Simultaneous Photodegradation and Biodegradation Processes in Photocatalytic Hybrid Sequencing Batch Reactor (PHSBR) for Mineralization of Phenol

by

NIK NOOR ATHIRAH BINTI NIK YUSOFF

1541211781

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UNIVERSITI MALAYSIA PERLIS

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DEDICATION

This dissertation is dedicated to my parents Nik Yusoff and Zaripah Hamzah and as an inspiration for my younger brother Nik Muzakkir and Nik Amer Aziden.
Love of my life.

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LIST OF ABBREVIATIONS

SBR	Sequencing Batch Reactor
PHSBR	Photocatalytic Hybrid Sequencing Batch Reactor
GAC	Granular Activated Carbon
POPs/EDCs	Persistence Organic Pollutant with Endocrine Effects
AOX	Absorbable Organic Halides
USEPA	United States Environmental Protection Agency
HGSBR	Hybrid Growth Sequencing Batch Reactor
NH_4^+	Ammonium
C_6H_5OH	Phenol
$-C_6H_5$	Phenyl Group
-OH	Hydroxyl Group
WHO	World Health Organization
UV	Ultraviolet
TiO_2	Titanium Dioxide
ZnO	Zinc Oxide
ECL	Electrogenerated Chemiluminescence
RBC	Rotating Biological Contactor
AOP	Advance Oxidation Process
COD	Chemical Oxygen Demand

Proses Fotodegradasi dan Biodegradasi Serentak Melalui Reaktor Hibrid Fotopemangkin dan Reaktor Urutan Berkumpulan (PHSBR) Untuk Penguraian Fenol

ABSTRAK

Bahan cemar organik seperti fenol adalah salah satu daripada bahan organik yang sukar dirawat dan boleh dikesan secara banyak di dalam air sisa industri. Rawatan fenol yang tidak sesuai akan mengakibatkan pelepasan sebatian fenol ke sumber air seterusnya mengakibatkan pelbagai kesan negatif. Sistem perawatan baru dibangunkan dengan mengabungkan proses fotopemangkin dan reaktor urutan berkumpulan (SBR) di dalam satu sistem untuk mengatasi keterhadan sistem rawatan melalui fizikal-kimia dan biologi. Kehadiran mikroorganisma sewaktu proses fotopemangkin dapat membantu penguraian fenol dan hasil penguraian dengan lebih cepat sejurus ia terbentuk. Pada masa yang sama, bahan sukar bio-urai akan diuraikan oleh radikal hidrosil yang terhasil daripada proses fotopemangkin. Bagi menggabungkan proses fotopemagkin dengan SBR, pembiakan mikroorganisma secara hibrid di dalam SBR (HGSBR) dibentuk untuk menjadikan ia sesuai untuk penggabungan. Kebolehan HGSBR untuk penguraian fenol turut dinilai di dalam pelbagai keadaan toksik. Seterusnya, reaktor hibrid fotopemangkin urutan berkumpulan (PHSBR) dibangunkan dan kebolehan foto-biodegradasi secara serentak dikaji. Penyingkiran COD secara total dapat dicapai oleh HGSBR untuk kepekatan fenol 50 mg/L. Kecekapan HGSBR meningkatkan kerana kewujudan enap cemar dan bio-filem yang menghasilkan kepekatan biojism yang tinggi. Biofilem terbentuk dengan seragam di atas permukaan bahan lapisan tetap dengan ketabalan adalah berbeza, bergantung kepada jenis bahan yang digunakan. Bio-filem yang tebal menunjukan kehadiran bakteria yang banyak di permukaan. Keadaan ini akan menggalakkan penyingkiran bahan di HGSBR. Model biokinetik iaitu *First-order*, *Stover Kincannon* dan *Grau Second-Order* diaplikasikan dalam HGSBR untuk penguraian fenol. Prestasi HGSBR berbeza di bawah tiga keadaan toksik yang berlainan (akut, toksik, kronik). Penguraian 100 mg/L fenol melalui fotodegradasi dan biodegradasi secara tunggal adalah sebanyak 64 % dan 53 %. Sementara itu, kadar penguraian meningkat kepada 92 % melalui proses rawatan serentak (PHSBR). Selain daripada penguraian fenol, penguraian ammonium (NH_4^+) melalui HGSBR juga dikaji. Fenol yang bersifat toksik dan berpotensi untuk menyekat proses nitrifikasi dapat dikurangkan melalui sistem rawatan PHSBR. Melalui PHSBR, kecekapan penyingkiran NH_4^+ meningkat berbanding kepada reaksi tunggal fotopemangkin dan nitrifikasi. Penyingkiran NH_4^+ sewaktu kepekatan fenol 50 mg/L adalah 94.4 %, manakala purata kecekapan penyingkiran NH_4^+ pada fenol 100 mg/L menurun kepada 92.9 %. Had penguraian fenol sewaktu tindak balas serentak dapat ditingkatkan kepada 300 mg/L. Kajian menunjukkan kadar penguraian fenol yang tinggi mampu dicapai melalui tindak balas serentak. PHSBR membenarkan kedua-dua reaksi berlaku secara serentak dan seterusnya mengatasi kelemahan satu proses dengan proses yang lain. Ini menyumbang kepada peratus penguraian fenol yang tinggi. PHSBR berpotensi dalam meyingkirkan fenol di dalam air sisa buangan secara menyeluruh dan memastikan tiada pelepasan ke dalam sumber air.

