

# DEGRADATION OF NAPHTHOL BLUE BLACK BY PHOTO-FENTON LIKE SYSTEM

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### DECLARATION

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28 MAC 2005

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### ABSTRACT

In this study, photochemical degradation of Naphthol Blue Black by advanced oxidation processes (AOPs) involving UV/H2O2/Fe(III) system were investigated at lab-scale. The degree of degradation was determined based on the measurement of absorbance at wavelength of 620 nm by UV-visible spectrophotometer. The study showed that the photo-Fenton like (a mixture of hydrogen peroxide and ferric ion), was the most effective treatment process under acidic conditions of pH 3, hydrogen peroxide-to-iron molar ratio of 1:20 and UV or solar irradiation. Finally the photo-Fenton like process was also conducted to compare its oxidation efficiency with the photo-Fenton process (a mixture of hydrogen peroxide and ferrous iron). The results showed that the photocatalytic oxidative degradation processes in the presence of UV/H<sub>2</sub>O<sub>2</sub>/Fe(II) are faster than the UV/H<sub>2</sub>O<sub>2</sub>/Fe(III). However, after 15 -20 min of reaction time using a photo-Fenton process, degradation of Naphthol Blue Black by UV/H2O2/Fe(III) was greater than 98.53% compared with the 97.02% for UV/H2O2/Fe(II) system.



### ABSTRAK

Dalam kajian ini, degradasi Naphthol Blue Black yang melibatkan proses pengoksidaan bertahap tinggi (AOPs) melalui UL/H2O2/Fe(III) telah dikaji dalam eksperimen ini. Darjah degradasi ditentukan berdasarkan kepada keserapan pada panjang gelombang 620 nm dengan menggunakan spektrofotometer UL-Nampak. Kajian didapati bahawa foto-Fenton like (campuran hidrogen peroksida dan ion ferik) merupakan proses rawatan yang paling berkesan dalam keadaan berasid dengan pH 3, nisbah hidrogen peroksida kepada besi dalam keadaan 1:20 dan UL atau penyinaran suria. Akhirnya proses foto-Fenton like juga digunakan untuk membandingkan kesan pengoksidaan dengan proses foto-Fenton (campuran hidrogen peroksida dan ion ferus). Keputusan menunjukkan bahawa proses degradasi pengoksidaan pemangkinanfoto dalam kehadiran UL/H2O2/Fe(II) adalah lebih cepat berbanding dengan UL/H2O2/Fe(III). Walaubagaimanapun, selepas 15-20 minit masa tindak balas dengan foto-Fenton, degradasi Naphthol menggunakan proses Blue Black oleh UL/H2O2/Fe(III) adalah lebih besar dengan 98.53% berbanding dengan 97.02% oleh sistem UL/H<sub>2</sub>O<sub>2</sub>/Fe(II).



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2.0x10<sup>-5</sup> mol/L;(c)  $[Fe^{2+}] = 1.0x10^{-5} mol/L;(d) [Fe^{2+}] = 4.0x10^{-6} mol/L;$ (e)  $[Fe^{2+}] = 2.5x10^{-6} mol/L;(f) [Fe^{2+}] = 2.0x10^{-6} mol/L$ 

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### LIST OF SYMBOLS AND ABBREVIATIONS

NBB Naphthol Blue Black

AOPs

Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV-A

Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>/UV-A

UV-A

•OH

ultra-violet light source, 365nm

advanced oxidation processes

photo-Fenton system

photo-Fenton like system

hydroxyl radical

wavelenghth

Abs

λ

absorbance



### **CHAPTER 1**

#### INTRODUCTION

### 1.1 TEXTILE INDUSTRY: DYE-BATH EFFLUENTS AND TREATMENT

Textile wastewater is strongly coloured which creates an environmental as well as aesthetic problems. Most of the chemical industries, especially textile industries use large amounts of water and chemicals for finishing and dyeing processes. The process of dyeing synthetic fabrics like alkantara, polyester, acetate of cellulose, acrylic and polyamide materials is mostly accomplished by the application of dispersed dyes (Szpyrkowiez et al., 2000). The chemical structures of dye vary enormously, and some organic compounds have complicated aromatic structures which can not be easily destructed to chemical or biological treatment (Lin and Peng, 1994; Tzitzi M et al., 1994). Biological treatment of wastewater is often the most costeffective alternative compared with other treatment option, but the process in dyeing and washing/rinsing of the fabrics produces bleaching effluents that contain toxic and non-biodegradable organic substances and thus it is not efficient to enhance this biotreatability of textile wastewater (Sarria et al., 2002). In other words, the complexity of dyes degradation comes from their strong colour property and their highly molecular structure constitution. Conventional waste water treatment, adsorption on activated and coagulation by a chemical agent followed by precipitation,



merely transfer dye from water to solid, hence further treatment is needed for ultimate solution.

