



Ozonation And Advanced Oxidation Process Of Wastewater Containing Azo Dye

by

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LIST OF ABBREVIATIONS

AOP	Advanced Oxidation Process
H ₂ O ₂	Hydrogen Peroxide
•OH	Hydroxyl Radical
O ₃	Ozone
UV	Ultraviolet
RB5	Reactive Black 5
RG19	Reactive Green 19
RBB	Remazol Brilliant Blue
RR120	Reactive Red 120
UV/Vis	Ultraviolet Visible
FTIR	Fourier Transforms Infrared
TOC	Total Organic Compound
COD	Chemical Oxygen Demand
kWh	Kilo Watt Hour
UV	Ultraviolet
BOD	Biochemical Oxygen Demand
GCMS	Gas Chromatograph Mass Spectrometer
IUPAC	International Union of Pure and Applied Chemistry
Pt-Co	Platinum-Cobalt Color

Pengozonan Dan Proses Pengoksidaan Lanjutan Air Sisa Mengandungi Pewarna Azo

ABSTRAK

Pengozonan (O_3) dan proses pengozonan lanjutan (AOP) melibatkan O_3/H_2O_2 merupakan teknologi baru untuk degradasi pewarna dalam tekstil dan bahan warna effluen dari perindustrian. Walaubagaimanapun, prestasi perbandingan proses ini dalam penyingkiran pewarna masih lagi tidak jelas. Oleh yang demikian, prestasi O_3 dan O_3/H_2O_2 dalam proses penyingkiran pewarna azo dalam effluen industri dikaji dalam kajian ini. Objektif khusus kajian ini adalah untuk membandingkan prestasi proses O_3 dan O_3/H_2O_2 untuk warna, COD dan penyingkiran TOC, serta menilai kesan kepekatan awal serta pH kepada prestasi proses O_3 dan O_3/H_2O_2 . Pewarna yang digunakan ialah Reaktif Hitam 5 (RB5), Remazol Brilliant Biru (RBB), Reaktif Hijau 19 (RG19) dan Reaktif Merah 120 (RR120). Eksperimen proses O_3 dan O_3/H_2O_2 ini dilakukan di dalam reaktor separa yang diperbuat daripada silinder kaca. Keputusan menunjukkan penyingkiran warna RB5, RBB, RG19 dan RR120 dalam proses rawatan O_3/H_2O_2 adalah lebih tinggi berbanding dengan rawatan O_3 untuk masa pengozonan kurang dari 5 minit dan perbandingan nilai adalah lebih kurang 0.2 % sahaja. Selain itu, penyingkiran warna sepenuhnya telah dicapai dalam masa lebih dari 5 minit pengozonan untuk kedua-dua proses. Keberkesanan kecekapan penyingkiran untuk kedua-dua proses O_3 dan O_3/H_2O_2 , menunjukkan bahawa kedua-dua proses ini memang efektif dalam penyingkiran warna reaktif. Di samping itu, proses O_3/H_2O_2 menunjukkan penyingkiran COD yang lebih efektif dan tinggi berbanding dengan proses O_3 untuk RB5, RBB, RG19 dan RR120. Perbandingan penyinkiran COD untuk kedua-dua proses untuk RB5, RBB, RG19 dan RR120 adalah 14.0, 19.5, 9.1 dan 10.5 %. Manakala, proses O_3/H_2O_2 menunjukkan penyingkiran TOC yang lebih efektif berbanding proses O_3 . Perbandingan penyinkiran TOC untuk kedua-dua proses untuk RB5, RBB, RG19 dan RR120 adalah 12.9, 10.4, 11.2 dan 11.3 %. Ia dapat disimpulkan bahawa, kedua-dua proses O_3 dan O_3/H_2O_2 mempunyai tahap kecekapan yang tinggi dalam penyingkiran warna, COD dan TOC. Kesan kepekatan awal terhadap kecekapan penyinkiran COD dan warna menghasilkan corak yang berbeza bagi proses O_3 dan O_3/H_2O_2 . Kecekapan penyinkiran COD dalam proses O_3/H_2O_2 bagi kepekatan awal yang tinggi (300 dan 500 mg/L) adalah hampir sifar berbanding dengan proses O_3 , ianya disyaki berpunca dari berlebihan H_2O_2 yang mengganggu nilai bacaan COD. Penyinkiran warna RBB untuk kepekatan yang lebih tinggi selepas 15 minit pengozonan menunjukkan kecekapan penyinkiran lebih daripada 99.0 %. Sementara itu, kecekapan penyinkiran warna bagi proses O_3/H_2O_2 adalah 99.0 % untuk pengozonan selama 10 minit. Keputusan ini menunjukkan perbezaan prestasi yang berbeza antara proses O_3 dan O_3/H_2O_2 pada kepekatan awal yang berbeza. Variasi pH tidak memberi kesan ketara terhadap kecekapan penyinkiran warna bagi proses O_3 yang mana masa lebih daripada 10 minit pada kepekatan awal 100 mg/L. Walaubagaimanapun, bagi proses O_3/H_2O_2 kecekapan penyinkiran menurun pada pH 11.0, penyinkiran warna sepenuhnya boleh di capai pada nilai pH sehingga 9.0 sahaja. Sementara itu, kepekatan COD bagi proses O_3 cenderung untuk menurun apabila nilai pH meningkat, ianya menggambarkan peningkatan penyinkiran COD pada nilai pH yang lebih tinggi. Namun demikian, nilai akhir COD bagi proses O_3/H_2O_2 menurun apabila nilai pH meningkat sehingga pH 7.0 dan berlaku peningkatan semula nilai sehingga nilai pH mencecah 11.0.