Simultaneous photodegradation and biodegradation processes in photocatalytic hybrid sequencing batch reactor (PHSBR) for mineralization of phenol

ABSTRACT

Organic pollutants such as phenol are one of the refractory organic pollutants that can be found widely in various industrial wastewaters. The improper treatment of phenol will lead to the discharge of phenolic compounds into the receiving waters which contribute to various adverse effects towards the environment. The new treatment systems were developed by integrating photocatalytic process and sequencing batch reactor (SBR) into a single system in order to overcome the limitation of physicochemical and biological treatment. The microorganisms were available during the photocatalytic process to assist the rapid degradation of the biodegradable intermediates as soon as they produced. Simultaneously, the bio-recalcitrant compounds were degraded by hydroxyl radicals from photocatalytic process. In order to integrate the photocatalytic process with SBR system, a hybrid growth SBR (HGSBR) was initially establish in order to make it compatible for the integration. The performance of HGSBR was evaluated for the mineralization of the phenol including under various toxicity conditions. Then, the photocatalytic hybrid sequencing batch reactor (PHSBR) was develop and the performance of the simultaneous photo-biodegradation process was studied. Complete COD removal was achieved by HGSBR for phenol concentration up to 50 mg/L. The co-existence of bio-sludge and biofilm increased the efficiencies of HGSBR due to high concentration of biomass. The biofilm develop on the fixed bed materials was homogeneous and the thickness varied from each materials. Thicker biofilm indicated that larger number of bacteria accumulated in the surface. This would promote the removal of substances in HGSBR. Bio-kinetics models First-order, Stover-Kincannon and Grau Second Order kinetic model were applied for HGSBR in degrading phenol. The performance of the HGSBR was different for the three conditions of toxicity studied (toxic, acute and chronic). The mineralization of 100 mg/L phenol in single photodegradation and biodegradation process recorded only 64% and 53% respectively. While, for the simultaneous process in PHSBR, the mineralization increased significantly to 92%. Besides the mineralization of phenol, the removal of ammonium (NH_4^+) in PHSBR was also investigated. The toxic characteristic of phenol that was subjected to inhibit the nitrification process was able to be reduced through PHSBR treatment system. In PHSBR the removal efficiency of NH_4^+ increased compared to the single reaction of photocatalytic and nitrification. The NH_4^+ removal during 50 mg/L of phenol was 94.4%, while for 100 mg/L of phenol, the average removal efficiency was slightly lower which is 92.9%. The threshold limit of phenol for NH_4^+ removal during the simultaneous reaction was increased to 300 mg/L. The results demonstrate the simultaneous reaction allowed for the higher mineralization rates of phenol. PHSBR allowed both reaction occurred simultaneously and consequently overcome the disadvantages of one process with another. This contributed to higher percentage mineralization of phenol. PHSBR highly potential in totally removed phenol from wastewater and ensure zero discharge into the water bodies.

