REMOVAL OF AZO AND ANTHRAQUINONE DYE FROM TEXTILE WASTEWATER USING OZONE-BASED ADVANCED OXIDATION PROCESSES

by

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TABLES OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AOPs	Advanced Oxidation Process
H_2O_2	Hydrogen Peroxide
$S_2O_8^{2-}$	Persulfate
•OH	Hydroxyl Radical
O_3	Ozone
UV	Ultraviolet
RR120	Reactive Red 120
RB19	Reactive Blue 19
O_3/H_2O_2	Peroxone
$O_3/S_2O_8^{2-}$	Ozone Persulfate
COD	Chemical Oxygen Demand
FTIR	Fourier Transforms-InfraRed
TDS	Total Dissolved Solid
BOD	Biological Oxygen Demand
CO_2	Carbon Dioxide
$SO_4^{\bullet}$	Sulfate Radical
RSM	Response Surface Methodology
BBD	Box Behnken Design
$Na_2S_2O_8$	Sodium Persulfate
H_2O	Hydrogen Dioxide
NaOH	Sodium Hydroxide
KI	Potassium Iodide
$K_2Cr_2O_7$	Potassium Dichromate
$HgSO_4$	Sulphuric Acid
Ag_2SO_4	Silver Sulfate
DOE	Design of Experiment
ANOVA	Analysis of Variance

PENYINGKIRAN PEWARNA AZO DAN ANTHRAQUINONE DARIPADA AIR SISA TEKSTIL MENGGUNAKAN PROSES PENGOKSIDAAN BERASASKAN OZON

ABSTRAK

Pengozonan (O_3) dan proses pengoksidaan lanjutan (PPL) yang melibatkan gabungan ozon dan persulfat ($O_3/S_2O_8^{2-}$) telah dianggap sebagai teknologi untuk merawat efluen daripada industri tekstil dan pewarna. Walau bagaimanapun, prestasi proses untuk penyingkiran pewarna masih tidak jelas. Oleh itu, kajian ini dijalankan untuk menilai prestasi dua kaedah rawatan dengan menggunakan O_3 dan $O_3/S_2O_8^{2-}$ untuk air sisa sintetik yang terdiri daripada azo Reactive Red 120 (RR120) dan anthraquinone Reactive Blue 19 (RB19). Objektif khusus kajian ini adalah untuk membandingkan prestasi proses O_3 dan $O_3/S_2O_8^{2-}$ untuk menyingkirkan warna dan keperluan oksigen kimia (KOK) untuk dua jenis pewarna yang berbeza. Ujikaji O_3 dan $O_3/S_2O_8^{2-}$ telah dijalankan dalam reactor separa kelompok daripada reaktor kaca silinder. Untuk lebih memahami proses ini, penyelidikan memberi tumpuan kepada parameter yang paling penting yang mengawal rawatan seperti kepekatan awal pewarna, masa rawatan, pH dan dos $S_2O_8^{2-}$. Selain itu, prestasi itu dibandingkan dan dinilai dengan menggunakan parameter seperti warna dan COD. Produk-produk degradasi dan pengoksidaan dicirikan berdasarkan perubahan dalam spektra transformasi UV-Vis (ultraviolet-visible) dan *Fourier transforms-infrared* (FT-IR). Di samping itu, pengoptimuman telah dilakukan menggunakan perisian Design Expert 7.1. Kajian ini mendapati bahawa rawatan oksidasi $O_3/S_2O_8^{2-}$ adalah baik terhadap penyingkiran warna RR120. Perubahan dalam spektrum UV-Vis dan FT-IR menunjukkan pemecahan struktur pewarna dan pembentukan perantaraan. Dos awal $S_2O_8^{2-}$, kepekatan pewarna dan pH memberi peranan yang sangat penting dalam penjanaan radikal hidroksil dan sulfat untuk merawat pewarna. Keputusan penyelidikan ini menunjukkan bahawa, penyingkiran sangat bergantung pada dos awal $S_2O_8^{2-}$. Kecekapan penyingkiran meningkat dengan peningkatan dos $S_2O_8^{2-}$ dan masa tindak balas. Walau bagaimanapun, kecekapan penyingkiran menurun peningkatan kepekatan awal pewarna.

