	-	Milileter
M	-	Molar
Nm	-	Nanometer
µm	-	Micrometer
s	-	Second
T	-	Temperature
W	-	Watt

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds, which contribute to an increasing environmental danger if not treated properly (Pouretedal and Keshavarz, 2010). The wastewater from dye industry containing toxic aromatic amine compounds are carcinogenic, harmful for skin, eye, blood and reproductive cell of human body, and threaten the aquatic organisms (Mohanta *et al*., 2013). There are more than 100,000 commercially available dyes with 7×10^5 tons of dyestuff production annually (Khataee *et al*., 2010; Darus *et al*., 2005) and the synthetic origin and complex aromatic structures of dyes make them stable and difficult to be biodegraded (Srinivasan and Viraraghavan, 2010).

Dye wastewater is one of the most difficult wastewaters to treat thus the removal of this toxic dye is considered as one of the important challenges in recent years (Abdel-Messih *et al.*, 2013). A wide range of methods has been developed for the removal of synthetic dyes from waters and wastewaters to decrease their impact on the environment (Forgacs *et al.*, 2004). The traditional wastewater treatment technologies including adsorption, coagulation or enzymatic decomposition have

proven to be markedly ineffective for handling wastewater of synthetic textile dyes because of the chemical stability of these pollutants. Besides that, the use of these techniques were also contribute to the production of secondary pollution, high cost and disable to treat all type of dyes (Lachheb *et al.*, 2002).

In recent time, advance oxidation process (AOP) appears to be promising technique to remove the pollutants because it is one of the simple and low cost processes. AOP rely on in situ generation of highly reactive radical species, mainly •OH by using solar, chemical or other forms of energy. The most attractive feature of AOPs is that this highly potential and strongly oxidizing radical allows the destruction of a wide range of organic chemical substrate with no selectivity (Gaya and Abdullah, 2008). Among AOP, heterogeneous photocatalysis using semiconductors such as TiO_2, ZnO, WO_3, Fe_2O_3, CuO, ZrO_2, and CdS has proved to be of real interest as efficient tool for degrading both aquatic and atmospheric organic contaminants. These semiconductors can convert a wide range of harmful dyes into non-toxic products, CO_2 and water at ambient temperatures (Houas *et al.*, 2001; Sapawe *et al.*, 2013a).

Among all the catalysts, TiO_2 is a well-known and most popular photocatalyst since it is relatively inexpensive to produce, non-toxic and chemically stable (Koodali and Zhao, 2010). It has a large number of applications such as environmental purification, decomposition of organic contaminants, generation of hydrogen gas, *etc* (Belhekar *et al.*, 2002). However, TiO_2 catalyst has some drawbacks such as wide band gap, high electron-hole recombination rate, large particle size and small surface area that limits its application range (Liu *et al*., 2015). To overcome those shortcoming, lot of researches nowadays focused on the modification of this catalyst by addition of mesoporous support.

From the practical point of view, the ideal support for photocatalysis must satisfy several criteria as follows: (i) strong adherence between catalyst and support, (ii) non-degradation of the catalyst reactivity by the attachment process, (iii) offer a high specific surface area and (iv) have a strong adsorption affinity towards the

pollutants (Shan *et al*, 2010). In addition, the catalyst support influences the catalytic performance through structural features and the interaction between the materials leads to enhancement of the contact between the surface and the irradiation (Zhang *et al*., 2010). Mesoporous silica (MS) is a suitable candidate to be used as a support due to its high surface area, highly uniform pore distribution, tunable pore size and unique hosting (Karim *et al*., 2012). Besides that, MS has high adsorption capacity that facilitate the photocatalytic reaction. In response to this, mesostructured silica nanoparticles (MSN) has become increasingly important because it also has such properties which offers considerable potential as an excellent solid support for immobilization of heterogeneous catalysts.

Regarding all the factors, herein, we report three types of TiO_2 supported on MSN and study its performance in photocatalytic decolourization of congo red (CR). Next, the potential of the catalyst was investigated on photodecolourization of simulated dye wastewater by using the optimum reaction condition.

1.2 Problem Statement

Recently, the disposal of untreated effluents from many dye industry to the environment often leads problems to humans and aquatic life. This phenomenon seriously affects the nature of water, inhibits sunlight penetration and reduces photosynthetic reactions. In addition, some dyes are either toxic or carcinogenic if not treated properly (Mittal *et al*., 2010). To overcome this problem, several methods for the removal of dyes have been reported, including chemical and biological oxidation, adsorption, coagulation and flocculation, electrochemical oxidation, ion exchange and membrane separation (Jusoh *et al.*, 2013; Sapawe *et al.*, 2013b). However, these methods have their own drawbacks of being time consuming, expensive, and commercially unattractive as well as the generation of secondary wastes.

The use of a heterogeneous photocatalysts for wastewater treatment has become more popular because it can be operated in mild conditions and transforms the toxic organic pollutants into nontoxic products (Zangeneh *et al*., 2015). In recent years, TiO_2 have attracted great interest of many researcher for their peculiar properties, such as photostability, largely available, inexpensive and non-toxic (Yang *et al*., 2006; Jaafar *et al*., 2015a). However, it also shows some disadvantages such as lower surface area, easy to agglomerate into large particles and the separation or recovery of catalyst is difficult which has limited its application (Kuwahara and Yamashita, 2011).