Ozonation And Advanced Oxidation Process Of Wastewater Containing Azo Dye

ABSTRACT

Ozonation (O_3) and AOP involving O_3/H_2O_2 have been considered as an emerging technology for degradation of dyes in textile and dyestuffs industrial effluent. However, the comparative performance of these processes for dye removal is remains unclear. Therefore, the performance of O_3 and O_3/H_2O_2 processes for azo dye removal in industrial effluent was evaluated in this study. The specific objectives of the research are to compare the performance of O_3 and O_3/H_2O_2 processes for colour, COD and TOC removal, and to evaluate the effect of initial concentration and initial pH on the performance of O_3 and O_3/H_2O_2 processes. The dyes used were Reactive Black 5 (RB5), Remazol Brilliant Blue (RBB), Reactive Green 19 (RG19) and Reactive Red 120 (RR120). The experiments of O_3 and O_3/H_2O_2 processes were conducted in a semi-batch reactor originated from cylindrical glass reactor. The result shows that the colour removal of RB5, RBB, RG19 and RR120 in O_3/H_2O_2 treatment was slightly higher than O_3 treatment for ozonation time less than 5 minutes and the comparison value approximately only 0.5 %. Moreover, complete colour removal was achieved for ozonation time more than 5 minutes in both processes. The significant removal efficiency of both O_3 and O_3/H_2O_2 processes showed that both processes are efficient for colour removal of reactive dyes. In addition, the O_3/H_2O_2 process shows higher COD removal efficiency than O_3 process for RB5, RBB, RG19 and RR120. The comparison of COD removal for both process for RB5, RBB, RG19 and RR120 are 14.0, 19.5, 9.1 and 10.5 %. Furthermore, the O_3/H_2O_2 process provide better TOC removal efficiency than O_3 process. The comparison of TOC removal for both process for RB5, RBB, RG19 and RR120 are 12.9, 10.4, 11.2 and 11.3 % respectively. In can be concluded that for both O_3 and O_3/H_2O_2 processes the highest order of removal efficiency is colour, followed by COD and TOC removal. The effect of initial concentration on the removal efficiency of COD and colour resulted in different trend for O_3 and O_3/H_2O_2 process. COD removal efficiency for O_3/H_2O_2 process for higher initial concentration (300 and 500 mg/L) are almost zero compare to O_3 process, its suspected to be due by the excess of H_2O_2 that interfere the COD measurement. In the view point of colour removal for higher initial concentration of RBB, after 15 minutes O_3 the removal efficiency is more than 99 %. Meanwhile, for O_3/H_2O_2 process the colour removal efficiency are 99 % for 10 minutes ozonation. This result show the different performance between O_3 and O_3/H_2O_2 process at different initial concentration. Variation of pH not significantly effect the colour removal efficiency, especially for O_3 process time longer than 10 minutes at initial concentration 100 mg/L. However, for O_3/H_2O_2 process the removal efficiency decreased at pH 11.0, the complete colour removal can be attained at pH value up to 9.0. Meanwhile, for O_3 process the COD concentration tend to be decreased as pH increased, which describe the increased in COD removal at higher pH. However, for O_3/H_2O_2 process the final COD value decreased as pH increased up to 7.0, and its increased again as pH increase up to 11.0.

