SYNTHESIS AND CHARACTERISATION OF NITROGEN AND MAGNESIUM-DOPED WITH TITANIUM DIOXIDE USING SOL-GEL METHOD

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DEDICATION

For my beloved father and mother that always give me support along the study. For my husband that always behind me along the research and thesis writing process

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ABSTRACT

Nowadays, too much pollution is happening surrounding us and one of them is water pollution which each becoming more severe and worse every day. One of the sources of water pollution comes from the industry which used dyes either excessively or not. In this particular case, the wastewater needs to be treated before releasing into the river or environment. Titanium dioxide (TiO_2) is one of the most powerful semi-conductors that chemically stable and widely used in the photodegradation of wastewater process. However, TiO_2 has wide band gap (3.2 eV) which only can be activated by using UV light. In order to overcome the weakness of this photocatalyst, doping technique is applied to modify the TiO_2. By doping technique, the band gap can be reduced and the modified TiO_2 can be applied under the visible light. The objectives of this research are to synthesise and analyse the characteristics of photocatalysts N-TiO_2 and Mg-TiO_2 on the phase and the morphology. Then, the objective is also to determine the maximum decolourisation efficiency on photodegradation Reactive Black 5 (RB 5) by N-TiO_2 and Mg-TiO_2 under visible light. In this research project, nitrogen and magnesium were used as dopants and sol-gel method is applied. Calcination temperatures were varied at 300 ^oC, 500 ^oC and 700 ^oC in order to analyse the phase and characteristics of samples at different calcination temperature. The results obtained from the experiment showed the band gap after doping for samples 0.5 wt.% Mg-TiO_2 and N-TiO_2 shifted to the lower value compared to the theory value of pure TiO_2 (3.2 eV) which are between 2.75 eV-2.98 eV . The phase structure of N-TiO_2 and Mg-TiO_2 at 300 ^oC and 500 ^oC were observed as pure anatase and at 700 ^oC , a mixture of anatase and rutile were found. The decolourisation of RB 5 achieved the highest efficiency at 83.46 % for 0.9 wt.% N-TiO_2 and 72.66 % for 0.7 wt.% Mg-TiO_2. Kinetic studies of zero order, first order and pseudo-first order were tested and it was found that the reaction followed pseudo-first order.

ABSTRAK

Pada masa kini, pencemaran terlalu banyak berlaku di sekeliling kita dan salah satunya adalah pencemaran air yang setiap hari memberi kesan buruk kepada alam sekitar. Salah satu sumber pencemaran air berasal dari industri yang menggunakan pewarna secara berlebihan. Oleh yang demikian, air sisa perlu dirawat sebelum dilepaskan ke sungai atau persekitaran. Titanium dioksida (TiO_2) adalah salah satu daripada semikonduktor yang stabil secara kimianya dan digunakan dengan meluas dalam proses pembersihan air kumbahan. Walau bagaimanapun, TiO_2 mempunyai jalur yang lebar (3.2 eV) yang hanya boleh diaktifkan dengan menggunakan cahaya UV. Untuk mengatasi kelemahan bahan ini, teknik doping digunakan untuk mengubahsuai TiO_2. Melalui teknik doping, jalurnya boleh dikurangkan dan TiO_2 yang telah diubah suai boleh digunakan di bawah cahaya nampak. Objektif kajian ini adalah untuk menghasilkan dan menganalisis ciri-ciri fotomangkin N-TiO_2 dan Mg-TiO_2 tehadap fasa dan morfologinya. Selain itu, objektif lain juga ialah untuk mengetahui kadar nyahwarna yang maksimum terhadap air yang mengandungi *Reactive Black 5* (RB 5) oleh N-TiO_2 dan Mg-TiO_2 di bawah cahaya nampak. Dalam projek penyelidikan ini, nitrogen dan magnesium digunakan sebagai dopan dan kaedah sol-gel digunakan. Suhu pemanasan diubah pada 300 ^oC, 500 ^oC dan 700 ^oC untuk menganalisis fasa dan ciri-ciri N-TiO_2 dan Mg-TiO_2 pada suhu berbeza. Keputusan yang diperolehi daripada eksperimen doping telah menunjukkan bahawa sampel 0.5 wt.% N-TiO_2 dan Mg-TiO_2 dapat mengurangkan nilai jalur lebih rendah daripada nilai teori TiO_2 yang tulen (3.2 eV) iaitu di antara 2.75 eV-2.98 eV. Struktur fasa N-TiO_2 dan Mg-TiO_2 pada 300 ^oC dan 500 ^oC ialah terdiri daripada anatase sahaja dan pada 700 ^oC, didapati terdapat campuran anatase dan rutil. Proses penyahwarnaan RB 5 mencapai kecekapan tertinggi iaitu 83.46% untuk 0.9 wt.% N-TiO_2 dan 72.66% untuk 0.7 wt.% Mg-TiO_2. Kajian kinetik diuji sama ada mengikut tertib sifar, tertib pertama dan tertib pseudo-pertama dan didapati bahawa tindak balas mengikuti tertib pseudo-pertama.

