PHOTODEGRADATION OF NAPHTHOL BLUE BLACK BY IMMOBILISED TiO_2 DOPED WITH Ag^+ ION

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I declare that this thesis is my original work, except for certain quotations and references that been duly cited in reference.

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ABSTRACT

Photodegradation of Naphthol Blue Black using TiO_2 thin film has been studied. The thin film was prepared by dip-coating the pyrex tube into a sol-gel and subsequently be heated in furnace at 2°C/min until achieving 550°C. The results showed that the oxidative activity of the thin film can be enhanced by doping the Ag^+ ion and the addition of H_2O_2 in term of degradation of NBB. Further, higher degradation degree of NBB was observed as the thickness of the film increased. The process of degradation is conform the kinetics of pseudo first-order reaction with the rate constant, *k*, ranges from 0.0009 to the highest 0.0103 min^{-1}.

FOTODEGRADASI *NAPHTHOL BLUE BLACK* (NBB) DALAM SISTEM TiO_2 SAPUT TIPIS YANG DIDOPKAN DENGAN ION Ag^+

ABSTRAK

Fotodegradasi *Naphthol Blue Black* dengan menggunakan TiO_2 saput tipis telah dikaji. TiO_2 saput tipis disediakan dengan langkah celup angkat tiub *pyrex* dalam sol-gel TiO_2 dan seterusnya dipanaskan dalam furnace dengan kadar 2°C/min sehingga mencapai 550°C. Keputusan yang didapati menunjukkan bahawa aktiviti *oxidative* TiO_2 saput tipis boleh dinaikkan dengan mendopkan ion Ag^+ dan penambahan H_2O_2 dalam keadaan degradation NBB. Selain daripada itu, kenaikan kadar degradasi NBB diperhatikan dengan penambahan ketebalan TiO_2 saput tipis. Proses degradasi adalah dikatakan mengikut pseudo tertib pertama dengan julat pemalar, k, yang diperolehi dalam kajian ini adalah 0.0009 yang terendah ke 0.0103 min^{-1} yang tertinggi.

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LIST OF SYMBOLS AND ABBREVIATIONS

AOPs	Advanced Oxidation Processes
UV	Ultraviolet
I_o	Intensity of incident light
I	Intensity of transmitted light
c	Molar concentration or velocity of light
l	Layer thickness or length of the sample cell (cm)
ε	Molar absorption coefficient
v	Frequency
λ	wavelength of the absorbed radiation
h	Plank's constant
ΔE	Energy differences
Abs	Absorbance
NBB	Naphthol Blue Black
λ_{max}	Maximum of absorbance
A_t	Absorbance at t min of reaction
A_α	Absorbance of the sample at t = α min
D_{Abs}	Degree of absorbance degradation
k	Rate constant
Ag^+	Argentum ion
T	Transmittance

CHAPTER 1

INTRODUCTION

1.1 AN OVERVIEW OF TEXTILE INDUSTRY AND ADVANCED OXIDATION PROCESSES (AOPs) IN WASTEWATER TREATMENT

Textile industry has expanded rapidly recent year. Considering both, the volume and chemical composition of the discharged effluent, the textile dyeing and finishing industry is one of the major polluters among industrial sectors. Textile industry is the largest consumer of dyestuffs. More than 300 000 tons of different dyestuffs are used per year for textile dyeing operation (Bechtold *et al.*, 2001). It is estimated that approximately 15% of synthetic dyes is lost annually during the dyeing process and 20% of the resultant colour enter the environment (Chen *et al.*, 2004). Dyes effluents would cause disturbance to the receiving waters and they are difficult to degrade with coventional biological or chemical methods. On the other hand, dyes are highly in composition. They have large pH and strong colour combination, high dissolved solid content and highly structured polymers results in high turbidity of the waste effluent (Balcioglu & Arslan, 1997; Sheng & Chi, 1993; Uygur 1997).

Among the dyestuffs, azo dyes are used in large amounts in the textile industry due to their important class of synthetic organic dyes. They are characterized by nitrogen to nitrogen double bond (N=N) and the colour of azo dyes is due to azo bonds and associated chromopheres (Ganesh *et al.*, 1994; So *et al.*, 2002). However, azo dyes are resistant to aerobic degradation and when under anaerobic conditions they can be reduced to potentially carcinogenic aromatic amines (Kiriakidou *et al.*, 1999). On the other hand, combination of biological oxidation and physical chemical treatment are ineffective in decolourization of wastewater since dyestuffs are one of recalcitrant nature and hardly removable by coagulation-flocculation or activated carbon absorption due to their low molecular weight and high water solubility. Thus, this has prompted further research efforts to develop economical and effective treatment methods in eliminating dyes from a waste stream to keep the stability of the ecological system (Arslan *et al.*, 2000).