CHAPTER 1

INTRODUCTION

1.1 Dye in Wastewater

Textile dyes were one of the popular used organic chemical; however it will cause significant environmental impact and low biodegradability (Zhang et al., 2012). Dyes are mainly consumed in textile, printing, leather and paint industries and the large volume of effluents released from these industries were discharge directly into surface and subsurface water bodies (Uma et al., 2013). Synthetic dyes are frequently used in the textile dyeing plant for aesthetic consideration of the products. In the dyeing process considerable amount of color effluents of high polluting degree are generated (Asghar et al., 2015). The increasing growth of textile, cosmetic, paper and pharmaceutical industry that demanding synthetic colouring agent in its production process has increased the consumption of synthetic dyes (Chang et al., 2001). The synthetic dye annual production capacity is approximately 0.7 million tons, in which azo dyes that containing azo group in its chemical structure are predominant amongst different types of synthetic dyes (Robinson et al., 2001). It is estimated that approximately 10 000 colors are produced on an industrial scale, 20 % of which are employed in the textile industry and 15 % are released into the environment during synthesis, processing or application (Liao et al., 2013). However, more than 10 % of the synthetic dyes used in those industries must be released as an industrial effluent containing dye and eventually lead to serious environmental problem due to their toxicity and non-biodegradable properties (Weber and Stickney, 1993). Consequently, the industries that released

wastewater containing synthetic dyes are forced to follow strict government legislations on the environmental quality standard (Shore, 1996). Therefore, the proper treatment method is necessary to remove or to reduce synthetic dyes concentration in the industrial wastewater. Treatment of industrial effluents containing carcinogenic and mutagenic azo dyes is necessary prior to their final discharge to the environment and meets the stringent environmental regulations (Saratale et al., 2011).

1.2 Treatment Method for Dye in Wastewater

Several physical and chemical treatment processes such as coagulation, adsorption, reverse osmosis and ultra-filtration have been proposed to treat wastewater containing dyes (Lu et al., 2009; Walker et al., 2003; Sheng and Cheng, 1999). However, these treatment methods transfer most of the contaminants from azo dyes, industrial effluent to the solid phase that requires post-treatment of solid wastes, which are expensive operations (Wu, 2008; Al Momani et al., 2002). Biological treatment offers an economical and environmentally friendly alternative when compared with chemical and physical treatment (Olukanni et al., 2009). Mabrouk and Yusef (2009) reported that aerobic treatment is the favourable biodegradation method for azo dye removal. Unfortunately, most of azo dyes are considered to be resistant to aerobic biodegradation (Adams and Kim, 1997). Traditional wastewater treatment technologies have proven to be markedly ineffective for handling the wastewater because of the toxicity and slow degradation of the azo dyes (Jonstrup et al., 2011). On the other hand, anaerobic treatment would be decomposing azo compounds lead to the formation of aromatic amines, which have higher toxicity and carcinogenicity, but easily biodegraded

by aerobic treatment (Suzuki et al., 2001). Therefore, anaerobic treatment on azo dyes will be effective if sequentially combined with aerobic treatment (Ong et al., 2005).

Nowadays, advanced oxidation processes (AOP's) involving O_3 , O_3/H_2O_2 , O_3/UV , UV/H_2O_2 , $O_3/UV/H_2O_2$ and Fe^{2+}/H_2O_2 have been considered as an emerging technology for degradation of azo dyes in textile and dyestuffs industrial effluent (Bidga, 1995; Ku and Hsieh, 1992). This technology, which is based on the production of OH radicals as oxidizing agent, is considered as a promising procedure for the treatment of textile wastewater for complete removal colour and reduction of organic pollutants in the wastewater (Hsing et al., 2007).

