PHOTOCATALYTIC DEGRADATION OF PHENOL AND FAST GREEN FCF USING LITHIUM DOPED ZnO UNDER FLUORESCENT LIGHT IRRADIATION

by

NOORUL AISYAH BINTI MD SUHAIMI

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LIST OF ABBREVIATIONS

AOPs	Advance oxidation process
BET	Brunauer-Emmett-Teller
BQ	*p*-benzequinone
CB	Conduction band
CO_2	Carbon dioxida
CH_3CN	Acetonitrile
C_6H_5OH	Phenol
DI	Distilled water
FGF	Fast Green FCF
H_2O	Water
HCl	Hydrochloric acid
HPLC	High performance liquid chromatography
H_2O_2	Hydrogen peroxide
L-H	Langmuir-Hinshelwood
Li	Lithium
$LiNO_3$	Lithium nitrate
NaI	Sodium Iodide
NaOH	Sodium Hydroxide
NHE	Normal hydrogen electrode
O_2	Oxygen
TiO_2	Titanium dioxide
TEM	Transmission electron microscopy
UV	Ultraviolet

UV-vis DRS	Ultraviolet-visible diffuse reflectance spectrophotometer
VB	Valance band
XRD	X-ray diffraction
ZnO	Zinc oxide

LIST OF SYMBOLS

C	Pollutant concentration at specific time	mg/L
C_o	Initial pollutant concentration	mg/L
c	Velocity of light	m/s
D	Crystallite size	nm
e^-	Electron	-
E_{bg}	Band gap energy	eV
h	Plank's constant	eVs
h^+	Hole	-
hv	Photon energy	-
K_{app}	Apparent rate constant	min^{-1}
K	Adsorption equilibrium constant	L/mg
k_r	Reaction rate constant	mg/L.min
$O_2^{\bullet -}$	Superoxide radical anion	-
OH^-	Hydroxyl ion	-
$HO_2^{\bullet}$	Hyperoxyl radical	-
$\bullet OH$	Hydroxyl radical	-
r	Reaction rate	mg/L.min
R^2	Correlation coefficient	-
θ	Bragg's angle in degree	-
λ	Wavelength	nm
pH_{zpc}	Point zero of charge	-
β	Full width at half maximum	-
$C_6H_5O^-$	Phenolate anions	-

PENURUNAN PEMFOTOMANGKINAN FENOL DAN FAST GREEN FCF MENGGUNAKAN ZnO TERDOP DENGAN LITHIUM DI BAWAH PENYINARAN CAHAYA PENDAFLUOR

ABSTRAK

Zink oksida (ZnO), memainkan peranan utama dalam jenis rawatan ini kerana ciri-ciri yang istimewa yang dipunyainya seperti kos yang rendah, sesuai untuk alam sekitar dan sangat stabil. ZnO fotopemangkinan telah diubahsuai dengan mendopkan bersama Lithium (Li) menggunakan kaedah pemendakan kimia. Fotopemangkinan ini telah berjaya disintesis dan telah dianalisa dengan menggunakan kaedah pencirian Pembelauan sinar-X (XRD), Microskop Imbasan Elektron (SEM), Mikroskop Penghantaran Elektron (TEM), Spektroskop menyerap pantulan (UV-vis DRS) dan analisis luas permukaan. Li merupakan dopan logam yang sangat baik kerana mampu memerangkap pasangan elektron dan lubang yang terhasil. Aktiviti pemfotomangkinan untuk ZnO yang tulen dan ketiga-tiga Li/ZnO dengan jumlah Li yang berlainan (5 wt%, 7 wt% dan 10 wt%) telah diuji untuk degradasi kedua-dua fenol dan Fast Green FCF di bawah penyinaran cahaya pendafluor. Keputusan menunjukkan aktiviti pemfotomangkinan untuk ketiga-tiga Li/ZnO lebih tinggi berbanding ZnO tulen yang disintesis dan TiO_2 komersial untuk penurunan fenol dan Fast Green FCF, terutamanya 7 wt% Li/ZnO yang menunjukkan prestasi pemfotomangkinan yang unggul berbanding yang lain. Seterusnya, kesan daripada pembolehubah proses seperti kepekatan awal bahan pencemar, bebanan fotomangkin dan pH larutan terhadap penurunan kedua-dua bahan pencemar juga telah dikaji.