The removal of dyes from the industrial effluent is a major concern in the textile industry followed by entrancement of stringent legislation. Textile effluent usually consists of a number of contaminants, including acids, bases, dissolved solid, toxic compounds and colour. Over 7 x 10<sup>5</sup> tons and 10000 different types of dyes and pigment are produced worldwide annually and it is estimated that 10 to 15% of the dye is lost in the effluent during the dyeing process (Yong and Jian, 1997; Danis et al., 1998). Furthermore, the fabrics absorb 50-70% of the hydrolyzed dye molecules during batch dyeing, and residual dye solution in the tank is diluted by 20-40% upon rinsing (Ince and Tezcanli, 1999). There are nearly 3000 different dyes in the commercial market and more half of them are azo compounds which are difficult to be biodegraded. Due to the variability of the organic dyes, wastewater containing dyes is difficult to treat by using traditional method. The removal of dyes using activated carbon adsorption process is given efficient result, but the cost of using this treatment is high (Malik and Saha, 2002). Some of the methods like ozone and hypochlorite are also efficient in decolourising the dyes, but they are not desirable because of the high cost of equipment, operating cost and the secondary pollution arising from the residual chlorine (Yoshida et al., 1999).

The chemical and biological limitations can be overcome by the development of so-call advanced oxidation processes (AOPs), due to the high oxidative power of the hydroxyl radicals (Alaton *et al.*, 2001). Advanced oxidation processes (AOPs) involving strong oxidizing agents (e.g. O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>) and/or catalysts (e.g. Fe, Mn, TiO<sub>2</sub>),



with or without UV irradiation source have been proposed as potential alternatives for colour and substantial COD and TOC removal from textile effluents. The advantage of AOPs is due to the absence of kinetic limitations, and the generation of highly reactive free radicals, especially hydroxyl radicals ( $\cdot$ OH) which are 10<sup>6</sup> to 10<sup>9</sup> times faster than other chemical oxidation processes, such as ozone and hydrogen peroxide (Bircher *et al.*, 1997). The most widely studied advanced oxidation processes include: heterogeneous photocatalytic oxidation, treatment with ozone (often combined with H<sub>2</sub>O<sub>2</sub>, UVA, or both), H<sub>2</sub>O<sub>2</sub> UV systems, Fenton and photo-Fenton type reactions (Francese *et al.*, 2004).

Among these processes, Fenton (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) effective for the decolourisation and degradation of dyes and have been widely applied in the treatment of nonbiodegradable wastewater. (Barbeni et al., 1987; Powell et al., 1994; Kuo., 1992; Kang et al., 2002). Recently, several studies have reported that the presence of Fenton-like reagents can increase the chain length by the formation of Fe (III)hydroxyl complexes, resulting in a more complete destruction of the organic compounds and / or dyestuffs (Ruppert et al., 1993). The involvement of high valence Fe intermediate responsible for the direct attack to organic matter and it is well known that the mixtures of Fe(III) + H<sub>2</sub>O<sub>2</sub> (Fenton-like reactions) have shown photon absorption up to 550nm. Fenton systems (Fenton reaction + Fenton-like reaction) have two limitations, the large production of iron sludge and slow reduction of ferric ions by H<sub>2</sub>O<sub>2</sub> in application; but it can be overcome by the addition of UV light (Walling and Goosen, 1973; Laat and Gallard, 1999). The advantages of the oxidative degradation of pollutants using Fenton and Fenton-like reagent over other oxidizing treatment methods are numerous including high efficiency, simplicity in destroying



the contaminants leaving no residue, stability to treat a wide range of substances and non-necessity of special equipment (Heeks *et a*l., 1991).

### **1.2 OBJECTIVES**

The homogeneous (photo) catalytic treatment using the dissolved iron such as the Fe(III)/H<sub>2</sub>O<sub>2</sub> and Fe(III)/H<sub>2</sub>O<sub>2</sub>/UV processes are known to be suitable for the treatment of wastewaters, with high concentrations of organics, due to their high performance and competitive economy (Lee and Yoon, 2004).

This research has focused on the degradation of simulated textile effluent using photo Fenton-like system ( $Fe^{3+}/H_2O_2/UV$ ).

The objectives of this research are:

- a) to investigate the degradation of Naphthol Blue Black in Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>/UV system.
- b) to evaluate the effects of the Fe(III) in the  $Fe^{3+}/H_2O_2/UV$  system.
- c) to compare the oxidative effectiveness of Naphthol Blue Black by  $Fe^{2+}/H_2O_2$ /UV and  $Fe^{3+}/H_2O_2/UV$  systems.



### 1.3 SCOPE OF THE RESEARCH

This research will analyze four main operational parameters-dye concentration,  $Fe^{2+}$  &  $Fe^{3+}$  concentration,  $H_2O_2$  concentration and temperature. UV-VIS spectrophotometer has been applied for the detection of dye concentration,  $H_2O_2$ concentration and  $Fe^{2+}$  and  $Fe^{3+}$  concentration. Napthol Blue Black solution has been chosen as a simulated as a textile dyeing effluent. Graf of Absorbance versus reaction time and In Absorbance versus reaction time have been plot to evaluate the degree of degradation and the chemical reactions.