REMOVAL OF AZO AND ANTHRAQUINONE DYE FROM TEXTILE WASTEWATER USING OZONE-BASED ADVANCED OXIDATION PROCESSES

ABSTRACT

Ozonation (O_3) and advanced oxidation processes (AOPs) involving ozone in combination with persulphate ($O_3/S_2O_8^{2-}$) has been considered as an emerging technology to treat dyes and dyestuff industrial effluents. However, the performance of dye removal remains unclear. Therefore, this research aim to evaluate the performance of two treatment methods by employing O_3 and $O_3/S_2O_8^{2-}$ for synthetic dye wastewater, consist of azo Reactive Red 120 (RR120) and anthraquinone Reactive Blue 19 (RB19). The main objective of the research are to compare the performance of O_3 and $O_3/S_2O_8^{2-}$ processes for colour, and chemical oxygen demand (COD) removal for two different types of dye. The experiments of O_3 and $O_3/S_2O_8^{2-}$ process were conducted in a semi-batch reactor originated from cylindrical glass reactor. For better understanding of the treatments, the research focused on the most significant parameter that govern the treatments such as initial dye concentration, contact time, pH and $S_2O_8^{2-}$ dosage. Furthermore, the performance is compared by evaluating the key parameters such as colour and COD. The degradation and oxidation products are characterized based on the change in ultraviolet-visible (UV-Vis) and Fourier transforms-infrared (FT-IR) spectra. In addition, the optimization of process parameters was performed by Design Expert 7.1 Software. This study has found that, the $O_3/S_2O_8^{2-}$ advanced oxidation treatment provides good performances in the colour removal of the RR120 in water. The change in the UV-Vis and FT-IR spectra indicated the cleavage of the dye structure and formation of intermediates. The initial $S_2O_8^{2-}$ dosage, dye concentration and pH play an important role in the generation of hydroxyl and sulphate radicals for the dye degradation. The results of this investigation show that, the decolourisation was strongly depending on initial $S_2O_8^{2}$ dosage. The decolourisation efficiency increased with increasing $S_2O_8^{2-}$ dosage and reaction time. While, decolourisation efficiency decreased with raising the initial dye concentration.

CHAPTER 1: INTRODUCTION

1.1 Industrial Water Pollution

Water contamination is one of the problematic issues that cause much of the concern to the society all around the world. The largest polluters is an industry with the generation of large quantity of wastewater used in processing activities. Although a wide range of industries are responsible for releasing the hazardous pollutants into the water bodies, textile dyeing industries is one of the major contributor (Alves & Pereira, 2012). The increasing usage of synthetic dyes are due to their wide colour variety, cost effective and easy to synthesize.

Up to 7 x 10^5 tons of these dyes are generated yearly worldwide and about 10 to 15% of the dyes are lost to effluents during dyeing and finishing process (Siti Zuraida et al., 2013). Dyeing process requires a large quantity of water to produce finished products and indirectly will release the equal amount of wastewater (Vijayaraghavan et al., 2013). These dyestuffs are found to be difficult to destruct due to their complex chemical structure and high stability.

In general, textile effluents consist of different composition of dyes and chemicals that bring out the environmental challenges such as deterioration of the quality of environment. The typical composition of textile effluents are shown in Table 1.1.

Table 1.1: Composite textile effluent characteristics (Al- Kdasi et al., 2005)

Parameters	Values
pH	7.0 – 9.0
Biological Oxygen Demand (mg/L)	80 – 6000
Chemical Oxygen Demand (mg/L)	150 – 12000
Total Suspended Solids (mg/L)	15 – 8000
Total Dissolved Solid (mg/L)	2900 – 3100
Chloride (mg/L)	1000 – 1600
Total Kjeldahl Nitrogen (mg/L)	70 – 80
Colour	50 – 2500

The textile wastewater can be characterized into three types which are high, medium and low strength wastewater based on their COD concentration as shown in Table 1.2.

Table 1.2: Characteristics of textile effluent (Alves & Pereira, 2012)

Wastewater type	COD (mg/L)	Conductivity (μm/cm)
High strength	1500	2900
Medium strength	970	2500
Low strength	460	2100

The dyestuffs that release from dyeing and finishing process are often having strong persistent colour, consists residues of dyes and chemicals such as high concentration of chemical oxygen demand (COD) and complex degradation materials which is environmentally unacceptable (Siti Zuraida et al., 2013; Yasar et al., 2007). Strong colour of textile waste effluents are respectively more difficult to treat due to the different compounds or composition, and concentrations it may contain. High strength of textile wastewater implies that the effluents consists of a large quantity of non-biodegradable organic matter. The major concern with colour and COD are high concentration of colour leads to high turbidity of the effluent, while high COD concentration lead to oxygen deficiency which both will cause negative impacts to aquatic environment (Uma et al.,2013).