1.3 Problem Statement

Ozonation (O_3) and AOP involving O_3/H_2O_2 have been considered as an emerging technology for degradation of dyes in textile and dyestuffs industrial effluent. Previously, several studies have been conducted to evaluate the performance of ozonation or other AOPs to reduce various contaminants in water and wastewater. Decontamination technologies such as: adsorption, coagulant, flocculation, sedimentation, bio-filtration and gas stripping, which very often shift the pollution issues from water to another medium, the utilisation of AOPs leads to the decomposition and mineralization of contaminants in water by in situ generation of active oxidising reagents such as hydroxyl radical ($OH\cdot$), superoxide ($\cdot O_2^-$), ozonide ($\cdot O_3^-$), photoproduced electronhole pairs (Mehrjouei et al., 2015). These oxidative species attack the existing pollutants in water and oxidise them gradually to less harmful substances. For instance, Takahashi et al. (2007) reported the performance of preozonation and subsequent biological treatment process for degradation of organic

pollutants and colour removal in the wastewater containing dyes. Ozone reacts slowly with certain organic substances such as inactivated aromatics or saturated carboxylic acids, and in many cases does not completely mineralise these organic compounds (Beltran et al., 2012). These disadvantages make the application of ozone alone to treat pollutes water economically undesirable and is the reason why ozonation processes are sometimes modified by addition of catalysts and/or irradiation to the oxidation medium to improve oxidation efficiency.

However, the comparison of dye removal efficiency and characteristic of the intermediate products in O_3 and O_3/H_2O_2 is remains unclear. Therefore, the performance of dye wastewater oxidation by O_3 and O_3/H_2O_2 should be further investigated in order to compare the efficiency of both processes. In addition, the characteristics of intermediate and final products for ozonation and AOP should be clarified in order to explain the mechanism of dye decomposition by both processes. The main problem of AOPs lies in the high cost or reagents such as ozone, hydrogen peroxide or energy sources such as ultraviolet light. Mean characteristic of the wastewater are presented in Table 1.1

Table 1.1 : Physico-chemical characterization of textile industrial wastewater (Balapure, K. et al., 2016).

Parameter	Concentration
pH	7.5 ± 0.3
Color (Pt-Co)	3340 ± 25.7
COD (mg/L)	10,000 ± 34.3
BOD ₅ (mg/L)	3330 ± 24.2
Total alkalinity (mg/L)	3950 ± 31.6
Total solids (mg/L)	4220 ± 25.4
Total suspended solid (mg/L)	1510 ± 20.8
Total dissolved solids (mg/L)	1960 ± 19.8
Chloride (mg/L)	2400 ± 14.8
Phosphate (mg/L)	650 ± 22.5
Sulphate (mg/L)	930 ± 29.5

1.4 Research Objectives

The general objective of this study is to evaluate the performance of O₃ and O₃/H₂O₂ processes to removal colour, COD and TOC of wastewater containing azo dye.

In detail, the objectives of the research are:

- i. To compare the performance of O₃ and O₃/H₂O₂ processes for colour, COD and TOC removal of Reactive Black 5 (RB5), Remazol Brilliant Blue (RBB), Reactive Green 19 (RG19) and Reactive Red 120 (RR120).
- ii. To evaluate the effect of initial concentration and initial pH on the performance of O₃ and O₃/H₂O₂ processes.

1.5 Research Scope

In this study, O_3 and O_3/H_2O_2 experiments were carried out in a semi batch reactor. The absorption of UV/Vis spectra, colour removal, COD removal and TOC removal were considered as the main parameters in evaluating the performance of these processes. These performance indicators were compared for each dye to observe the trend of dye degradation and explaining the possible reason that affecting the different in performance. Some set of experiments that were conducted within the range of ozonation time from 0 to 20 minutes at constant pH of 7.0 were used as the basis of performance evaluation. To further investigate the mechanism of oxidation process in O_3 and O_3/H_2O_2 treatment, chemical functional group transformation were determined using Fourier transforms infrared (FT-IR) analyser.