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LIST OF ABBREVIATIONS

NIOSH	-	National Institute for Occupational Safety and Health
FESEM	-	Field Emission Scanning Electron Microscopy
XRD	-	X-Ray Diffraction
TGA/DTA	-	Thermogravimetric and Differential thermal analysis
DR-UV Vis	-	Diffuse Reflective Ultra Violet spectrophotometer
Ppm	-	Part per million

LIST OF SYMBOLS

TiO_2	-	Titanium Dioxide
RB5	-	Reactive Black 5
N	-	Nitrogen
Mg	-	Magnesium
k	-	the reaction rate constant (min^{-1})
k_{app}	-	adsorption coefficient of the pollutant (L/mg)
TTIP	-	Titanium (IV) isopropoxide

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CHAPTER 1

INTRODUCTION

1.1 Overview

Water pollution have become a serious issue nowadays especially in the textile industry, printing industry, food manufacturing and cosmetic industry. These industries contribute to water pollution as they release wastewater that contains azo dyes. Azo dyes are widely used as the pigmentation and bright colour that is highly demanded especially by the textile industry. Based on a previous research, about 10% to 15% of dyes used is released together with the wastewater and the complex chemical structure of dyes has caused the difficulties in wastewater treatment (Harikumar et al,. 2013).

The structures of azo dyes may contain with one or more azo group (-N=N-) as a chromophore in the molecular structure. The azo dyes are synthesised from aromatic compound and basic aqueous solution (the presence of N=N may reduce the unpaired electron pairs in nitrogen atoms). Most of them belong to the non-biodegradable and recalcitrant type of water pollutant, which cause activated sludge treatment methods to be inadequate (Muqing et al., 2014). The uncontrollable releasing of wastewater contaminants with dyes can cause environmental issues including the reduction of light absorption due to the organisms that inhabit the aquatic environments and production of different amines under anaerobic conditions (Harikumar et al., 2013).

Since the environmental issues that have become serious day by day, many researchers have shown their interests in solving the problem with few methods of water treatment including carbon adsorption, ultrafiltration, coagulation using chemical method, biodegradation using microbes, ozonation and also advanced oxidation process (Akpan, & Hameed, 2009a). One of the popular methods is photocatalysis process that has been widely used in the degradation of azo dyes. Photocatalysis is known to be a friendly environmental process which will totally degrade the pollution into water and carbon dioxide (Ferreira et al., 2015).

In photocatalysis, titanium dioxide is often used as the catalyst because of it is cheap raw materials, easy to obtain and environmental friendly. There is no side product that will harm the environment discharged from the process as semiconductor catalysts such as TiO_2 and ZnO. These types of catalysts have been widely used to mineralise harmful organic pollutants in wastewater into harmless inorganic nontoxic compounds such as CO_2, HCl and water, thus it is very recommended to be applied in the wastewater treatment process (Mondal, & Sharma, 2005). TiO_2 is made up of TiO_6 octahedral. This arrangement of octahedral makes the structure consist of three different polymorphs which are anatase, rutile and brookite as shown in Figure 1.1 (Nolan et al., 2011). Basically, the rutile part is thermodynamically stable, while anatase and brookite are categorised as metastable.

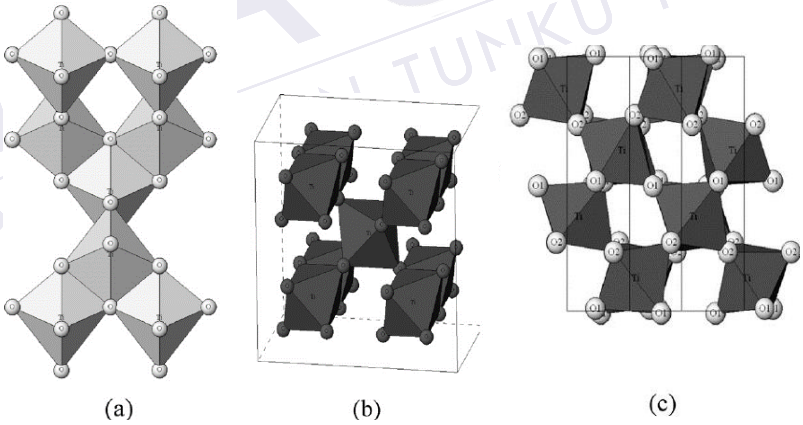

Figure 1.1: Crystalline structures of titanium dioxide (a) anatase, (b) rutile, (c) Brookite (source: Pelaez et al., 2015).