CHAPTER 1: INTRODUCTION

1.1 Research Background

One of the most significant current discussions regarding to the environmental issues is clean water. The past decade has seen the rapid development in construction and industrial. These rapid developments increase the demand for efficient wastewater treatment in order to ensure the environmental conservation parallel with the development of the country. One of the refractory organic pollutants from industrial that have high ability to give a negative effect towards water consumers is phenol. Phenol can be life threatening to human being and ecosystems due to its biorecalcitrant and acute toxicity behavior (Ahmed et al., 2010).

The effluent wastewater that contains phenol compound need to be treated until fulfilled the legal requirement enacted by Malaysia Environmental Quality Act 1974, Environmental Quality (Industrial Effluent) Regulations 2009, which is 0.001mg/l for Standard A and 1.0 mg/l for Standard B. Despite the low concentration, phenol treatment has become issue due to its toxicity, genotoxicity and extremely high potency of endocrine disrupting (Ahmed et al., 2010).

Phenol in wastewater can be mineralized through photodegradation and biodegradation process. Photodegradation through the photocatalytic reaction process is a combination of heterogeneous catalyst with radiation such as solar (Beydoun et al., 1999) and UV light. There are three major components which are crucial for the photocatalytic reaction to occur; an emitted photon with appropriate wavelength, catalyst surface, and oxidizing agent such as oxygen and air (de Lasa et al., 2005).

Biodegradation through biological remediation approaches has been gaining tremendous attention worldwide, especially in wastewater treatment process. The approaches were found to be more economical and often have a better acceptance rate from the public than the conventional physical and chemical approaches. Biodegradation is usually defined as the breakdown of organic contaminants that occurs due to the microorganism's activity. The microorganisms can be obtained from various sources such as activated sludge. One of the variant from the conventional activated sludge process is known as sequencing batch reactor (SBR). As compared to other biological treatments, SBR possess the advantage of process flexibility in the single-tank design which satisfies different treatment requirements.

Biological treatment processes under aerobic conditions were divided into three types of microorganism's growth categories which are suspended, attached and hybrid (combined) growth process. Individually, all types of growth systems have associated advantages and disadvantages and most of the research works focus on suspended growth and attached growth in SBR system separately.

In suspended growth process, the biological treatment occurs in which the microorganisms responsible for the conversion of the organic matter to gasses and cell tissue are maintained in suspension within the liquid. The attached growth will promote the development of biofilm. The biofilm has the capability to promote high active biomass concentration and consequently high reaction rates.

Hybrid growth is the result of combined processes; part of the microorganism is attached to support materials in the biological reactor where they cohabit with free microorganism flocs. In this research, hybrid growth was selected to increase the resistance by allowing the co-existence of microorganism from activated sludge in form of bio-sludge and biofilm within a single reactor.

However, one of the drawbacks of biological treatment is the possibility of less versatile in term of types of pollutant as microbial activities are more easily affected by the toxicity. While, for photocatalytic it has potential to produce more toxic and biorecalcitrant intermediate products. Hence, suitable and effective methods must be developed to reduce the inhibitory effects and achieve total mineralization. Scott and Ollis, (1995) identified several types of wastewater as potentially treatable by combined photocatalytic/biological degradation.