1.6 Thesis Outline

This study was carried out to achieve the objectives outlined in the previous section. To accomplish these objectives, the thesis outline was arranged in five chapters as follows:

In Chapter 1, the introduction of the study, problem statement, objectives and scope of the study were described. This chapter justifies the rationale why this study should be conducted and what benefit could be gained at the end of the study. The thesis organization was also included in the last section of this chapter.

Chapter 2 (Literature Review) covers the review on the colourant, types of dye in the environment and contribution of this colourant towards environmental pollution. In addition, this chapter also discusses on the conventional dye wastewater treatment

methods and its complications. Moreover, the information on ozonation and AOP treatment for these dye effluents are also discussed in this chapter.

Chapter 3 (Methodology) presented the research methodology, starting from explanation on chemical and materials used throughout the research. It is followed by the detailed experimental procedure which includes the O_3 and O_3/H_2O_2 processes by varying contact time, pH and ozone dosages. In order to evaluate the performance of O_3 and O_3/H_2O_2 processes, various qualitative and quantitative analytical procedures were employed. UV/Vis spectrophotometer was used for characterization and colour analysis. COD was analyzed by using the Hach DR2800 Spectrophotometer and TOC was analyzed by HACH Direct Method. Chemical functional group in raw wastewater and intermediate products was analyzed by using FTIR.

Chapter 4 (Results and Discussion) presented the result and discussion base on the specific objective set in Chapter 2. The results started with elution of UV/Vis spectra of various dyes that exposed to O_3 and O_3/H_2O_2 processes, which reflect the colour removal during the processes. Furthermore, the results of COD and TOC removal were also correlated with colour removal to evaluate the performance of O_3 and O_3/H_2O_2 processes for dye removal. The characterization of intermediate products during the O_3 and O_3/H_2O_2 processes of dyes that identified by the change in FTIR spectra was also clarified to justify the effect of these process on functional group transformation in dye molecule. In addition, the results on the effect of operating parameters such as initial pH and concentration were also presented.

Chapter 5 (Conclusions and Recommendations) summarized the main results in this study and recommended the suggestions for improvement in the future studies in the related research area.

CHAPTER 2

LITERATURE REVIEW

2.1 Colourant and Environment

Colourant is an important element that forms the variety of appearance in the environment. All the things that can be seen in our surrounding will have their own colours. Colours are very important for us to identify all the things and for pleasant view since wonderful colour can lighten up our heart. First-order colours refer to yellow, blue and red. These are the primary colours that will make up other colours through mixing (Berns, 2000). Different colours are visible to us because of that our eyes can absorb different spectrum range of visible light. Red has the longest wavelengths, followed by the greens and finally the blues. Hence, we can see the colour is because of that colour emitted the wavelength. Different colour will have different wavelength (Bohren, 2006).

Colourant is materials that are added to something else to cause a change in the colour. It can be dyes, pigments, inks or paints (Finlay and Victoria, 2003). Dyes and pigments will be seen in colour as they absorb some wavelength of light more than others. Differ from dye, pigment is insoluble and has no affinity for the substrate. Some dyes are soluble and can be dissolved in wastewater stream, whereas pigments will retain in particle or crystal form. Therefore, it is very hard for the pigments to be reacting with their characteristics. This has caused the pigments could not be used in some purpose of manufacturing, as compared to dyes. However, this also shows that dyes will not be easy to be monitored since it is in liquid form. It can dispersed fast and hard to withdraw back after it flows to the water body, such as the river and sea (Allen,

1971). In particular, some dyes have toxic, carcinogenic and even genotoxic effects on the human (Saroj et al., 2014). Thus is important to remove dyes in the textile wastewater before discharging to receiving water bodies (Wang et al., 2013). However the removal of different dyes is always a remarkable challenge (Tian et al., 2013). Gupta et al., conducted a review study from 1988 to 2015 to present the different diversified attempts, such as photodecolorization, combination of coagulation with catalytic oxidation, adsorption, photocatalysis etc., used for decolorization and degradation of a mixture of dyes, where the problem of dye removal become more difficult for effluents containing a dye matrix.