Many researchers focused on synthesis of mesoporous titania with high specific surface area or loading TiO_2 with porous materials such as zeolite to improve its activity (Li *et al*., 2005; Yang *et al.*, 2006). However, like most of the conventional zeolites, it is suffers from intracrystalline diffusion limitations due to the small size of its micropores. Accordingly, intensive research has been done to overcome this limitation, focusing on the synthesis of Ti-containing materials with enhanced accessibility to the reactive sites with large pores such as mesoporus silica (MS) (Corma *et al*., 1999; Cundy *et al*., 2003; Ke *et al*., 2007). Linking chemically TiO_2 particles and dispersing them inside the pores of MS materials allows the suitable mean pore size induce and control the oxide particle growth, uniformity of size, as well as to stabilize and prevent agglomeration of the particles (Acosta-Silva *et al.*, 2011). Thus, this approach generates a large number of active sites which are used for adsorption/desorption of reactants or products. MS also have high surface area with a uniform and tunable pore size, which offers considerable potential as an excellent solid support for immobilization of heterogeneous catalysts and enhances the photocatalytic activity (Jusoh *et al.*, 2013). In this study, we reported e new method preparing TiO_2 supported onto MSN and it is expected that the introduction of TiO_2 on MSN can increase the surface area and number of active sites, thus enhance the photocatalytic activity.

1.3 Objective of Study

The aims of this study are:

1. To synthesize TiO_2 and TiO_2 supported on MSN using different preparation method and study the physico-chemical properties of a catalysts.
2. To investigate the photoactivity of the catalysts on decolourization of congo red (CR).
3. To study the mechanism and kinetics of the CR photodecolourization over the catalyst
4. To optimize the photocatalytic decolourization by response surface methodology (RSM).
5. To test the potential of catalysts on photodecolourization of simulated dye wastewater.

1.4 Scope of Study

The mesoporous TiO_2 nanoparticles (MTN) and TiO2 catalysts were prepared by the microwave and electrolysis methods, respectively. Then, the MTN was loaded onto MSN by impregnation method (MTN/MSN) and, TiO_2 were supported on MSN by in-situ electrolysis (TiO_2/MSN-E) and impregnation electrolysis (TiO_2/MSN-I) methods, accordingly.

The physical and chemical properties of the catalysts was characterized using various method which could be explained as below. The structural and textural properties of the catalysts were recorded using X-ray diffraction (XRD) and N_2 adsorption-desorption isotherms, respectively. The chemical properties were

elucidated by Fourier transform infrared (FTIR) spectroscopy, electron spin resonance (ESR), ^{29}Si magic angle spin nuclear magnetic resonance (^{29}Si MAS NMR).

The photoactivity of the TiO_2/MSN-E was evaluated by the decolourization of congo red (CR) under varying parameters such as pH (5-11) and catalyst dosage (0.375-1.5 g L^{-1}). Then, the best reaction conditions was applied for photoactivity of CR using MTN/MSN and TiO_2/MSN-I. The mechanism pathway to prepare the catalyst was investigated based on the interaction between TiO_2 and MSN framework support. A new structural model for the catalyst was established on the basis of characterization results. Next, the kinetic study of the photodecolourization was described by pseudo first-order Langmuir-Hinshelwood model.

Response surface methodology (RSM) using central composite design (CCD) was carried out to optimize the conditions of photodecolourization using the high potential catalyst under three parameters including pH (5-9), catalyst dosage (0.5-1.5 g L^{-1}) and TiO_2 loading (3-10 wt%). Finally, the potential of the related catalyst was tested for photodecolourization of simulated dye wastewater which contained of four types of dyes with 10 mg L^{-1} of initial concentration, including congo red (CR), methyl orange (MO), methylene blue (MB) and rhodamine B (RhB).

1.5 Significant of Study

This study was conducted to synthesize MTN/MSN and TiO_2/MSN for photocatalytic decolourization of CR. A detail investigation of physico-chemical properties of the catalysts as well as the photocatalytic activity was also conducted. The TiO_2 catalyst attracts great intention on photocatalytic activity of CR due to low cost, environmental benignity, plentiful polymorphs, good chemical and thermal stability. However, it also has some drawbacks such as easy to agglomerate and

difficult to separate. In response to this problem, the TiO_2 has been modified by synthesizing mesoporous TiO_2 and introducing TiO_2 onto MSN. Additionally, the introduction of TiO_2 onto MSN was improved the properties of the catalyst by increasing the adsorption capability and surface area while reducing the particle size. This catalyst was expected to give high percentage of photodecolourization of CR and consequently have great potential to be applied into various dyes samples in textile wastewater.

1.6 Thesis Outline

This thesis was divided into five chapters. In chapter 1, an introduction is given about the commercial use of dyes in industries and the significant of dyes removal that cause a problem to the environment and human health. The conventional removal techniques of dyes were also mentioned. Besides that, the potential of TiO_2 as semiconductor photocatalyst and MSN as support material were highlighted. The problem of the current research was stated to give the clear objectives of the present study, while the scopes of study covered the research work to meet these objectives.

Chapter 2 which is a literature review covers the details on previous studies that have been done in order to get the clear view in the synthesis, characterization and photocatalytic efficiency of catalyst.

Chapter 3 described the experimental procedure which gives details on the chemicals and materials used in the present work, the procedure for catalyst preparation, characterization and photocatalytic reaction which includes experimental setup and analysis calculation.

Chapter 4, results and discussion are discussed in four parts, (i) physico-chemical properties of catalysts (ii) photocatalytic activity of the catalysts (iii) optimization of photodecolourization of CR by RSM and (iv) potential of catalyst on photodecolourization of simulated dye wastewater. The result are presented and discussed comprehensively

Finally, the conclusion about the study and the recommendation for future studies were simplified in the last chapter which is chapter 5.

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