Despites of all the advantages of this photocatalyst, titanium dioxide is capable to act as sensitiser for light which will reduce the redox process due to their electronic structure. The best part is that the TiO_2 can be chemically activated by light, thus in the industry, water treatment, air-cleaning or self-cleaning for the building often used titanium dioxide which helps the cleaning process becomes easier.

However, TiO_2 can be applied only when the Ultra Violet (UV) light is present in order to activate the electrons because of the high band gap energy (3.2 eV), which will cause the process become very costly (Sikirman et al., 2014). In that case, the band gap energy need to be narrowed in order to enable the process operate under the visible light ($400 < \lambda < 500$) by modifying the photocatalyst. One of the easiest ways to reduce the band gap energy is by doping with suitable dopants. There are others ways including sputtering, ion implantation, pulser laser deposition, hydrothermal and solvothermal synthesis but sol-gel method will be chosen as the method since it is easy to be applied than the other as the process only need to operate at low temperature normally less than 700^{o}C and low cost involved (Sikirman et al., 2014). Doped TiO_2 will be applied on Reactive Black 5 dye and the result will be analysed (Segne et al., 2011).

A non-metal dopant, as an example, nitrogen is considered as the most effective dopant to be incorporated with TiO_2 as the size is smaller and the source is cheaper. Besides, many research showed significant results when nitrogen doped TiO_2 were used on methylene blue and methyl orange. Some researchers believed that the nitrogen atoms substitute the oxygen atom in the lattice of TiO_2 molecule (Nolan et al., 2011).

Magnesium is one of the abundant alkaline earth metal and less hazardous to be used in the water treatment process which will cause a more environmental friendly process. Magnesium is a type of metal dopant and a study of doping with magnesium ion that have nearly equivalent atomic radius to titanium, may give a better insight into doping process in detail and the effect of dopant size on the photocatalytic activity (Avasalara & Bojja, 2016). Besides, the insertion of metal ions into TiO_2 structure can decrease the band gap and based on the research, metals are found to be able to lower the electron-hole recombination rate and trap the electrons (Behnajady et al., 2011).

1.2 Problem Statement.

The photocataytic of TiO_2 is effective in dye removing and phenolics compound from aqueous solutions than the conventional techniques. Pure TiO_2 can affect the photocatalytic effectiveness which consists of large bandgap, high aggregation tendency and difficult to separate and recover after the treatment process (Haoran et al., 2015). Because of that, doping with metal and non-metal has been done in this study so that the energy band gap can be lowered and shifted to the visible light region. By introduced dopants to TiO_2, the band gap can be lower than 3.2 eV can be activated using the visible light.

Thus, this study is carried out to improve the present photocatalytic process using N-TiO_2 and Mg-TiO_2. Nitrogen and magnesium will be used as dopants to enhance the photocatalytic activity of the catalyst. This is because the band gap of TiO_2 can be narrowed by introducing metal and non-metal ion into TiO_2 (Etacheri et al., 2015).

Water treatment using TiO_2 photocatalyst is no longer a new method in the industries, many research have been carried out including doping technique with a particular materials including metals and non-metals doping (Lucas et al., 2012). However, there are few limitations in this technique which need to be improved. Disadvantages on having agglomerated particles, inefficient exploitation of visible light, and post-recovery of the TiO_2 particles after water treatment have become limitations for photocatalytic process to perform the higher rate of decolourisation of pollutants (Haoran et al., 2015). Hence, many studies have been conducted with the objective to improve or eliminate the limitations.

Therefore, doping with another species either metal or non-metal is one of the proposed methods in order to promote the separation of the electron-hole pair, improve the photocatalytic efficiency and at the same time reducing the possibility for the recombination of electron charge carriers to occur (Palaez et al., 2012). When doping technique is applied, the band gap of titanium dioxide can be narrowed and new energy level will be produced. This is the reason why visible light can be applied to the photocatalytic process despite of using UV light when doping technique is used to modify the semiconductors (Banarjee, et al., 2015).