Number of studies has reported the combination of photocatalytic and biological treatment in sequential either as pre-treatment or post-treatment (Rizzo et al., 2008; L'Amour et al., 2008; Barreto-Rodrigues et al., 2009; Banu et al., 2008; Gulyas et al., 2009; Sirtori et al., 2009). Based on the concept of the combined treatment system, a novel reactor called photocatalytic hybrid sequencing batch reactor (PHSBR) were develop. The PHSBR was a combination of two types of treatment which is photocatalytic process and sequencing batch reactor (SBR). Rather than in sequence, PHSBR differ from common combined treatment system. The PHSBR applied the hybrid concept which allows both of the treatment process to occur simultaneously in a single reactor. During the simultaneous reaction, the photocatalytic would partial oxidize the biological persistent compounds to produce the biodegradable intermediates.

Either in sequential or simultaneous reaction, the mineralization of the pollutant should be at optimum rate during the chemical treatment. The reaction must be not too short or too long because the intermediates that formed might be structurally similar to the parent compound and become non-biodegradable. Compared to sequential reaction, the mineralization of pollutant in simultaneous reaction was easy to control. The microorganism would immediately select the biodegradable intermediates for their metabolic activities. The metabolism activities of microorganisms during simultaneous reaction were more active since more biodegradable compound available. This will enhance the degradation of the toxic organic compound such as phenol and reduce the treatment cost compare to the sequential treatment system. A novel design of this hybrid reactor is necessary to overcome the limitation of physicochemical and biological treatment.

1.2 Problem statement

Rapid development in industries has heightened the need for appropriate treatment of the industrial effluent especially those containing toxic substances such as phenol. Major heavy industries such as petroleum refinery, petrochemical industries, pulp and paper mills, liquefaction process, coal gasification operation, dye synthesis unit, resin manufacturing industries and pharmaceutical industries contribute to the phenol contamination in wastewater (Kulkarni and Kaware, 2013).

Due to the toxic characteristic of the phenol, it was expressed in various term such as environmental recalcitrant compound (Kulkarni, 2012), persistence organic pollutant with endocrine effects (POPs/EDCs) (Yusoff et al., 2015) and adsorbable organic halides (AOX) (Savant et al., (2006). The improper treatment of phenol will lead to the discharge of phenolic compounds into the receiving waters which contribute to various adverse effects towards the environment. Phenol molecules will bio-accumulate in fish tissue and cause carcinogenic, endocrine, clastogenic, and mutagenic affects (Goh et al., 2009). Subsequently, it will pose problems to human consuming the contaminated fish.

United States Environmental Protection Agency (USEPA) limit the discharged of phenol in wastewater to 0.5 mg/L for surface and 1 mg/L for sewerage system and listed phenol as priority pollutant. While phenol content in potable and mineral water were limited to 0.5 μg/L. Even though phenol is toxic and claimed to be life threatening, the proper treatments of phenol are still neglected by some industries compare to other types of pollutant. The conventional treatment method for phenol can be classified into physical, chemical and biological method.

The most common applied physical treatment such as air stripping and adsorption, are not reliable to be applied due to the production of extended pollutant from the treatment such as activated carbon. The spent activated carbon is usually disposed by incineration and eventually generated dioxin and furan which are severe to human health (Kulkarni et al., 2008). Besides the behavior of the removal are non-destructive. The chemical oxidation treatment method such as ozonation and electrochemical degradation (Lim et al., 2013) is a promising technology. Unfortunately, most of the solvents such as ozone and chlorine dioxide are expensive and lead to the formation of by-products such as benzoquinone and organic acids. The debate over phenol treatment method is very complicated.

Some researchers have concluded that biological treatment is a safe and applicable treatment method. Activated sludge system, oxidation ponds and aerated lagoons are widely applied in small industries (Nigam et al., 1995). However, phenol can be biodegraded efficiently only under low concentration (Youssef and Rodríguez, 2011; Wosman et al., 2016). Moreover, at higher concentration, phenol molecule capable to affects the mobility of cell membrane (Davidson and Branen, 1981; Wosman et al.,

2016) and showing some inhabitation effect. Thus, it will lead to failure of whole wastewater treatment system.

