# การเตรียมตัวเร่งปฏิกิริยาเหล็กที่เคลือบบนถ่านกัมมันต์เพื่อสลายฟีนอลในน้ำด้วยเครื่องปฏิกรณ์ฟลูอิดไดซ์เบดแบบสามวัฏภาค

นางสาวพิลาสินี ลิ้มสุวรรณ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
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ปีการศึกษา 2551

# PREPARATION OF Fe CATALYST COATED ON ACTIVATED CARBON FOR DECOMPOSITION OF AQUEOUS PHENOL IN THREE-PHASE FLUIDIZED BED REACTOR

Miss Pilasinee Limsuwan

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
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| Thesis Title | PREPARATION OF Fe CATALYST COATED ON ACTIVATED CARBON FOR DECOMPOSITION OF AQUEOUS PHENOL IN THREE-PHASE FLUIDIZED BED REACTOR |
| By | Miss Pilasinee Limsuwan |
| Field of Study | Chemical Engineering |
| Thesis Principal Advisor | Associate Professor Tawatchai Charinpanitkul, D.Eng. |
| Thesis Co-Advisor | Professor Wiwut Tanthapanichakoon, Ph.D. |

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Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

.................................... Dean of the Faculty of Engineering
(Associate Professor Boonsom Lerdhirunwong, Dr. Ing)

THESIS COMMITTEE

.................................... Chairman
(Associate Professor Seeroong Prichanont, Ph.D.)

.................................... Thesis Principal Advisor
(Associate Professor Tawatchai Charinpanitkul, D.Eng.)

Wiwut Tanthapanichakoon ....Thesis Co-Advisor
(Professor Wiwut Tanthapanichakoon, Ph.D.)

.................................... Member
(Assistant Professor Joongjai Panpranot, Ph.D.)

Pratarn Wongsarivej ..... External Member
(Pratarn Wongsarivej, D.Eng)

พิลาสินี ลิ้มสุวรรณ : การเตรียมตัวเร่งปฏิกิริยาเหล็กที่เคลือบบนถ่านกัมมันต์เพื่อสลายฟีนอลในน้ำด้วยเครื่องปฏิกรณ์ฟลูอิดไดซ์เบดแบบสามวัฏภาค (PREPARATION OF Fe CATALYST COATED ON ACTIVATED CARBON FOR DECOMPOSITION OF AQUEOUS PHENOL IN THREE-PHASE FLUIDIZED BED REACTOR) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร. ธวัชชัย ชรินพาณิชกุล, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ศ.ดร. วิวัฒน์ ตัณฑะพานิชกุล, 91 หน้า

ในงานวิทยานิพนธ์นี้ ได้ทำการศึกษาการกำจัดฟีนอลในน้ำ (สารละลายฟีนอล) ด้วยกระบวนการดูดซับ และการสลายตัว โดยใช้เครื่องปฏิกรณ์ฟลูอิดไดซ์เบดแบบสามวัฏภาค โดยวัฏภาคแก๊ส คือ ฟองอากาศที่มีหรือไม่มีโอโซน วัฏภาคของเหลว คือ สารละลายฟีนอล ส่วนวัฏภาคของแข็ง คือ เม็ดถ่านกัมมันต์ ที่มีเหล็กและไม่มีเหล็กเคลือบอยู่บนผิวตามลำดับ ในการทดลองนี้ได้กำหนดอัตราการไหลของก๊าซ และ ของเหลวให้คงที่ เท่ากับ 1 ลิตร/นาที และปริมาณตัวเร่งปฏิกิริยา เท่ากับ 5 กรัมต่อกะ จากผลการทดลองในการกำจัดสารละลายฟีนอลความเข้มข้น 10 มิลลิกรัมต่อลิตร ปริมาตร 2 ลิตร ในขณะเดียวกันผลิตภัณฑ์ขั้นกลางที่เกิดขึ้นระหว่างปฏิกิริยาการกำจัดฟีนอล เช่น ไฮโดรควิโนน และ คาทิชอลนั้น พบว่า จะถูกกำจัดต่อไปจนเหลือ $CO_2$ และ $H_2O$ โดยถ่านกัมมันต์ทั้งสองชนิดคือ AC1 และ AC2 มีพื้นที่ผิว 1,106 และ 1,150 ตารางเมตรต่อกรัม ส่วนขนาดรูพรุนโดยเฉลี่ยมีค่า 2.3 และ 1.7 นาโนเมตร ตามลำดับ เมื่อเปรียบเทียบถ่านกัมมันต์ทั้งสองชนิด จะเห็นว่า AC1 ที่มีทั้งระดับเมโซพอร์ และไมโครพอร์มากกว่า AC2 จะกำจัดสารผลิตภัณฑ์ขั้นกลางที่เกิดขึ้นระหว่างปฏิกิริยาการกำจัดฟีนอลได้ดีกว่า AC2 ดังนั้น AC1จึงถูกเลือกใช้ในการทดลองลำดับต่อมา จากนั้นทำการเปรียบเทียบประสิทธิภาพการกำจัดฟีนอล และ TOC สำหรับกรณีต่อไปนี้ 1) โอโซนจากออกซิเจน หรืออากาศ 2) ถ่านกัมมันต์ 3) ถ่านกัมมันต์ที่มีเหล็กเคลือบอยู่บนผิว 4) และ 5) โอโซนร่วมกับกรณี 2) และ 3) ตามลำดับ จากนั้นเรียงลำดับประสิทธิภาพการกำจัดฟีนอลจากมากไปน้อยดังนี้ 5) ( 100% ที่ 15 นาที ) > 4) ( 100% ที่ 30 นาที ) > 3 ) ( 100% ที่ 45 นาที ) ≈ 2 ) ( 100% ที่ 45 นาที ) > 1) จากออกซิเจน ( 100% ที่ 90 นาที ) > 1 ) จากอากาศ ( 100% ที่ 150 นาที ) ในขณะที่ลำดับประสิทธิภาพการกำจัด TOC จากมากไปน้อยเป็นดังนี้ 4) ( 89% ที่ 150นาที ) > 5 ) ( 83% ที่ 150 นาที ) > 2 ) ( 79% ที่ 150 นาที ) > 3 ) ( 77% ที่ 150 นาที ) > 1 ) จากออกซิเจน ( 70% ที่ 150 นาที ) > 1) จากอากาศ ( ไม่กำจัดTOC ) สรุปแล้วการใช้ถ่านกัมมันต์ร่วมกับโอโซนจากอากาศเหมาะสมาที่สุดสำหรับการกำจัด TOC และ ราคาการดำเนินงาน

ภาควิชา.....วิศวกรรมเคมี...ลายมือชื่อนิสิต พิลาสินี ลิ้มสุวรรณ
สาขาวิชา...วิศวกรรมเคมี...ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์หลัก..........................
ปีการศึกษา..........2551......ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์ร่วม..........................

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KEY WORD: PHENOL/ THREE PHASE FLUIDIZED BED/ Fe CATALYST/ ACTIVATED CARBON

PILASINEE LIMSUWAN: PREPARATION OF Fe CATALYST COATED ON ACTIVATED CARBON FOR DECOMPOSITION OF AQUEOUS PHENOL IN THREE-PHASE FLUIDIZED BED REACTOR. THESIS PRINCIPAL ADVISOR: ASSOC. PROF. TAWATCHAI CHARINPANITKUL, D.Eng. THESIS CO-ADVISOR: PROF. WIWUT TANTHAPANICHAKOON, Ph.D., 91 pp.

A lab-scale three-phase fluidized-bed reactor was used for removal of aqueous phenol by adsorption and decomposition. The gas, liquid and solid phases were air bubbles with or without ozone, aqueous phenol, and granular activated carbon (AC) with and without Fe on AC, respectively. Both the gas flow and liquid recirculation rate were controlled at 1 L.min$^{-1}$ and the catalyst loading was 5 g per batch. The experiments were carried out using 2 L of 10 ppm phenol solution. Some intermediate products such as hydroquinone (HQ) and catechol (CC) were also detected but they were eventually decomposed to $CO_2$ and $H_2O$. First, two types of AC (AC1 and AC2) with BET surface areas of 1,106 and 1,150 m$^2$.g$^{-1}$ and average pore diameters of 2.3 and 1.7 nm, respectively, were compared. It was found that AC1 with more mesopores removed the intermediate products better than AC2 with more micopores. Since both AC removed phenol with the same efficiency, AC1 was selected for use in all subsequent experiments. Comparison of the phenol and TOC removal efficiencies were made for the following cases: 1) only $O_3$ from pure $O_2$ or air, 2) only AC, 3) only Fe/AC, 4 and 5) $O_3$ in combination with cases 2) and 3), respectively. The sequence of decreasing phenol removal efficiency was as follows: 5) (100% at 15 min) > 4) (100% at 30 min) > 3) (100% at 45 min) ≈ 2) (100% at 45 min) > 1) from pure $O_2$ (100% at 90 min) > 1) from air (100% at 150 min). Meanwhile, the sequence of decreasing TOC removal efficiency was as follows: 4) (89% at 150 min) > 5) (83% at 150 min) > 2) (79% at 150 min) > 3) (77% at 150 min) > 1) from pure $O_2$ (70% at 150 min) > 1) from air (negligible removal). In conclusion, the use of AC with $O_3$ from air was a best compromise in terms of TOC removal efficiency and operation costs.

Department.........Chemical Engineering....Student's signature Pilasinee Limsuwan
Field of Study....Chemical Engineering....Principal Advisor's signature............
Academic Year...............2008.............Co-advisor's signature............

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Finally, she also would like to dedicate this thesis to her parents, a brother and Mr. Tissanaphol Dissarabhong for total support, inspiration and everything in my life.

# CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

**Figure** **Page**

# CHAPTER I

# INTRODUCTION

## 1.1 Background

Waste products, generated from industrial processes, are considered as a certain kind of pollutants giving deteriorative effects to our environment. Some waste is reported to exhibit toxicity, carcinogenic and mutagenic properties. Such industrial waste also exerts negative effects on economic aspects as well. Among various waste, the organic compound is one of the most serious problems to the environmental concern since it is difficult to remove by means of conventional wastewater treatment technologies **[1]**. Though there are many organic compounds contaminated in public reservoirs, phenol and its derivatives is a crucial one because they could hardly be decomposed in nature. Phenol presents widely as a contaminant in many industrial processes, such as, wood preservative, pesticide, textile, paper and dye industrial **[2]**. Moreover, phenolic compounds can stand conventional removal methods, including biological decomposition or adsorption by activated carbon. Consequently, alternative high-performance wastewater treatment systems have also been required.

Meanwhile, catalytic oxidation system is recognized as a promising alternative, due to its various advantages, such as non-toxicity and high stability of decomposing pollutants. Moreover, the use of such catalysts can lead to a higher mineralization of the organic refractory pollutants which will flavor a further biological treatment **[3]**. Especially, once a super oxidizing agent, such as, ozone, is incorporated with the catalytic oxidation process, it will drastically help increase decomposition rate.

At the moment, more and more attention turns to the three-phase reactors, because they could provide intimate contact of gases, liquid, and solid phases. It also possesses the characteristic of simplicity in construction and operation, low operating cost and flexibility for liquid and solid phase residence times. In accordance with fluidization technology proposed for the improvement of the system, some novel catalysts have been introduced for decomposing the phenolic compounds with the catalytic oxidation reaction **[2]**.

The present research is aimed at the application of an effective wastewater treatment for removing phenol dissolved in wastewater Fe catalyst impregnated on activated carbon. Performance of a lab-scale fluidized-bed reactor with Fe/Ac catalyst and/or activated carbon (solid phase) and air (oxygen) and/or ozone (gas phase) will be investigated experimentally. It is well-known that the oxidation of phenol often leads to numerous hard-to-remove intermediate products. To monitor the presence and removal of the intermediate products, the TOC concentration of the treated wastewater is also measured.

## 1.2 Objectives of research

The objective of this research is to investigate and compare a decomposition rate of aqueous phenol by using a lab-scale fluidized bed reactor with catalyst immobilized on activated carbon (adsorption and catalytic oxidation) and / or ozone (ozonation reaction).

## 1.3 Scopes of research

1.3.1 Phenol is dissolved in de-ionized water to make synthetic aqueous phenol.

1.3.2 Investigation of phenol removal by two types of activated carbons and choosing the better activated carbon to apply in lab-scale fluidized bed reactor.

1.3.3 Prepare a Fe/activated carbon (Fe/AC) catalyst

- Activated carbon: 5 g.
- Fe/AC: 5 %wt.

1.3.4 Test the decomposition of phenol.

- Phenol concentration: 10 ppm.
- Catalyst loading: 5 g.
- The liquid flow rate: 1 L/min.
- The gas flow rate: 1 L/min.

1.3.5 Analyze the decomposition of phenol and intermediate product by

- HPLC (High performance liquid chromatography, Shimadzu column class VP)
- TOC (Total organic carbon analyzer, Shimadzu TOC-VCPH)

## 1.4 Benefit of this research

The expected benefit from this research is the knowledge to develop effective wastewater treatment for removing phenol dissolved in wastewater by using a lab-scale fluidized bed reactor with catalyst immobilized on activated carbon (adsorption and catalytic oxidation) and / or ozone (ozonation reaction). In addition, this reactor developed will be useful for scale-up of the system for application.

# CHAPTER II

# LITERATURE REVIEW

## 2.1 Wastewater treatment methods

In the recent years, many studies on various catalysts for pollution treatment have been conducted. Among all the organic materials that we are concerned with, phenol is important. Phenol and phenolic substances are used widely as raw materials for organic compounds, such as dyes, pharmaceuticals, plasticizers, and antioxidants. However, phenol, in addition to having a strong disagreeable odor and taste in water even at very small concentrations, is extremely toxic to aquatic life and resistant to biodegradation. There are classified the treatment processes for phenolic wastewater into two principal categories: destructive process such as destructive oxidation with ozone, hydrogen peroxide, or manganese oxides and recuperative processes such as adsorption into porous solids, membrane separation and solvent extraction. At present, several treatment methods are available as follows

### 2.1.1 Adsorption and Oxidation

James **[3]** studied that activated carbon removes organic compounds from aquaria by adsorption and absorption principles. Both processes involve the transfer of the adsorbate (pollutant) from the liquid phase (water) to the solid phase (carbon). Adsorption is the primary sorption mode relying on electrostatic Van der Walls forces. This attractive “force” forms relatively weak bonds between the carbon and adsorbate. In theory activated carbon could release or desorb what it removed at some point. But practical experience with aquarium filtration and laboratory experiments show desorption rarely occurs or causes any type of “toxic release”. Bacteria readily colonize the outer surface of the activated carbon and consume some of the sorbed organics. The bacterial action reactivates a small portion of the carbon and perhaps prevents desorption. Absorption refers to the diffusion of a gas or compound into the porous network where a chemical reaction or physical entrapment takes place. Ozone for example is absorbed into activated carbon where it oxidizes a portion of the carbon’s surface. Ozone ($O_3$) is reduced to oxygen ($O_2$) thus “detoxified” and made safe for the aquarium. Ozone does not accumulate or build-up in the carbon structure. A third process called chemisorption forms an irreversible chemical bond between the carbon surface and the adsorbate. Pollutants are tightly bound to the sorbent. All three sorption processes occur simultaneously in the aquarium. The sorption process takes place in three stages:

1) Organic laden water contacts the activated carbon particle.

2) The adsorbate diffuses into the porous network.

3) Sorption onto the carbon occurs.

The sorption process has been described as the activity observed in a parking lot. Vehicles (organics) are moving freely on the main highway (aquarium water). Gradually vehicles enter the lot (pore) in search of a parking space (sorption site). As the parking lot becomes filled the sorption rate slows down. Sorption of large organic compounds takes longer than smaller compounds. The sorption rate is also influenced by water temperature, pH, and salinity, but these factors will not be discussed since they are "constants" in the marine aquarium.

Banat et al. **[4]** evaluated the potential of bentonite for phenol adsorption from aqueous solutions was studied. Batch kinetics and isotherm studies were carried out to evaluate the effect of contact time, initial concentration, pH, presence of solvent, and the desorption characteristics of bentonite. The adsorption of phenol increases with increasing initial phenol concentration and decreases with increasing the solution pH value. The adsorption process was significantly influenced by the solvent type in which phenol was dissolved. The affinity of phenol to bentonite in the presence of cyclohexane was greater than that in water and was lowest in the presence of methanol. Methanol was used to extract phenol from bentonite. The degree of extraction was dependent on the amount of phenol adsorbed by bentonite. X-ray diffraction analysis showed that the crystalline structure of bentonite was destroyed when cyclohexane was used. The ability of bentonite to adsorb phenol from cyclohexane decreased as the water to cyclohexane ratio was increased. Furthermore, hysteresis was observed in phenol desorption from bentonite in aqueous solutions. The equilibrium data in aqueous solutions was well represented by the Langmuir and

Freundlich isotherm models. The removal of phenol from aqueous solutions was observed without surface modification.

Mccallum et al. **[5]** developed experimental and molecular simulation results are presented for the adsorption of water onto activated carbons. The pore size distribution for the carbon studied was determined from nitrogen adsorption data using density functional theory, and the density of acidic and basic surface sites was found using Boehm and potentiometric titration. The total surface site density was 0.675site/nm$^2$. Water adsorption was measured for relative pressures $P/P_0$ down to 10-3. A new molecular model for the water/activated carbon system is presented, which we term the effective single group model, and grand canonical Monte Carlo simulations are reported for the range of pressures covered in the experiments. A comparison of these simulations with the experiments shows generally good agreement, although some discrepancies are noted at very low pressures and also at high relative pressures. The differences at low pressure are attributed to the simplification of using a single surface group species, while those at high pressure are believed to arise from uncertainties in the pore size distribution. The simulation results throw new light on the adsorption mechanism for water at low pressures. The influence of varying both the density of surface sites and the size of the graphite microcrystals is studied using molecular simulation.

Polaert et al. **[6]** interested a two-step adsorption–oxidation process for treatment of aqueous phenolic effluents has been investigated. This process is based on the use of activated carbon as adsorbent in the first step and as oxidation catalyst in the second step, in a single bi-functional reactor. The main advantage of this process concerns the regeneration–oxidation step, for which only a small quantity of liquid has to be heated and pressurised, reducing then the heat consumption. Calculations and design were performed based on the experimental results obtained separately for the adsorption and the oxidation steps. This two-step adsorption–oxidation process appears to offer good potentialities for treating moderate flow rates of wastewater, especially when the effluent is dilute.

### 2.1.2 Ozonation

In an ozonation process two possible ways of oxidizing action may be considered: the direct way, because of the reaction between the ozone and the dissolved compounds, and the radical way owing to the reactions between the generated radicals produced in the ozone decomposition (hydroxyl radicals) and the dissolved compounds. Kinetic models for the reaction of ozone with different organic and inorganic compounds have been established by Hoigne and Bader **[7].**

Mokrini et al. **[8]** studied ozone appeared few minutes after the begining of all experiments with ozone (**Figure 2.1**). And, proposed the following mechanism of phenol oxidation by molecular ozone:

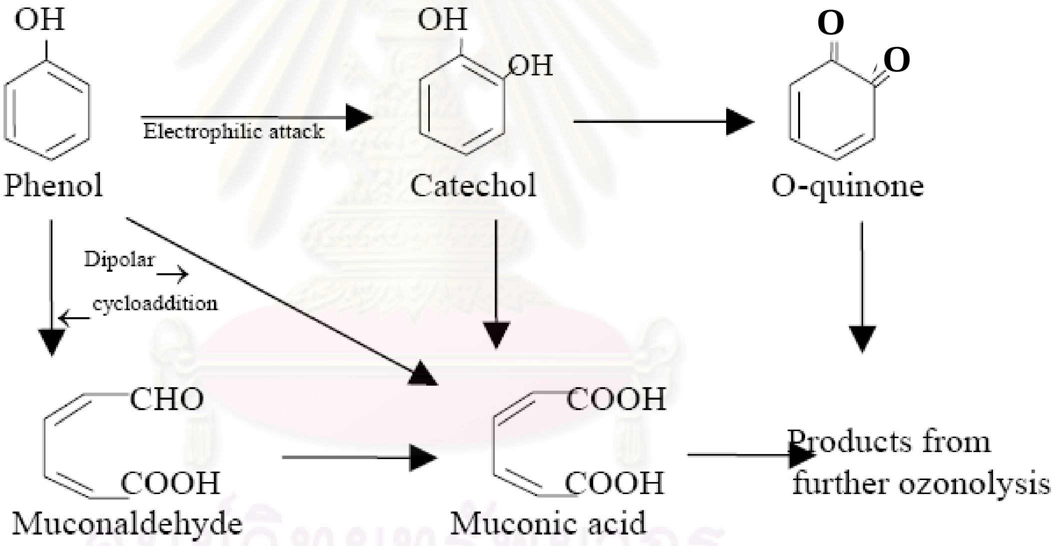


**Figure 2.1** Mechanism of phenol oxidation by molecular ozone

Bozena et al. **[9]** studied the influence of ozonation on the activated carbon adsorption, a model solution containing approximately 8 mg/dm$^3$ of humic acid and approximately 1 mg/dm$^3$ of phenol has been ozonated, and then adsorption kintetics and adsorption isotherm experiments have been performed. The applied ozone doses ranged from 1 to 3 mg $O_3$/dm$^3$, and a contact time was 1 min. In the adsorption experiments, the commercial activated carbon CWZ-30 has been used. Phenol adsorption under equilibrium conditions was determined by the Freundlich isotherm equation, and the modified Freudlich isotherm equation has been employed for the determination of humic acid equilibrium adsorption. The applied oxidation conditions resulted in color, chemical oxygen demand (COD), total organic carbon (TOC) and UV 254 absorbance removal, by 4 – 13%, 3 – 6%, 3 – 7%, respectively. After ozonation, phenol concentration decreased by 6%– 23%. These changes in the model solution did not affect the humic acid adsorption, however, they deteriorated phenol adsorption. The applied oxidation conditions (1-min contact time and ozone dose ranging from 1 to 3 mg $O_3/dm^3$) resulted in partial decomposition of phenol and humic acid molecules. These changes in the model solution did not affect humic acid adsorption on the PAC, however, they deteriorated phenol adsorption.

### 2.1.3 Catalytic Oxidation

Levec and Pintar. **[10]** were presented about a potential catalytic liquid-phase oxidation of aqueous solutions of organics, advanced waste water treatment technology. Catalysts are briefly reviewed first, followed by mechanistic speculations and kinetics that have been proposed for liquid-phase oxidation of some model pollutants. Subsequently, oxidation reactors and potential process schemes are discussed. The key issue of the effective catalytic oxidation of organics in waste water is the catalyst. Oxidation most probably undergoes a complex redox and/or heterogeneous nonbranched-chain free radical mechanism. In order to develop effective catalyst and process, more kinetic and mechanistic studies with different systems in aqueous solutions are needed.