Kajian menunjukkan kondisi terbaik untuk kepekatan awal fenol dan Fast Green adalah pada 5 mg/L. Di samping itu, bebanan fotomangkin yang terbaik untuk penurunan fenol dan Fast Green FCF didapati pada 2g/L. Tambahan lagi, fotodegradasi fenol dan Fast Green FCF yang baik telah diperhatikan masing-masing pada pH 5.8 dan 4.4. Penggunaan semula yang tinggi dan keupayaan pemisahan yang tinggi untuk 7 wt% Li/ZnO mencadangkan potensi penggunaannya untuk aplikasi praktikal dalam rawatan air kumbahan. Spesis aktif yang terlibat dalam penurunan fenol dan Fast Green FCF telah dikaji dengan menambahkan bahan kimia tertentu dalam tindakbalas larutan. Kemudian, radikal hidroksil dan anion superoksida masing-masing dikenalpasti sebagai spesis aktif untuk penurunan fenol dan Fast Green FCF. Selain itu, beberapa produk semasa penurunan fenol telah dikesan menggunakan kromatografi cecair prestasi tinggi (HPLC), dan laluan tentatif degradasinya telah dicadangkan. Analisis Kinetik penurunan fenol dan Fast Green FCF dengan menggunakan 7 wt% Li/ZnO telah mematuhi kinetik tertib-pertama diwakili oleh model Langmuir-Hinshelwood.

PHOTOCATALYTIC DEGRADATION OF PHENOL AND FAST GREEN FCF USING LITHIUM DOPED ZnO UNDER FLUORESCENT LIGHT IRRADIATION

ABSTRACT

Zinc oxide (ZnO), plays a main role in this treatment due to its special characteristic such as, non-toxic, low cost, environmental friendly and stable. However, modification has to be done to improve its limitation. ZnO photocatalyst was modified by doping with lithium (Li) using chemical precipitation method. It has been successfully synthesized and synthesized photocatalyst was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-Vis diffuse reflectance spectroscopy (UV-VIS DRS), and surface analyzer. Li was found o be a promising metal dopant due to ability for trapping the photogenerated electron hole pairs from recombine. The photocatalytic activities of pure ZnO and three Li/ZnO with different Li loading (5 wt%, 7 wt% and 10 wt%) were being evaluated for the degradation of phenol and Fast Green FCF under fluorescent light irradiation. Results showed that the photocatalytic activities of all three Li/ZnO were higher than synthesized pure ZnO and commercial TiO_2 for both phenol and Fast Green FCF degradation, especially 7 wt% Li/ZnO which gives superior photocatalytic performance compare to others. Next, effects of operating parameters such as initial pollutant concentration, photocatalyst loading and solution pH towards the photocatalytic degradation of both pollutants were investigated. Results showed that the best conditions of initial phenol and Fast Green FCF concentrations were found to be 5 mg/L. Besides, the optimal photocatalyst loading

was found at 2 g/L for both phenol and Fast Green FCF degradation. In addition, favorable photodegradation of phenol and Fast Green FCF were observed at pH 5.8 and 4.4, respectively. The high reusability and high sedimentation test of 7 wt% Li/ZnO were achieved suggested its potential usage for practical applications in wastewater treatment. The actives species involved in phenol and Fast Green FCF degradation were also investigated by adding certain chemical into the solution reaction. Then, hydroxyl radical and superoxide anion radical are detected as active species for phenol and Fast Green FCF degradation, respectively. In addition, several intermediates product during phenol degradation were detected using high performance liquid chromatography (HPLC), and its tentative pathway degradation has been proposed. The kinetics analysis of the degradation of phenol and Fast Green FCF was over 7 wt% Li/ZnO fitted well by the first-order kinetics represent by the Langmuir-Hinshelwood model.

CHAPTER 1

INTRODUCTION

1.1 Water contamination

Water is the important natural resource in all aspects of human life including community health, food production, economic vitality and ecosystem biodiversity. As technology improves, there are many industries which threaten water quality. Industrial waste is the major source of water pollution; they consist of both organic and inorganic pollutants. Pollutants such as dyes, pharmaceuticals, pesticides, metals and endocrine disrupting chemicals (EDCs) have contributed to the contamination of fresh water in ecosystem which is extremely harmful to human and environment.

The world population is expected to reach between 8.3 and 10.9 billion by 2050 (Wikipedia, 2015). In general, along with increasing the population growth, the requirements of clean water for household purposes will be increased. The high population density also affects the water quality because large number of contaminants will be dumped into the water supply. Furthermore, by increasing the population growth, food supply demand also will be increased. Thus, more pesticides are used and released into the water supply and trigger the water pollution.