1.2 Textile Industry

There are many industries that give benefit to the economy around the world, which includes light and heavy industries. Heavy industry involves heavy appliances including development, automobile, and housing industries. Light industries depend on human work and only use the small equipment. These light industries include agriculture, textile, and printing industries. The textile industry is one of the largest industries in the world in terms of its output or production and employment. A textile sector is a group of related industries which is use variety of natural, such as wool, cotton and other beside it also related to synthetic fibre that produces fabric (Rosi et al, 2007).

Generally, textile industries play an important role in the world in providing the basic need of people and improving the quality of life. The industry comes with a unique process, from the production of raw materials to the distribution to the market. Therefore, it can contribute to the national economic growth. The industry always has to meet customers need, in order to avoid losses (Yilmaz et al, 2015). Textile industry provides various choice according to the customer requirement especially in order of colour (Khatri et al, 2011).

The supplying chain of textile industry involves the use of raw material in the textile plants. Next, the textile plants will through some processes such as spinning, weaving, dying, knitting and printing the raw material. Finally, the product will distribute to the retail stores and sold to the customer. Figure 1.1 shows the flow diagram for textile industries production in details. For fibre sector, the source can be made or taken from animals and plants. The raw materials from plant source are cotton, silk and wool. The source must be cleaned and safe before sent to the primary sector. The materials undergo spinning, texturing, knitting, weaving and dying (Wang et al., 2011). Finally, printing and finishing. All the processes can be done by machine or human. The worker can produce more quality and unique product compared to a machine. However, the machine can speed up the production process. Then, the product will produce into furnish, apparel or other under making-up sector.

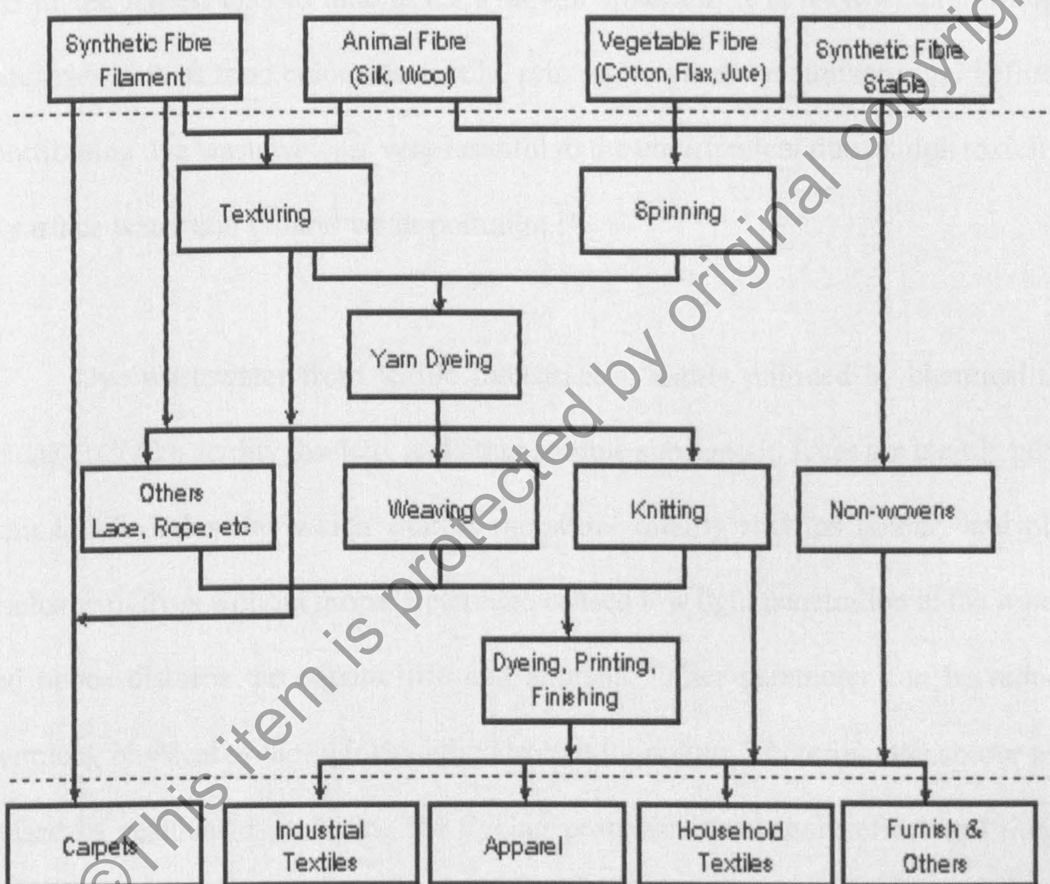

Figure 1.1: Textile industries production (Wang et al., 2011)

1.3 Problem Statement

Nowadays, the colour of effluent discharge from industrial wastewater to the receiving water bodies has become the critical environmental problem. Dyes constitute one of the larger groups of pollutants in effluents discharged from various industries. More than 100,000 commercially available dyes are known (Stolz, 2001). Azo dyes are one of the largest classes among the synthetic colorant. It is used widely in important industries such as food colorants, textile, printing, cosmetic manufacturing. Effluent that contributing dye wastewater is very harmful to the environment due to high toxicity leads to surface water and ground water pollution.