Pirkanniemi and Sillanpa. **[11]** studied dealing with heterogeneous catalytic raw water treatment processes including oxidation and hydrogenating processes. If catalyst in water phase process is dissolved homogeneous, separation processes possibly have to be adapted. In many cases, separation would be technically and/or economically unachievable. In addition, many active homogeneous catalysts, such as some metal salts are a potential environmental problem. Under these circumstances, there is a need for heterogeneous catalytic procedures where the catalyst is in different phase and therefore more likely easy to separate. However, heterogeneous processes are usually more complicated to control. Since surface plays an important role in adsorption and desorption, appropriate support selection may therefore have a remarkable effect on reaction rate. This is possibly a field of the most rapid development in heterogeneous catalysis during past 10 years. This review consists of publication concerning environmental heterogeneous catalytic water phase applications. All the most important processes, catalysts, and supports are listed. The reference material included has mostly been published during past five years. However, some older papers were included when found fruitful.

Quintanilla et al. **[1]** has been tested a Fe/activated carbon (Fe/AC) catalyst for the wet oxidation of phenol in a fixed bed reactor at relatively mild conditions. Using the incipient-wetness impregnation method, a catalyst containing 2.4 wt% of Fe on the active carbon was prepared. An aqueous solution of $Fe(NO_3)_3•9H_2O$ was employed as iron precursor. Impregnation was followed by drying at room temperature for 2 h and overnight at 60 °C. The sample was then heated up to 200 °C within 2 h at two temperature rates and then calcined at 200 °C during 4 h. The organic compounds present in the effluent were identified and quantified by HPLC. Total organic carbon (TOC) measurements were accomplished with TOC analyzer. Iron in the reactor effluent was analyzed by total reflection X-ray fluorescence (TXRF).The Fe/AC shown a complete phenol conversion and 80% TOC removal at 127 °C and shown chemical stability in long-term experimental. Research in course is addressed to optimize the preparation of Fe/AC catalysts for their application in catalytic oxidation treatments of real industrial wastewaters.

## 2.2 Fluidized bed reactor

Nam et al. **[12]** was carried out in two different types of fluidized bed reactors with $TiO_2$ powder in this research the photocatalytic oxidation of methyl orange under weak illumination conditions One is the typical type of FBR (fluidized bed reactor) and the other is the FBR with an internal draft tube (Draft tube fluidized bed reactor, DTFBR). Two FBRs of experimental test set-up is shown in **Figure. 2.2**

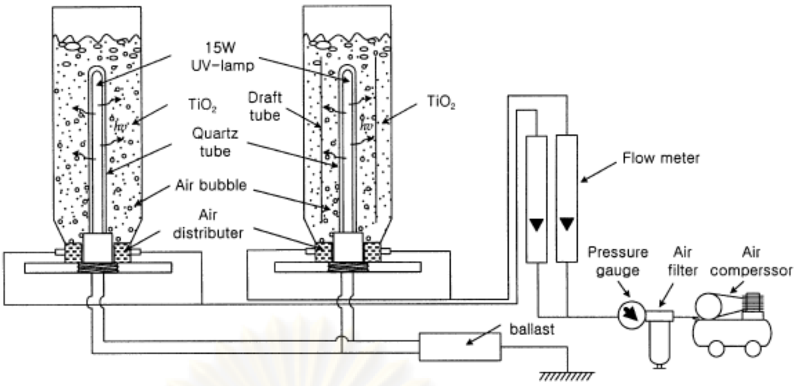


**Figure 2.2** The schematic diagram of experimental test set-up.

In this study, factors affecting the decolorization rate of methyl orange in a three-phase FBR are investigated such as catalyst loading, pH, air flow rate, initial concentration of target compound, and reactor geometry. The methyl orange solution was successfully decolorized by the photocatalytic reaction in the FBRs under weak illumination conditions. It was also found that pH is another important parameter in determining the reaction rate and the acidic condition was favorable for the methyl orange and $TiO_2$ system. The higher initial concentration decreased the light penetration thus decreased the relative reaction rate of photocatalytic reaction. It was also observed that there was an optimum amount of catalyst loading which does not prevent screening effect to illumination. There was no significant difference of geometric effect on reaction rate under the covered experimental conditions.

Trivedi et al. **[13]** shown in the **Figure. 2.3**, a liquid–solid circulating fluidized beds (LSCFB) system is composed of two interconnected fluidized beds, namely, a riser and a down-comer. The other important components of the LSCFB involves a liquid–solid

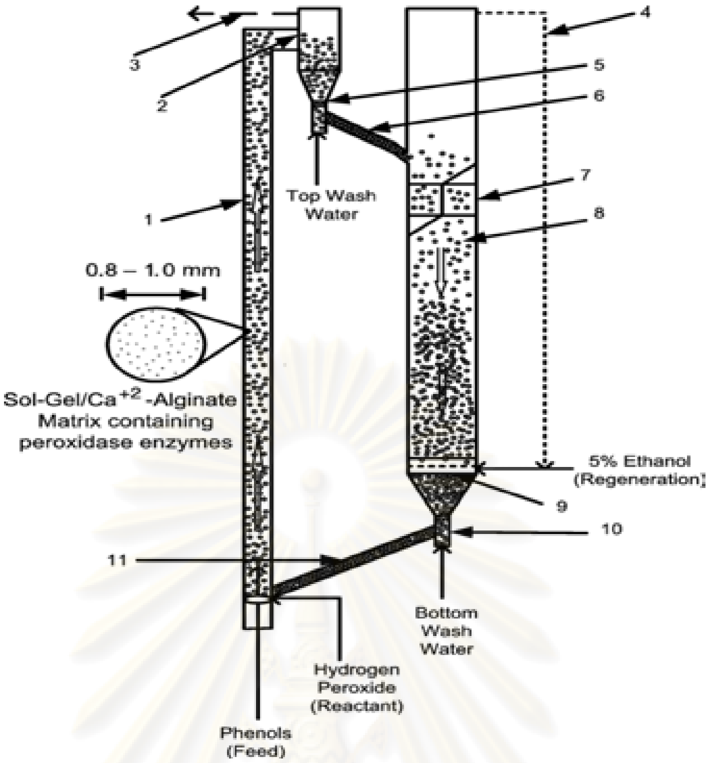


**Figure 2.3** Schematic of a liquid–solid circulating fluidized bed bioreactor system containing entrapped soybean seed hull peroxidase enzymes within the sol-gel/calcium-alginate matrices.

separator, a top particles returning pipe from riser to the down comer, a bottom particles returning pipe from down-comer to the riser, a top washing section and a bottom washing section. A liquid–solid circulating fluidized bed (LSCFB) system consisting of 3.8 cm I.D. and 4 m high riser and 12 cm I.D. and 3.5 m high down comer was investigated in this study for the continuous polymerization of phenol. Approximately 8.5 kg immobilized particles containing soybean seed hull peroxides enzymes were applied in the LSCFB system. The continuous enzymatic polymerization was carried out in the riser section by introducing phenol and hydrogen peroxide at the entrance of the riser. Under optimized hydrodynamic conditions and by keeping the molar concentration ratio of phenol to $H_2O_2$ of 1:2, 54% conversion of phenol was achieved. The down-comer of the LSCFB was utilized for the regeneration of the coated immobilized enzyme particles. The effect of the superficial liquid velocity and an initial substrate concentration was studied. Our experimental results show that an enzymatic reaction and the regeneration of the biocatalysts can be carried out simultaneously and independently in the LSCFB system. Furthermore, this work opens the possibilities for many bioprocesses where the deactivation of the biocatalysts is a major problem and the regeneration of the biocatalysts is required. This study shows that the LSCFB is an attractive alternative for processes where deactivation of the biocatalysts occurs and regeneration is needed. For such processes, the LSCFB system can offer a simultaneous reaction and regeneration continuously. Further studies on the down-comer side in the LSCFB device is in progress including the recovery of the polymeric material and the recirculation of the regeneration stream.

### 2.3 Combination of wastewater treatment methods and fluidized bed reactor.

Kabir et al. **[14]** was exploited in this research effect of $H_2O_2$ addition on phenol degradation in the photocatalytic fluidized bed reactor. Laboratory optimized integrated photocatalyst adsorbent was used as the supported photocatalyst. Overall, it was found that addition of hydrogen peroxide to the photocatalytic system was beneficial and it was demonstrated that the desired enhancement can be achieved with small doses of hydrogen peroxide, which is promising from economic perspective since it requires miniscule consumption of the non-recyclable agent, $H_2O_2$.

# CHAPTER III

# FUNDAMENTAL KNOWLEDGE

## 3.1 Wastewater treatment

Human ingenuity has produced well over fourteen million chemicals substances which have never before been part of the terrestrial environment and the rate of discovery is increasing every day. Some of these newly synthesized compounds, such as substances containing heavy metals and persistent organic pollutants, have been known to be dangerous for many years already, while fears have been raised about many others recently. In addition to chemicals that are placed on the market, either as intermediates within a production process, or as part of final products, there is the unintentional formation of chemical by-products in many industrial processes, which can also impact on the environment. Clearly, solutions must be tailored to the properties and uses of each particular chemical and groups of chemicals, as well as to each country's unique circumstances. But action must be taken quickly. Each year that passes without effective action will result in decades of additional, unintended exposure to chemicals that are likely to be harmful to human health and the environment. Water is a key resource for our quality of life. Access to clean water for sanitary purposes is a precondition for human health and well-being. Almost all human activities can and do impact adversely upon the water. Discharges from wastewater treatment plants and industry are caused pollution by oxygen consuming substances, nutrients and hazardous substances. The adverse impacts depend very strongly upon the degree to which (if at all) such discharges are treated before reaching waterways. Thus, challenges faced by chemical and related industries, due to unprecedented market demands and public environmental concern, are to imagine efficient and cost-competitive remediation processes and minimization strategies for water pollution problems.

Wastewater typically can be divided in two categories: urban and industrial. In the urban residues, the main pollutant load is organic, mostly non toxic and biodegradable. Usually, this kind of wastewater is treated in conventional wastewater treatment plants (WWTP) based on biological oxidation. On the contrary, industrial effluents usually have a very complex and toxic composition, depending on the industry that generates them, which often requires more severe remediation treatments. Examples of toxic and therefore non biodegradable organic pollutants are phenols, surfactants, chlorinated compounds, pesticides, polyethylene and aromatic hydrocarbons, among many others. Organic pollutants tend to accumulate in the tissues of animals and plants, often becoming more concentrated as they move up through the food chain. Many times, the symptoms of contamination may not manifest themselves until several generations after initial contact with the chemical of concern.

The importance of phenolic effluents, a part from their potential toxicity, is outlined by the high quantities that are eventually rejected in the environment. In addition, phenol is considered to be an intermediate product in the oxidation pathway or higher-molecular-weight aromatic hydrocarbons. Thus, it is usually taken as a model compound for wastewater treatment studies, as it is for the present research work.

There is no doubt that water pollution is a continuing and even growing problem that arises from human activities. No unique solution seems possible for destroying all kind of water pollutants due to the heterogeneous composition of real wastes as well as the diversity of new chemical compounds that are continuously being synthesized. Some waste treatments merely transfer the toxic component from one phase to another. While this may serve to concentrate the wastes in a more readily disposable form, it does not alter the chemistry of the pollutants. Other processes use chemical reactions to transform the wastes into less toxic by-products or harmless end products such as $CO_2$ and water. It is clear that the selection of the correct process or the combination of treatments is a difficult task and should be generally made depending on the treated wastewater characteristics and the destination of the effluent **[15].**

## 3.2 Phenol and Activated carbon

### 3.2.1 General information of phenol

Phenol is usually in the form of colorless or white crystals. It has a sickly sweet smell and a sharp burning taste. Phenol occurs naturally as coal tar, and is formed during decomposition of organic materials. Much of the phenol that is present in the environment is due to anthropogenic activities such as wood burning, smoking, rubbish incineration and car exhausts. One of the main uses for phenol is for the production of phenolic resins, bisphenol-A, used to make epoxy resins and caprolactam used to make nylon. It is also used to make adhesives, paint, rubber, ink, dyes perfume and soap. Phenol may also occur in rain, surface water and ground water. Occupational exposure may occur during the production of phenol and phenol products and during the application of phenolic resins as well as other industrial processes. For the general population the largest exposure will come from smoking or inhaling air containing phenol and to a lesser extent from eating smoked food. Exposure to phenol causes both local effects at the site of exposure as well as systemic effects on other organs in the body. Eating food or drink contaminated with phenol for a short period can cause burning to the mouth and throat, wounds to mouth, esophagus and stomach, abdominal pain, vomiting and diarrhea. Ingestion of a significant concentrated dose or of significant amounts of a concentrated dose is usually fatal. Breathing in air contaminated with phenol for a short period is irritating to the lungs and may cause wheezing. Inhalation can also cause anorexia, headache, weight loss, vertigo and dark urine. If the skin comes into contact with phenol the area becomes numb, hence its use as a local anesthetic. If contact continues, pain, inflammation and discoloration/blanching can occur. If ingesting phenol for a longer time, severe stomach irritation can occur as well as heart and breathing effects, mouth sores and production of dark urine. Long term skin contact causes wounds on the skin and can make the skin yellow. If phenol is absorbed into the body, it can cause headaches, dizziness, high blood pressure, heart effects, shallow breathing, wheezing, coughing, vomiting, stomach ulceration and eventually death. These health effects are the same whether absorption is due to eating contaminated food or drink, inhaling contaminated air or from skin absorption. Phenol and its compounds are not classifiable as to their carcinogenicity to humans by the International Agency for Research on Cancer. Phenol is largely used in the manufacture of phenolic resins and plastics. It is also used in the manufacture of explosives, fertilizers, paints, rubber, textiles, adhesives, drugs, paper, soap and wood preservatives. It is also mixed with other reagents and used as a disinfectant for toilets, floors and drains **[16]**.

#### 3.2.1.1 Chemistry of phenol

Phenol is the simplest member of a family of compounds in which an -OH group is attached directly to a benzene ring. The molecular formula of phenol is $C_6H_5OH$ (see the molecular structure in **Figure. 3.1**).

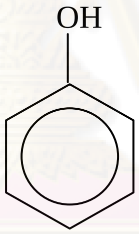


**Figure 3.1** Molecular structure of phenol

#### 3.2.1.2 Physical properties of phenol

Pure phenol is a colourless or white solid with sweet and acrid odors. Phenol has a molecular weight of 94.11, a melting point of 43°C and a boiling point of 182°C at 760 mm Hg. The pKa for phenol is 9.9 to 10 and it readily reacts with strong bases such as NaOH or KOH to form phenoxides. Not only do these phenolic compounds differ in chemical structure and environmental behaviour, they also differ in toxicity. Phenolic compounds are weakly acidic and can be more toxic at low pH because of increasing proportions of free phenol.

#### 3.2.1.3 Solubility in water of phenol

The simplest phenolic compounds, such as phenol, cresol and xylenol are highly soluble in water and are easily degradable. Phenol has a water solubility of 6.7 g/100 mL at 16°C and is fully soluble in water at 66°C. Phenol can remain in water for up to six days, but is generally present for much shorter durations. Sorption to sediments is not an important transport mechanism of phenol to water.

#### 3.2.1.4 Handling and storage of phenol

Take precautionary measures against static discharges. To avoid ignition of vapours by static electricity discharge, all metal parts of the equipment must be grounded. Keep away from food, drink and animal feeding stuffs. Easy access to as emergency shower and eye wash facility is required. To be handled by trained personnel only. Ensure adequate ventilation. The following measures are recommended: Closed systems for handling, process and storage. Keep away from sources of ignition-No smoking. Avoid contact with skin, eyes and clothing. Avoid inhalation of vapour or mist. Suitable container: stainless steel. Unsuitable container: aluminium, zinc, lead, copper, copper alloys, unlined steel. Keep away from incompatible materials. Keep container tightly closed and in a well-ventilated place. Keep under nitrogen.

#### 3.2.1.5 Personal protection of phenol

Avoid and prevent all spillage, contact and exposure. Smoking, eating and drinking should be prohibited in the application area. Wash hands before breaks and immediately after handling the product. In case of insufficient ventilation: Respirator with filter or self-contained breathing apparatus. Wear suitable gloves: Polyvinylchloride (PVC), neoprene breakthrough time > 480 min; thick PVC, neoprene breakthrough time > 60 min; Polyvinylchloride (PVC), neoprene. Wear suitable protective clothing and rubber boots.

#### 3.2.1.6 Stability and reactivity of phenol

Phenol is stable under normal conditions exposure to air and sunlight. Keep away from heat and sources of ignition. It reacts violently with: Strong oxidizing agents, sulphuric acid, nitric acid, aluminium chloride and corrosive effects: Aluminium, zinc, lead, copper, copper alloys, unlined steel. Phenol may attack many plastics, rubbers and coatings. Heating or fire can release toxic gases **[6].**

#### 3.2.1.7 Industrial effluent quality standards in Thailand of phenol

The acceptable phenolic compound concentration to be treated in central wastewater treatment process must be controlled at the industrial effluent standard (1.0 mg/L). This means that any particular plant (located in the industrial estates) which discharges phenolic and related compounds greater than the Industrial Estate Authority of Thailand (IEAT) acceptable limits (1.0 mg/L for phenolic compounds) must have their own effective wastewater treatment unit before transferring the wastes to the central treatment process.

#### 3.2.1.8 Wastewater treatment methods

Variation of component in wastewater is high, contains a large number of different compounds arise from raw material. Several methods have been studied for treating dye wastewater. However, these effluent treatments have different advantages and disadvantages as shown in **Table 3.1**.

**Table 3.1** Summary the advantages and disadvantages of methods for treating dye wastewater**. [17]**

| **Method** | **Advantages** | **Disadvantages** |
|---|---|---|
| Activated carbon adsorption | -Suspended solids and organic substances well reduced | -Blocking filter |
| Advanced chemical oxidation | -Non-hazardous end products | -High cost |
| Electrochemical oxidation | -Removes small colloidal particles<br>-Breakdown compounds are non-hazardous<br>-No chemical use | - High cost |
| Biological process | -Environmentally friendly<br>-Rates of elimination by oxidizable substances about 90%<br>-Economically attractive | -Low biodegradability of phenol<br>-Needs adequate nutrients<br>-Narrow operating temperature range |

### 3.2.2 Activated carbon

Activated carbon, also called activated charcoal or activated coal, is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions **[18].** The word activated in the name is sometimes substituted by active. Due to its high degree of microporosity, just one gram of activated carbon has a surface area of approximately 500 $m^2$, as determined typically by nitrogen gas adsorption. Sufficient activation for useful applications may come solely from the high surface area, though further chemical treatment often enhances the adsorbing properties of the material. Activated carbon is usually derived from charcoal.

### 3.2.2.1 Granular activated carbon (GAC)

Granular activated carbon has a relatively larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface. Diffusion of the adsorbate is thus an important factor. These carbons are therefore preferred for all adsorption of gases and vapors as their rate of diffusion are faster. Granulated carbons are used for water treatment, deodourisation and separation of components of flow system. GAC is designated by sizes such as 8x20, 20x40, or 8x30 for liquid phase applications. The most popular aqueous phase carbons are the 12x40 and 8x30 sizes because they have a good balance of size, surface area, and heedless characteristics.

### 3.2.2.2 Environmental applications

Carbon adsorption has numerous applications in removing pollutants from air or water streams both in the field and in industrial processes **[19].**

### 3.2.2.3 Porous activated carbon

The activated carbons have been used in several applications. In the adsorption process, we should consider appropriation between molecular size and the suitable pore width of activated carbon. Pores are usually characterized in terms of their width, meaning the diameter of a cylindrical pore or the distance between sides of a slit-shaped pore. Their different structures are shown in **Figure 3.2.**

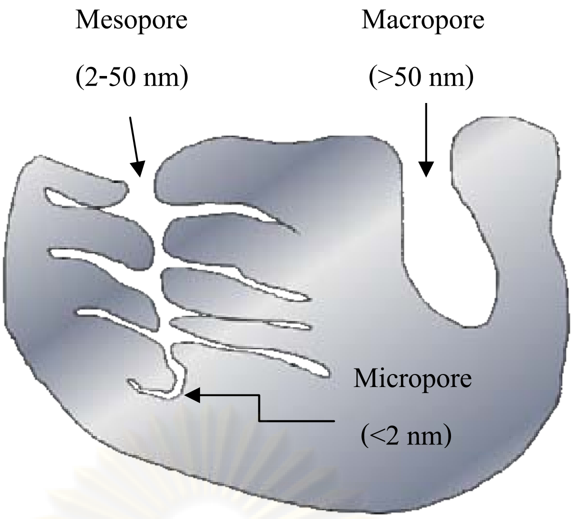


**Figure 3.2** Schematic of the pore structure observed in AC

The range of pore sizes which is defined according to the International Union of Pure and Applied Chemistry (IUPAC).

### 3.2.3 Intermediate products

#### 3.2.3.1 Hydroquinone

Hydroquinone, also benzene-1,4-diol or quinol, is an aromatic organic compound which is a type of phenol, having the chemical formula $C_6H_4(OH)_2$. Its chemical structure, shown in the table at right, has two hydroxyl groups bonded to a benzene ring in a *para* position. It is a white granular solid at room temperature and pressure. (see the molecular structure in **Figure. 3.3**).

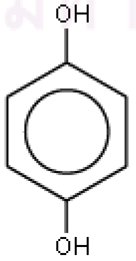


**Figure 3.3** Molecular structure of hydroquinone

### 3.2.3.2 Catechol

Pyrocatechol, more commonly known as catechol, is the organic compound with the formula $C_6H_4(OH)_2$. It is one of three isomeric benzenediols. This colourless compound occurs naturally, but about 20000 tons are manufactured each year, mainly as precursors to pesticides, flavors, and fragrances.

**Figure 3.4** Molecular structure of catechol. **[20]**

Three planar structures are possible for catechol. Our calculated structure for catechol, is in excellent agreement with previous calculations (a wide variety of theoretical methods have been applied) and the accepted crystal structure. For example, the C–O bond length is within 0.011 Å of the expected value (average experimental: 1.373 Å vs. calculated: 1.378 and 1.362 Å), the difference in the –C–O–H bond angle is only 0.6° (121.0 vs. 120.4°) and the deviation from the expected 120° ring bond angle is only 0.5°. For the carbon–carbon bond length at the reaction site, the calculated bond length is 0.015 Å greater than the experimental value of 1.389 Å. The lowest energy structure for *cis*-catechol has an intramolecular hydrogen bond, as shown in **Figure 3.4.** One expects, however, that rotation of the hydroxyl groups would not be hindered by a significant barrier. This possibility was explored by allowing the hydroxyl groups to rotate through an angle of 180° around the C–O bonds. The barrier between the two identical catechol forms was found using the QST3 procedure to be 3.4 kcal $mol^{-1}$, a value lower than the energy of a typical hydrogen bond. This relatively low barrier indicates that the vicinal groups can easily rotate, and change conformation during the formation of an activated complex.

