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**PHOTODEGRADATION OF NAPHTHOL BLUE BLACK BY USING  
IMMOBILISED TITANIUM DIOXIDE DOPED WITH COPPER ION**

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PERPUSTAKAAN  
UNIVERSITI MALAYSIA SABAH

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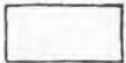
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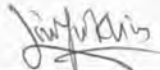
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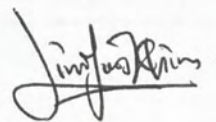
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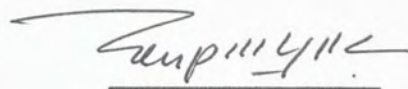
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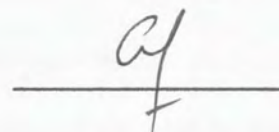


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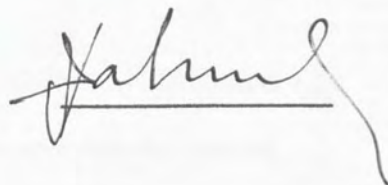
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## ABSTRACT

The photocatalytic activity of  $\text{TiO}_2\text{-Cu}^{2+}$  thin film has been studied over Naphthol Blue Black (NBB) in aqueous solution. The thin film has been prepared by sol-gel dip-coating method and the photocatalytic degradation of NBB was carried out in a 400-mL cylindrical photoreactor. The results showed that the photoactivity of  $\text{TiO}_2$  thin film was enhanced by doping  $\text{Cu}^{2+}$  ion into the film (as  $\text{TiO}_2\text{-Cu}^{2+}$  thin film) and also the addition of  $\text{H}_2\text{O}_2$  into the system. On the other hand, it also found that higher thickness of the thin film has contributed to the higher degree of NBB degradation. The best experimental condition was comprised of 10-layer  $\text{TiO}_2\text{-Cu}^{2+}$  thin film and  $1 \times 10^{-4}$  mol/L  $\text{H}_2\text{O}_2$  with the existence UV radiation where 24% of the NBB in the aqueous solution was successfully degraded.



## **FOTODEGRADASI BAHAN PEWARNA NAPHTHOL BLUE BLACK (NBB) MENGUNAKAN TiO<sub>2</sub> SAPUT TIPIS DENGAN PENAMBAHAN ION Cu<sup>2+</sup>**

### **ABSTRAK**

Aktiviti pemangkinanfoto TiO<sub>2</sub>-Cu<sup>2+</sup> saput tipis telah dikaji terhadap larutan Naphthol Blue Black (NBB). Saput tipis TiO<sub>2</sub> telah dihasilkan melalui kaedah celup angkat dan fotodegradasi NBB telah dijalankan dalam fotoreaktor 400mL. Keputusan eksperimen menunjukkan pemangkinanfoto TiO<sub>2</sub> telah ditingkatkan dengan penambahan ion Cu<sup>2+</sup> pada saput tipis ( TiO<sub>2</sub>-Cu<sup>2+</sup> saput tipis) dan juga penambahan H<sub>2</sub>O<sub>2</sub> dalam sistem degradasi. Didapati juga ketebalan saput tipis yang lebih tinggi mendapat kadar degradasi NBB yang lebih baik. Keadaan eksperimen yang optimum didapati ialah 10 lapis TiO<sub>2</sub>-Cu<sup>2+</sup> saput tipis dan 1 x 10<sup>-4</sup> mol/L H<sub>2</sub>O<sub>2</sub> dengan kehadiran sinar UV, dimana 24% NBB dalam larutan dikaji telah didegradasikan.