Advanced Oxidation Processes (AOPs) that are combination of powerful oxidizing agents with UV or near-UV light have been applied for the complete degradation of dyes (Arslan *et al.*, 2000; Tanaka *et al.*, 2000). Among AOPs, heterogeneous photocatalytic process seems to be most attractive method because they hold out the total mineralization of organics pollutants, like converting the C to CO_2, and N to NO_2 (Bose *et al.*, 1998). Another advantages of this method that the photocatalyst, usually TiO_2 (titania or anatase) is non-toxic, insoluble, comparatively cheap, available in some forms having high photoactivity and it can be activated by sunlight (Matthews, 1991). However, this method are highly energy demanding. Thus different approaches have been taken to improve the performance of these oxidation processes. Photocatalysis system has been combined with UV light, H_2O_2, Fe^{2+}, Pb^{2+}, Zn^{2+}, Ca^{2+} *etc*., in attempt to increase its effectiveness. During the AOP, the hydroxyl radicals ($\cdot OH$) have been identified as the most reactive oxidant or strong electrophiles, are generated in solution and they are responsible in disrupting, oxidizing and destroying organic pollutants to more biodegradable species or even achieving mineralization (Kiriakidou *et al.*, 1999). However, the oxidation reactivity of the photocatalyst-assisted system is varies with different operational parameters, such as pH of the solution, incident photon energy, dye concentration and the concentration of additional oxidant (Arslan *et al.*, 2000; Kiriakidou *et al.*, 1999). Therefore, a good combination of operational parameters of AOP is important to obtain optimum or desirable degradation rate of textile effluent.

1.2 OBJECTIVE OF THE RESEARCH

This research focused titania-assisted oxidation process as the treatment method of the simulated textile wastewater, Naphthol Blue Black solution. The objective of the studies is:

i. To determine the effect of different thickness TiO_2 thin film doped with Ag^+ ion in the mentioned oxidation system,

ii. To determine the effect of H_2O_2 in the mentioned oxidation system, towards the degradation of textile-dyeing effluent.

1.3 SCOPE OF THE RESEARCH

"Photodegradation of Naphthol Blue Black by Using Immobilised TiO_2 Doped with Ion Ag^+" had been investigated. This experiment was carried out in lab-scale using 600-mL photor-reactor with Naphthol Blue Black solution as a simulated textile dyeing effluent. The samples collected were evaluated by UV-Visible analysis and determine the performance of the oxidation system in degrading dye with different thickness in operational parameter of H_2O_2 and TiO_2 film Doped with Ion Ag^+.

CHAPTER 2

LITERATURE REVIEW

2.1 COLOUR AND LIGHT

Light or electromagnetic energy exist in a wide number of wavelengths, called spectrum. The regions of electromagnetic spectrum start from gamma rays (0.01 nm) to radio waves (10 m). However, the part of the electromagnetic spectrum visible to man is in the range of wavelength, between 380-760 nm (Raheel, 1996; Tortora and Collier, 1997; Zollinger, 1991). Physically, molecules (gases, liquid and solids) with different number of conjugated double and single bonds absorbed light completely, partially or even reflected wavelengths. The particular colour of a dye is determined by which wavelengths are absorbed and which reflected (Tortora and Collier, 1997).

If electromagnetic energy distribution in the visible range corresponds to that of sunlight on earth, reach a solid which reflects all visible light, it appears white to human eye. On the other hand, if the solid absorbed all light, it appears black. Gray objects absorb a constant fraction of light in the whole range between 400-700 nm (Zollinger, 1991). White, black and gray are characterized by a constant absorption in the range between 400-700nm are called achromatic colours. On the other hand, chromatic colours like orange, violet, blue and green show one or more bands that have absorption maxima and minima in the visible spectrum (Zollinger, 1991).

2.2 PHOTON ABSORPTION BY MOLECULES

The energy of visible light and ultraviolet is absorbed by molecule and used to promote one of the electrons to a level of higher energy. The molecule is capable of certain limited motion relative to each other. Moreover, the internal energy of a molecule (excluding translation) may be written as:

$$\text{Internal energy, } E = E_{rotation} + E_{vibration} + E_{electron} \tag{2.1}$$

Absorption of radiation in the far infrared causes the molecular rotation. Combination of molecular rotation and vibration responsible for the absorption in the near infrared (Atkins, 1998). However, absorption in the visible and ultraviolet regions, which dyes and related substances are concerned, is electrons in origin (Abrahant, 1977).