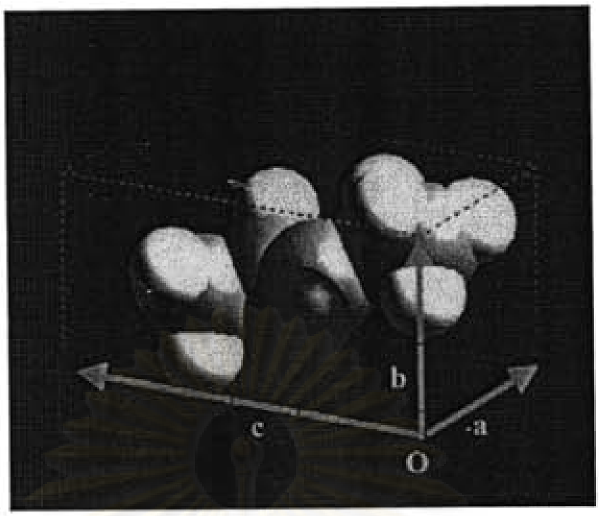


**Figure 3.5** Hydroquinone placed in an optimized periodic cell and compass force field were used for calculation. **[21]**

The molecular size was calculated for phenol, catechol and hydroquinone by periodic molecular mechanics optimization and compass force field set were used for the calculation. Calculations were done as follows. (1) a molecule was put in a rectangular periodic cell. (2) structure of the molecule and cell volume were optimized while cell angles were fixed at $\alpha$, $\beta$ and $\gamma$=90°. The cell size was optimized in which a molecule feeling force exerted by replicas in surrounding cells. Therefore, the optimized cell size is expected to be roughly equal to void space by a molecule. Hydroquinone in an optimized periodic cell is shown in **Figure 3.5** as a typical result. The cell lengths (*a*, *b* and *c*) were listed in **Table 3.2** and used as a measure of size of a molecule **[21]**.

**Table 3.2** Molecular size **[21]**

| *Molecule* | *a(nm)* | *b(nm)* | *c(nm)* |
|---|---|---|---|
| Phenol | 0.4792 | 0.4908 | 0.5090 |
| Hydroquinone | 0.4559 | 0.4934 | 0.5193 |
| Catechol | 0.4857 | 0.4869 | 0.5126 |

The molecular size of phenol, catechol and hydroquinone calculated by periodic molecular mechanics using compass force field are listed in **Table 3.2.**

## 3.3 Degradation of reactions

For the past few decades, there have been many ways for removal of phenol from flow effluents such as biological and chemical oxidation, adsorption on granular activated carbon, chlorination and ozonation.

In biological system, pH and temperature control are necessary and a large land space is required while in chemical system, hydrogen peroxide and potassium permanganate, this method is more expensive and appear to be a reasonable method of phenol treatment for smaller flows. For carbon adsorption, phenol in the final effluent is produced in the low level but the cost of this method included the carbon contact vessel, carbon regenerated system and an associated apparatus is expensive. With chlorination, there are several shortcomings such as the sophistication of correct chlorine dosage, the need of pH control and the generated more toxic phenol. Meanwhile in ozonation, it should be cautioned that ozone may be toxic depending upon exposure. Direct extended contact with ozone should be avoided [22].

The treatment of many industrial waste streams by traditional non-catalytic chemical process may be too energy intensive with adaptable catalyst, energy consumption of various oxidation procedures may be decreased [23]. Nowadays an advance oxidation process using a metal oxide catalysts for decomposing the phenolic compounds are developed for the use of wastewater treatment system. In this research the removal of phenol is investigated under the ozonation, catalytic oxidation, photo catalytic oxidation and the ozonation combined with one of them.

### 3.3.1 Adsorption

Adsorption is an effective separation process for treating industrial and domestic effluents. Activated carbon is the most widely used adsorbent. It has the advantage of high adsorption capacity for organic compounds, but its use is usually limited due to its high cost. The adsorption characteristics of phenol on various adsorbents have previously been extensively investigated for many purposes of separation and purification. However, most of the work was on the adsorption behavior of activated carbon. The adsorption of phenol from aqueous solution by using carbonized beet pulp was investigated. The result indicated that adsorption capacity of the adsorbent was considerably affected by initial pH, temperature and initial phenol concentration.

#### 3.3.1.1 Methods of Adsorption

Adsorption into porous solids may be considered to occur by mechanisms involving either diffusion through a barrier or a purely diffusional process along the pore. There are, of course, instances where the mechanism may not be clear cut and it is in these cases that a combination of approaches must be considered.

#### 3.3.1.2 Methods of Diffusion

Diffusion may be considered as the process by which molecules are transported from one part of the porous system to another. The process is dependent both upon the ratio of the adsorbate molecule size to the pore width and the concentration of the adsorbing molecule. The mechanism and methods involved in the adsorption of an adsorptive are indicative of the pore-filling processes which occur and also provide a means to evaluate the kinetics of the adsorption process. The adsorption isotherm describes the equilibrium states of an adsorbate within an adsorbent hence does not afford any information regarding the rate of adsorption and such quantities must be measured directly. The method of diffusion is heavily dependent on pore width and as the pores become progressively narrower the mechanism may be subject to change. The mechanism of diffusion begins with free diffusion, where the average path length of the molecule is small compared to the pore diameter. As the diameter of the pores become smaller capillary or Knudsen diffusion dominate, both involve surface diffusion and exhibit Arrhenius temperature dependence. At the point where the pore diameter becomes comparable to the admolecule activated diffusion occurs due to the strong interactions between the admolecule and the pore walls. Activated diffusion is sometimes referred to as micropore diffusion, not an entirely suitable title as the pore width at which activated diffusion occurs is obviously dependent on the molecular dimensions of the adsorbate and this is not necessarily the micropores.

### 3.3.2 Catalytic oxidation

Different methods for treating industrial waste water containing organic pollutants have been widely reported. The choice of treatment depends on the level of phenol concentration, on economics and easy control, reliability and treatment efficiency. Oxidation of dilute aqueous solutions of refractory pollutants by using oxygen over a solid catalyst offers an alternative to the techniques (for example, noncatalytic wet-air oxidation, biological oxidation, oxidation in supercritical water, and physical adsorption) as a means of purifying waste waters.

The key issue in the process of effective oxidation of phenolics in water is the catalyst which must have high mechanical strength, chemical stability, and hydrophobicity; actively participate in the oxidation reactions; to be stable in water and facilitate the complete oxidation of the phenolics to carbon dioxide. Transition-metal oxides have proved to be active in the catalytic reactions of complete degradation of phenol and its derivatives in waste waters **[24]**.

Metal oxides can be classified according their physico-chemical properties. One of these properties is the stability of metal oxide. Metals with unstable high oxidation state oxides, such as Pt, Pd, Ru, Au, and Ag do not perform stable bulk oxides at moderate temperatures. Most of the commonly used metal oxide catalysts (Ti, V, Cr, Mn, Zn, and Al) have stable high oxidation state oxides. Fe, Co, Ni, and Pb belong to group with intermediate stability of high oxidation state oxides. It is a well-known fact that metal oxides are usually less active catalysts than noble metals. Nevertheless, to majority of applications metal oxides are more suitable since they are more resistant to poisoning. In addition, combining two or more metal oxide catalysts may improve non-selectivity and catalytic activity **[23]**.

### 3.3.2.1 Mechanism of catalytic oxidation [25]

The mechanism of the oxidation of phenols is extremely complex and is not yet fully understood. It is generally accepted that the oxidation of phenol by molecular oxygen is basically an electrophillic reaction and the rate limiting step is the reaction between the aryloxy radical with oxygen [26]. In accordance with the proposed scheme (see **Figure 3.6**), the oxidation process starts with the adsorption of the substrate (PhOH) on the catalyst surface and the simultaneous tearing off of an H-atom from the phenolic OH‾group, which combines with the active oxygen (O–) of

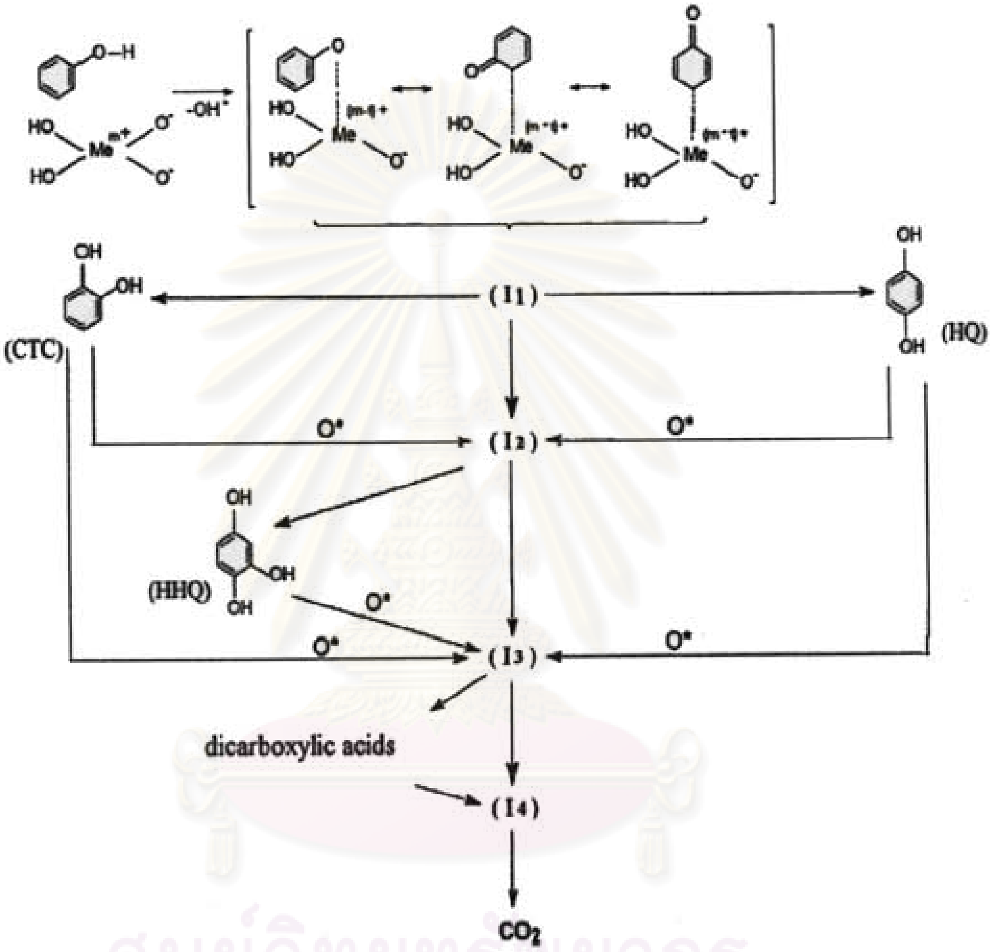


**Figure 3.6** Mechanism proposed for the catalytic oxidation of phenol under basic conditions by metallic catalysts. [25]

the catalyst to form surface $OH^{\bullet}$. The chemisorbed phenol forms a complex $I_1$ with the reduced form of the catalyst cation ($Me.^{(n-1)+}$). The latter passes consecutively via a series of surface complexes ($I_2$–$I_4$) with a different degree of oxidability, which possess probably the following nature respectively: $I_2$ —phenoxyradical type, similar to $I_1$; $I_3$ — carboxilate complex, while $I_4$ has a carbonate character.

### 3.3.3 Ozonation [27]

Ozone is a very powerful oxidizing agent that can react with most species containing multiple bonds (such as C=C, C=N, N≡N, etc.) It is intensively used in water and waste water treatment, disinfection, bleaching and industrial oxidation processes. The practical applications are based on the very high oxidizing power of ozone. Ozonation of water and wastewater is carried out by dispersing ozone gas into the liquid phase. Ozone has been employed as oxidants in many water and wastewater treatment applications. Theoretically, ozone should be able to oxidize inorganics to their higher oxidation states while oxidizing organic compounds into carbon dioxide and water. There are two possible ways of oxidizing action in an ozonation process, direct way and radical way.

In the direct way, ozone react directly with phenol molecules and cleavage the ring to finally yield an organic acid molecule as represented in **Figure 3.7.**

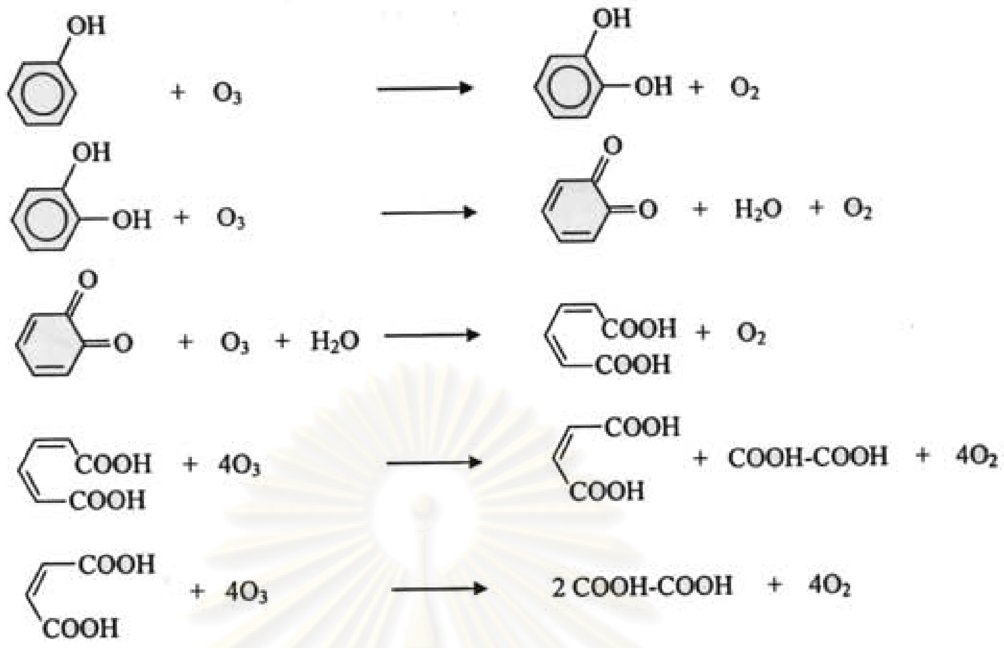


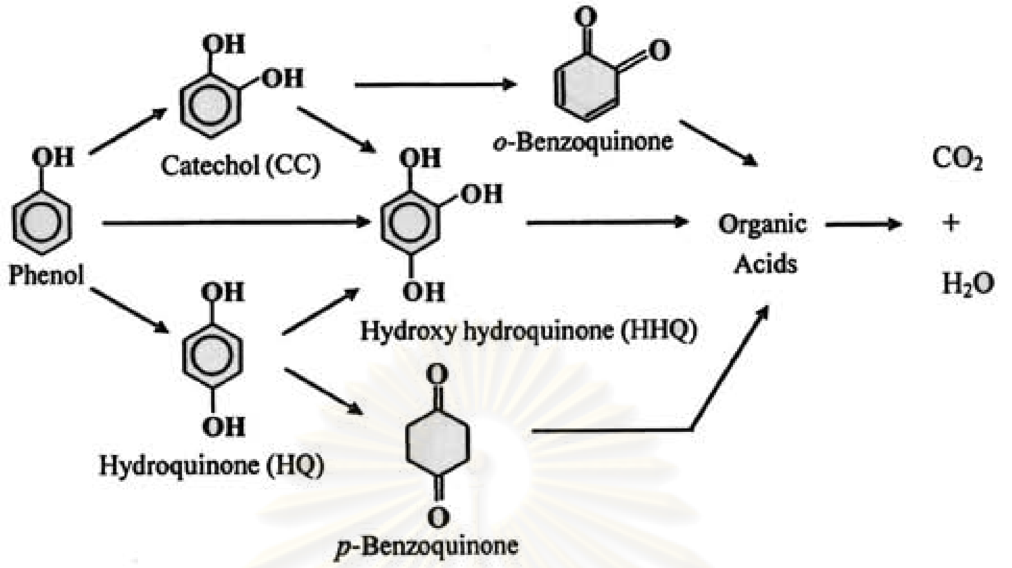
Figure 3.7 Pathways of phenol decomposition by ozonation reaction. **[28]**

Meanwhile the radical way owing to the reactions between the generated radicals, hydroxyl radicals ($OH^{\cdot}$), produced in the ozone decomposition and the dissolved compounds. The global reaction of ozone decomposition to yield hydroxyl radical is **[29, 30]**:

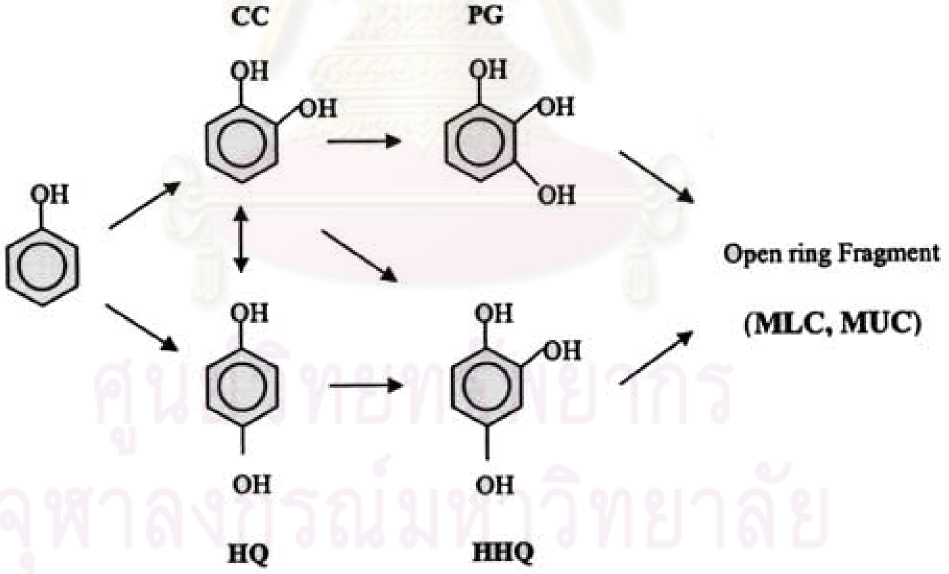
$$O_3 + H_2O \xrightarrow{h\nu} 2OH^{\cdot} + O_2$$

## 3.4 Pathways of the intermediate products of phenol

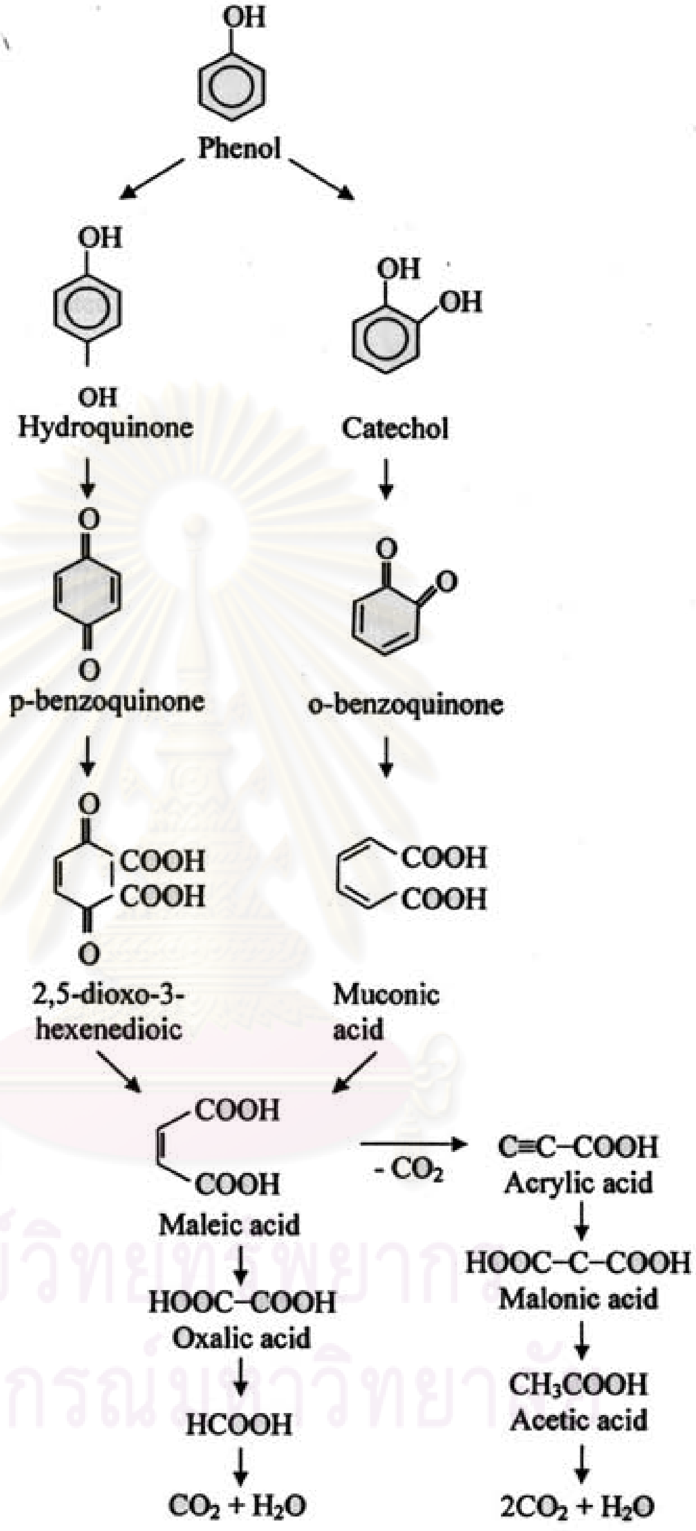
When phenol is degraded, catechol, hydroquinone and hydroxyl hydroquinone are generated as the products of the initial stage of degradation. These aromatic intermediates undergo to *o*, *p*-benzoquinone and further ring cleavage to yield carboxylic acids such as muconic acid, maleic acid, oxalic acid, etc. which subsequently become $CO_2$ and $H_2O$ due to decarboxylation. Pathways of the intermediate products were summarized in **Figure 3.8.**


OH
Phenol
OH
OH
Catechol (CC)
O
O
o-Benzoquinone
OH
OH
OH
Hydroxy hydroquinone (HHQ)
OH
OH
Hydroquinone (HQ)
O
O
p-Benzoquinone
Organic Acids
CO2
+
H2O

(a)


CC
OH
OH
PG
OH
OH
OH
OH
OH
OH
HQ
OH
OH
OH
HHQ
Open ring Fragment
(MLC, MUC)

(b)



(c)

**Figure 3.8** Pathways of the phenol intermediate products (a) [31], (b) [32] and (c) [33]

### 3.5 Gas-Liquid-Solid fluidization [34]

The expression of three-phase fluidization was used to describe fluidization of solid particles by two fluids. A gas and a liquid were the fluidizing media used in the applications. Studies of three-phase fluidization had been of interest and their numerous applications existed in various industrial processes, which varied in size from bench to commercial scale. In such system, the individual phases could be reactants, products, catalysts, or inert. Some examples of three-phase fluidization applications were shown in **Table 3.3.**

**Table 3.3** Examples of applications of three-phase fluidized bed processing.

| Physical processing | Chemical processing | Biochemical processing |
|---|---|---|
| Drying of calcium carbonate and polyvinylchloride | Production of zinc hydrosulfite | Aerobic biological waste treatment |
| Dust collection | Methanol fermentation | Production of animal cells |
| Crystallization | Electrode | Enzyme immobilization |
| Sand filter cleaning | Coal liquefaction | Ethanol fermentation |
| Drying of granular material | Coal gasification | Antibiotic production |
| Lactose granulation | Fuel gas desulfurization | Conversing of sucrose to glucose by plant cells |

As mentioned previously, the gas-liquid-solid fluidization was an operation, in which the solid particles layer, fluidized by gas and liquid and then behaved like a fluid. In general, the state of the particle motion in the fluidized bed operation by the upward flow of the fluid could be subdivided into three basic operating regimes: the fixed bed regime, the expanded bed regime, and the transport regime.