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## LIST OF SYMBOLS & ABBREVIATION

NBB	Naphthol Blue Black salt
UV-Vis	Ultra Violet-Visible spectrometer
AOP	Advanced Oxidation Process
Abs	Light absorptivity
$\Phi$	Quantum yield
T	Transmittance
$P_T$	Electromagnetic radiation exiting sample
$P_0$	Electromagnetic radiation incident on sample
$A_{bs}$	Absorbance
$\varepsilon$	Molar absorptivity
TiO <sub>2</sub> / H <sub>2</sub> O <sub>2</sub> /UV	Titania-assisted photodegradation system
%D <sub>Abs</sub>	Degradation degree
$A_t$	Absorptivity at contact time, t
$A_0$	Initial absorptivity
$k$	Rate constant



## CHAPTER 1

### INTRODUCTION

#### 1.1 AN OVERVIEW OF TEXTILE WASTEWATER TREATMENT

In the year of 2003, textile industry in Malaysia ranked among the top five export earners with overseas sales reaching RM8.5 billion from RM8.4 billion in 2002. The industry also contributed 2.4 per cent to the country's total exports of manufactured goods and employed over 70,000 workers (British High Commission, 2003). However, the textile industry had made a big amount of dye-containing wastewater that is not amendable by the conventional treatment techniques, therefore the necessity of finding an effective and economical process to clean wastewater from textile dyes has motivated important research efforts on several aspects of the problem (Giovana *et al.*, 2004; Anna *et al.*, 2002; Poullos and Tsachpinis, 1999).

Elimination of toxic chemicals from textile wastewater is a important subjects in pollution control, expecially in dyeing processes which produced strong colour, high and unstable pH, and high chemiccal oxygen demand (COD) which are hardly eliminated by biological process (Poullos and Tsachpinis, 1999).



Biological treatment is unefficient to degradate the dye, therefore conventional oxidants had been used as the standard chemical method in wastewater treatment. However these procedures needs long time and costly, thus the advanced oxidation processes or techniques, which generate powerful hydroxyl radicals ( $\bullet\text{OH}$ ,  $E^\circ = 2.8 \text{ V}$  vs. normal hydrogen electrode), have been proposed for colour removal and degradation of dyes (Goi and Trapido, 2000). These processes had been found most suitable for azo-dyes which mostly used among textile colorants. (Stock *et al.*, 2000).

Photocatalytic reaction using  $\text{TiO}_2$  to decompose the hazard organic materials has been confirmed. The  $\text{TiO}_2$  photocatalyst has the capability of removing  $\text{NO}_x$  and can play an important role in removing other environmental contaminants (Kamat, 1996). The nature and properties of photocatalyst  $\text{TiO}_2$  have been described as various applications of anti-bacteria effect, self-sterilization effect, deodorizing effect, self-cleaning effect, anti-fogging effect, air purification, and water purification. Generally  $\text{TiO}_2$  has been utilized as an additive or pillar to bright pigment, ink, plastic, paper, rubber and textile. Treatment of water can be accomplished by adding a powdered form of  $\text{TiO}_2$  to the water, or it can be immobilized on a substrate. If  $\text{TiO}_2$  is in solution then some sort of recovery system is necessary in order to reuse the catalyst. (Ganesh *et al.*, 2004).





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## 1.2 OBJECTIVE

This project focuses titania-assisted oxidation process as the treatment technique of the simulated textile wastewater. The objective of this project is to evaluate the effect of  $\text{TiO}_2$  film doped with ion copper towards the degradation of NBB solution.

## 1.3 SCOPE OF THE PROJECT

Photodegradation of Naphtol Blue Black was carried out using  $\text{TiO}_2$  film doped with copper ion with the presence of  $\text{H}_2\text{O}_2$  and UV radiation. The scope of this study is to examine the performance of the oxidation system in degrading dye with the effect of the doped copper ion using  $\text{TiO}_2$  thin film. This project was conducted at lab scale using 400-mL photo-reactor with Naphthol Blue Black solution as a simulated textile dyeing effluent. The sample collected were analysed under UV-Visible spectrophotometer and the performance of the mentioned oxidation system in degrading the dye solution is evaluated.



## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 LIGHT AND COLOUR

When we discuss about colour, it is related to light. Electromagnetic energy, or light, travels in waves, and one way it designated was the length of the waves, or “wavelength”, that can be measured in nanometers, nm ( $10^{-9}$  m) (Suppan, 1994). The perception of colour is an ability of human to detect some wavelengths (400nm-700nm) of the electromagnetic radiation (light) differently from other wavelengths. The colour appearance of an object depends on several processes. The colour appearance of an object depends on the source of illumination, the object’s interaction with light, and the response of sensors in the observer’s eye to the light reflected from the object (Allen, 1971; Zollinger, 1991).

##### 2.1.1 Classification of Colour Vision

The electromagnetic spectrum ranges from very short wavelengths such as gamma rays ( $10^{-11}$  m =  $10^{-2}$  nm), to the much longer radio waves (10 m =  $10^9$  nm). The human eye, however is only able to see light in the range of approximately 400-700





nm, which is a very small portion of the electromagnetic spectrum, consists of the colours ranging from blue (400nm) to red (700nm) (Zollinger, 1991; Völz, 1995).

In 1666, Sir Isaac Newton split white light with prism into its component colours, the spectrum, and assigned the seven colours, red, orange, yellow, green, blue, indigo, and violet (Jacqueline *et al.*, 1993). The spectral colour, saturation, chroma, tone, or purity is the attributes used in descriptions of colour. When the light reaches an object which reflects all the light, it appears white. Meanwhile, if it absorbs all light, we see it as black. If it absorbs a constant fraction of light in the range between 400-700nm it appears grey. We recognized different colours because there are different absorption band for various object. For example, if the absorption band of an object is located in 400-430nm, the part of light will be absorb and the rest will be reflected and human eye detected the solid as yellow. This is how Naphthol Blue Black dye solution employed in textile industry appears blue with their absorption peak at 621 and 427 nm (Zollinger, 1991).

### 2.1.2 Colour Hue

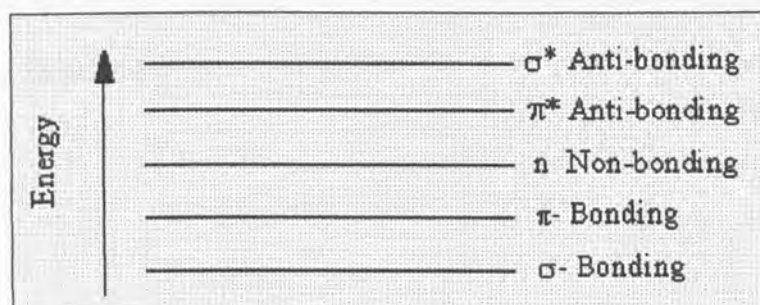
The absorption of light in a molecule to appear colour is not depend on the maximum of absorption of wavelength but also the the shape of the band. The smaller the width and the steeper the slopes of a band, the purer and the more brilliant the hue appear (Zollinger, 1991). Witt (1876) postulated that a compound is coloured due to the presence of particular groups, the chromophores, which must be linked to the system of conjugated double bonds. The hue is primarily defined by the pattern of chromophores, which is responsible for the absorption of visible light (Suppan, 1994).





### 2.1.3 Photon Absorption from Quantum Chemistry Theory

The energy of visible light and also ultraviolet (10-400nm) is absorbed by the molecules. There are used to increase energy of an electron to transit from the (electronic) ground state to one of its (electronic) excited states, and the downward transition which will release energy is the process of emission or luminescence (Suppan, 1994). Generally, the most probable transition is from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). This energy corresponds to 170 to 300 kJ mol<sup>-1</sup> for the visible spectrum and 300 to 12000 kJ mol<sup>-1</sup> for near and far ultraviolet light (Zollinger, 1991). For most molecules, the lowest-energy occupied molecular orbital are the  $\sigma$  orbital, which correspond to  $\sigma$  bonds. The  $\pi$  orbitals lie at somewhat higher energy levels, and orbital that holds unshared pairs, the nonbonding ( $n$ ) orbitals, lie at even higher energies. The unoccupied or antibonding orbitals ( $\pi^*$  and  $\sigma^*$ ), are the orbitals of highest energy as shown below (Harvey, 2000):



