Study on Photocatalytic Mineralization of Various Azo Dyes under Solar Light Irradiation

by

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LIST OF ABBREVIATIONS

Ag_2SO_4	Silver sulfate
AOPs	Advance Oxidation Processes
AO7	Acid Orange 7
BOD_5	Biochemical Oxygen Demand for five days
CdS	Cadmium sulfide
Cl^-	Chloride ion
COD	Chemical Oxygen Demand
CO_2	Carbon dioxide
CuO	Copper(II)oxide
Cu_2O	Cuprous oxide
E.coli	*Escherichia coli*
Fe_2O_3	Iron(III)oxide
Fe_2O_3/UV	Iron(III)oxide/Ultraviolet
H_2O	Water
H_2O_2	Hydrogen peroxide
H_2O_2/UV	Hydrogen peroxide/Ultraviolet
H_2SO_4	Acid sulfuric
IC	Ion Chromatography
$K_2Cr_2O_7$	Potassium dichromate
MB	Methylene Blue
MnO_4	Permangate
NaOH	Sodium hydroxide
NC	New Coccine
NO_2^-	Nitrite ion
NO_3^-	Nitrate ion
$\bullet O_2^-$	Superoxide radical anion
O_3	Ozone
O_3/ H_2O_2/UV	Ozone/ Hydrogen peroxide/Ultraviolet
O_3/UV	Ozone/Ultraviolet
OG	Orange G
•OH	Hydroxyl radical
OH^-	Hydroxide ions
RB	Rhodamine B
RB5	Reactive Black 5
RG19	Reactive Green 19
SEM	Scanning Electron Microscope
SO_4^{2-}	Sulfate ions
TiO_2	Titanium(IV)oxide
TSS	Total Suspended Solid
UV	UltraViolet
UV-Vis	UltraViolet-Visible
WO_3	Tungsten oxide
XRD	X-Ray Diffraction
ZnO	Zinc oxide

LIST OF SYMBOLS

%	Percent
°C	Degree Celcius
C	Concentration
C_0	Concentration at time = 0
C_t	Concentration at time = t
e^-	Excited electron
h	Hour
h^+	Electron hole
k	Reaction rate constant
mg/L	Miligram per litre
mM	Milimolar
nm	Nanometer
$\bullet O_2^-$	Superoxide radical anions
•OH	Hydroxyl radical
t	Time
µm	Micrometer

Kajian Fotopemangkinan ke atas Penguraian Pelbagai Pewarna Azo di Bawah Cahaya Penyinaran Suria