1.3 Objectives of study

The objectives of this study are:

1. To synthesise and analyse the characteristics of photocatalysts N-TiO_2 and Mg-TiO_2 on the phase and the morphology.
2. To determine the maximum decolourisation efficiency on photodegradation Reactive Black 5 by using modified photocatalysts under visible light.

1.4 Scope of Study

The research will be conducted on specific criteria and conditions:

1. The method involved in this experiment is the sol-gel method for doping titanium dioxide and photocatalytic degradation to test the samples performance.
2. Parameters that will be investigated are including the doping weight percentage, type of dopants and calcination temperature of the samples during the photocatalytic activity
3. The samples will be collected for each parameter and undergo analysis using Ultra Violet-spectrophotometer, Field Emission Scanning Electron Microscopy (FESEM), Thermogravimetric and Differential Thermal analysis (TGA/DTA), diffuse reflectance UV-vis spectroscopy (DR-UV) Vis spectrophotometer and X-Ray Diffraction (XRD).
4. The photocatalyst will be used in the decolouriasation process of the Reactive Black 5 under visible light.
5. Representative dyes that will be used is Reactive Black 5, which is a diazo type of dyes.

1.5 Significance of Study

Water is a precious commodity to living things and environment which cannot be replaced by man for his daily requirement, development and industrialisation. The quality of water is decreasing due to the growth of industrialisation and increasing of population of living things. Water is also an important raw material for most of the industries and it is necessary to find an efficient wastewater treatment at industrial level in order to sustain and protect the water resource. An efficient and applicable wastewater treatment method needs to be identified. The environmental problems created by the textile industry have received much attention because contaminated and polluted effluent mainly generated by this industry.

Dye adsorbs and reflects the sunlight entering water, which will interferes the growing process of aquatic species and hinder photosynthesis to occur. Hence, as the photosynthesis is disturbed, the oxygen level will be decreasing. In addition to being toxic, dye also carcinogenic, mutagenic to various organisms (Ratna & Padhi, 2012). As an example, benzidine (BZ) based azo dyes are widely used in dye manufacturing, textile dyeing and coloured paper printing. The National Institute for Occupational Safety and Health (NIOSH) published a data on 1980 after conducting survey on the experimental animals and epidemiological studies on workers that have been exposed to the dyes. BZ has been recognized as a human urinary bladder carcinogenic and workers could be exposed directly to the carcinogen since they work in dyeing industry (Puvaneswari et al., 2006).

Many treatment methods are available for the wastewater treatment, but they are unable to remove completely the dyes and pigments from the wastewater. Some of the wastewater treatment methods depend on the formation of the secondary pollutants and these methods are not suitable and applicable in preserving the environment. In addition, these methods involve high-cost, difficult to perform and not a sustainable way for wastewater treatment (Shivaraju et al., 2017). Chemical method like ozonation has been extensively applied for remediation of industrial effluent, the ozone cleaves with conjugated double bonds of the chromophere are proved to be resulting in decolourisation even though this process will lead to the formation of toxic by-products (Ratna & Padhi, 2012). Photocatalysis is highly effective and economical process among all of the mentioned methods because it can complete the mineralisation of the pollutants, involving only UV or solar light, and operate near room temperature which has become the advantages of this process (Shrivastava, 2012; Wang et al., 2007).

The wastewater that has been discharged from industries consists of several harmful chemicals. These chemicals will affect the water resource and thus maintaining the water quality is necessary. Hence, in order to maintain the water quality, this study is significant to improve the present method of photocatalysis in treating the wastewater. More research and development on this issue are required to be conducted in order to seek for a viable and reliable ways in wastewater treatment process.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Recently, water pollution has become a critical issue that has been discussed globally as 70 % of untreated wastewater is released from the industry without any filtering and processing. The amount of drinkable water is believed to be run out every day due to the few factors including natural disasters, increasing in population and water pollution (Tan et al., 2011). Water pollutants can be classified as physical (odour, colour, solids, or temperature), biological (pathogens), or chemical (organic or inorganic compounds) (Mahlambi et al., 2015).

Nowadays, the textiles industries use the complex synthetic organic dyes extensively as the colouring agents to obtain bright and vibrant colours. However, this type of dyes is not completely absorbed by the fabrics and the excess dye will be released without proper treatment to the environment. Other than that, colours are the first pollutants to be recognized in wastewater and need to be removed before released into environment. The visual quality of water will be affected even by small amount of dye in watercourses (Shah, 2018).

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