**Figure 2.1** The comparison among different electron transition orbital levels

The energy differences  $\Delta E$ , of the ground states and excited electronic states of the molecule and ion are directly proportional to the observed frequency  $\nu$ , which can be expressed by the Einstein-Bohr frequency condition.

$$\Delta E = E_1 - E_0 = h\nu = \frac{hc}{\lambda} \quad (2.1)$$

where

$\nu$  = frequency

$c$  = velocity of light ( $3.0 \times 10^8 \text{ ms}^{-1}$ )

$\lambda$  = wavelength of the absorbed radiation

$h$  = Planck's constant ( $6.63 \times 10^{-34} \text{ Js}$ )

Harvey (2000) mentioned that when a molecule or ion absorbs ultraviolet or visible radiation, it undergoes a change in its valence electron configuration. The valence electron in organic molecules and inorganic anions such as  $\text{CO}_3^{2-}$ , occupied quantized sigma bonding,  $\sigma$ , pi bonding,  $\pi$ , and non-bonding,  $n$ , molecular orbital. Four types of transitions between quantized energy levels account for molecular UV-Visible spectra are as follow (Harvey, 2000):



Transition	Wavelength range (nm)	Examples
$\sigma \rightarrow \sigma^*$	< 200	$C-C, C-H$
$n \rightarrow \sigma^*$	160-260	$H_2O, CH_3OH, CH_3Cl$
$\pi \rightarrow \pi^*$	200-500	$C=C, C=O, C=N, C \equiv C$
$n \rightarrow \pi^*$	250-600	$C=O, C=N, N=N, N=O$

**Table 2.1** Types of electronic transition, their wavelength range and examples.

Not all of the transitions that at first sight appear possible are observed. Certain restrictions, called selection rules have to be considered. One called “forbidden” transitions where transitions that involve a change in the spin quantum number of an electron during the transition are not allowed to take place. Other rules which deal with the numbers of electrons that may be excited, symmetry properties of the molecule and electronic states also involved (Pavia *et al.*, 2001).

#### 2.1.4 Spectroscopy: UV-Visible Absorption

Most of the organic molecules and functional groups are transparent in the portions of the electromagnetic spectrum (ultraviolet and visible) region, where the wavelength range from 190-800 nm. UV-visible data is often used to predict the concentration of an organic compound in the solution. The operational theory of this spectrometry technique is simply based on absorption theory (Harvey, 2000). The absorption of the band as a function may be expressed according to the Beer-Lambert Law (Equation 2.2):





$$A = \log ( I_o/I ) = \epsilon cl \quad (2.2)$$

where  $A$  is the absorbance,  $I_o$  is the intensity of light (at a particular wavelength),  $I$  is the intensity of transmitted light through a sample,  $c$  is the molar concentration of an absorbing species ( $\text{mol L}^{-1}$ ) and  $l$  is layer thickness or length of the sample cell (cm). The quantity  $\epsilon$  is named the molar absorption coefficient which depends on the frequency of the incident radiation and is greatest where the absorption is most intense (Pavia *et al.*, 2001).

## 2.2 COLOURANTS

Colourants are the organic and inorganic compounds that able to absorb visible light (400 to 700nm) so that they can appear to be coloured (Suppan, 1994). Each of these two groups can be subdivided further into natural and synthetic compounds. Colourants can be either dyes or pigment. Most organic pigments are closely related to dyes, there are dyes which become pigments after application (vat dyes). Dyes are aromatic compounds, they must have at least one aryl ring (often called a phenyl or benzene ring) in their structure. The delocalized electrons in this aryl ring are the fundamental cause of the absorbance of electromagnetic radiation in organic compounds, and consequently the appearance of colour in dyes. Dye are applied to various substrates (textile materials, leather, *etc.*) from a liquid in which there a soluble; pigments are practically insoluble in the media which they are applied, they have to be attached to substrates by additional compounds, *e.g.* by a polymer in a paint or in a plastic (Zollinger, 1991).





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