ABSTRAK

Pewarna azo yang diwakili oleh *azo chromophores* (-N = N-) merupakan kelas pewarna terbesar yang digunakan dalam kebanyakan industri terutamanya industri-industri tekstil. Bahan-bahan kimia lain yang bersifat mutagenik atau toksik kepada alam sekitar dan kehidupan manusia akan hadir dalam badan-badan air jika efluen air sisa daripada industri dilepaskan tanpa merawat mereka dengan betul. Terdapat banyak kaedah rawatan yang biasa digunakan untuk menghapuskan pewarna azo di dalam air sisa, sebagai contoh, penyerapan, membran penapisan, penukaran ion dan sebagainya. Walau bagaimanapun, kaedah-kaedah rawatan ini memerlukan kos yang tinggi dan menghasilkan pencemar yang susah untuk dimusnahkan. Untuk mengurangkan kos merawat sisa air, tetapi berkesan untuk menghapus pewarna azo, fotopemangkinan telah dikaji oleh pengkaji-pengkaji terdahulu. Oleh itu, tujuan utama kajian ini adalah untuk menilai uraian pelbagai pewarna azo oleh proses fotopemangkinan. Pemangkin dan pewarna azo utama yang digunakan dalam kajian ini masing-masing adalah zink oksida (ZnO) dan *New Coccine* (NC). Dalam bahagian pertama, kajian ini adalah untuk membandingkan fotopemangkinan antara penyahwarnaan *Orange G* dan *New Coccine*. Perbandingan antara pewarna azo telah ditentukan melalui beberapa parameter operasi seperti dengan dan tanpa penyinaran cahaya suria, kepekatan awal pewarna, dos pemangkin, pH, dengan dan tanpa pengudaraan. Hasil kajian menunjukkan bahawa kepekatan NC menurun dengan cepat dalam setiap parameter dan hampir mencapai 100 % kecekapan penyingkiran berbanding OG. Bahagian kedua dalam kajian ini adalah untuk menilai kesan struktur molekul lima pewarna azo (Asid Orange 7, *Orange G*, *New Coccine*, Reaktif Hitam 5, Reaktif Hijau 19) dalam penguraian fotopemangkinan di bawah penyinaran cahaya suria. Di antara pewarna-pewarna azo ini, Reaktif Hijau 19 menunjukkan prestasi yang terbaik dalam proses fotopemangkinan dan mencapai 100 % daripada kecekapan penyingkiran di bawah cahaya penyinaran suria. Selain itu, kajian ini juga memberi tumpuan kepada keberkesanan fotopemangkin lain (CuO, Fe_2O_3, TiO_2) pada degradasi pewarna. Luas permukaan dan corak untuk semua pemangkin juga diperiksa. Pengurangan kepekatan pewarna ditentukan dengan UV-Vis spektrofotometer. Penguraian pewarna diperiksa oleh ion kromatografi (IC) dan pengukuran permintaan oksigen kimia (COD). Kepekatan akhir New Coccine mencapai penyingkiran 100 % selepas 5 jam di bawah penyinaran cahaya suria. Antara semua fotopemangkin, ZnO menunjukkan penyingkiran tertinggi yang mencadangkan bahawa ia menyerap sebahagian besar spektrum solar dan penyerapan lebih quanta cahaya. Air sisa batik juga menunjukkan penyingkiran warna yang tinggi dalam 10 jam pensampelan dan kepekatan COD yang menurun daripada 1332 mg/L hingga 286 mg/L selepas 12 jam masa radiasi. Kedua-dua pewarna azo dan fotopemangkin mengikuti kadar tetap pseudo-pertama-susunan dan sangat sesuai dengan model kinetik Langmuir-Hinshelwood. Kesimpulannya, sama ada pewarna sintetik atau air sisa tekstil sebenar, kedua-duanya boleh degradasi dan dimusnahkan oleh pemangkin dengan kehadiran cahaya suria.

Study on Photocatalytic Mineralization of Various Azo Dyes under Solar Light Irradiation

ABSTRACT

Azo dyes represented by azo chromophores (-N=N-) are the largest class of dyes used in many industries especially textile industries. Other chemicals that mutagenic or toxic to the environment and human life will present in the water bodies if the wastewater effluent from industries was released without treating them properly. There are many conventional treatment methods in order to remove azo dyes in wastewater, for example adsorption, membrane filtration, aerobic or anaerobic process and others. However, these conventional treatment methods required high cost and generated other pollutants which difficult to be destroyed. In order to minimize the cost for wastewater treatment but effective in removal of azo dye, solar photocatalytic had been discovered by previous researchers. Therefore, the main purpose of this research was to evaluate the mineralization of various azo dyes by solar photocatalytic process. The main photocatalyst and azo dye used in this study was zinc oxide (ZnO) and New Coccine (NC), respectively. In the first section, the study was to compare the solar photocatalytic between decolorization of Orange G and New Coccine. The comparison between the azo dyes was determined through several operating parameters such as with and without solar light irradiation, initial dye concentration, catalyst dosage, pH and with and without aeration. The results showed that concentration NC decreased rapidly in each parameter and almost achieved 100 % removal efficiency compared to OG. The second section in this study was to evaluate the effect of molecular structure of five azo dyes (Acid Orange 7, Orange G, New Coccine, Reactive Black 5, Reactive Green 19) in photocatalytic mineralization under solar light irradiation. Among these azo dyes, Reactive Green 19 showed great performance in photocatalytic process and achieved 100 % of removal efficiency under solar light irradiation. Moreover, this study also focused on the effectiveness of other photocatalysts (CuO, Fe_2O_3, TiO_2) on the degradation of dye and showed that photocatalyst with higher band gap (ZnO) rapidly decolorized and mineralized the azo dye. The surface area and patterns of all photocatalysts were also examined. The reduction in dye concentration was determined by UV-Vis spectrophotometer. The mineralization of dye was examined by ion chromatography (IC) and chemical oxygen demand (COD) measurement. The final concentration of New Coccine achieved 100 % removal after 5 h irradiation time. Among all the photocatalysts, ZnO showed highest removal which suggesting that it absorbs large fraction of the solar spectrum and absorption of more light quanta. *Batik* wastewater also showed great color removal within 10 h sampling and its COD concentration decreased from 1332 mg/L to 286 mg/L after 12 h irradiated time. Both of azo dyes and photocatalysts followed pseudo-first-order rate constant and well fitted the Langmuir-Hinshelwood kinetic model. In conclusion, either synthetic dye or real textile wastewater, both of them can be degraded and mineralized by photocatalyst with presence of solar light.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Dyes and pigments are produced more than 7 x 10^5 ton and approximately 10,000 dyes used annually world-wide (Akhtar et al., 2005). Generally, these dyes and pigments are widely used by many types of industries such as textiles, pharmaceuticals, paints, food and leather. All of these products used 60-70 % of azo dyes, which molecules with one or more azo (-N=N-) and linked to the aromatic structure (Zee et al., 2003; Davies et al., 2006). However, 15 % of these dyes is lost during the dyeing process and released as textile effluents.