2.2 Dyes

2.2.1 General Overview on Dyes

Dyes are commonly used as an additive in materials to impart colour and become integrated with the materials. Dyes contain chromophores, which also known as conjugated double bond and auxochromes, which is the electron-donating substituent. Chromophore of a dye can be defined as functional group that give colour, which is represented by group of azo (N=N) in azo dye. The $-N=N-$ double bond in the azo dyes is the chromophoric group for color (Aljamali, 2015). The aromatic structure such as benzene, naphthalene or anthracene rings is classified as chromogen in dye. In addition, other functional group such as carbonyl ($=C=O$), carbon-nitrogen ($>C=NH$ or $-CH=N-$), nitro ($-NO_2$ or $=NO-OH$), nitroso ($-NO$ or $N-OH$) are also classified as chromogen. On the other hand, sulfonic group or their derivatives, hydroxyl, amine and carbonyl are acted as auxochrome or bonding affinity groups. The colour of dyes can be detected within the visible wavelength in the range of 350nm to 700nm. In the synthesis of dye,

the correlation between chromogen-chromophore and auxochrome will determine the color of dye. Generally, dye can be formed from the reaction of organic compounds such as naphthalene with an acid or alkali along with an intermediate, such as a nitrating or a sulfonating compound, and a solvent. They will be synthesized through sulfonation, halogenations, amination, diazotization and coupling followed by separation processes that include distillation, precipitation and crystallization (Zollinger, 2003).

2.2.2 Classification of Dyes

Dyes can be classified according to structure varieties as follows: azo, diazo, acidic, basic, anthraquinone based, disperse and metal complex dyes (Ahmad et al., 2003). Acetate rayon dyes are the dyes synthesized for application in synthetic fibers and cellulose acetate. These dyes are normally applied to the nitrogenous fibers of fabrics in organic or inorganic acid solutions by binding to the cationic NH_4 ions of the fibers. The three most commercially important acid dyes are azo, anthraquinone and triarylmethane. They have poor wet fastness (Kulkarni et al., 1985).

Azoic dyes are the dyes containing the azo group as the chromophore and formic acid, caustic soda, metallic compounds, and sodium nitrate. The azo dye is widely used for colouring the cotton. They are applied by combining two soluble components impregnated in the fiber to form an insoluble colour molecule. In addition, basic dyes are cationic compounds that are used for dyeing acid-group containing fibers. The basic dye contains softening agents, acetic acid and the amino derivatives in its molecular structure.

Direct dyes can be coming from the azo dyes, and sodium salts, fixing agents, and metallic compounds, such as chrome and copper. Direct dye bonds to fibers by

electrostatic forces and are highly soluble in cold water. They are usually the azo dyes with more than one azo bond.

Mordant or chrome dyes are the dyes with metallic salt or lake formed directly on the fiber by the use of aluminum, chromium, or iron salts that cause precipitation in situ. Sulfur or sulfide dyes contain sulfur and can precipitate from sodium sulfide bath with the furnished of dull shades with good fastness to light, washing, and acids but susceptible to chlorine and light. It is primarily for cotton and rayon, but not applicable to wool and silk as it can damage them by dyeing process. Vat dyes can impregnate into fiber under reducing condition and reoxidize to an insoluble colour.

Disperse dyes are colloidal and have very low water solubility. They are used for polyester, nylon, acetate and triacetate fibers. High temperature will sublime the dye and once it is inside the fiber, the dye will condense to a solid colloidal state and is adsorbed on the fiber.

2.2.3 Reactive Dyes

The reactive dye has an active group that determines the specific reactive properties by forming the covalent bonds with $-OH$ groups of cotton through substitution and addition mechanism (Khatri et al., 2011). Covalent bonds can be formed when reactive dyes are attached with the fiber molecules. Molecules of reactive dyes are much smaller than the complex molecules of direct dyes. The dye is more expensive than the direct dyes, but it has the excellent shade reproducibility and good leveling properties with excellent wet fastness. It will become the integral part of textile fiber that is dyed.