Dye wastewater from textile industries is highly polluted by chemical oxygen demand (COD), acidity, basicity and other soluble substances. Dyes are mainly generated from textile industries which change the water quality such as colour, and pH. The discharge of dyes without proper treatment, caused low light penetration in the water body and hence disturbs the aquatic life and animals. Other parameter can be reduced by chemical, physical or biological method except for colour. Therefore, the colour problem caused by residual dyes during the dyeing processes need more effort and time to be studied and investigated (Muqing et al., 2014).

Due to longer time needed of removing dye residue from the textile wastewater by conventional method wastewater treatment methods such as carbon adsorptions and flocculation, advanced oxidation processes (AOPs) become the most suitable procedures to treat textile wastewater containing dye residue in terms of effective decolourization and reduction of the refractory pollutants. Recent year, ozonation and AOPs involving ozone in combination with hydrogen peroxide (O_3/H_2O_2), photolytic H_2O_2 oxidation (UV radiation with H_2O_2) and advanced fenton have been the new technology to treat dyes textile and dyestuff industrial effluent.

However, the ozone-based concept has been extended to the oxidation processes with sulfate radicals ($SO_4^{\bullet -}$); ozone persulfate ($O_3/S_2O_8^{2-}$). This new treatment has some operational advantage over conventional processes such as wide pH range, low cost of oxidant precursors (Ammonium sulphate or sodium persulfate), no post-treatment steps and complete mineralization of pollutants into harmless products (Abdul Aziz et al., 2014). However, there are only a few research about the $O_3/S_2O_8^{2-}$ process. Thus, a study on dye degradation by $O_3/S_2O_8^{2-}$ process for various dye types and optimized by using Response Surface Method (RSM) are being carried out in this research. Two types of dyes were selected as model of dyestuff effluents, consisting of Reactive Red 120 (RR120, di-azo) and Reactive Blue 19 (RB19, anthraquinone). Azo and anthraquinone dye types are mostly found in textile industry (Chang et al., 2009).

Lastly, the present research is very significant for the development of the efficient and economical treatment for the mineralization of the industrial dye wastewater (Rauf & Salman Ashraf, 2009). Therefore, this current study will investigate the efficiency of industrial dye wastewater treatment by using O_3 and $O_3/S_2O_8^{2-}$.

1.4 Research Objectives

The research is to investigate the effectiveness of O_3 and $O_3/S_2O_8^{2-}$ treatment for synthetic dye wastewater consist of diazo RR120 and anthraquinone RB19. In specific, the objectives of the research are:

1. To evaluate the performances of O_3 and $O_3/S_2O_8^{2-}$ treatment for colour and COD removal of azo and anthraquinone dye.

2. To investigate the effect of operational parameters of ozone-based AOPs treatment performance.

3. To determine the optimum operational parameters by using Response Surface Methodology (RSM) by Box Behken Design (BBD).

1.5 Scope of Research

The main objective is to evaluate the performance of ozone-based AOPs on the degradation of dyes in the presence of synthetic wastewater. Experiments were carried out using laboratory scale semi-batch ozonation via the single-stage flow-through system. For $O_3/S_2O_8^{2-}$ system, sodium persulfate ($Na_2S_2O_8$) was introduced into the ozone reactor prior ozonation.

The performance for two different treatments evaluated based on colour and COD removal of dye wastewater. The research is focused on the most significant operational parameters that affect the treatments such as initial dye concentration (100, 300, 500 mg/L), contact time (0, 1, 2, 3, 4, 5, 10, 15, 20 min), pH (3, 5, 7, 9, 11), and $S_2O_8^{2-}$ dosage (0, 2, 4, 6 g dye/ g $S_2O_8^{2-}$). The treatment process optimized by using Response Surface Methodology (RSM). Furthermore, Box-Behnken Design (BBD) is used to investigate the effect of operating parameters on decolourisation and COD removal efficiency. Finally, the oxidation products will be characterized based on the change in the ultra-violet (UV-Vis) and Fourier transform-infrared (FT-IR) spectra.