There are many disadvantages and side effects of these effluents either to human or environment as well as aquatic life. The untreated effluents from pulp and paper mill, for example, will cause thermal impacts, slime growth, color problems and also increase the amount of toxic substances in the water stream, which will cause death to aquatic life, especially fish and zooplankton (Pokhrel and Viraraghavan, 2004). In addition, high level of NH_4-N and enormous quantities of leachates also posed a serious pollution threat to the water environment and lost aesthetical aspects to the environment (Connolly et al., 2004).

Dyes produce from *batik* industrial processes have obtained notoriety as hazardous substances, because most of them are persistent and toxic to the environment (Al-Momani et al., 2002). Disposal of large amount of colored effluent produces severe environmental hazards due to the organic compounds that contain in the effluent which are not easily degraded by conventional wastewater

treatment such as adsorption, coagulation, biological treatment and others (Shanthi and Kuzhalosai, 2012).

In recent years, there has been an increasing interest in advanced oxidation processes (AOPs) as an effective wastewater treatment. The pollutants in wastewater such as toxic organic and inorganic contaminants will completely destroy by •OH which are generated from AOPs (Ghaly et al., 2011). The photo-Fenton process, UV photolytic process, Fenton process, sonolysis and ozonation are several of the examples in AOPs for treating contaminants such as dye, phenol and leachate.

Among various treatment methods in AOPs, photocatalytic process by semiconductor materials is a promising technology in dealing with worldwide pollution problems (Gokakakar and Salker, 2009). Photocatalysis is a highly effective and inexpensive process compared to other methods and it is one of the potential techniques to either reduce or oxidize hazardous pollutants (Joshi and Shrivastava, 2011). Moreover, Sharma et al. (2012) also stated that solar photocatalytic is an efficient technique to eliminate the pollutants from aqueous and gaseous media.

The purpose of the photocatalyst is to generate reactive •OH upon absorption of UV or visible light, which in turn causes the destruction of chemical structure of organic pollutants (Chaturvedi et al., 2003). The most semiconductors used as photocatalyst are TiO_2, ZnO, WO_3, CdS, Fe_2O_3 and others. There are several studies about solar photocatalytic by other researchers for decolorizing of either synthetic dyes or real textile wastewater (Lu et al., 2008; Solarska et al., 2005; Stroyuk et al., 2007).