The fixed bed regime existed when the drag force on the particle induced by the flow of a gas-liquid mixture was smaller than the effective weight of the particle layer. With an increase in gas and/or liquid velocity, the drag force counterbalances the effective weight of the particles then the bed would achieve the state of minimum fluidization and marked the onset of the expanded bed regime. With a further increase in gas and/or liquid velocity beyond the minimum fluidization velocity, the solid bed would change to the expanded bed regime until the gas or liquid velocity reached the terminal velocity of the particles in the medium ($U_t'$). At the gas or liquid velocity above $U_t'$, operation would be considered as the transport regime.

### 3.5.1 Hydrodynamics [34]

Hydrodynamic behavior of three-phase fluidized bed reflected, the complex interactions between the individual phases. The most prominent interaction occurred between the rising gas bubbles and the surrounding liquid-solid mixture. Three distinct regions above the gas-liquid distributor were identifiable based on the prevailing physical phenomena: the distributor region, the bulk fluidized bed region, and the free board region. A schematic diagram was shown in **Figure 3.9.**

The distributor region referred to the region immediately above the gas-liquid distributor where gas spouts might occur. It included the region from initial bubble formation to the establishment of the final bubble shape. The hydrodynamic behavior in the distributor region inherently depended on the gas-liquid distributor design and the physical properties of the liquid-solid medium.

The bulk fluidized bed region included the main portion of the fluidized bed. The hydrodynamic behavior in the bulk fluidized bed region varied drastically over large ranges of operating conditions. However, for a given operating condition, there was a minimum axial transport property variation in the region.

Drastically different from the previous regions, the freeboard region mainly contained entrained particles from the bulk fluidized bed region. Particle entrainment led to a solids hold up profile above the fluidized bed surface that decreased axially in a manner similar to that in a gas-solid fluidized bed. Generally, the demarcation between the freeboard region and the bulk fluidized bed region was much more distinct for large/heavy particles than for small/light particles.

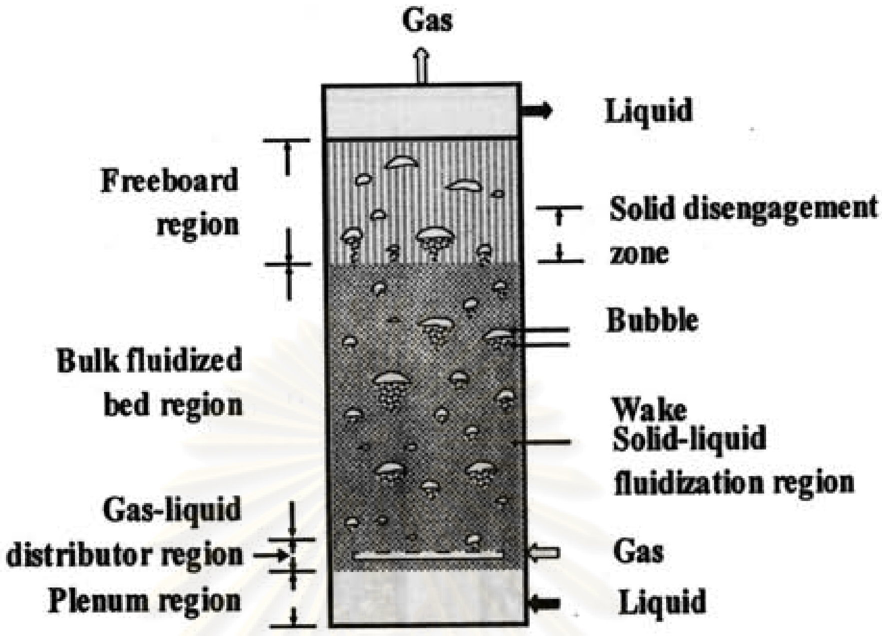


**Figure 3.9** Schematic representation of gas-liquid-solid fluidized bed for co-current upward gas-liquid-solid systems with liquid as the continuous phase

### 3.5.1.1 Hydrodynamic relations for gas-liquid-solid fluidized bed reactor

Understanding the flow pattern of gas-solid in the system is needed. Several flow patterns have been identified following gas velocity as shown in **Figure 3.10.** The hydrodynamic flow pattern of gas-solid mixture in fluidized bed system is called fast fluidization regimes, which is considered to be high-velocity fluidization. In fast fluidization regimes, the particles are transported out at the top and must be replaced by adding solids near the bottom. Clusters or strands of particles move downward mostly near the wall while gas and entrained widely dispersed particles move upward in the interior. From the complexity of this regime, fluidized bed system are often characterized by complex flow phenomena such as non-uniform spatial distribution of particles, large slip velocities between the phases, and the existence of several possible pressure gradients and solids holdups for specified values of gas and solid flowrate. Also, the particle concentration profile can influence the distribution of residence time of particles. It may lead to recirculation of particles against the direction of their net motion. Thus, the hydrodynamics of fluidized bed system concern with the gas mixing, solid mixing and particles motion.

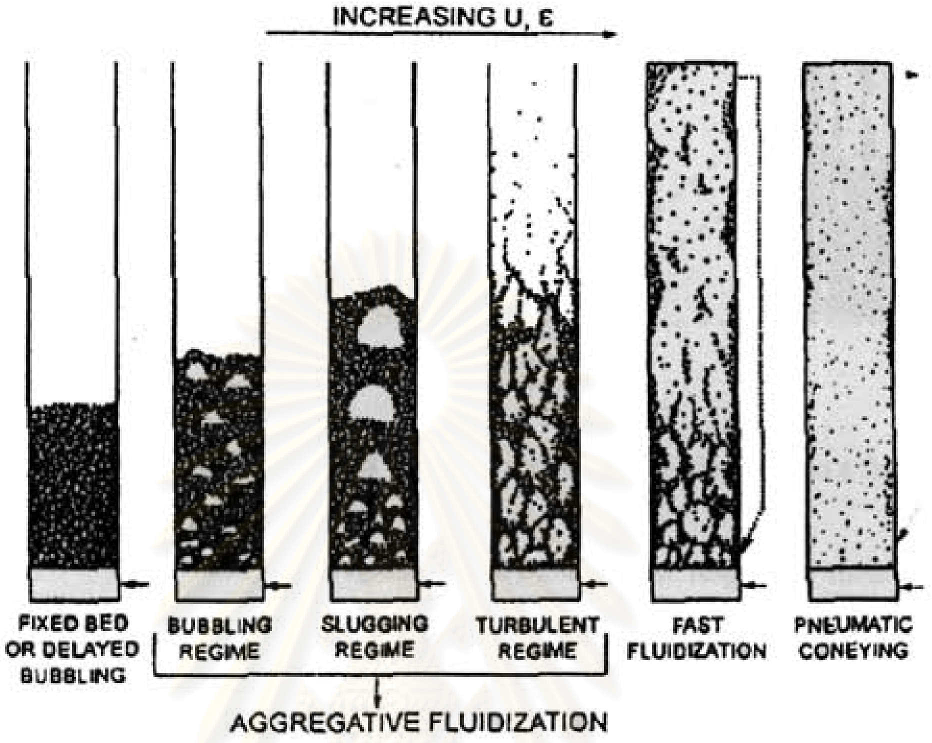


**Figure 3.10** Flow patterns in gas solids fluidized beds. [35]

Some general models of gas-liquid-solid fluidized-bed reactors for the gas phase reactant $A$ for a single solid catalyzed reaction $A \longrightarrow$ to products are represented in this section. Starting with information about the particle size, density of each phase and viscosity of liquid, the provided hydrodynamic relations may be used to determine bed characteristics such as the minimum fluidization velocity, particle terminal settling velocity, and so on. The equations in this section (3-1 to 3-6) are referred from [36].

*Particle motion and solids mixing mechanisms*

Fluidized bed hydrodynamics can be generally divided into four regions as shown in **Figure 3.11.**

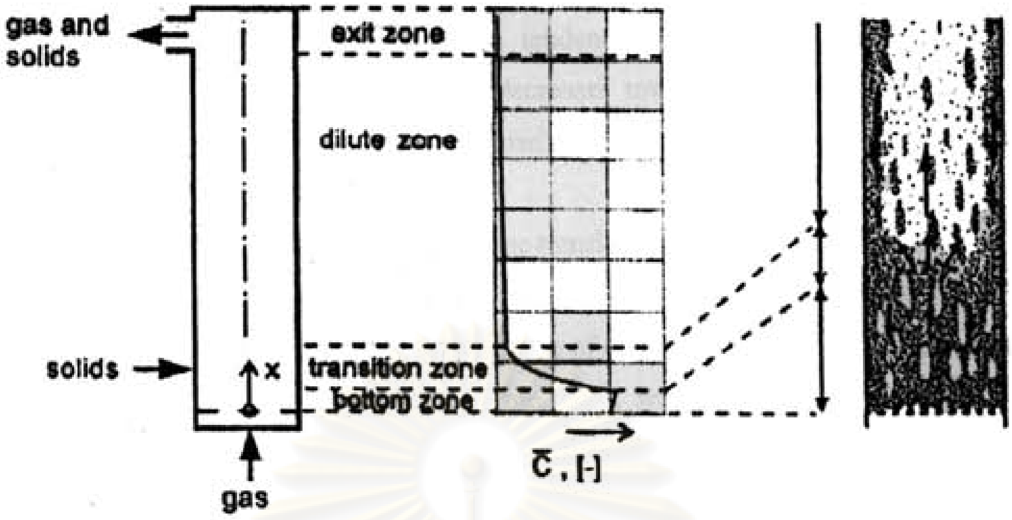


Figure 3.11 Zones of different solids volume fractions and solid motion in a fluidized bed. [35]

These four regions are separated with respect to their solids volume concentrations. The acceleration of the solid particles takes place in the bottom zone. The dilute zone is characterized by low solids volume concentration. Solids mixing in these regions are discussed in detail in the following sections.

a. Particle motion in the bottom zone

The bottom zone of a fluidized bed is similar to bubbling or turbulent fluidized beds with fluidization gas passing through the bottom zone in form of voids. When these voids reach the surface of the bottom zone, they break and eject solids into the transition zone. The transport in the wakes of rising voids is the essential mixing mechanism. Due to the high of turbulent mixing of particles, this region was assumed as a continuous stirred tank reactor or perfect mixing in some models.

b. Particle motion in the dilute zone

The solid motions in the dilute zone can be determined by the upflowing and downfalling phases. The dilute zone is characterized by the existence of two phases; a lean phase and a dense phase. The lean phase consists of an upward flowing dilute suspension. The dense phase is formed by downward travelling particle clusters or strands. It is predominantly found in the region near the wall and shows that it has higher solids concentrations than lean phase. The upward solids mass fluxes reach their largest values at the riser center and decrease towards the wall whereas the downward mass fluxes show a reverse tendency. Therefore, the highest solids velocities occur at the riser center and decreases towards the walls. The negative values of velocity are obtained in the dense phase near the wall. They indicate the dominant downward flow of the solids.

c. Particle motion in the transition zone

In the transition zone, a transition occurs from the dense bottom zone to the dilute zone. The frequency and size of clusters diminish with height. Large amounts of solids are ejected by bursting voids from the bottom zone into the transition zone. Downfalling clusters carry solids from the dilute zone back into the transition zone. Thus, the transition zone is a region of high intensity solids mixing.

d. Particle motion in the exit zone

The particle motion of the exit zone depends on the exit geometry. There are two types of exit geometry; smooth and abrupt exit. The abrupt exit is an exit configuration where the roof is higher than the top of the exit channel. Therefore, a dense suspension zone forms under the roof and many heavy particles are reflected back down the column. This movement of solids contributes to axial gas dispersion in this area. The smooth exit is another configuration where short radius bends smoothly connect the top of riser to the cyclone entrance. The apparent suspension density continues to decrease over the top because a greater proportion of solid leaves directly through the exit.

*Minimum fluidization velocity, $U_{mf}$*

Minimum fluidization velocity was the velocity of fluid, which the solid particles moved apart and few vibrate. The equation for minimum fluidization velocity for gas-liquid-solid fluidized bed reactor was

$$U_{mf} = U_{mf,LS}[1 - 376U_G^{0.327}\mu_L^{0.227}d_p^{0.213}(\rho_S - \rho_L)^{-0.423}] \qquad (3\text{-}1)$$

$$U_{mf,LS} = \frac{\mu_L(\sqrt{1135.69 + 0.0408Ar} - 33.7)}{d_p\rho_L} \qquad (3\text{-}2)$$

$$Ar = \frac{\rho_L(\rho_S - \rho_L) g d_p^3}{\mu_L^2} \tag{3-3}$$

where $U_{mf}$ = minimum fluidization velocity (m/s)

$U_{mf,LS}$ = minimum fluidization liquid velocity (m/s)

Ar = Archimedes number (-)

$U_G$ = gas velocity (m/s)

$\mu_L$ = liquid viscosity (m/s)

$d_p$ = diameter of particle (m)

$\rho_S$ = density of solid (kg/m$^3$)

$\rho_L$ = density of liquid (kg/m$^3$)

*Terminal velocity, $U_t$*

Terminal velocity of a single particle could be considered with an assumption that the particle moving through a fluid under the action of an external force. The external force was the acceleration of gravity, *g*, which was constant. Also, the drag force always became larger with an increasing in velocity. The particle quickly reached a constant velocity, which was the maximum attainable under the circumstances, and which was called the terminal velocity. The equation for the terminal velocity was

$$U_t = \frac{g d_p^2(\rho_S - \rho_L)}{18\mu_L} \qquad K < 2.6 \tag{3-4}$$

$$U_t = 1.75\sqrt{\frac{g d_p(\rho_S - \rho_L)}{\rho_G}} \qquad K > 60 \tag{3-5}$$

$$K = d_p\left(\frac{g\rho_L(\rho_S - \rho_L)}{\mu_L^2}\right)^{1/3} \tag{3-6}$$

### 3.5.1.2. Pressure Drop and Phase Holdup [37]

#### 3.5.1.2. Pressure Drop and Phase Holdup [37]

When consider a fluidized bed column, which was partly filled with a fine granular material as shown schematically in **Figure 3.12**. The column was opened at the top and had a porous plate at the bottom to support the bed and to distribute the flow uniformly over the entire cross section. Fluid was admitted below the distributor plate at a low flow rate and passes upward through the bed without causing any particle motion. If the particles were quite small, flow in the channels between the particles would be laminar and the pressure drop across the bed would be proportional to the superficial velocity. As the fluid velocity was gradually increased, the pressure drop increased, but the particles did not move and the bed height remained the same. At a certain velocity, the pressure drop across the bed counterbalances the force of gravity on the particles or the weight of the bed, and any further increase in velocity caused the particles to move. This was point A on the graph. Sometimes the bed expanded slightly with the grains still in contact, since just a slight increased in porosity, $\varepsilon$ could offset an increase of several percent in superficial constant and keep pressure drop, $\Delta P$ constant. With a further increase in velocity, the particles became separated enough to move above in the bed, and true fluidization begins (point B).

Once the bed was fluidized, the pressure drop across the bed became constant, but the bed height continues to increase with increasing flow. The bed could be operated at quite high velocities with very little or no loss of solids, since the superficial velocity needed to support a bed of particle was much less than the terminal velocity for individual particles.

If the flow rate to the fluidized bed was gradually reduced, the pressure drop remained constant, and the bed height decreased, following the line BC that was observed for increasing velocities. However, the final bed height might be greater than the initial value for the fixed bed, since solids dumped in a column tended to pack more tightly than solids slowly settling from a fluidized bed state. The pressure drop at low velocities was then less than in the original fixed bed. On starting up again, the pressure drop offset the weight of the bed at point B, and this point, rather than point A, should be considered to give the minimum fluidization velocity, $U_{mf}$ To measure $U_{mf}$, the bed should be fluidized vigorously, allowed to settle with the fluid turn off, and the flow rate increased gradually until the bed starts to expand. More reproducible value of $U_{mf}$ could sometimes be obtained from the intersection of the graphs of pressure drop in the fixed bed and the fluidized bed.

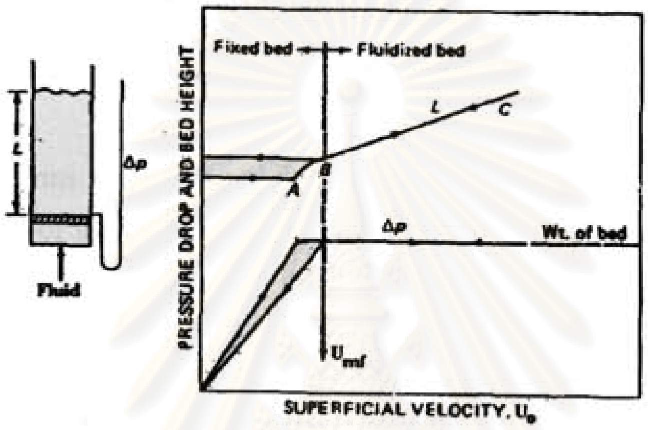


**Figure 3.12** Pressure drop and bed height and superficial velocity for a bed of solid. (Redrawn from *McCabe et al*, Unit operation of chemical engineering. 1993, p.1 65)

The pressure drop through the bed was strongly related to the individual phase holdup in the bed. The phase holdup was defined as the fraction of the solids, liquid or gas phase to volume of the column. In the fluidized bed with low solids entrainment rates, the volume fraction of the solids, or can be expressed in terms of the total mass of solids ($W_s$), the solid density ($\rho_s$), the cross section of the column (A), and the effective bed height (H), as (see in **Figure 3.12**)

$$\varepsilon_s = 1 - \varepsilon = \frac{W_s}{\rho_s A H} \tag{3-7}$$

where is the solids holdup and $\varepsilon_s$ is the bed porosity. A necessary requirement of the phase volume fraction, or individual phase holdups, is

$$\varepsilon_G + \varepsilon_L + \varepsilon_S = 1 \qquad (3\text{-}8)$$

where $\varepsilon_s$ and $\varepsilon_L$ are the gas and liquid holdups, respectively.

At steady state conditions with low or moderate liquid and gas velocities, the total vertical pressure gradient (static pressure gradient) can be readily obtained from

$$\frac{-dP}{dZ} = (\varepsilon_G \rho_G + \varepsilon_L \rho_L + \varepsilon_S \rho_S)g \qquad (3\text{-}9)$$

In this equation the frictional drag on the column wall and the acceleration terms for the gas and liquid flows are neglected. Since the contribution of the gas phase of usually negligible compared to the other terms, Eqn. (3-9) can be simplified to

$$\frac{-dP}{dZ} = (\varepsilon_L \rho_L + \varepsilon_S \rho_S)g \qquad (3\text{-}10)$$

Equation (3-10) permits evaluation of individual phase holdups from the pressure gradient. $\varepsilon_s$ can be directly obtained from Eqn. (3-7) with the measured effective bed height. $\varepsilon_L$ can be calculated from the total pressure gradient based on Eqn. (3-10) and $\varepsilon_G$ is obtained by the difference based on Eqn.(3-8)

However, behavior of gas holdup in the freeboard region strongly depended on the flow regimes and hence, on both particle and liquid properties. Gas holdup in three-phase fluidized beds could be lower than that in a corresponding bubble column because the particles promoted bubble coalescence, however it could also be higher than that in a corresponding bubble column when the particles helped break up gas bubble in some certain operating ranges. Furthermore, gas holdup was important for determining residence time of the gas in liquid.

Fan [36] measured the gas holdup in the freeboard region of a bed containing 3 mm glass beads. In their apparatus, the independent nozzles (2.54 cm ID) used as the gas distributor produced a spouted behavior of the gas phase at the bottom of the bed. They found that gas holdup decreased significantly with increasing liquid velocity. They proposed a correlation for $\varepsilon_G$ in the freeboard region for $U_L$ / ( $U_L$ + $U_G$ )> 0.08 as

$$\varepsilon_G = 0.066\left[\frac{U_L}{(U_L + U_G)}\right]^{-0.424} \tag{3-11}$$

Fan [36] using a porous plate gas distributor with 2 mm holes to ensure a uniform gas distribution, found that the gas holdup in the freeboard region but smaller than that in a bubble column. They proposed the following correlation for estimating gas holdup in the freeboard region:

$$\varepsilon_G = \frac{0.3W^{1.3}}{(1 + 1.1W^{1.15})} \tag{3-12}$$

where the parameter W is defined as

$$W = \left(\frac{gD_c^2\rho_L}{\sigma}\right)^{0.198}\left(\frac{gD_c^3}{\nu_L^2}\right)^{0.035}\left(\frac{U_G}{\sqrt{gD_c}}\right) \tag{3-13}$$

According to Eqn. (3-13), W is inversely proportional to the liquid viscosity to the 0.07 power, but is independent of column diameter. Note that no significant axial variation of gas holdup in the freeboard region is evident for a given operation.

where $\varepsilon_G, \varepsilon_L, \varepsilon_S$ = gas, liquid, and solid holdup (-), respectively.

$\rho_G \rho_L \rho_G$ = gas, liquid, and solid density (kg/m$^3$), respectively.

$W$ = weight of solid particle in the bed (kg).

$A$ = cross-section area of empty column (m).

$H$ = effective height of bed expansion (m).

g = gravitational acceleration (m/s$^2$).

$\frac{dP}{dZ}$ = static pressure gradient.

$D_c$ = column diameter (m)

$\sigma$ = surface tension (mN/m)

$\nu_L$ = kinematic liquid viscosity ($m^2/s$)

$U_G$ = gas velocity (m/s)

The frictional drag on the wall of the column and the acceleration of the gas and liquid flows could be neglected. In equation (3-9), the term $\varepsilon_G \rho_G$ in the right hand side was usually negligibly small compared to the other terms. The evaluation of individual phase holdups based on the pressure gradient method, $\varepsilon_S$ could be directly obtained from equation (3-7) with the height of bed expansion measured experimentally while $\varepsilon_G$ could be directly calculated from equation (3-12). Finally, $\varepsilon_L$ could be calculated from equation (3-8) and (3-9) simultaneously with the experimentally measured static pressure gradient [38].