Lately, toxic contaminants such as dyes and phenolic compounds are of concerned. These contaminants whose sources are mainly industrial waste are harmful to the environment, hazardous to humans and difficult to degrade (Fernandez et al., 2010). Several solutions have been proposed in this regard, including chemical, biological and physical treatment. Unfortunately, physical and biological treatments have some drawbacks such as there are simply transfers the pollutant from one phase to another phase and might be expensive (Panda et al., 2010; Kuyukina et al., 2009; Laoufi et al., 2008). Furthermore, large scale implementations of these methods have some limitations, owing to the expensive equipment involved in these processes (Panda, 2010). An ideal wastewater treatment process to mineralize the entire toxic compound into the harmful by-products is needed. Therefore, researchers have focused to develop effective methods to convert the hazardous chemical to harmless compounds.

1.2 Photocatalysis in wastewater treatment

Advanced Oxidation Processes (AOPs) are well known method due to their competency in degrading and mineralizing mostly all organic pollutants (Jantawasu et al., 2009). Heterogeneous photocatalysis is one of the AOPs which are versatile, low- cost and the ideal technique to control the organic pollutants in water and air (Shu et al., 2010). AOPs are defined as process which is concerned with the in-situ generation of highly chemical oxidants such as hydroxyl radicals (•OH) or superoxide anion radicals (•O_2) to significantly enhance the oxidation and degrade the organic pollutant (An*et al*., 2010; Khatee and Kasiri, 2010; Krishnakumar and Swaminathan, 2011). Besides photocatalysis, there are some processes which can also obtain these radicals, such as ozonation, electrochemical oxidation, Fenton, and Fenton-like process (Asgar *et al*., 2015). However, the process that has gained attention is heterogeneous photocatalysis because it can be reusable and does not require the addition of any other strong oxidants. The main advantages of the heterogeneous photocatalysis over the conventional methods include (Malato et al., 2009):

1. The photocatalytic reaction takes place at ambient temperature and pressure

2. Complete mineralization of oxidation substances into CO_2 and harmless compound is possible
3. Atmospheric oxygen is used for the reaction.
4. The photocatalysts are low cost, non- toxic and can be recycled
5. The photocatalytic activation can occur under sun light irradiation.

ZnO and TiO_2 are among the semiconductor materials that have been used as photocatalyst due to their high photocatalytic ability in the wastewater treatment. But, ZnO is preferred to TiO_2, due to its high quantum efficiency, and applicability in large-scale wastewater treatment (Kansal *et al*, 2007; Etacheri *et al*., 2012). In addition, the advantages of ZnO are the ability to absorb and utilize large fraction of solar spectrum, large band gap, non-toxicity nature and low cost (Chakrabarti and Dutta, 2004; Sakthivel et al., 2003; Kansal et al., 2009). However, the photocatalytic activity of ZnO is highly dependent on the operating conditions such as photocatalyst loading, solution pH, initial concentration and oxidizing agent. Therefore more investigations are still needed on ZnO photocatalyst for excellent use in photocatalysis.

1.3 Problem statements

Currently, environmental pollution is one of the most important issues faced in the world. It has increased exponentially in the past few years and reached worse level in terms of its effects on living creatures. Phenol has been detected as common organic pollutant in wastewater since it is widely used as raw material industries such as chemical, petrochemical and pharmaceutical (Naem and Ouyang, 2013; Hasanoglu, 2013). Nowadays, phenol has attracted great concerns because it can disrupt the normal regulatory function of the endocrine system. There are several adverse effects in bodies such as it will damage the liver, kidneys, respiratory, nervous, and cardiovascular system; and it is also possible to cause death (McManamon et al., 2011). Widespread occurrences of phenol have been reported in Taihu Lake at concentrations ranging from 675.2- 3346.1 ngL^{-1}(Zhong, et al., 2010).

Besides phenol, dyes also have been detected in wastewater and can cause environmental problems. Dyes are quiet useful for human, but some of them are toxic and carcinogenic in nature. Fast Green FCF (FGF) is a triarylmethane food dye, which is widely used as food colorant, and protein stain in the electrophoresis (Dixit and Goyal 2012; Mittal et al., 2008). However, due to its carcinogenic effects, its usage is prohibited in most of the developed countries (Brown et al., 1978; FAO, 1970). It has shown tumorigenic effects in experimental animals and mutagenic effects in both experimental animals and humans. Furthermore, it can causes irritation of eyes, skin, digestive tract, respiratory tract and inhibits the release of neurotransmitter (Mittal et al., 2008; Bhati et al., 2010). Therefore, there is a need to develop treatment methods that are effective in eliminating both phenol and FGF.

The ZnO-mediated photocatalysis has been proven to be an important and effective method for degradation of various organic pollutants including phenol and