1.2 Problem statement

Paper and pulp mill industries, textile industries and rubber sheet industries are some of the industries that consumed dyes and colorants for their products. The wastewater that released from industries without treating them will give harmful effect to the human, aquatic life and also environment. The conventional treatment method such as membrane filtration will remove all types of dyes, however, it will create concentrated sludge which are difficult to be destroyed. The compounds that present in the dyes can breakdown by electrochemical destruction method, but it requires high cost of electricity. Ozonation is one of the techniques in AOPs and also had been widely applied for color removal, but it has short half-time which is only 20 minutes. Besides that, Fenton's reagent also effective for decolorization of both soluble and insoluble dyes, but at the end of this treatment, it will generate sludge. Solar photocatalytic is an alternative treatment method instead of UV light for degradation of organic pollutants which is an eco-friendly process and more economical. Moreover, the application of this treatment method in the industries is not much as other treatment methods. This treatment method is suitable to be applied in Malaysia because of ample amount of solar light is available in this country. The degradation of dyes and other organic pollutants also depend on the photocatalyst that had been chose and in this study, ZnO was used as photocatalyst due to its low cost, has higher larger quantum efficiency as well as photocatalytic efficiency.

1.3 Objectives

There are four objectives for this study, which are:

i. To investigate the effects of operating parameters of Orange G and New Coccine by solar photocatalytic process.

ii. To study the effect of molecular structure of azo dyes in photocatalytic mineralization under solar light irradiation

iii. To study the effect of different semiconductors on photocatalytic degradation rate and its characterization.

iv. To apply the photocatalytic processes in real industrial wastewater.

1.4 Scope of study

The scope of this study was to evaluate the effect of operating parameters such as presence of solar light irradiation, initial dye concentration, catalyst dosage, pH and addition of aeration on the degradation of azo dyes by solar photocatalytic activity. Other than that, this study also investigates the effect of different number of sulphonate groups of five azo dyes (Acid Orange 7, Orange G, New Coccine, Reactive Black 5 and Reactive Green 19) on photodegradation rates. Four catalysts or semiconductors which are CuO, Fe_2O_3, TiO_2 and ZnO had been studied for the effect of semiconductor towards the degradation of azo dye. The characterization of these catalysts such as surface morphology and their patterns also has been examined by SEM and XRD, respectively. Besides that, this study also applied to the real textile industrial wastewater which was *batik* wastewater and all the operating parameters such as pH, catalyst dosage and aeration were examined.

The mineralization of synthetic dyes and *batik* wastewater was analyzed by the changes of UV-Vis spectrum and chemical oxygen demand (COD). Ion chromatography also used in this study to determine the concentration of sulfate ion in the dye during photocatalytic reaction. The sample of azo dye was analyzed for each irradiation time.

The Langmuir-Hinshelwood kinetic model and pseudo-first-order had been used in this study to the degradation rate of azo dyes under solar photocatalytic process using ZnO and other catalysts.

CHAPTER 2

LITERATURE REVIEW

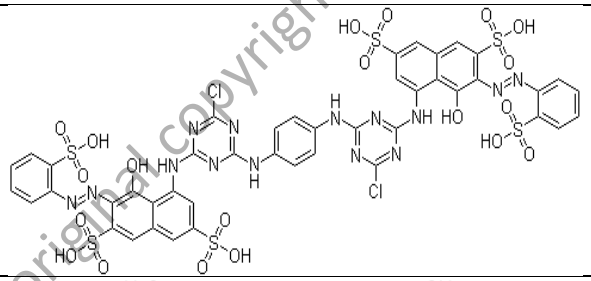
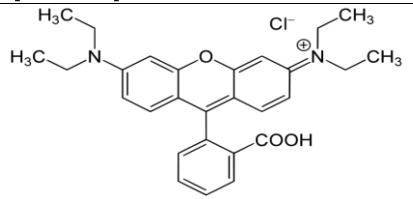
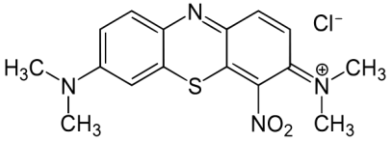
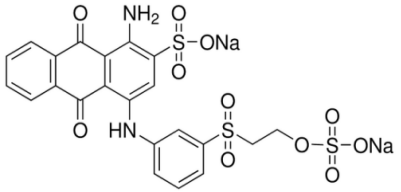
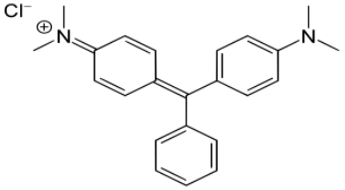
2.1 Definition and classification of dyes