#### 3.5.1.3. Flow Regime

Three flow regimes could be identified based on the bubble flow behavior in three-phase fluidized bed: the coalesced bubble, the dispersed bubble, and the slugging regimes. In the coalesced bubble regime, bubbles tended to coalesce and both the bubble size and velocity became large and shown a wide distribution. Coalesced bubbles rose near the column near the column center with high velocity and stirred the bed violently. The coalesced bubble regime predominated at low liquid and high gas velocities. In the dispersed bubble regime, no bubble coalescence occurred and the bubbles were of uniform, small size. The dispersed bubble regime predominated at high liquid velocities and at low and intermediate gas velocities. In a small diameter column (e.g., $D_c < 15$ cm), the gas bubble could easily grew to the size of the column diameter at high gas flow rates creating "slug" bubbles which occupied nearly the whole cross section. In columns of large diameter, however, slugging might not occur. The flow regimes varied significantly with the column diameter. Particle properties also profoundly affected the prevailing flow regime at given gas and liquid velocities and terminal velocity of the fluidized particles affected the liquid velocity of transition from the coalesced to the dispersed bubble regime [38].

# CHAPTER IV

# EXPERIMENTAL

This chapter describes the experiment in details. The chemicals, the catalysts and the experimental system are shown in sections 4.1, 4.2 and 4.3, respectively. In sections 4.4, 4.5, and 4.6, the equipment, the experimental procedure and analytical instrument are explained.

## 4.1 Chemicals

Phenol and intermediate products solution, hydroquinone and catechol, for testing the reaction and preparing HPLC standard are prepared from:

1) Phenol, $C_6H_6O$, available from Polski Odczynniki Chemiczne S.A., 99.9%
2) Pyrocatechol, $C_6H_6O_2$, available from Fluka, 98%
3) Quinol, $C_6H_4(OH)_2$, available from APS Chemicals, 99.8%

In addition the HPLC mobile phase, Acetonitrile, is:

4) Acetonitrile, $CH_3CN$, available from Fisher Scientific, 99.99%

## 4.2 Catalyst

The metallic catalysts, Iron (III) Nitrate•9-hydrate ($Fe(NO_3)_3 \cdot 9H_2O$) were supplied by Ajax Finechem on activated carbon, were prepared by wet impregnation techniques. The activated carbons were heated and held at 473 K for 4 hrs to eliminate their impurities, then impregnated with a solution of $Fe(NO_3)_3 \bullet 9H_2O$ to yield 5 %w/w of Fe. The supported activated carbon was prepared by wet impregnation of 5 %w/w Fe on 1 g of activated carbon mixed with 10 ml of Fe solution. The sample was dried under vacuum at temperature 333 K. Then, calcinations at 773 K under $N_2$ flow 5 h and Oxidation at 473 K under air flow to constant weight. After impregnation, the samples were dried overnight at 353 K and subsequently calcined at 773 K under nitrogen atmosphere for 5 hrs.

Granulated activated carbons made from coal by Calgon Company (Cod.102514100; pz: 0.60-2.36 mm: AC1) and from coconut shell by Carbokarn Company (pz: 0.42-1.70 mm: AC2) were used. The main characteristics of the activated carbons used in the present investigations are presented in **Table 4.1.**

**Table 4.1** Characteristics of catalysts

| Physical properties | AC 1 | AC 2 |
|---|---|---|
| Particle Size Distribution (mm.) | 0.60-2.36 | 0.42-1.70 |
| Moisture (%W/W) | MAX . 2 | MAX . 8 |
| Ash (%W/W) | MAX . 10 | MAX . 3.5 |
| Iodine Number (mg/g) | MIN . 900 | MIN . 1100 |

## 4.3. Experimental system

As illustrated in **Figure. 4.1**, the experimental apparatus consists of a lab-scale 3-phase fluidized bed reactor, hold-up tank, magnetic stirrer, liquid pump, flow meter, 3-way valve, ozone generator, and oxygen cylinder. The liquid solution and gas were separately fed through a distributor into the fluidized catalyst bed. Gas flow was exhausted from the top of the reactor while the liquid solution was totally circulated and intermittently sampled. A fixed amount both of ACs and Fe/AC1 5 g were used. Aqueous phenol 10-ppm 2 L in the hold-up tank were charged into the fluidized bed reactor.

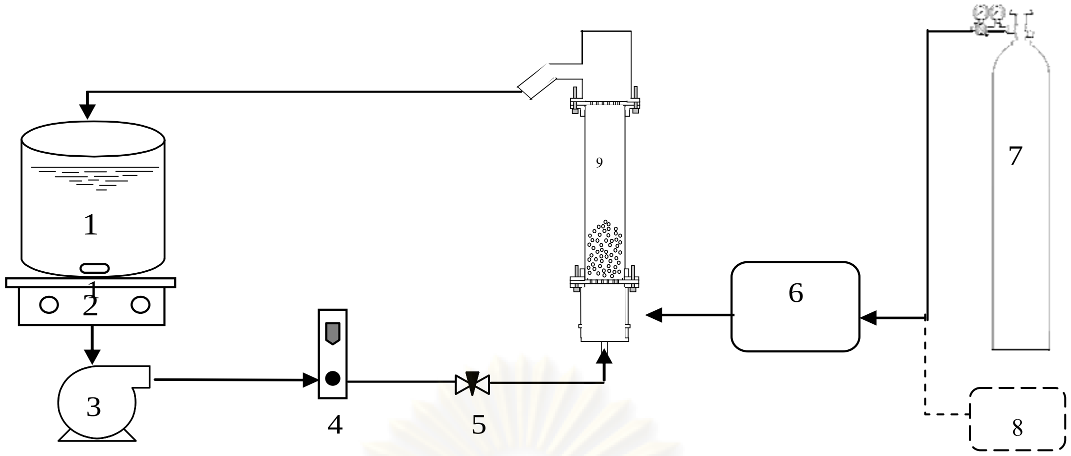


**Figure 4.1** Diagram of experimental apparatus, 1. hold-up tank, 2. magnetic stirrer, 3. liquid pump, 4. flow meter, 5. 3-way valve, 6. ozone generator, 7. oxygen cylinder, 8. air pump and 9. fluidized bed reactor.

## 4.4 Apparatus

### 4.4.1 Reactor

The reactor is made of quartz tube with an inside diameter and high of 31.6 and 300 mm, respectively.

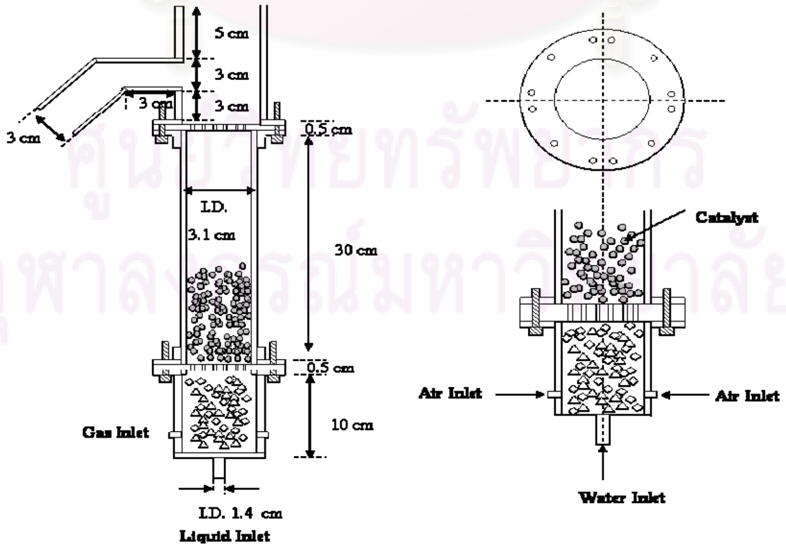


**Figure 4.2** Construction diagram of a lab-scale fluidized bed reactor

**Figure 4.3** Fluidized bed reactor

### 4.4.2 Ozone generator

**Figure 4.4** is shows a photo of the ozone generator model SO-O3UN-OX. Its technical specifications are shown in **Table 4.2**. This apparatus uses oxygen or air as a source of ozone production. When oxygen is used, a much higher ozone production rate could be obtained. Moreover, the gas flow rate can be varied in the range of 1-5 L/min., and the ozone generation rate is between 1.4-5.7 g/h depending on the gas flow rate. The ozone concentration slightly decreases with an increase in gas flow rate.

**Figure 4.4** Ozone generator model SO-O3UN-OX of Tokyu Car Co., Ltd

**Table 4.2** Specification of the ozone generator model SO-O3UN-OX

| Oxygen flow rate [L/min.] | $O_3$ concentration [g/m$^3$] | $O_3$ generation rate [g/h] |
|---|---|---|
| 1 | 24.39 | 1.46 |
| 2 | 22.73 | 2.73 |
| 3 | 21.29 | 3.83 |
| 4 | 19.85 | 4.76 |
| 5 | 18.77 | 5.63 |

Model: SO-03UN-OX03007, Source: Oxygen ($O_2$), Oxygen flow rate: 1-5 L/min., Room temperature: approx. 23 $^oC$, Room humidity: approximately 70%, Pressure of supplied oxygen: 2 $kg_f/cm^2$.

## 4.5 Experimental procedure

Granulated activated carbons were heated and held at 473 K for 4 hrs to eliminate their impurities, then impregnated with a solution of $Fe(NO_3)_3{\cdot}9H_2O$ to yield 5 % w/w of Fe. The metal catalyst, Fe, was loaded on 1 g of AC was mixed with 10 ml of metal solution in an vacuum evaporator at 333 K until the aqueous phase could no longer be observed. After impregnation, the samples were dried overnight at 353 K and subsequently calcined at 773 K under $N_2$ for 5 hrs. All experiments were carried out with co-current upward flow of gas (1 L.min$^{-1}$) and liquid (1 L.min$^{-1}$). In each run, the phenol-containing liquid and gas were fed in at the bottom, came out from the top and the entire liquid was recirculated via the hold-up tank. Ozone was produced either from air or from pure $O_2$ by passing it through an ozone generator (Tokyu Car Corporation, SO-O3UN-OX). Intermittently samples were withdrawn at the times of interest for chemical analysis, filtered through filter paper (0.45µm pore size), and then analyzed by HPLC and TOC analyzer.

## 4.6 Analytical instruments

The concentration of phenol was analyzed by a high-performance liquid chromatography (HPLC) using a Shimadzu column (Class VP), with 25% acetronitrile: 75% water as the mobile phase and the UV-vis detector using 254 nm wavelength. The total organic carbon analyzer (TOC analyzer, TOC-VCPH, Shimadzu, Japan) was used to find the concentration of the intermediates in terms of TOC. The details of the equipment are described next.

### 4.6.1 Nitrogen physisorption

The sample's Brunauer-Emmett-Teller (BET) surface area was determined by nitrogen adsorption in a BEL Japan Inc., (BelSorb 2). All the samples were thermally treated at 150 $^{o}$C for 30 min in a 30% $N_2$-helium flow prior to BET measurements.

### 4.6.2 High performance liquid chromatography (HPLC)

The concentration is measured by HPLC (Shimadzu column class VP). It can be used for indicating the compounds and the number of the compounds in the sample as well. The result from the sample taken in sequent of time is exhibited in graph form. Peak area of each compounds occurred at the individual resident time were brought to calculate the concentration. In addition the degradation time of each batch can be found by HPLC. 25% acetonitrile 75% demineralized water (conductivity < 2 microziemen) were mobile phase. The total flow rate of mobile phase was 0.6 $cm^3$/min. The column Phenomenex C18 was operated at 31.5 °C. The wavelength of UV-vis detector was 254 nm. Figure 4.5 shows the picture of this tool.

**Figure 4.5** The picture of HPLC (Shimadzu column class VP)

### 4.6.3 Total organic carbon (TOC)

The TOC disappearance was obtained from Shimadzu TOC-VCPH. It could be used for indicating the total mineralization of phenol. The picture of TOC analyzer is shown in **Figure 4.6.**

**Figure 4.6** The picture of TOC analyzer (Shimadzu TOC-VCPH)

# CHAPTER V

# RESULTS AND DISCUSSION

AC1, AC2 and Fe/AC are employed for investigating the phenol decomposition efficiency and the possibility in fluidized bed reactor for application on wastewater treatment.

## 5.1 Catalyst characteristics

The metallic catalysts, Iron (III) Nitrate•9-hydrate ($Fe(NO_3)_3 \cdot 9H_2O$) were supplied by Ajax Finechem on activated carbon, were prepared for wet impregnation method. Granulated activated carbons made from coal by Calgon Company (Cod.7440-44-0; pz: 0.60-2.36 mm: AC1) and from coconut shell by Carbokarn Company (pz: 0.42-1.70 mm: AC2) were used. The main characteristics of the activated carbons used in the present investigations are presented in Table 5.1. The specific surface areas and porosities of these activated carbons were determined from $N_2$ adsorption-desorption isotherms measured at 77 K using an automated adsorption apparatus (BELSORP 28, BEL Japan, Japan, or AUTOSORB-1-C, Quantachrome, USA). The specific surface areas were calculated by the BET method. The MP method yielded the pore volume and pore size distribution from the curvature of the t-plot. It should be noted that two types of activated carbon have significantly different characteristics. The pore size distributions of the two materials have been given elsewhere **[39].**

**Table 5.1** Characteristics of catalysts

| Type | BET surface area ($m^2g^{-1}$) | Particle size (mm) | Total pore vol. ($cm^3g^{-1}$) | Micropore vol. ($cm^3g^{-1}$) | Ave. pore diameter (nm) |
|---|---|---|---|---|---|
| AC1 | 1060 | 0.60-2.36 | 0.61 | 0.49 | 2.3 |
| AC2 | 1154 | 0.42-1.70 | 0.49 | 0.49 | 1.7 |
| Fe/AC1 | 888 | - | 0.49 | 0.39 | 2.2 |

**Table 5.1** shows a comparison of the surface area, micropore volume, total pore volume and average pore diameter for the two types of carbons.

## 5.2 Surface functional groups

### 5.2.1 FT-IR analysis

The FT-IR spectroscopy provides information on the chemical structure of the material in activated carbon samples. The functional groups of all the activated carbon samples spectra were determined by a handbook of standard FT-IR spectra **[40].** Wavenumber assignments for the spectra of the activated carbon sample was summarized in **[39]**, which indicates that the sample contain a number of atomic groupings and structures. The commercial activated carbon sample and its possible FT-IR peak assignments by FT-IR spectroscopy for the samples showing in **Figure 5.1** was obtained from **[39].** Infrared spectroscopy was an extremely powerful analytical technique for both qualitative and quantitative analyses. **Figure 5.1** shows FT-IR spectra of the activated carbon. It was well known that the position of the band for free hydroxyl groups is normally observed around 3700cm$^{-1}$. However, the position of the OH band in **Figure 5.1** was shown in the range of 3400 cm$^{-1}$.

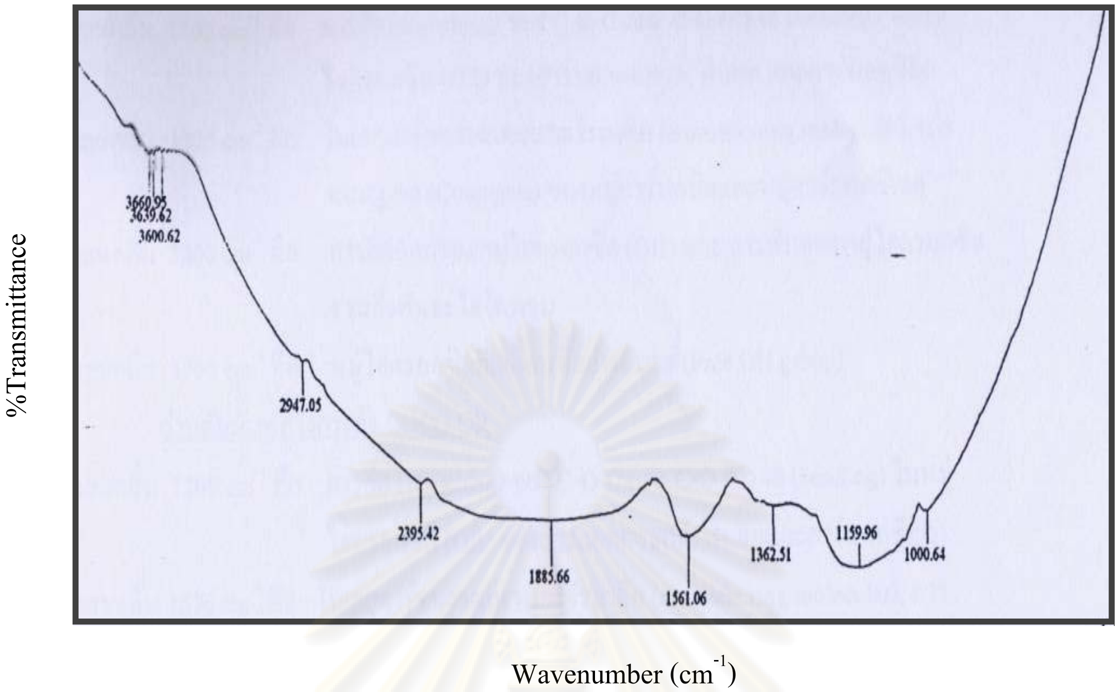


**Figure 5.1** FTIR spectrum of activated carbon 1 (AC1). **[39]**

The Fourier transform infrared spectra of activated carbon (AC1) were shown in **Figure 5.1.** At 1576 cm$^{-1}$, the specific peak for the aromatic ring and carbonyl groups were observed for the activated carbon. They also found a peak near 1200 cm$^{-1}$, due to stretching of aliphatic ethers and bending of hydroxyl groups for alcohol, phenol and carboxylic acid groups.

### 5.2.2 Boehm's titration carboxylic, lactone, and phenolic groups

The Boehm titration method allows the determination of the surface functional groups such as phenolic group (–OH), lactone group (C=O) and carboxylic group (–COOH). **Table 5.2** shows the results of surface functional groups of various activated carbon samples by the Boehm's method.

**Table 5.2** Surface function groups of activated carbon fibers by Boehm’s method**[39].**

| **Samples** | **Funtional of groups (meq/gAC)** | | | |
|---|---|---|---|---|
| | **Phenol** | **Lactone** | **COOH** | **Total** |
| AC1 | 0.026 | 1.164 | 0.196 | 1.386 |
| AC2 | 0.196 | 0.197 | - | 0.393 |

Numerous studies on surface functional groups of carbon were already demonstrated by the Boehm’s method. The changes of the surface acidity developed from $HNO_3$ and NaOH treatment were detected by Boehm’s titration measurement and were summarized in **Table 5.2.** The three bases used in the titration were regarded as approximate probes of acidic surface groups: $NaHCO_3$ (carboxyl), $Na_2CO_3$ (carboxyl and f-lactonic) and NaOH (carboxyl, f-lactonic and phenolic). **Table 5.2** indicated that the nitric acid treatment produces a lot of acidic surface groups and that leads to an increase in the amount of base required to neutralize the oxidized carbon. On the other hand, the sodium hydroxide treatment of AC resulted in a decrease of carboxyl surface groups. It was clear that the chemical nature of surface functionality was significantly altered by the nitric acid and sodium hydroxide treatments **[41].**

## 5.3 Comparison of two types of activated carbon

The comparison of two types of activated carbon is conducted for selection of the best activated carbon of which phenol removal performance was taken into account.

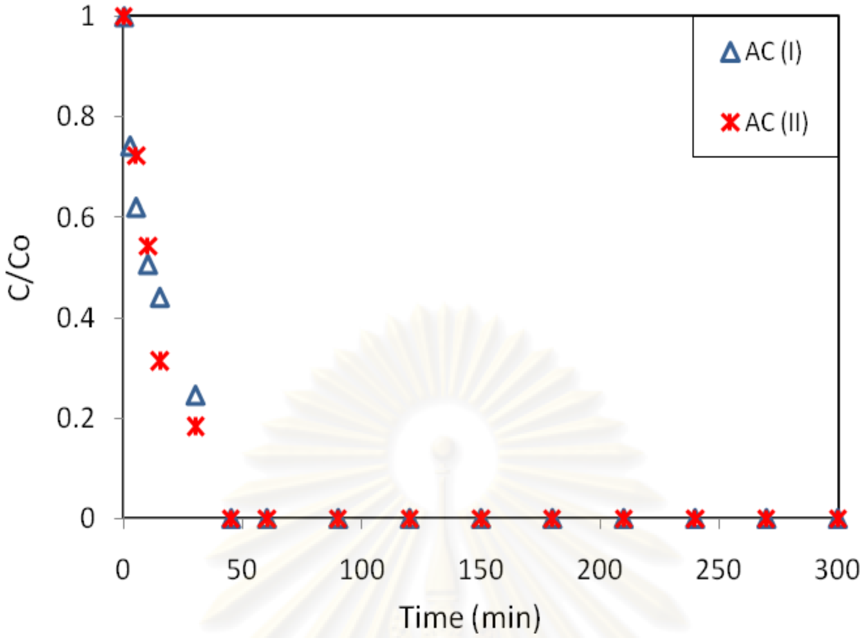


**Figure 5.2** Phenol concentrations as a function of time for AC1 and AC2

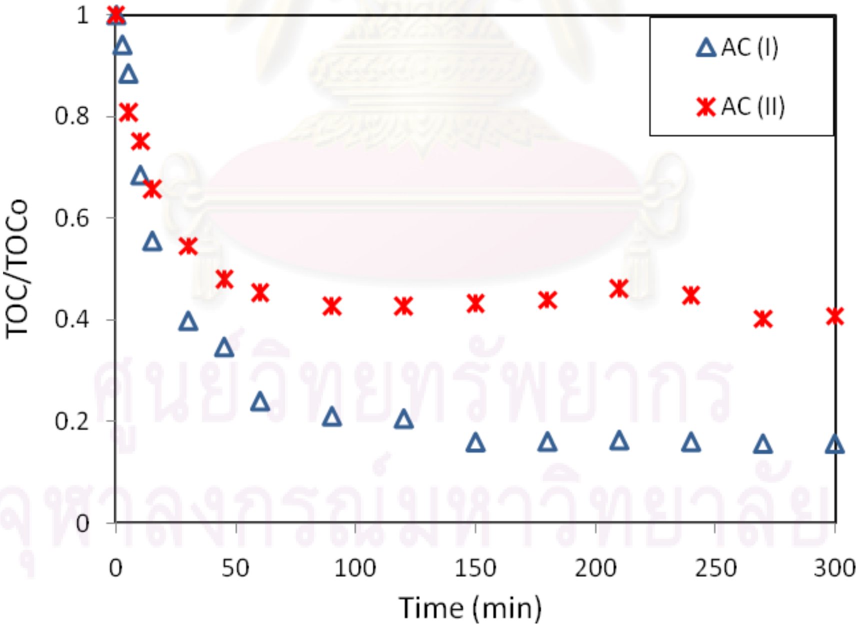


**Figure 5.3** TOCs as a function of time for AC1 and AC2

**Figures 5.2 and 5.3** represent the effect on the removal of phenol and TOC by AC1 and AC2. In order to test for removal efficiency, experiments were conducted with 2 liters of 10 mg/l. phenol solution. As shown in **Table 5.1**, both AC1 and AC2 possess large surface areas for adsorption of hydrophobic compounds, including aqueous phenol. Here air was sent co-currently through the reactor while the ozone generator was switched off. The experimental results shown in **Figures 5.2 and 5.3** can be interpreted in terms of conversion with respect to decomposition term (see **Table 5.3**). Phenol conversion, $X_{ph}$, is defined as:

$$X_{Ph} = \frac{[Ph]_0 - [Ph]_t}{[Ph]_0} \times 100 \tag{5.1}$$

**Table 5.3** Phenol removal efficiency (%) and TOC removal efficiency (%) for AC1 and AC2.

| **Type** | **Phenol removal (%)** | | | **TOC removal (%)** | | |
|---|---|---|---|---|---|---|
| | 30min | 45min | 300min | 30min | 45min | 300min |
| **AC (I)** | 75 | 100 | 100 | 60 | 65 | 84 |
| **AC (II)** | 81 | 100 | 100 | 46 | 52 | 59 |

## 5.4 Treatment of aqueous phenol in a lab-scale fluidized bed reactor

This part aimed at the application of an effective wastewater treatment for removing phenol dissolved in wastewater Fe catalyst impregnated on activated carbon. Performance of the lab-scale fluidized-bed reactor with Fe/AC catalyst and/or activated carbon (solid phase) and air (oxygen) and/or ozone (gas phase) was investigated experimentally. It is well-known that the oxidation of phenol often leads to numerous hard-to-remove intermediate products. To monitor the presence and removal of the intermediate products, the TOC concentration of the treated wastewater was also measured.