Recently, it can be best explained by considering another promising technology for organic pollutant remediation at ambient conditions known as photocatalytic. The main advantages of this method are inexpensive as oxidizing chemicals are not consumed in this treatment. It only involves the non-hazardous photocatalyst and the oxidant is atmospheric oxidant. As photocatalytic process contributes to phenol removal, photocatalyst played a key role in accomplishing this treatment. In this study zinc oxide (ZnO) was chosen as the photocatalyst. However, the application of photocatalytic process into the real wastewater treatment is still under research stage. In order to make it applicable, several attempts have been made to combine the photocatalytic and biological treatment process. Most of the researches conduct the combined process in a sequential and separate reactor (Wang et al., 2008; Sarria et al., 2001; Bijan and Mohseni, 2005; Balcioglu et al., 2006; Di laconi et al., 2002; Rizzo et al., 2008; L'amour et al., 2008; Banu et al., 2008; Gulyas et al., 2009; Sirtori et al., 2009), which will require high cost and space.

Moreover, during the sequential process, some of the compound might be over or less mineralized, and yields the unsuitable intermediates to be removed in the secondary or tertiary treatment. This undesirable condition occurred due to the difficulty to control the mineralization of the compound during the sequential treatment process. This condition affects the total mineralization or lowered the treatment efficiency especially when dealing with toxic organic pollutant such as phenol.

This research will solve the problem by combining two treatment processes simultaneously into a single unit reactor which known as photocatalytic hybrid sequencing batch reactor (PHSBR) with the goal to shorten the reaction time and totally mineralized the toxic organic compound and other biological nutrient.

1.3 Objectives

The overall aim of this research was to develop a hybrid reactor for the simultaneous photodegradation and biodegradation reaction. This research will solve the problem by combining two treatment processes simultaneously into a single unit reactor which known as photocatalytic hybrid sequencing batch reactor (PHSBR) with the goal to shorten the reaction time and totally mineralized the toxic organic compound and others biological nutrient. The main objectives of this research are to:

1. To establish the hybrid growth sequencing batch reactor (HGSBR) for mineralization of phenol.
2. To evaluate the performances of hybrid growth sequencing batch reactor (HGSBR) for biodegradation of phenol under various toxicity conditions
3. To develop the simultaneous photo-biodegradation process in photocatalytic hybrid sequencing batch reactor (PHSBR) for mineralization of phenol.
4. To evaluate the nitrification process during mineralization of phenol through photocatalytic hybrid sequencing batch reactor (PHSBR).

1.4 Scope of Study

In this research, photocatalytic hybrid sequencing batch reactor (PHSBR) was developed. By definition of PHSBR, “P” denoted as photocatalytic process being integrated into biological reactor known as sequencing batch reactor denoted as “SBR” in the abbreviation. Term of hybrid abbreviated as "H" defined two different meaning which is the hybrid growth of microorganism in SBR and also; the hybrid reaction of photodegradation and biodegradation. This research was divided into three consecutive stages of study as shown in Figure 1.1.