Dye is a colored substance which generally applied in an aqueous solution. Dye molecules comprise of two components which is chromophores and auxochromes. The chromophores are responsible for producing or giving color to the dye, meanwhile auxochromes will render the dye molecule to be soluble in water and enhanced the attachment of affinity towards the fibers. There are three ways to classify the dyes. First, dye can be classified according to their chemical and/or physical properties. Second, dyes also can be classified based on their origin either natural or synthetic. The third way is through their characteristics which related to the application process in industries. There are six types of dyes which commonly used by industries for coloring their products or by previous researcher in their studies. These dyes are differentiated according to their chemical structure as shown in Table 2.1.

2.2 Azo dye

Azo dyes are the largest class of synthetic dyes amongst various dyes which manufactured annually and used worldwide in industries ranging from pharmaceuticals to textile (Jain et al., 2012). The azo dye is characterized by the presence of azo bond linkage (-N=N-) in its molecular structure. Besides that, the azo dye also may contain one (mono), two (di) or three (tri) azo bond linkage. Acid Orange 7, Orange G and New Coccine are examples of

Table 2.1: Classification of dye according to chemical structure (Nidheesh et al., 2013)

Types	Example	Molecular structure
Azo dye	Reactive Red 120	
Xanthene	Rhodamine B	
Thiazine	Methlyene green	
Anthraquinone	Remazol Brilliant Blue R	
Triphenylmethane	Malachite Green	

monoazo dyes while Reactive Black 5 and Reactive Green 19 are considered as diazo dye. Due to their resistance to chemical photodegradation and degradation, dyes would persist in natural setting which can cause problems in aesthetic and environment (Tsang et al., 2007). For example, Acid Yellow 36 used in textile, tannery, paper and soap is acute toxicity to heteropneustes fossilis and toxic and carcinogenic to nature (Malik, 2003). Another diazo dye such as Direct Red 23 also used in production of textile, tannery and paper and its dose will not allow solar light to penetrate into rivers or streams which then affects the photosynthesis of aquatic plants (Abdelwahab et al., 2005). An acute exposure to Methylene Blue will cause increased heart rate, jaundice, vomiting and Heinz body formation (Hameed and Ahmad, 2009).

2.3 Treatments of dye

Physical methods such as adsorption techniques and membrane-filtration processes are commonly treatment that used by many industries in treating wastewater. Nakamura et al. (2003) in their study suggested that charcoal from coffee ground is useful for decolorization of Acid Orange 7. Even adsorption methods have attracted considerable interest due to their higher efficiency for the removal of dye, it is not often been used due to high cost of adsorbents especially activated carbon (Robinson et al., 2001). Another physical treatment method is ion exchange. The colored wastewater passed over the ion exchange resin until the available exchanged sites are saturated. Both of anionic and cationic dyes can be removed efficiently by employing this wastewater treatment method and there is no loss of adsorbent on regeneration, however it cannot accommodate a wide range of dyes (Wu et al., 2008). Filtration such as nanofiltration, microfiltration and ultrafiltration also effective in treating wastewater contains dye, however, this treatment method required high working pressure, energy consumption and also cost of membrane (Gupta and Suhas, 2009).

Chemical oxidation methods especially use various oxidizing agents, such as hydrogen peroxide (H_2O_2), permanganate (MnO_4) and ozone (O_3) enable the decomposition or destruction of dye molecules. Ozonation, for example, has been found to be effective due to its high reactivity with many azo dyes and good color removal efficiencies (Alaton et al., 2002). The ozone used can selectively oxidize unsaturated bonds (-N=N- or -C=C-) and also aromatic compounds. However, high cost of ozone and low COD removal capacity will limit the practical application of this technique in industries (Anjaneyulu et al., 2005). The Fenton's reagent process is the combination of hydrogen peroxide (H_2O_2) which activated with Fe (II) salts and it was effectively remove either soluble or insoluble dyes from wastewater. This process involved flocculation where the impurities from wastewater are transferred to the sludge which did not settle if released to the environment.