### 5.4.1 Effect of ozonation using either pure oxygen or air

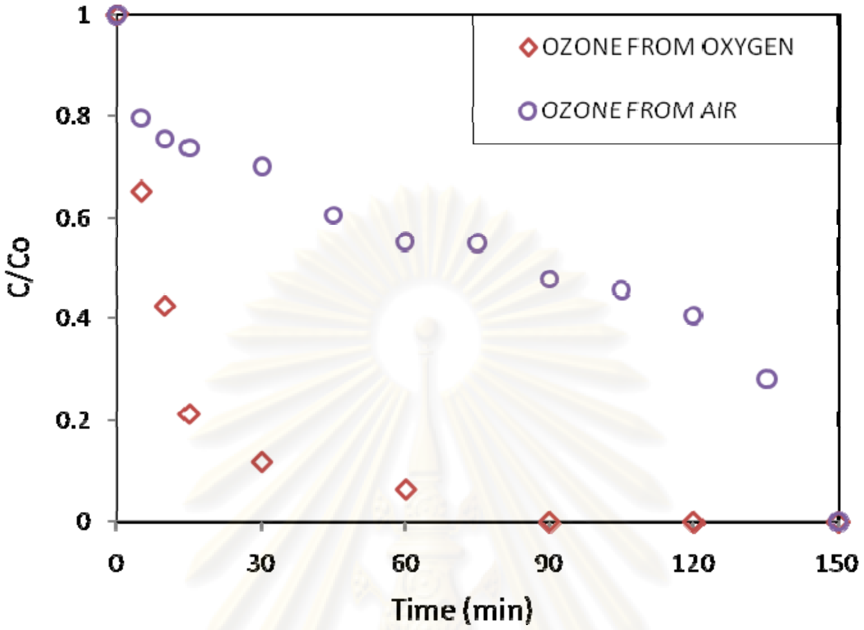


**Figure 5.4** Phenol concentrations as a function of time in ozonation with two oxygen sources

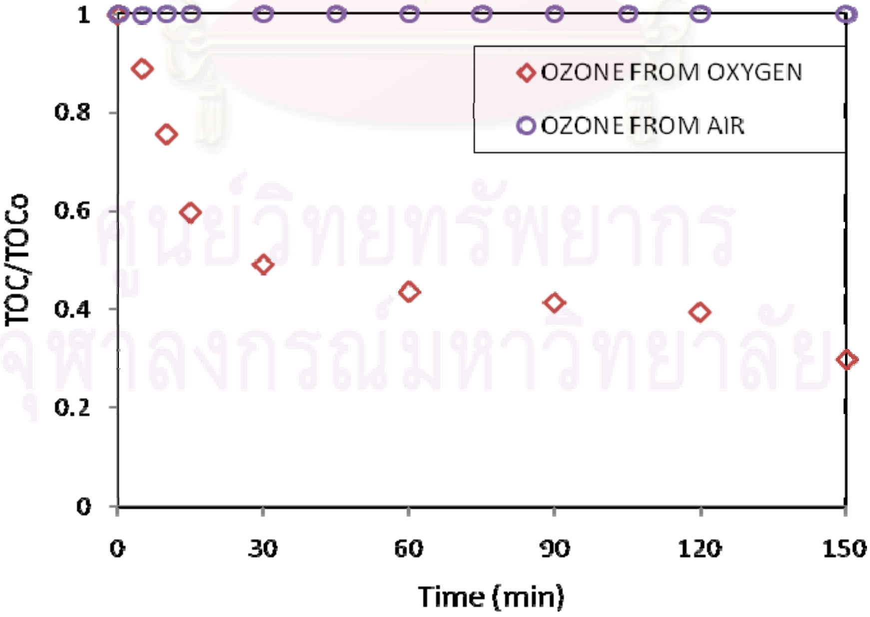


**Figure 5.5** TOCs as a function of time in ozonation with two oxygen sources

Here pure oxygen gas and air were used as the two sources of ozone generation. In the present ozonation process, the ozone-containing gas was introduced into the reactor along with a co-current phenol-containing liquid stream. At the beginning, ozone could transfer from the gas phase to the liquid phase due to its concentration difference. Then ozone would self-decompose in water to produce •OH radicals **[42].** The hydroxyl radicals were consumed by aqueous phenol oxidation and reactions between the radicals. A logical analysis of the oxidation reaction between ozone and phenol was presented by Zhong et al **[43]. Figures 5.4 and 5.5** show the residual phenol and TOC concentrations as a function of time for the two cases of ozone generated from pure oxygen and air. Obviously the removal efficiency differed significantly for the two sources of ozone. In the case of ozone from pure oxygen, phenol and TOC removals were 100% and 70%, respectively, at 150 min. However, in the case of ozone from air, phenol removal was 100% and TOC removal was negligible at 150 min. for two reasons. First, air contains 70 mol% nitrogen so that the rate of ozone generation should be less than one-fifth of that from pure oxygen. Second, when air contains moisture, the already much smaller quantity of ozone is further consumed in the formation of nitrogen oxides **[44].** Obviously using pure oxygen as a gas source will increase the ozone concentrate. Nevertheless, if we could sufficiently compensate for the drop in removal efficiency by coupling the ozonation system with activated carbon, the use of ozone generated from air should offer a suitable cost-effective alternative.

**Table 5.4** Phenol removal efficiency (%) and TOC removal efficiency (%) for ozonation with two oxygen sources

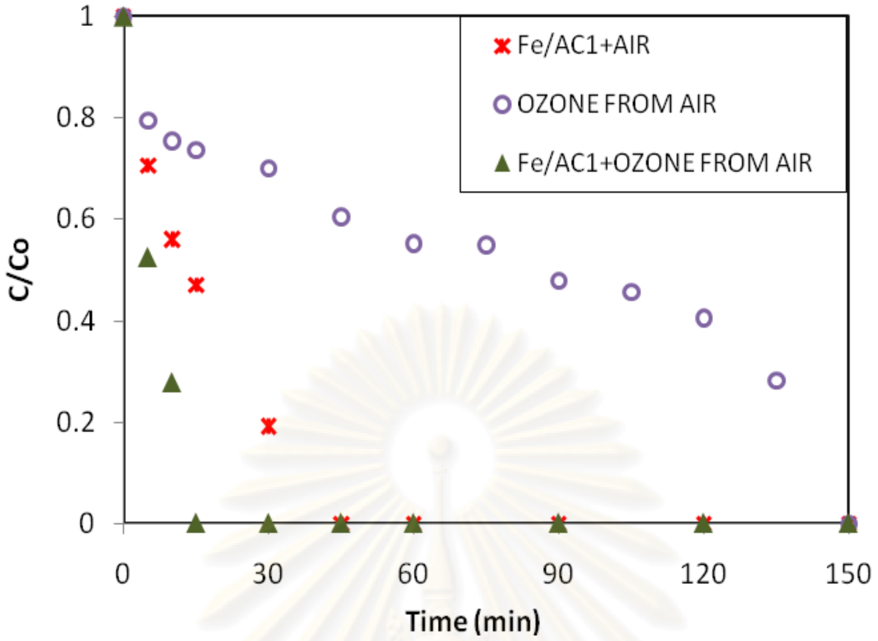
| **Type** | **Phenol removal (%)** | **TOC removal (%)** |
|---|---|---|
| | 150 min | |
| **OZONE (Pure $O_2$)** | 100 | 70 |
| **OZONE (Air)** | 100 | Negligible removal |

### 5.4.2 Effect of activated carbon

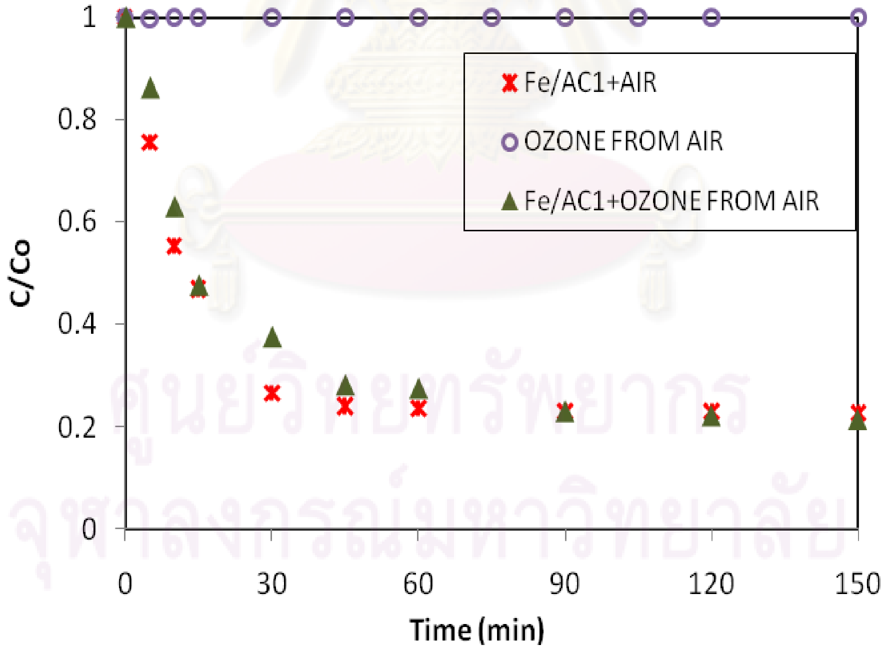
As shown in **Table 5.1,** both AC1 and AC2 possess large surface areas for adsorption of hydrophobic compounds, including aqueous phenol. Here air was sent co-currently through the reactor while the ozone generator was switched off. If only adsorption takes place without any oxidative decomposition of the adsorbed phenol to some intermediate products, the drop in the normalized TOC concentration must essentially equal that of phenol, and the residual phenol concentration will finally reach an equilibrium value. **Figures 5.2 and 5.3** show the normalized residual phenol and TOC concentrations as a function of time for the cases of AC1 and AC2. In the former first 10 minutes, the rates of reduction in phenol and TOC concentrations were essentially the same. This implies that both of them were removed by adsorption on the activated carbon. After that the reduction rate of TOC became slower than that of phenol. This implies that a portion of the adsorbed phenol was decomposed to intermediate products such as hydroquinone and catechol, which started to desorb from the activated carbon and entered the bulk liquid, thereby contributing to a slower drop in the residual TOC concentration. Since the intermediates were resistant to further oxidative decomposition on the activated carbon, their TOC value reached an asymptote, which reflects their adsorption equilibrium on the activated carbon. The findings are consistent with the published results **[45, 47].**

### 5.4.3 Effect of Fe/AC catalyst for phenol removal

Investigation of a decomposition rate of aqueous phenol by using a lab-scale fluidized bed reactor with Fe catalyst coated on activated carbon (catalytic oxidation) and / or ozone (ozonalysis reaction) was obtained in **Figures 5.6 (a and b)**



(a) Concentration removal of phenol



(b) TOC removal of phenol.

**Figure 5.6** Comparison of Fe/AC, $O_3$ and Fe/AC enhanced with $O_3$ by (a) Concentration removal of phenol and (b) TOC removal of phenol.

The degradation efficiency of phenol from the initial concentration of 10 ppm by treatment with Fe/AC, $O_3$ and combination of Fe/AC and $O_3$ was presented in **Figures 5.6 (a and b).** By using only Fe/AC (50% and 100% efficiency at 10 min and at 150 min, respectively) was more effective than degradation of phenol by using only $O_3$ from air (25% and 100% efficiency at 10 min and at 150 min, respectively). The efficiency of the combination of Fe/AC and $O_3$ was 72% and 100% at 10 min and 150 min, respectively. At 10 min of degradation, the efficiency of combination treatment was higher than the sum of efficiency of using only $O_3$ and only Fe/AC. Moreover, the result of TOC removal after 150 min of water treatment treated by Fe/AC, $O_3$ and Fe/AC enhanced with $O_3$ was reached an asymptote. The possible pathways of substrate degradation and the interactions of catalysis and ozonalysis were summarized by ZHU Xiang-feng and XU Xin-hua **[48].** During ozonalysis without catalytic, ozone moves from the gas phase into solution and then react in bulk solution either directly with the substrate or indirectly via reactions with radicals generated by $O_3$ auto-decomposition. By only catalysis, the substrate can undergo direct pyrolysis. However, in the combined system, the above pathways may be altered by the addition of other pathways that only occur by the direct interaction of catalysis and ozonation. For example, catalysis could enhance the decomposition of $O_3$, generating $^{\bullet}OH$ to react the substrate. Furthermore, Fe/AC could enhance the mass transfer of $O_3$ to disperse thorough the solution. Under the experimental conditions described here, phenol degradation obeyed the pseudo-first-order rate law. **Table 5.5** lists the first-order degradation rate constants of catalysis, ozonation and Fe/Ac enhanced with $O_3$ by decomposing of phenol. For the purpose of discussion, $k_{Fe/AC}$ $k_{O_3}$, and $k_{Fe/AC + O_3}$ were defined as the overall pseudo-first-order degradation rate constants for catalysis, ozonalysis, and the combination of Fe/AC and $O_3$, respectively.

**Table 5.5** Phenol removal efficiency (%) and TOC removal efficiency (%) for Fe/AC, $O_3$ and Fe/AC enhanced with $O_3$

| **Type** | **Phenol removal (%)** | | | | **TOC removal (%)** | | | |
|---|---|---|---|---|---|---|---|---|
| | 10 min | 15 min | 45 min | 150 min | 10 min | 15 min | 45 min | 150 min |
| $O_3$ FROM AIR | 25 | 26 | 40 | 100 | Negligible removal | | | |
| Fe/AC + AIR | 50 | 53 | 100 | 100 | 45 | 69 | 76 | 77 |
| Fe/AC + $O_3$ FROM AIR | 72 | 100 | 100 | 100 | 37 | 52 | 72 | 78 |

In this report, the efficiency for decomposing of 2 l of 10 ppm phenol solution with catalyst loading 5 g was revealed in term of $-\ln(C/C_0)$ to express the rate constant (*k*). The disappearance of phenol followed pseudo first order kinetics. Initial rate constants were determined from the slope of $-\ln(C/C_0)$ vs t (min) plots **(Figure 5.7 and Table 5.6)**, where $C_0$ and C were the phenol concentration at initial and time t, respectively.

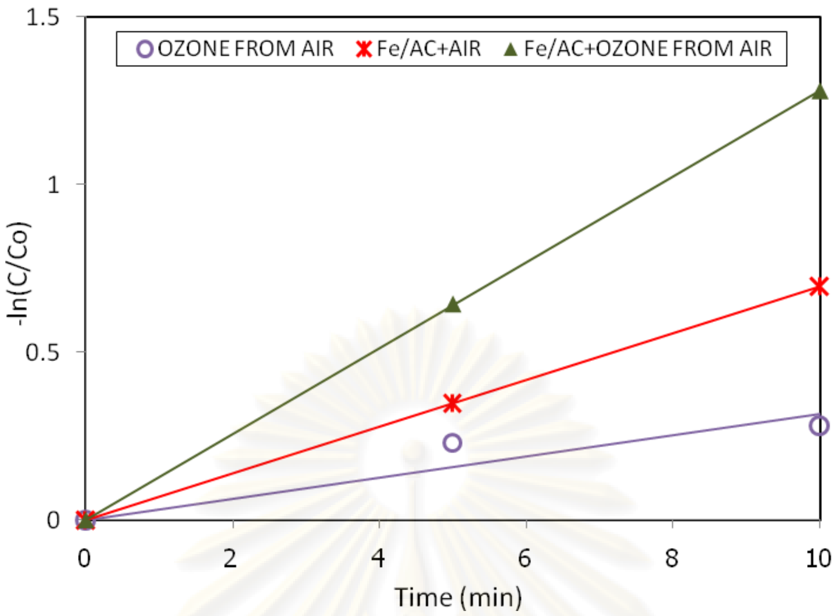


**Figure 5.7** Phenol decomposition rates by three processes of phenol degradation (Fe/AC, $O_3$, and Fe/AC enhanced with $O_3$).

**Table 5.6** Pseudo first order rate constant for decomposition of aqueous phenol

| **Condition** | **Phenol** | |
|---|---|---|
| | **$R^{2a}$** | **k ($min^{-1}$)$^b$** |
| $O_3$ 1 L/min ($O_2$) | 1.0 | 0.0317 |
| Fe/AC + $O_3$ 1 L/min ($O_2$) | 1.0 | 0.0698 |
| Fe/AC 5%wt 1L/min ($O_2$) | 0.9 | 0.1283 |

[a] Correlation coefficient of the straight line

[b] Pseudo first order rate constant determined for the 10 min of reaction

To compare the activity of any reactant or chemical reaction, the study of kinetic reaction was very important. By this purpose, the rates of reaction for two reactions were computed. The reaction rate constant of different reactions estimated from our measurement is 0.0317, 0.0698, and 0.1283 $min^{-1}$ for $O_3$, Fe/AC, and Fe/AC enhanced with $O_3$ respectively.

The degradation of phenol by Fe/AC with $O_3$ in aqueous solution was measured in fluidized bed reactor. Fe/AC was more efficient than Ozonation for the degradation of phenol, and the combination of the two resulted in a synergetic increase in the overall process rate. The synergy observed in combined schemes was mainly due to the effects of catalysis in enhancing the decomposition of $O_3$ in collapsing bubbles to yield additional free radicals. Set of possible reactions to explain the degradation process was suggested.

### 5.4.4 Combination effect of activated carbon and/or ozone

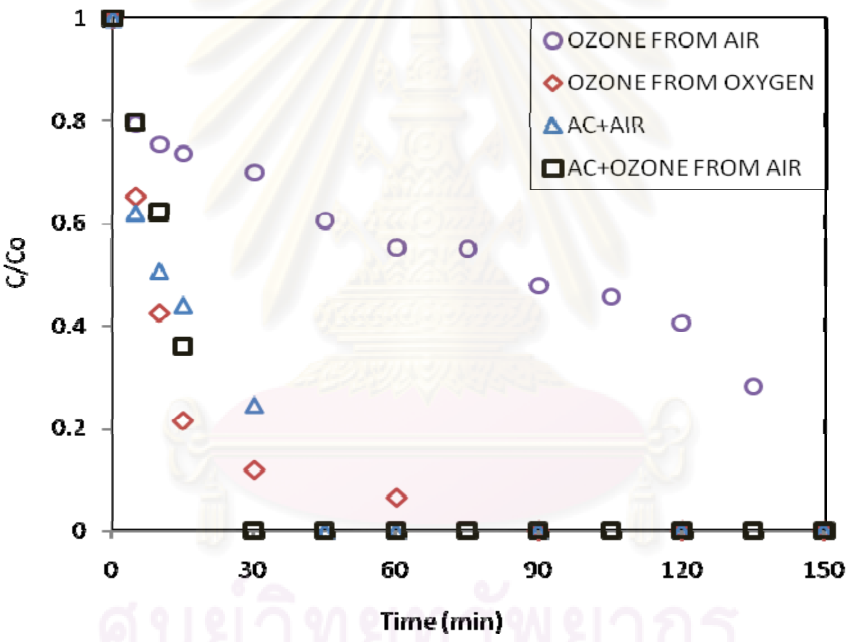


**Figure 5.8** Phenol concentration as a function of time for AC1 and/or ozone

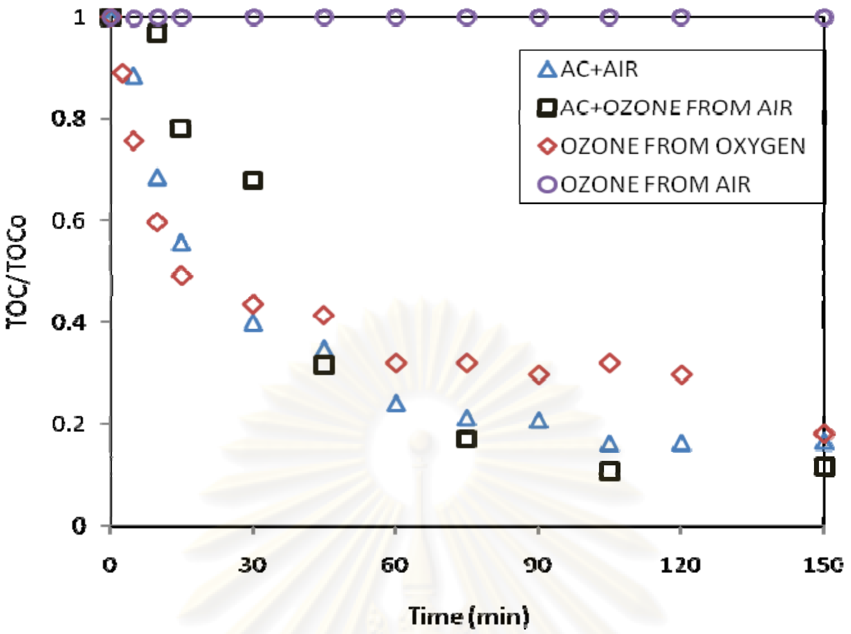


**Figure 5.9** TOCs as a function of time for AC1 and/or ozone

**Table 5.7** Phenol removal efficiency (%) and TOC removal efficiency (%) for AC1 and/or ozone

| **TYPE** | **Phenol removal (%)** | | | | | **TOC removal (%)** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 10 min | 15 min | 30 min | 45 min | 150 min | 10 min | 15 min | 30 min | 45 min | 150 min |
| AC(1)+AIR | 49 | 56 | 75 | 100 | 100 | 31 | 44 | 60 | 65 | 83 |
| AC(1)+OZONE FROM AIR | 38 | 64 | 100 | 100 | 100 | 5 | 22 | 32 | 68 | 89 |

Here only AC1 in combination with ozone generated from air was investigated. **Figures 5.8 and 5.9** show the residual phenol and TOC concentrations as a function of time for the present case of interest. For comparison, the cases of ozone from pure oxygen and from air as well as the case of AC1 with pure air are also included in the figure. In the first 10 minutes, activated carbon with air gave higher phenol removal and faster removal rate than activated carbon with ozone from air because the phenol adsorption effect was more prominent in the former case. In the latter case AC1 adsorbed not only phenol but also the dissolved ozone. However, the situation was reversed after 15 min. This may be ascribed to the fact that activated carbon quickly decomposed the adsorbed ozone on its surface to hydroxyl radicals, a powerful oxidant that reacted non-selectively with organic compounds at a faster rate than ozone **[40-48].** In fact the adsorption of phenol on the surface of activated carbon initially limited the available surface for ozone decomposition **[49].** Meantime, the contact and reaction between the adsorbed phenol and the active radicals on the carbon surface was enhanced due to the presence of the surface radicals from the very beginning of the process, as reported by Ko et al. **[50].** As a consequence the initial removal rate of phenol in both AC1 cases was enhanced compared to the case of ozone only.