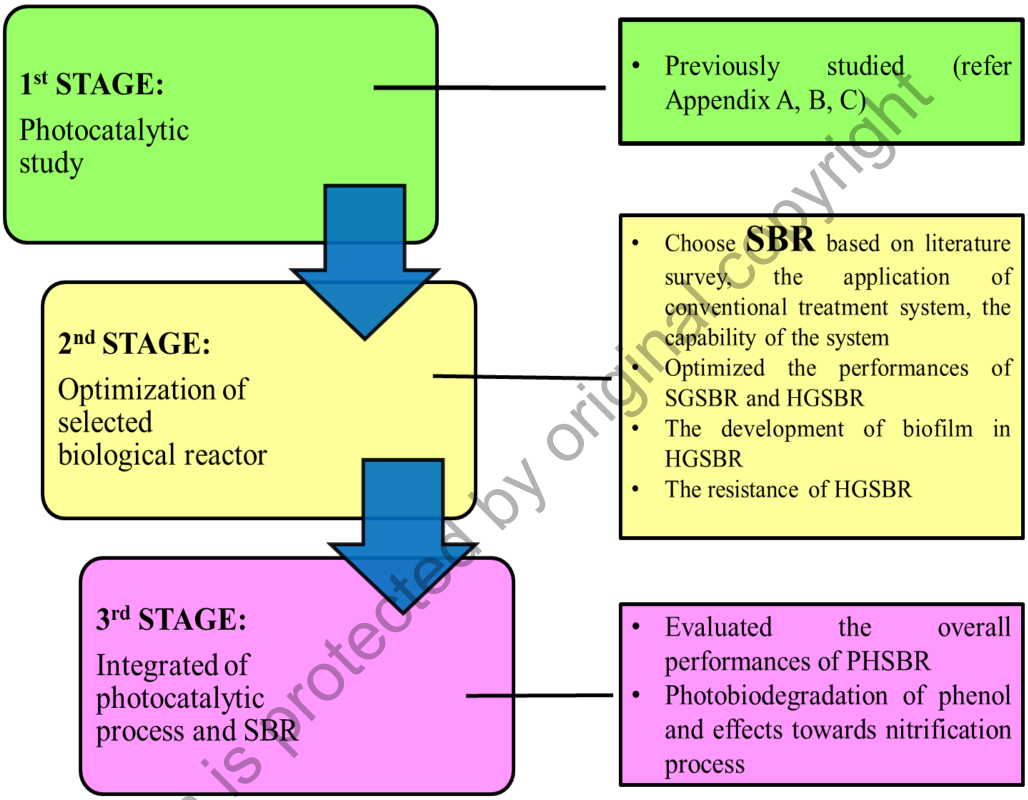

Figure 1.1 Research flow

The first stage which is photocatalytic study that has been completed in previous study and not detailed discuss in this research. However, the results and discussions related to the photocatalytic study were presented in Appendix A, B and C. Three journal articles was published discussed the performances of photocatalytic process for degradation of phenol. The first article (Appendix A) discussed the photocatalytic degradation of phenol with commercial zinc oxide as photocatalyst under solar irradiation. The operating parameters studied such as initial phenol concentration, catalyst loading, pH, effect of aeration, H_2O_2 dosage and effect of solar light. In the second and third articles (Appendix B and C), synthesized zinc oxide through precipitation, hydrothermal and sol-gel method was studied. The performances of the synthesized zinc oxide were compared with the commercial zinc oxide for the photodegradation of phenol.

The second stage of this research is the optimization of biological reactor before being integrated with photocatalytic process. For biodegradation process, the sequencing batch reactor (SBR) was used to optimize the performances of the biological reactor. The microorganisms were grown in hybrid growth condition. Hybrid (combined) growth microorganism is a combination of suspended and attached growth. Microorganisms in form of bio-sludge were co-existed with microorganisms in form of biofilm in a single reactor. The theoretical developments of the biofilm in hybrid growth SBR (HGSBR) are important to understand the formation of biofilm. The resistances of the hybrid growth type of SBR were evaluated. The removal performances, microbial growth, development of biofilm and resistances towards various toxicity conditions were evaluated for the optimization. The biodegradation of phenol at different concentration were compared with the microorganism's community growth which are able to indicate whether the microorganisms were affected by phenol toxicity. The development of biofilm on the packing materials was observed in this hybrid growth SBR (HGSBR).

The third stage is the integrated of photocatalytic process and SBR treatment system into a single treatment system called PHSBR. For the PHSBR, the overall performances during phenol removal were evaluated. The degradation of phenol was evaluated in both photocatalytic and biological compartment for detailed explanation of occurring sequence in both reactions. Kinetics and modeling of phenol degradation provides the