Organic compounds absorb light or energy in the visible and ultraviolet region which involves promotion of electrons in σ, π and n-orbitals from the ground state to higher energy states. Through equation 2.2:

$$\Delta E = hv \tag{2.2}$$

From the relation $\Delta E = hv$, it will be seen that the higher the frequency, the less the energy needed for excitation (Pavia *et al.*, 1996). The wavelengths of ultraviolet and visible light absorbed by a molecule are determined by the electronic energy differences between orbitals in the molecule (Bruice, 2001).

All coloured organic compounds contain carbon to carbon double bonds, which are formed by a chemical bond called σ-bond and a second chemical bond called π-bond, which are overlapping by two sp^2 orbitals. According to Pauli Exclusion Principle, these bonds are molecular orbitals. Each being occupied by two electrons and have opposite spin (Abrahant, 1997; Allen, 1971). At the same time, these σ- and π-bonding orbitals are created, two other anti-bonding orbitals are also formed as σ^* and π^* which are unoccupied when the molecule in the ground state. An electron can be excited from the π-bonding orbital to the π^*-antibonding by the absorption of a photon with the right amount of energy (Bruice, 2001). In the other condition which may involved in the colour formation is if the molecule contains a nitrogen or an oxygen atom in certain position, the orbital occupied by two electrons, which are not involved in bond formation such as 'lone pair' or n(non-bonding) electrons. Each of these orbital has specific energy level and these are represented by an energy level diagram (Abrahant, 1977; Allen, 1971), as shown below (Figure 2.1):

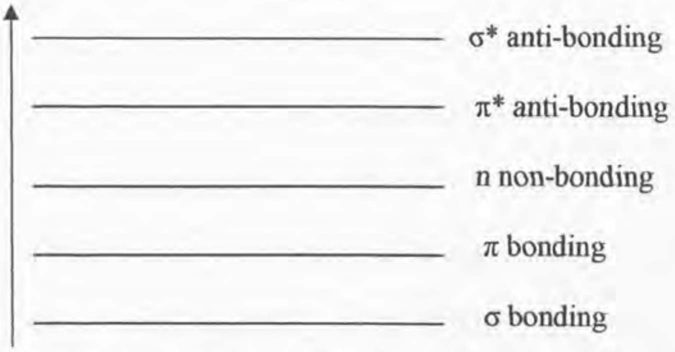

Figure 2.1 Type of molecular orbital with different energy levels.

Generally colourless organic substances absorb radiation in the ultraviolet, high energy are required to raise the molecule from the ground state E_0 to excite state E_1 (Abrahant, 1997; Pavia *et al.*, 1996). An n, σ or π electron is in excited state when ultra-UV is absorbed. Clearly, the energy to bring about transitions from highest occupied energy level (HOMO) in the ground state to the lowest unoccupied energy level (LUMO) is less than the energy required to bring about a transition would have lower energy than a $\pi \rightarrow \pi^*$ transition (Pavia *et al.*, 1996).

According to quantum theory, energy transformations on an atomic or molecular scale occur discontinuously in discrete packets or quanta (Moh, 2002).

$$\Delta E = E_1 - E_0 = hv = hc/\lambda \tag{2.3}$$

Where,

v = frequency

c = velocity of light (3.0×10^8 ms^{-1})

λ = wavelength of absorbed radiation

h = Planck's constant (6.6×10^{-34} Js)

Transition from σ electron to an σ^* anti-bonding orbital where the energy required corresponds to radiation in far ultraviolet can be ignored. But, a π or n electron can be promoted to a π^* anti-bonding orbital by visible light (Moh, 2002). These transitions are important as far as colorants are concerned: $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and charge transfer. Conjugated system contains an electron-donor subsituent such as —NH_2 or —OH and an electron-acceptor substituent such as —C=O or —NO_2 may prompt to a charge transfer transition. In this condition, electron promotion that is accompanied by an intra-molecular charge transfer will cause a marked increase in the polarity of the excited state and a marked change in chemical reactivity (Mclaren, 1983).

2.3 SPECTROSCOPY: UV-VISIBLE ABSORPTION

The range of ultraviolet and visible light lies from $\lambda = 190$ nm to $\lambda = 800$ nm. Most of the organic compounds and functional groups are colourless in the region of this electromagnetic spectrum. The spectroscopy of UV-visible absorption of organic compounds is related with the chemical bond and substituent (Tortora & Collier, 1997).