After the decomposition reaction had proceeded for 30 min, desorption of the intermediate products continuously provided additional sites for further adsorption and decomposition, thereby resulting in higher phenol removal than activated carbon with air or ozone alone. At 45 min AC1 with ozone from air achieved the highest phenol removal compared with the other two cases **[51]**. Similarly, AC1 with ozone from air also yielded the highest TOC removal at 45 min. Maximal TOC removal of 70.2%, 83.5% and 89.3% were achieved at 150 min by ozone from pure oxygen, AC1 with air, and AC1 with ozone from air, respectively. It should be noted that ozone from air could decompose phenol well but it failed to remove the intermediate products.

Our results are consistent with the following effects reported by Amin et al**.** **[51]** to support the application of activated carbon and ozone to remove organic contaminants from water: (1) activated carbon is a strong adsorbent for phenol, (2) when in contact with activated carbon, ozone undergoes rapid decomposition to generate highly oxidative radicals **[51]** and (3) in this way, organic compounds adsorbed by activated carbon can be oxidized by ozone, thereby restoring its porous structure for further adsorption. In fact, activated carbon initiates the transformation of ozone to hydroxyl radicals, which are not bound to the surface of carbon but are free to react with the organic compounds in the aqueous solution **[48, 51].**

### 5.4.5 Overall comparative investigation of catalytic and/or ozone

All the experiments in the presence of: only ozone ($O_3$), only AC, only Fe/AC and ozone in combination with one of the mentioned catalysts were carried out under the same operation conditions (1 l/min of liquid and/or gas flow rate and 5 g of catalyst loading). For the sake of comparison, phenol concentration change with respect to decomposition time which was obtained from each experiment was plotted in **Figure 5.10**

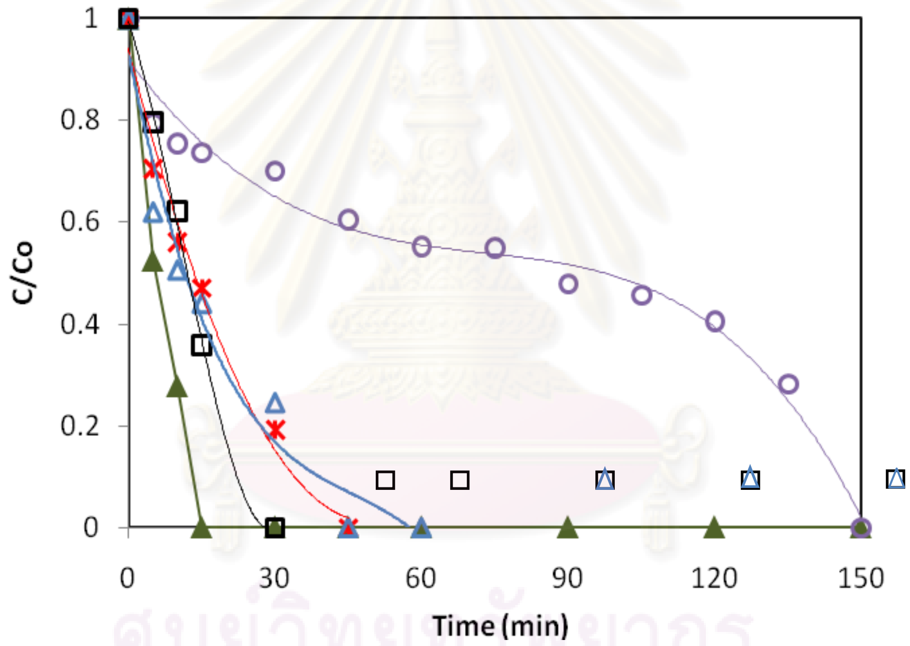


**Figure 5.10** Comparison of phenol degradation efficiency in the presence of: ozone generated from air (o), AC1+air (Δ), Fe/AC1+air (*), AC with ozone generated from air (□) and Fe/AC1 with ozone generated from air (▲).

First, consider the cases of using only ozone or a catalyst. The comparison between Fe/AC1 (*) and AC1 (Δ) show that Fe/AC1 was more effective than AC1. In addition, comparing between Fe/AC1 (*) with ozone from air (o) reveals that the metallic catalyst has a decomposition higher efficiency than that of the ozone generated from air. Evidently Fe/AC1 was more effective than the ozone from air. Next the experiments were focused on the case of Fe/AC1 together with ozone from air. The results came out as predicted. Decomposing phenol by Fe/AC1 combine with ozone generated from air (▲) gave the best result. It is noteworthy that in an actual wastewater treatment process it is crucial to minimize the total costs of the treatment system. Therefore the most appropriate case should use Fe/AC1 combined with ozone generated from air.

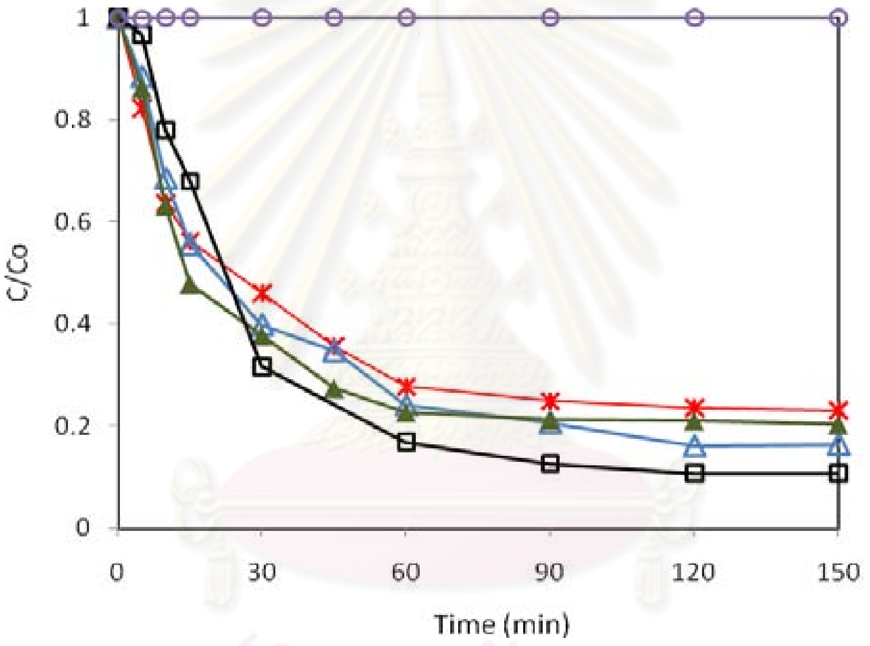


**Figure 5.11** Comparison of TOC removal of efficiency in the presence of: only ozone generated from air (O), only AC1+air (Δ), only Fe/AC1+air (*), AC with ozone generated from air (□) and Fe/AC1 with ozone generated from air (▲).

In addition, the TOCs removal come from the intermediate product (hydroquinone (HQ) and catechol (CC) concentrations are expressed in **Figure 5.11**. The results from **Figure 5.11** shows that the TOCs removal in each case was produced in an insignificant amount and it was finally decomposed to a concentration about 1 ppm in 150 min. Meanwhile the decomposition reaction had proceeded for

30 min, desorption of the intermediate products continuously provided additional sites for further adsorption and decomposition, thereby resulting in higher phenol removal than activated carbon with pure oxygen or ozone alone. Consider the cases of using only ozone or a catalyst. The comparison between Fe/AC1 (*) and AC1 (Δ) show that AC1 (Δ) was more effective even though the amount of Fe. In addition, comparing between both Fe/AC1 and AC1 (* and Δ) with ozone from air (o) reveals that the both Fe/AC1 and AC1 have a decomposition higher efficiency than that of the ozone generated from air. Evidently both Fe/AC1 and AC1 were more effective than the ozone from air. Next the experiments were focused on the case of metallic catalyst together with ozone. The results came out as predicted. It should be noted that ozone from air could decompose phenol well but it failed to remove the intermediate products. TOCs removal of phenol by AC1 combine with ozone generated from air (□) gave the best result and both Fe/AC1 and AC1 were more efficient than the case of ozone generated from air. It is noteworthy that in an actual wastewater treatment process it is crucial to minimize the total costs of the treatment system. Therefore the most appropriate case should use both Fe/AC1 and AC1 combined with ozone generated from air.

# CHAPTER VI

# CONCLUSIONS AND RECOMMENDATIONS

Conclusions and recommendations for the future investigation are presented in this chapter.

## 6.1 Conclusions

The conclusions of this research are as follows,

1. In the 3-phase fluidized bed reactor, AC1 was more effective than AC2 in the removal of aqueous phenol and TOC and AC shows two primary capabilities of adsorption and catalytic oxidation.

2. The removal of phenol using only $O_3$ gave the worst result when compared to the other cases which employed activated carbons.

3. From the viewpoint of operating costs, the use of ozone generated air in the combined system was significantly less expensive than the use of ozone generated pure oxygen.

4. Applying Fe/AC with ozone generated from air gives the best results for phenol removal. However, using air instead of pure oxygen can save more costs whereas the total efficiency differs insignificantly.

5. As the best case for TOC removal, a combination of AC1 and ozone generated air can remove nearly 90% of the intermediates (TOC) at could also be decomposed within 150 min.

## 6.2 Recommendations for future studies

From the previous conclusions, the following recommendations for future studies are proposed.

1. The system in the section of dissolving ozone into the water should be measured.

2. To apply these metallic catalysts to a wastewater treatment system, an effective regeneration method of the metallic catalysts is an issue to be investigated further.

3. There are some fine powders detaching from the carbon support after testing for a while. Therefore an improvement of these metallic catalysts stability is needed.

4. The catalytic efficiency in reaction of heterogeneous catalysts where the chemical environment of iron is modified by mixing with $H_2O_2$ to be investigated further.

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# APPENDICES

# APPENDIX A

## Publications Resulting from This Research Work

### National Proceedings

1. **Limsuwan, P.,** Chaeysiri, S., Sano, N., Yamamoto, T., Wongsarivej, P., Tongpram, P., Soottitantawat, A., Tanthapanichakoon, W., and Charinpanitkul, T. Removal of aqueous phenol in a three-phase fluidized bed reactor using activated carbon and/or ozone. *Proceeding of the First Asian Conference on Innovative Energy & Environmental Chemical Engineering (ASCON-IEEChE),* pp.563-568. August 31 to September 3, 2008, Sapporo, Japan, 2008.
2. Wongsarivej, P., Tongprem, P., **Limsuwan, P.,** Chaeysiri, S., Soottitantawat, A., Charinpanitkul, T., and Tanthapanichakoon, W. Investigation of catalytic decomposition of phenol in lab scale three-phase fluidized bed reactor using Fe on activated carbon support. *Proceeding of the 2nd Thailand Nanotechnology Conference 2008,* August 13-15, 2008, Phuket, Thailand, 2008.
3. Wongsarivej, P., Tongprem, P., Chaeysiri, S., **Limsuwan, P.,** Soottitantawat, A., Charinpanitkul, T., and Tanthapanichakoon, W. Investigation of catalytic decomposition of phenol in pilot scale three-phase fluidized bed reactor using Fe on activated carbon support. *Proceeding of the First Asian Conference on Innovative Energy & Environmental Chemical Engineering (ASCON-IEEChE),* pp.369-372. August 31 to September 3, 2008, Sapporo, Japan, 2008.
4. Chaeysiri, S., Charinpanitkul, T., **Limsuwan, P.,** Soottitantawat, A., Tongprem, P., Wongsarivej, P., and Tanthapanichakoon, W. Preparaton of fe catalyst supported on activated carbon for phenol decomposition. *Proceeding of* the *Nano Thailand Symposium 2008 International Conference & Exhibition*, November 6-8, Bangkok, Thailand, 2008.

# Removal of aqueous phenol in a three-phase fluidized bed reactor using activated carbon and/or ozone

P. Limsuwan[1], S. Chaeysiri[1], N. Sano[2], T. Yamamoto[3], P. Wongsarivej[4], P. Tongpram[4],
A. Soottitantawat[1], W. Tanthapanichakoon[1], and T. Charinpanitkul[1]

*[1]Center of Excellence in Particle Technology (CEPT), Faculty of Engineering,*
*Chulalongkorn University, Patumwan, Bangkok, Thailand, 10330.*
*[2] University of Hyogo, Department of Mechanical and*
*System Engineering, 2167 Shosha, Himeji, Hyogo 671-2201, Japan*
*[3] National Institute of Advanced Industrial Science and Technology,*
*Central 5, 1-1-1 Higashi, Tsukuba, Ibaragi 305-8565, Japan*
*[4] National Nanotechnology Center (NANOTEC), NSTDA, Pathumthani, Thailand, 12120*

## Abstract

A lab-scale three-phase fluidized-bed reactor was used for removal of aqueous phenol by adsorption and decomposition on activated carbon surface. The gas, liquid and solid phases were air bubbles with or without ozone, aqueous phenol and granular activated carbon (AC), respectively. Two types of AC (AC1 and AC2) with BET surface areas of 1,106 and 1,150 $m^2.g^{-1}$ and average pore diameters of 2.3 and 1.7 nm, respectively, were employed. The removal of phenol by ozone alone, and either activated carbon with or without ozone was experimentally investigated at a fixed initial phenol concentration of 10 ppm. Both the gas flow and liquid recirculation rate were controlled at 1 $L.min^{-1}$. The fastest initial removal of phenol was with AC1 alone, whereas the slowest was with ozone alone. Some intermediate products, such as hydroquinone and catechol, still remained at 150 min even after phenol was completely removed. Between the two ACs, AC1 with more mesopores removed the intermediates better than AC2 with more micopores. At 150 min AC1 with ozone was found to have the highest complete removal of phenol and removal of the intermediates of up to 89% as represented by TOC.

**Keywords**: Phenol, Three phase fluidized bed, metallic catalyst, and activated carbon

## 1. Introduction

Most wastewater pollutants emitted from industrial chemical processes are not only toxic but also hard to degrade with conventional treatments[1]. Though public reservoirs are contaminated by many organic compounds, phenol and its derivatives are widely detected and are harmful to human health at dilute concentrations. Phenol is widely used in many industrial products and processes such as wood preservative, pesticide, textile, paper and chemical dye[2]. Consequently, development of high-performance aqueous phenol treatment systems is of interest here.

Activated carbon exhibits high adsorption capacity for aqueous phenol and possesses various advantages, such as high surface area per unit mass[3]. Moreover, the employment of activated carbon coupled with a super-oxidizing agent such as ozone is expected to result in a higher degree of mineralization of the organic refractory pollutants, which may be followed by further biological treatment.

Recently, increasing attention has turned to the three-phase fluidized-bed reactor, because it readily provides intimate contact between the gas, liquid and solid phases. It also possesses several advantageous characteristics such as simplicity in construction and operation, low operating cost, and high flexibility for liquid and solid phase residence times. Our system applies ozonation for the decomposition of aqueous phenol together with activated carbon[2].

The present research is aimed at the application of an effective wastewater treatment for removing phenol dissolved in wastewater. Performance of a lab-scale fluidized-bed reactor with two types of activated carbon (solid phase) and/or ozone in air or oxygen (gas phase) will be investigated experimentally. It is well-known that the oxidation of phenol often leads to numerous hard-to-remove intermediate products. To monitor the presence and removal of the intermediate products, the TOC concentration of the treated wastewater is also measured.

## 2. Experimental

### 2.1 Materials

Phenol was purchased from Polski Odczynniki Chemiczne S.A., 99.9%. Granulated activated carbons made from coal by Calgon Company (AC1) and from coconut shell by Carbokarn Company (AC2) were used. The main characteristics of the activated carbons used in the present investigations are presented in Table 1. The specific surface areas and porosities of these activated carbons were determined from $N_2$ adsorption-desorption isotherms measured at 77 K using an automated adsorption apparatus (BELSORP 28, BEL Japan, Japan, or AUTOSORB-1-C, Quantachrome, USA). The specific surface areas were calculated by the BET method. The MP method yielded the pore volume and pore size distribution from the curvature of the t-plot. It should be noted that two types of activated carbon have significantly different characteristics. The pore size distributions of the two materials have been given elsewhere[4]

Table 1. Characteristics of the activated carbons

| Type | BET surface area ($m^2g^{-1}$) | Particle size (mm) | Total pore vol. ($cm^3g^{-1}$) | Micropore vol. ($cm^3g^{-1}$) | Ave. pore diameter (nm) |
|---|---|---|---|---|---|
| AC1 | 1060 | 0.60-2.36 | 0.61 | 0.49 | 2.3 |
| AC2 | 1154 | 0.42-1.70 | 0.49 | 0.49 | 1.7 |

### 2.2 Apparatus and procedure

As illustrated in Fig. 1, the experimental apparatus consists of a lab-scale 3-phase fluidized bed reactor, hold-up tank, magnetic stirrer, liquid pump, flow meter, 3-way valve, ozone generator, and oxygen cylinder. The reactor is made of quartz tube with an inside diameter and length of 3.16 and 45 cm, respectively. The liquid solution and gas were separately fed through a distributor into the fluidized catalyst bed. Gas flow was exhausted from the top of the reactor while the liquid solution was totally circulated and intermittently sampled.

A fixed amount of activated carbon 5 g was used. Aqueous phenol 10-ppm 2 L in the hold-up tank were charged into the fluidized bed reactor.

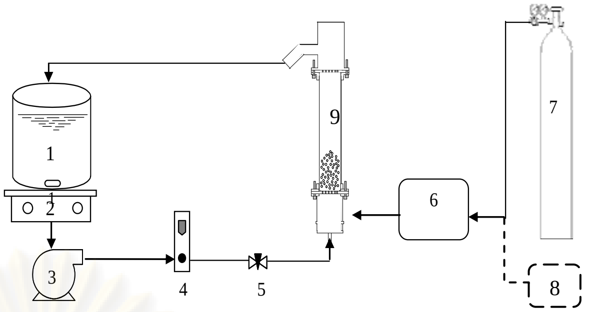

Fig.1 Diagram of experimental apparatus, 1. hold-up tank, 2. magnetic stirrer, 3. liquid pump, 4. flow meter, 5. 3-way valve, 6. ozone generator, 7. oxygen cylinder, 8. air pump and 9. fluidized bed reactor

All experiments were carried out with co-current upward flow of gas (1 L.min$^{-1}$) and liquid (1 L.min$^{-1}$). In each run, the phenol-containing liquid and gas were fed in at the bottom, came out from the top and the entire liquid was recirculated via the hold-up tank. Ozone was produced either from air or from pure $O_2$ by passing it through an ozone generator (Tokyu Car Corporation, SO-O3UN-OX). Intermittently samples were withdrawn at the times of interest for chemical analysis, filtered through filter paper (0.45μm pore size), and then analyzed by HPLC and TOC analyzer.

2.3 Analysis for phenol and TOC

The concentration of phenol was analyzed by a high-performance liquid chromatography (HPLC) using a Shimadzu column (Class VP), with 25% acetronitrile: 75% water as the mobile phase and the UV-vis detector using 254 nm wavelength. The total organic carbon analyzer (TOC analyzer, TOC-VCPH, Shimadzu, Japan) was used to find the concentration of the intermediates in terms of TOC.

## 3. Results and Discussion

To investigate the influence of different treatment options on the efficiency of the wastewater treatment process, the experimental funs can be classified as follows:

a. Removal of phenol and TOC by ozone generated from pure oxygen or air
b. Removal of phenol and TOC by two different types of activated carbon
c. Removal of phenol and TOC using a combination of activated carbon and ozone

3.1 Removal of phenol and TOC by ozone generated from pure oxygen or air

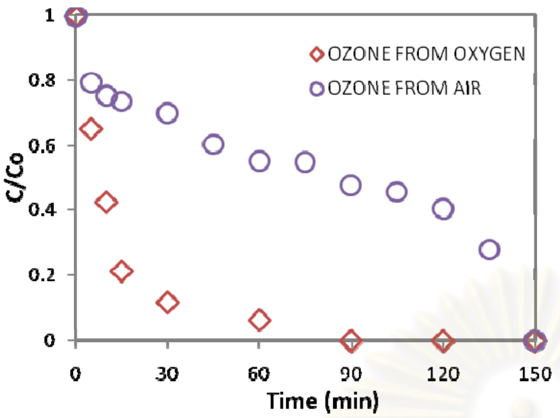

Fig. 2(a). Phenol concentrations as a function of time in ozonation with two oxygen sources

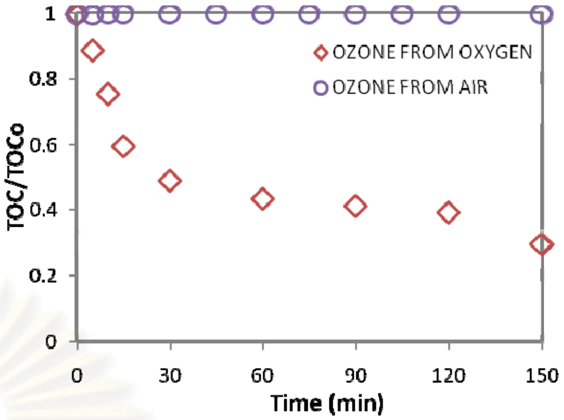

Fig. 2(b). TOCs as a function of time in ozonation with two oxygen sources

Here pure oxygen gas and air were used as the two sources of ozone generation. In the present ozonation process, the ozone-containing gas was injected into the reactor along with a co-current phenol-containing liquid stream. At the beginning, ozone transfers from the gas phase to the liquid phase. Then ozone self-decomposes in water to produce •OH radicals[6]. The hydroxyl radicals were consumed by aqueous phenol oxidation and reactions between the radicals. A logical analysis of the oxidation reaction between ozone and phenol was presented by Zhong et al.[5]. Figs. 2 (a, b) show the residual phenol and TOC concentrations as a function of time for the two cases of ozone generated from pure oxygen and air. Obviously the removal efficiency differed significantly for the two sources of ozone. In the case of ozone from pure oxygen, phenol and TOC removals were 100% and 60.6%, respectively, at 120 min. However, in the case of ozone from air, phenol removal was 59.3% and TOC removal was negligible at 120 min for two reasons. First, air contains 70 mol% nitrogen so that the rate of ozone generation should be less than one-fifth of that from pure oxygen. Second, when air contains moisture, the already much smaller quantity of ozone is further consumed in the formation of nitrogen oxides[7]. Nevertheless, if we could sufficiently compensate for the drop in removal efficiency by coupling the ozonation system with activated carbon, the use of ozone generated from air should offer a suitable cost-effective alternative.