Biological treatment is another ways that applied by industries to treat their wastewater before releasing them into water stream. Biodegradation methods such as fungal decolorization, bioremediation systems and biomass commonly applied to treat the effluents due to the microorganisms such as yeasts, bacteria and fungi that are able to degrade and accumulate different pollutants (Fu et al., 2001). Herrera-Robledo et al. (2010) have recently studied anaerobic membrane bioreactor for treating municipal wastewater and found that the systems produced a clear effluent free of suspended solids. However, longer time is required in biological treatment especially for growth of microorganism. Moreover, large land area is required and lifetime of microorganisms also plays an important role for biological treatment (Fu and Viraraghavan, 2001). Even though bacteria showed great dye removal rate, but the fermentation process will limit the applicability of this treatment methods to cope with larger volume of colored effluents.

2.4 Advanced oxidation processes (AOPs)

Advanced oxidation processes (AOPs) are one of the techniques under chemical methods that constitute a promising technology to treat wastewaters contain non-easily removable organic compounds such as color and all AOP are designed to produce hydroxyl radical (Sharma et al., 2011). The main advantage of this degradation method is that it can be carried out under ambient conditions which lead to complete mineralization of organic carbon (Pare et al., 2008). The examples of AOPs treatment methods to degrade organic pollutants and dyes are O_3/UV, H_2O_2/UV, O_3/H_2O_2/UV, Fe_2O_3/UV and photolysis processes. Lü et al. (2013) conducted a study that showed ozonation in combination with UV irradiation of 185 W had a synergistic effect on the decolorization of methyl orange and the effect was more pronounced on the COD removal rate during the degradation process. Soares et al. (2006) carried out a research to study the influence of operating parameters by ozonation treatment for decolorization of textile effluents and dye solutions under continuous operation and they found that this treatment method was effective for dye removal but less effective in TOC removal. Peternal et al. (2006) studied the mineralization of reactive azo dye through UV-based (UV/H_2O_2, UV/O_3, UV/H_2O_2/O_3) processes and found that complete bleaching was achieved by all applied processes. He et al. (2008) investigated the mineralization of Reactive Blue 19 by combination of ozonation and sonolysis and the results showed that combination of both these processes gave great performance. Among all these AOPs, solar photocatalytic oxidation process has attracted wide attention due to clean, green technology and cost effective in removing toxic organic and inorganic pollutants from wastewater (Pruden and Ollis, 1983; Gupta et al., 2011a).

2.4.1 Solar photocatalytic

Solar photocatalytic is the advanced method or technology which has been used nowadays by many researchers to treat colorant in wastewater. Since solar energy is a natural energy source, photodegradation of pollutants using semiconductor with solar light can make it as an economically viable process (Muruganandham and Swaminathan, 2004). The exploration of renewable energy sources with minimal adverse effect to the environment is necessary in order to maintain the sustainable global development (Subash et al., 2013). Among the renewal energy sources, solar light is the largest global energy source and in photocatalytic, it had been captured to induce a series of redox reactions for degradation of pollutants (Baxter et al., 2009). Nagaveni et al. (2004) showed that degradation rates of methylene blue, remazol brilliant blue R and orange G by synthesized nano TiO_2 through solar photocatalytic process was higher than commercial Degussa P-25 TiO_2. Solar photocatalytic water detoxification of paper mill effluents by Sattler et al. (2004) proved that this treatment method can be very effectively degraded the non-biodegradable substances. Vineetha et al. (2013) found that photocatalytic degradation process using solar light irradiation showed potential application for removal of color and COD in the treatment of distillery effluent.

Figure 2.1 explained the mechanism of solar photocatalytic for organic pollutant. Light energy from solar is made to fall on to a semiconductor which in this study is catalyst (Chatterjee and Dasgupta, 2005). When the energy irradiated from solar is equivalent to or greater than band gap energy of catalyst, an electron would be excited out from the valence band to the conduction band of catalyst and will cause a hole in the valence band (Chatterjee and Dasgupta, 2005). The photogenerated holes can react with H_2O or OH^- and oxide them into $\bullet OH$ (Saquib and Muneer, 2003). The photogenerated electrons could reduce the dye or react with electron acceptors which dissolved in water and reducing it to superoxide radical anion, $\bullet O_2^-$ (Saquib and Muneer, 2003).