CHAPTER 2: LITERATURE REVIEW

2.1 Dye Classification

Dye is a colorant which can be used to dye textile fibres, which means that it has an affinity to the material to which it is applied. The colour of dyes is caused by the presence of chromophore group which is known as auxochromes and conjugated bond. Besides, it is also known as an electron-donating substituent. In addition, the bonding affinity groups or auxochromes are sulfonic radicals, amine, hydroxyl, carboxyl, or their derivatives. The wavelength of dyes is within the visible range of 350 – 700 nm. Dyes are usually water-dispersible or water-soluble organic compounds. It is also capable of being absorbed into the substrate destroying the crystal structure of the substance. The molecules dyes are normally bond chemically to the surface and become a part of the material on which it is applied (Moussavi & Mahmoudi, 2009).

Dyes have many different classes, which can be classified according to their method of application or by the structure. The classes of dyes are basic, acidic, disperse, azo, diazo and metal complex dyes. It is reflected by the chromophoric structure of their constituent molecules.

2.1.1 Classification of Dye by Method of Application

Acid dyes are containing one or more sulfonic acid substituents or other acidic groups; which are water-soluble anionic dyes. Acid Yellow 36 is an example of the acid dyes class. Acid dyes are used to some extent for paper, leather, ink-jet printing, food, and cosmetics. The ionic bonding between the fibre and the dye is the produce the reaction of the amino groups on the fibre with acid groups on the dye. The rate of dye can diffuse through the fibre under the conditions of washing is depends on the fastness of dyes (Carmen & Daniela, 2010).

Azo dyes are the dyes containing at least one -N=N- as a chromophore in an aromatic system (Manu & Chaudhari, 2003). It is a group of dyes, with the azo group and formic acid, caustic soda, sodium nitrate, and metallic compounds. This group is depending on the number of azo groups present they are called as monazo, diazo, triazo, tetrakisazo and polyazo dyes (Ashraf et al., 2009). The azo pigments initially are colourless particles, and then have been coloured using the azo compound. In the industries, the azo are among the most common synthetic dyes both in terms of the number and amount produced with –N=N– groups (Muqing et al., 2014). The azo dye wastewater has high biological oxygen demand (BOD) and chemical oxygen demand (COD) content that visible colour which can obstruct light penetration and oxygen transfer into water bodies. Futhermore, azo dyes account for approximately 60 to 70% of all dyes used in food and textile manufactures (Rauf & Ashraf, 2009).

Anthraquinone dye is a group of organic dyes having molecular structures based upon anthraquinone. It is the second most important class of dye. The group is subdivided according to the methods best suited to their application to various fibres (Christie, 2001). Anthraquinone acid dyes contain sulfonic acid groups that render them soluble in water and substantive for wool and silk; that is, they have an affinity for these fibres without the aid of auxiliary binding agents. The principal reasons why anthraquinone dyes are less widely used commercially than azo dyes is simply that they are less cost effective.

Basic dyes or also known as cationic dyes are water-soluble and able to produce colour cations in solution. Basic dyes are normally substituted amino or amino compound that soluble in acid. It is attached to the fibre by the formation of an ionic bond with anionic groups in fibre. Generally, there are used to dye modified nylon, modified polystyrene, paper, and polyacrylonitrile. Basic brown 1 is an example of basic dyes (Rauf & Ashraf, 2009).

Direct dyes are used for the direct dyeing of cotton and regenerated cellulose, paper and leather. They are water-soluble anionic dyes but are not categorized as acid dyes. In addition, direct dyes can be metallic compounds, fixing agents, sodium salts and azo dyes (Odaro & Wang, 2009). Besides, direst dyes are highly soluble in cold water and bond with fibre by electrostatic forces. They are normally azo dyes that contain more than one azo bond. Direct orange 26 is the example of direct dyes group. Disperse dyes are substantially water-insoluble non-ionic dyes which are also known as acetate dyes. They are applied as very fine divided materials which are absorbed into the fibre and then form a solid solution. These dyes are normally used to dye nylon, hydrophobic fibres and cellulose acetate (Carmen & Daniela, 2010).

Disperse red 4 is the example of disperse dyes. Reactive dyes able to form covalent bonds with fibre molecules. They also can form covalent bonds with –OH groups of cotton through addition and substitution mechanism (Khatri et al., 2011). They used to dyed cotton, rayon, and some nylons. These reactive dyes chemical principal classes are azo, anthraquinone and others. The molecules of reactive dyes are very small compared to complex molecules of direct dyes. Reactive dyes used in printing textiles due to colour brightness are wet fast. Reactive blue 5 is the example of reactive dyes. Table 2.1 shows the classification of dye by application.