3.2 Removal of phenol and TOC by two different types of activated carbon

As shown in Table 1, both AC1 and AC2 possess large surface areas for adsorption of hydrophobic compounds, including aqueous phenol. One important fringe benefit is that the concentration of adsorbed phenol will be much higher than that in the bulk liquid. Here air was sent co-currently through the reactor while the ozone generator was switched off. If only adsorption takes place without any oxidative decomposition of the adsorbed phenol to some intermediate products, the drop in the normalized TOC concentration must essentially equal that of phenol, and the residual phenol concentration will finally reach an equilibrium value. Figs. 3 (a, b) show the normalized residual phenol and TOC concentrations as a function of time for the cases of AC1 and AC2. In the first 10 minutes, the rates of reduction in phenol and TOC concentrations were essentially the same. This implies that both of them were

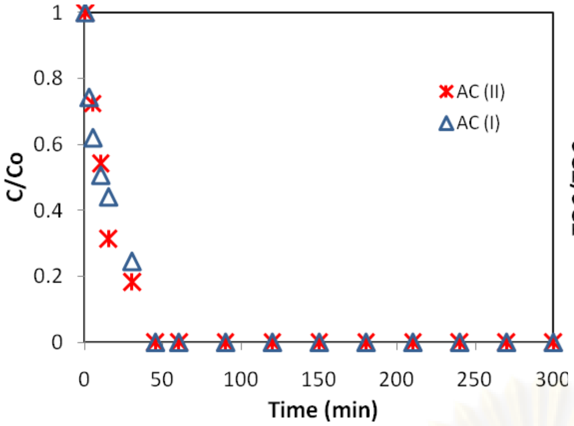

Fig. 3(a). Phenol concentrations as a function of time for AC1 And AC2

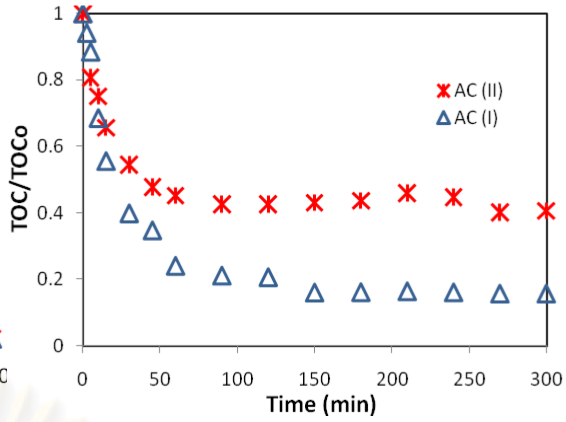

Fig. 3(b). TOCs as a function of time for AC1 And AC2

removed by adsorption on the activated carbon. After that the reduction rate of TOC became slower than that of phenol. This implies that a portion of the adsorbed phenol was decomposed to intermediate products such as hydroquinone and catechol, which started to desorb from the activated carbon and entered the bulk liquid, thereby contributing to a slower drop in the residual TOC concentration. Since the intermediates were resistant to further oxidative decomposition on the activated carbon, their TOC value reached an asymptote, which reflects their adsorption equilibrium on the activated carbon. The findings are consistent with the published results[8-9].

More specifically, at 45 min, the phenol and TOC removal efficiencies of AC1 were 100% and 65.3%, respectively. In contrast, the corresponding removal efficiencies of AC2 were 100% and 52%, respectively. The higher TOC removal efficiency of AC1 may be attributed to its possession of more mesopore and larger average pore diameter than AC2. Nevertheless, some hard-to-decompose intermediate products, such as hydroquinone and catechol, still remained even after phenol was completely removed.

### 3.3 Removal of phenol and TOC using a combination of activated carbon and ozone

Here only AC1 in combination with ozone generated from air was investigated. Figs. 4 (a, b) show the residual phenol and TOC concentrations as a function of time for the present case of interest. For comparison, the cases of ozone from pure oxygen and from air as well as the case of AC1 with pure air are also included in the figure. In the first 10 minutes, activated carbon with air gave higher phenol removal and faster removal rate than activated carbon with ozone from air because the phenol adsorption effect was more prominent in the former case. In the latter case AC1 adsorbed not only phenol but also the dissolved ozone. However, the situation was reversed after 15 min.

This may be ascribed to the fact that activated carbon quickly decomposed the adsorbed ozone on its surface to hydroxyl radicals, a powerful oxidant that reacted non-selectively with organic compounds at a faster rate than ozone [8-10]. In fact the adsorption of phenol on the surface of activated carbon initially limited the available surface for ozone decomposition[11]. Meantime, the contact and reaction between the adsorbed phenol and the active radicals on the carbon surface was enhanced due to the presence of the surface radicals from the very beginning of the process, as reported by

Ko et al.[11]. As a consequence the initial removal rate of phenol in both AC1 cases was enhanced compared to the case of ozone only.

After the decomposition reaction had proceeded for 30 min, desorption of the intermediate products continuously provided additional sites for further adsorption and decomposition, thereby resulting in higher phenol removal than activated carbon with air or ozone alone. At 45 min AC1 with ozone from air achieved the highest phenol removal compared with the other two cases [12]. Similarly, AC1 with ozone from air also yielded the highest TOC removal at 45 min. Maximal TOC removal of 70.2%, 83.5% and 89.3% were achieved at 150 min by ozone from pure oxygen, AC1 with air, and AC1 with ozone from air, respectively. It should be noted that ozone from air could decompose phenol well but it failed to remove the intermediate products.

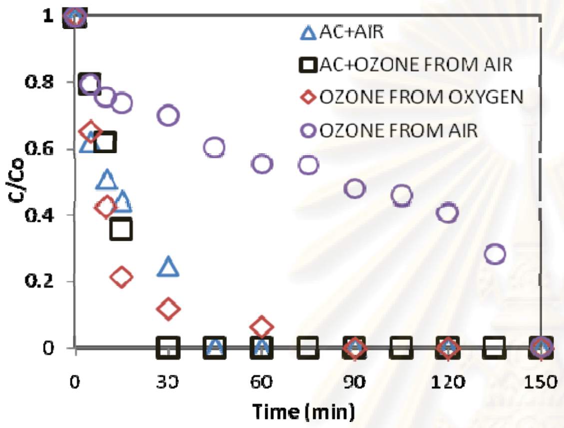

Fig. 4(a). Phenol concentration as a function of time for AC1 and/or ozone

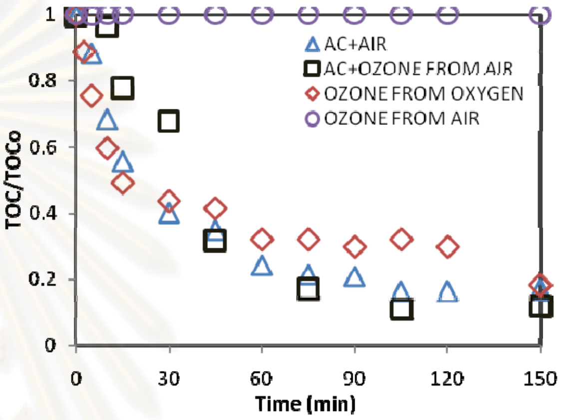

Fig. 4(b). TOCs as a function of time for AC1 and/or ozone

Our results are consistent with the following effects reported by Amin et al.[12] to support the application of activated carbon and ozone to remove organic contaminants from water: (1) activated carbon is a strong adsorbent for phenol, (2) when in contact with activated carbon, ozone undergoes rapid decomposition to generate highly oxidative radicals [13] and (3) in this way, organic compounds adsorbed by activated carbon can be oxidized by ozone, thereby restoring its porous structure for further adsorption. In fact, activated carbon initiates the transformation of ozone to hydroxyl radicals, which are not bound to the surface of carbon but are free to react with the organic compounds in the aqueous solution[12, 14].

## 4. Conclusion

(1) In the 3-phase fluidized bed reactor, AC1 is more effective than AC2 in the removal of aqueous phenol and TOC.

(2) A combination of AC1 and ozone from air can remove aqueous phenol completely as well as nearly 90% of the intermediates in terms of TOC.

(3) From the point of view of operational costs, the use of ozone from air in the combined system will be significantly less expensive than the use of ozone from pure oxygen.

**Acknowledgements**

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# Investigation of catalytic decomposition of phenol in a lab scale three-phase fluidized bed reactor using Fe on activated carbon support

**Pratarn Wongsarivej**[1], Pornsiri Tongprem[1], Pilasinee Limsuwan[2], Sukhum Chaeysiri[2],
Apinan Sootitantawat[2], Tawatchai Charinpanitkul[2] and Wiwut Tanthapanichakoon[2]

[1]National Nanotechnology Center, Bangkok 12120
Phone 0-2564-7100 (6564), Fax. 0-2564-6989, E-Mail: pratarn@nanotec.or.th
[2]Department of Chemical Engineering, Faculty of Engineering,
Chulalongkorn University, Bangkok, 10330

## Abstract

A lab-scale three-phase fluidized-bed reactor was used to investigate the decomposition of 10 ppm aqueous phenol. Comparison of the phenol decomposition rates under the three different conditions: a) employing only Fe catalyst on activated carbon support (Fe/Ac), b) employing only ozone ($O_3$) and c) employing Fe/Ac enhanced with $O_3$, were carried out. The gas and liquid flow rate were kept constant at 1 L/min and the catalyst loading was 5 g. The liquid was circulated through the reactor and its phenol concentration was measured with respect to time. The experimental results of the decomposition of 2 L of phenol solution revealed that using only Fe/Ac without $O_3$ gave the worst result ($k = 0.026\ min^{-1}$). However, when employed with only $O_3$ generated from pure $O_2$, the result was better ($k = 0.052\ min^{-1}$). In the case of using Fe/Ac enhanced with $O_3$, it provided the best result ($k = 0.241\ min^{-1}$). In the best case, the complete degradation of phenol can be essentially achieved within 20 min whereas the total organic carbon (TOC) was reduced to less than 2 ppm in 120 min.

## 1. Introduction

Recently water pollution is a crucial environment problem that important and continuous increasing. Some of wastewater comes from industrial development for example: wastewater from process line, cooling tower drainage and domestic waste. Most of industrial wastewater composes of phenolic compound which is difficult to decompose by conventional treatment [1]. Phenol and its derivatives have highly influence to water quality that directly affected to human and aquatic animals [2]. The recent research works are in progress to study for understanding the complex phenomena of phenolic oxidation using activated carbons and/or ozone [3-4]. High quality system is extremely important for wastewater treatment. In this research, knowledge and existing experiences are uses for actual waste treatment.

## 2. Material and method

### 2.1 Catalyst preparation

Catalytic support, microporous granulated activated carbons, (Ac) were purchased from Carbokarn Co., Ltd. (Thailand). Ac was previously sieved to a particle size diameter in the range of 0.4-2.0 mm. It was pretreated by heating at 473 K for 4 hrs to eliminate the impurities, sequentially impregnated with a solution of $Fe(NO_3)_3{\cdot}9H_2O$. The Ac impreged with iron, (Fe/Ac) catalyst was prepared by incipient wetness impregnation method. The concentration of Fe on the Ac is constantly controlled at 5%Fe (w/w) which prepared by using metal solution 0.5 ml. per gram of Ac. The solution is slowly dropped on Ac and continuously stirred by glass rod in water bath which constantly controlled at 353 K. After impregnation, Fe/Ac was dried overnight at 353 K and calcinated at 773 K under $N_2$ flow for 5 hrs.

### 2.2 Experimental

The laboratory scale three-phase fluidized bed reactor is used as test system. It consists of hold up tank, magnetic stirrer, liquid pump, liquid flow meter, three way valve, ozone generator, oxygen tank and reactor. The schematic diagram and the fluidized bed reactor are shown in Fig. 1&2, respectively. The reactor with effective volume 235 ml is made from transparent quartz tube that easily observe the phenomenon occurring inside. The inside diameter and height of reactor are 31.6 and 300 mm, respectively. Phenol 10 mg/l and $O_3$ 1.46 g/h were used as tested and oxidizing agents with 5 g catalyst. Phenol and $O_3$ were continuously fed to the reactor at equal constant flow rate 1 l/min with co-current and up-flow. Two liters of phenol was circulated through the reactor and return to the hold up tank. The aqueous temperature in the tank was approximately 17-25°C. The ozone generator model SO-03UN-OX used to generate $O_3$ from oxygen tank. Comparison of the phenol decomposition rates under the three different conditions: a) employing only Fe catalyst on activated carbon support, b) employing only ozone, and c) employing Fe/Ac enhanced with $O_3$, were carried out. The samples were collected from the hold up tank respect to time and analyze with HPLC and TOC.

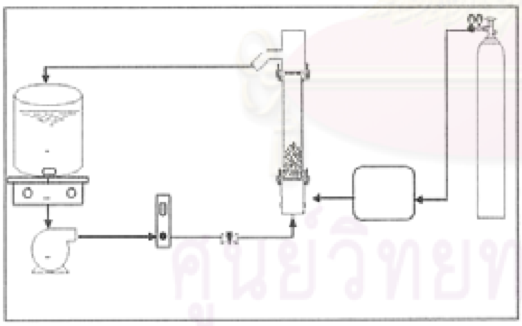

Fig. 1 The schematic diagram of fluidized bed reactor

Fig. 2 Fluidized bed reactor

## 3. Results and Discussion

The degradation of phenol from the initial concentration of 10 ppm by treatment with lab scale fluidized bed reactor under three different conditions: a) employing only Fe/Ac, b) employing only $O_3$, and c) employing Fe/Ac enhanced with $O_3$ are presented in Fig. 3. It is found that the condition of using only Fe/Ac has the worst result of phenol degradation ($C/C_0 = 0.20$ at 20 min.). However, the phenolic decomposition in condition of using only $O_3$, conducted the better results ($C/C_0 = 0.05$ at 60 min). The best decomposition of phenol result occurring in condition of using Fe/Ac enhanced with $O_3$, ($C/C_0 = 0.00$ at 60 min.). In the best case, the complete degradation of phenol can be essentially achieved within 20 min while in the worst case, the complete degradation of phenol must be extensively operated over 120 min.

The total organic carbon (TOC) degradation at different times on stream is shown in Fig. 4 under three different conditions as same as Fig.3. It is found that case b) has the worst result ($TOC/TOC_0 = 0.45$ at 60 min.). However, the phenolic decomposition in case a), conducted the better results ($TOC/TOC_0 = 0.37$ at 60 min). The best decomposition of TOC result occurring in case c), ($TOC/TOC_0 = 0.30$ at 60 min.). In the best case, TOC can be reduced to less than 2 ppm in 120 min.

The efficiency of phenolic decomposition was revealed in term of $-\ln(C/C_0)$ to express the rate constant (k). Rate constants were determined from the slope of $-\ln(C/C_0)$ vs. t as shown in Fig. 5. The experimental results of the decomposition of phenol solution revealed that using only Fe/Ac gave the slowest result ($k = 0.026$ min$^{-1}$). However, the result was better in condition of using only $O_3$ ($k = 0.052$ min$^{-1}$). Finally, condition of using Fe/Ac enhanced with $O_3$ provided the best result ($k = 0.241$ min$^{-1}$).

In case a), the phenolic decomposition taken place by adsorption process, on the other hand, the degradation of phenol in case b) comes from oxidation process. Moreover, in case c), phenol decomposed beneath influent of both of adsorption and oxidation processes. The comparison of rate constant between cases a) and b) showed that adsorption effect by Fe/Ac is weaker than reaction effect by $O_3$. In addition, case c) obtained the faster phenolic removal than case a) and b) since the both of adsorption and ozonation effects.

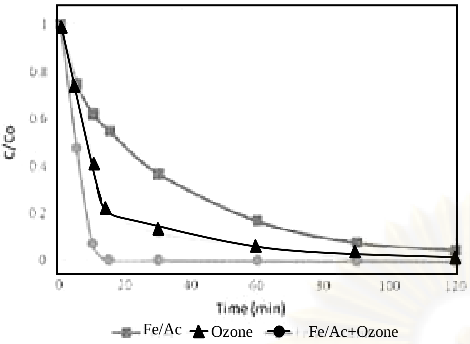

Fig. 3 Concentration removal of phenol

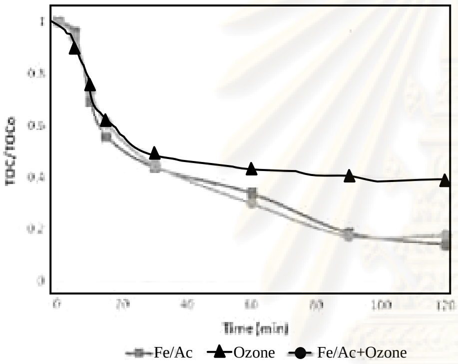

Fig. 4 TOC removal of phenol

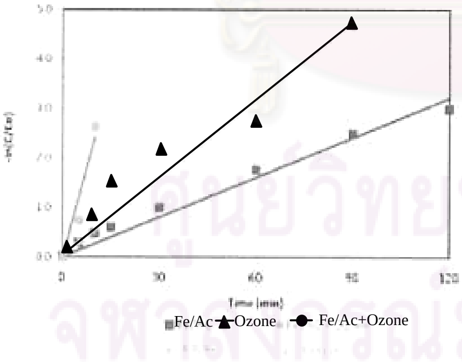

Fig. 5 Decomposition rate of phenol

## 4. Conclusions

Oxidation of phenol by a lab scale three-phase fluidized bed reactor using Fe on activated carbon catalyst and/or ozone has been examined. The conclusions obtained as follow

1. The phenolic degradation using only Fe/Ac gave the worst result.
2. The phenolic degradation using Fe/Ac enhanced with $O_3$ provides the best result.
3. Treating phenol, effect of adsorption by Fe/Ac is weaker than effect of oxidation reaction by $O_3$.

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# APPENDIX B

## CALCULATION OF THE HYDRODYNAMICS

In chapter V, there are mentioned about the hydrodynamic of three-phase fluidized bed reactor. According to the relations in chapter V, minimum fluidization velocity was preliminary calculated by using the physical properties which measured in this work. These properties and results from calculation are shown in below table.

**Table B.1** Hydrodynamics data of lab-scale experiment

**Lab-scale**

| Properties | symbol | Value | SI unit | Remark |
|---|---|---|---|---|
| Density of liquid | $r_L$ | 1000 | $kg/m^3$ | |
| Viscousity of liquid | $m_L$ | 0.001 | kg/m.s | |
| Density of wet particle | $r_S$ | 1330 | $kg/m^3$ | |
| Diameter of particle | $d_p$ | 0.0006 | m | |
| Density of ozone | $r_G$ | 1.2 | $kg/m^3$ | |
| Gravitional acceleration | g | 9.8 | m/s | |
| Flow rate of gas | $F_G$ | 0.000017 | $m^3/s$ | 1 L/min |
| Flow rate of liquid | $F_L$ | 0.000017 | $m^3/s$ | 1 L/min |
| Diameter of reactor | $D_R$ | 0.0316 | m | |
| Cross section area of reactor | $A_R$ | 0.000784 | $m^2$ | |

| Calculation | symbol | Value | SI unit |
|---|---|---|---|
| Superficial gas velocity | $U_G$ | 0.02126 | m/s |
| Superficial liquid velocity | $U_L$ | 0.02126 | m/s |
| Archimedes number | Ar | 698.544 | - |
| Minimum fluidization velocity of liquid | $U_{mf,LS}$ | 0.00070 | m/s |
| Minimum fluidization velocity | $U_{mf}$ | 0.000424 | m/s |

# APPENDIX C

# CALIBRATION CURVE FOR HPLC

## Phenol

**Table C.1** The peak area data of phenol from HPLC

| Concentration (ppm) | Peak area |
|---|---|
| 20 | 122487 |
| 40 | 242991 |
| 60 | 358838 |
| 80 | 472311 |
| 100 | 593542 |

Cal range: 0 – 100 ppm

Method: 75% water / 25% acitonitrile at 254 nm UV-Vis

Linear fit: C (ppm) = a (Peak area) + b

a = 0.000168134

b = 0

Goodness of fit: $r^2$ = 0.999604

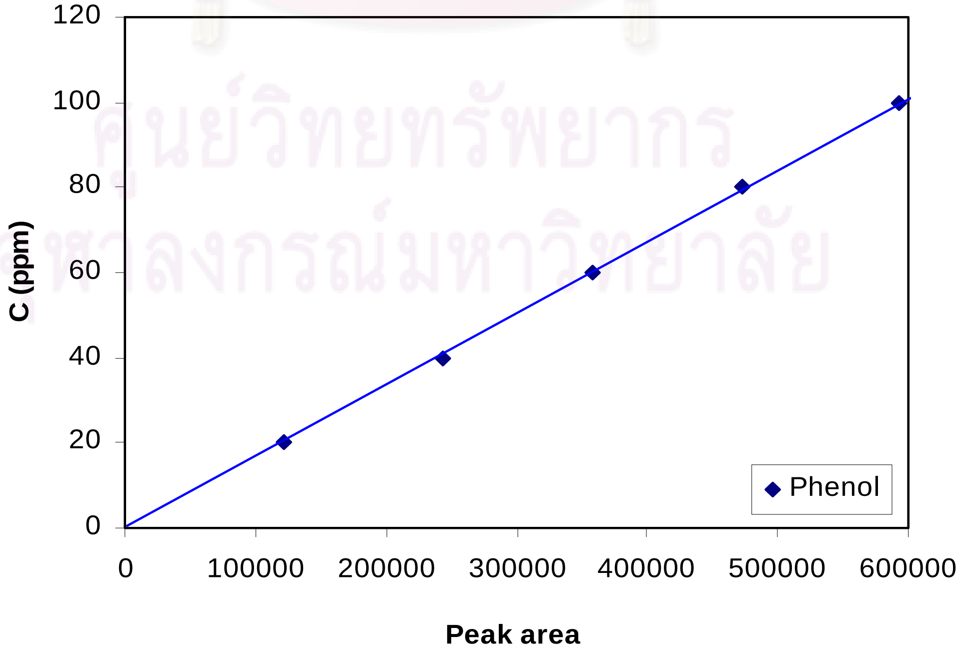

**Figure D.1** The calibration curve of phenol

# VITA

Miss Pilasinee Limsuwan was born on January 10, 1984 in Bangkok, Thailand. She studied in primary and secondary educations at Samsen Wittayalai School. In 2006, she received the Bachelor Degree of Chemical Engineering from Faculty of Engineering, Burapha University. She continued her Master’s study at Chulalongkorn University in September 2008.