In this research, UV-visible absorption spectroscopy of organic compounds is very important because the collected UV-visible data is the function of the concentration the organic compounds in the solution. The relationship between UV-visible absorption and concentration of organic solution is stated in Beer-Lambert law (Pavia *et al*., 1996; Bruice, 2001):

$$A = \log (I_0/I) = \varepsilon\, c\, l \qquad (2.4)$$

Where,

I_0 = Intensity of incident light (at a particular wavelength)

I = Intensity of transmitted light through a sample

c = Molar concentration of an absorbing species (mol/L)

l = Layer thickness or length of the sample cell (cm)

ε = Molar absorption coefficient (molar extinction coefficient)

The molar absorption coefficient depends on the frequency of the incident radiation and is greatest where the absorption is most intense. Its dimensions are 1/(concentration x length), and it is normally convenient to express it in L $\text{mol}^{-1}\text{cm}^{-1}$. The dimensionless product $A = \varepsilon\, c\, l$ is called the absorbance of the sample, and the ratio I_0/I is the transmittance T. These two quantities are related as below:

$$\text{Log } T = - A \qquad (2.5)$$

Hence, the absorption can be measured experimentally by determining the ratio of the incident to emergent intensities and taking the logarithm (Atkins, 1998).

2.4 DYES

Dyes are characterized by their ability to absorb visible light from 400-700 nm which giving it a coloured appearance (Allen, 1971). There are natural and synthetic dyes. Synthesis organic dyes are essential to satisfy the ever growing demands, in terms of quality, variety, fastness, and other technical requirements, for colouration of a growing number of substances (Tortora and Collier, 1997). In most cases the material to be dyed such as paper, fiber, plastic, hair or foodstuff possesses a natural affinity for appropriate dyes and readily absorbs them from solution or aqueous dispersion under suitable conditions of concentration and temperature; the presence of auxiliary substances may be necessary to control the rate of dyeing, and pH suitably adjusted (Nassau, 1983).

2.4.1 Classification of Dyes

Dyestuffs are divided according to chemical guidelines (characteristic chemical groups) or by colour aspects which application in dye works. Below are some examples of dyes classification and they application in the textile industry:

Basic dyes or *cationic dyes* are water soluble with a coloured cation (Carr, 1995). They contain positively charged amino groups that are attracted to negative groups in fibers; for this reason, they are known as cationic dyes (Tortora and Collier, 1997). Wool and silk have negative acid groups and acrylic fibers usually have sulfonic aid groups added to the polymer for dyeing with basic dyes (Carr, 1995; Tortora and Collier, 1997). Recent developments of basic dyes for synthetics produce excellent colorfastness.

Disperse dyes are applied for colouring cellulose acetates, used to colour many other manufactured fibers and almost insoluble in water. Particles of dye disperse in the water without dissolving but dissolve in the fibers. Disperse dyes can be applied to a wide variety of fibers, including acetate, acrylic, aramid, modarcrylic, nylon, olefin, polyester, saran, and triacetate (Carr, 1995; Tortora and Collier, 1997).

Acid dyes are applied in acid solution; they react chemically with basic groups in the fiber structure to from ionic bonds. They are widely used for dyeing cotton, wool, silk, nylons, acrylics, paper and leather (Tortora and Collier, 1997). Acid dyes also known as anionic dyes. The chromogen in acid dyes is substituted with a sulphonic acid group produces an anionic dye (Carr, 1995). Acid dyes have one to four negatively charged functional groups. They react chemically with he basic groups in the fiber structure to form ionic bonds when applied in acid solution (Tortora and Collier, 1997). Acid dyes can be utilized for dyeing wools, nylon and, to a lesser extent, for acrylics, some modified polyesters, polypropylene, and spandex. However, acid dyes cannot be used on cellulosic fibers because these fibers are susceptible to damage from acids. On the other hand, metal complex dyes or premetallized dyes also classified with acid dyes. All acid dyes donor H^+.

In this research, Naphthol Blue Black (NBB) had been evaluated. The structure of NBB was illustrated as in Figure 2.4.

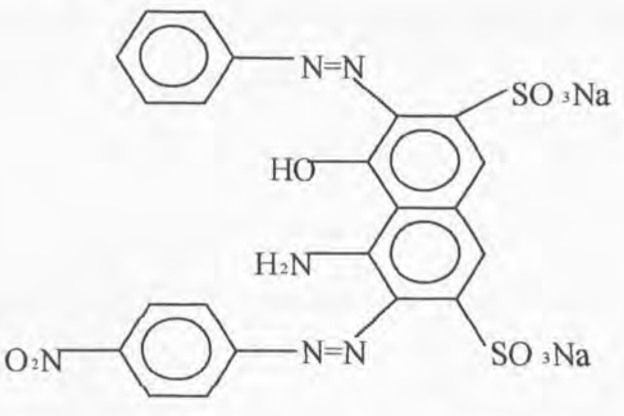

Figure 2.4 The structure of Naphthol Blue Black

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