### **CHAPTER 2**

### LITERATURE REVIEW

#### 2.1 DYES

Dyes are classified as colorants, before it can be considered as a dye it must also be able to impart colour to something else on a reasonably permanent basis. The purpose of dye is usually to be exclusively natural products and help the purchaser sell his product to customer, but sometimes it has special uses, such as radiation detectors and photosensitive dyes for papers and posters (Hans, 1995). Most of the dyes in the commercial market contain considerable unsaturation and usually in the form of aromatic rings with nitrogen unsaturation of several types common to many dyes. (Heaton, 1994)

Ever since the beginning of humankind, people have been using colorants for painting and dyeing of their surroundings, their skins and their clothes. Until the middle of the 19th century, all colorants applied were from natural origin. Inorganic pigments such as soot, manganese oxide, hematite and ochre have been utilised within living memory. Palaeolithic rock paintings, such as the 30,000 year old drawings that were recently discovered in the Chauvet caves in France, provide ancient testimony of their application (Bandara *et al.*, 1997). Organic natural colorants have also a timeless



history of application, especially as textile dyes. These dyes are all aromatic compounds, originating usually from plants (e.g. the red dye alizarin from madder and indigo (Figure 2.1) from woad) but also from insects (e.g. the scarlet dye kermes from the shield-louse *Kermes vermilio*), fungi and lichens.



Figure 2.1 Structure Indigo

Synthetic dye manufacturing started in 1856, when the English chemist W.H. Perkin, in an attempt to synthesise quinine, obtained instead a bluish substance with excellent dyeing properties that later became known as aniline purple, Tyrian purple or mauveine. Perkin, 18 years old, patented his invention and set up a production line. This concept of research and development was soon to be followed by others and new dyes began to appear on the market, a process that was strongly stimulated by Kékulé.s discovery of the molecular structure of benzene in 1865. In the beginning of the 20<sup>th</sup> century, synthetic dyestuffs had almost completely supplanted natural dyes (Walker and Weatherly, 1997)

Dye wastewater also consists of number of contaminants, including acids, bases, dissolved solids, toxic compound and color (Herbst and Hunger, 1993). They are three main classes for dyes; azoic dyes, vat dyes, sulfur dyes, reactive dyes, direct or substantive dyes are most often used on cellulose fibers. Second's class of dyes



used primarily for protein fibers are acid dyes, chrome or mordant dyes. The third class of dyes usually used for manufactured fibers, they are disperse dyes, basic dyes an pigment colours. (Tortora and collier, 1997). Dyes also can be characterized according to their chemical structures and application method. For example azo dyes, anthraquinone dyes, heterocyclic dyes are categorize base of chemical structures and vat dyes, reactive dyes, disperse dyes, direct dyes, acid dyes and basic dyes base of application method (Malik and Saha, 2002). Figure 2.2 shows the structure formulas of several dyes.

The vast array of commercial colorants is classified in terms of colour, structure and application method in the Colour Index (C.I.) which is edited since 1924 (and revised every three months) by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists. The Colour Index (3rd Edition, issue 2) lists about 28,000 commercial dye names, representing ~10,500 different dyes, 45,000 of which are currently produced. Each different dye is given a C.I. generic name determined by its application characteristics and its colour (Bandara *et al.*, 1997).





Figure 2.2 Structure formulas of several dyes (Bandara et al., 1997)



### 2.1.1 Dyes Constitution

All aromatic compounds absorb electromagnetic energy but only those that absorb light with wavelengths in the visible range (~350-700 nm) are coloured. Dyes contain chromophores, delocalised systems with conjugated double bonds, and auxochromes, electron-withdrawing or electron-donating substituents the cause of intensify the colour of the choromophore by altering the overall energy of the electron system (Hung *et al.*, 2001).

The chromogen is an aromatic body containing colour-giving group or the presence of certain groups of atoms, commonly called the chromophore. The chromogen (electron acceptor) as a colour-producing structure and the auxochrome (electron donor), a part to regulate the solubility and dyeing properties are two part consists in the dyes, without both parts, the material is simply a coloured body but does not have the ability to bind with the substrates (Glenn and Gold., 1983).

Chromophore groups cause colour by altering absorption bands in the visible spectrum. Examples of common chromophores group are (Moh, 2002):

- azo group: -N=N-
- ethylene group: C=C
- carbonyl group: > C=0
- carbon-nitrogen group: > C=NH and -CH=N-
- carbon-sulfur group:  $\rangle$  C=S and  $\rightarrow$  C-S-S-C  $\stackrel{\checkmark}{\leftarrow}$
- nitro group: -NO<sub>2</sub> (or =NOOH)

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