

ZEOLITE-SUPPORTED TRANSITION METAL CATALYSTS TO ENHANCE
THE OZONATION OF AQUEOUS PHENOL

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THE OZONATION OF AQUEOUS PHENOL

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*To my beloved mother, father, sister and Waheguru
for their love and support*

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ABSTRACT

In this research, zeolite HZSM-5, H- β , H-Mordenite and H-USY were used to evaluate the aqueous phenol and its corresponding chemical oxygen demand (COD) removals in a semi-continuous ozonation system. Screening for the best zeolite was held at different levels of phenol concentration (100 to 3340 ppm), temperature (30 to 70°C), ozonated air flow rate (0.5 to 1.5 L/min) and pH (5 to 9). The phenol adsorption tests were also performed. Results revealed that the presence of zeolites, except H-Mordenite, induced better results in terms of phenol and COD removals than ozonation alone. HZSM-5 (80) and H-USY were the most promising zeolites to treat phenol less and above 750 ppm of phenol, respectively. HZSM-5 (80) and H-USY were also found to be the best phenol adsorbents at 100 and 3340 ppm phenol, respectively. Effect of variables showed that the removal of phenol is almost independent of temperature at 100 ppm phenol, but very much affected by the ozonated air flow rate and pH at both the concentration levels. The study on HZSM-5 (80) was sustained by impregnating transition metals (Ti, Mn, Fe and Cu) onto it to improve its activity in ozonation of phenol. Based on the results obtained, a 2 wt.% Mn/HZSM-5 is the most promising catalyst with phenol and COD removals of 95.78% and 70.17%, respectively in two hours. In addition, ozonation tests were also carried out using GAC and alumina in order to compare the effectiveness of phenol treatment with different groups of catalysts. The tests with alumina indicated that although it inherits a poor adsorption capacity, its activity was tremendously enhanced in the presence of ozone. Whereas, for GAC, its combination with ozone for phenol treatment produced a more significant improvement with total phenol elimination and a more complete COD removal in two hours of treatment compared to alumina, HZSM-5 (80) and Mn/HZSM-5. In all the ozonation systems tested, adsorption of phenol by the zeolites and GAC was observed to play a vital role in determining their activity in phenol and COD removals.

ABSTRAK

Kesan kehadiran zeolit HZSM-5, H- β , H-Mordenite dan H-USY terhadap penyingkiran fenol and COD dalam ujikaji pengozonan telah dijalankan. Zeolit yang paling sesuai dipilih berdasarkan keberkesanannya merawat fenol pada kepekatan (100 -3340 ppm), suhu (30-70°C), kadar alir gas (0.5-1.5 L/min) dan pH (5 hingga 9) yang berbeza. Ujikaji penjerapan fenol ke atas zeolit juga dijalankan. Hasil yang diperolehi membuktikan bahawa kehadiran zeolit, kecuali H-Mordenite, menyingkirkan lebih banyak fenol and COD berbanding dengan kehadiran ozon sahaja. HZSM-5 (80) merupakan zeolit yang paling efektif untuk merawat fenol yang berkepekatan kurang daripada 750 ppm, manakala zeolit H-USY pula memberikan peratusan penyingkiran yang paling berkesan pada kepekatan melebihi 750 ppm. HZSM-5 (80) dan H-USY juga merupakan penjerap terbaik, masing-masing pada kepekatan 100 dan 3340 ppm. Penyingkiran fenol dan COD didapati kurang bergantung kepada suhu pada kepekatan 100 ppm, tetapi sangat dipengaruhi oleh kadar alir gas and pH pada kedua-dua kepekatan tersebut. Kajian lanjut melibatkan peningkatan aktiviti HZSM-5 (80) dengan memuatkan logam peralihan besi, titanium, kuprum dan mangan ke atasnya. 2 wt.% Mn/HZSM-5 didapati mangkin yang paling sesuai. Ia berjaya menyingkirkan fenol dan COD sebanyak 95.78% dan 70.17% dalam masa dua jam. Sebagai perbandingan dengan kumpulan mangkin yang lain, pengozonan juga dijalankan menggunakan GAC dan alumina. Alumina didapati tidak efektif menjerap fenol tetapi penambahan ozon meningkatkan penyingkiran fenol and COD secara mendadak. Walaubagaimanapun, pengozonan dengan GAC menyumbang kepada 100% penyingkiran fenol serta penyingkiran COD yang lebih lengkap berbanding alumina, HZSM-5 (80) dan Mn/H-ZSM-5. Hasil kesemua ujikaji pengozonan menjelaskan bahawa penjerapan fenol ke atas permukaan zeolit dan GAC adalah faktor penting yang mempengaruhi keberkesanannya untuk menyingkirkan fenol dan COD dalam larutan.

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LIST OF SYMBOLS

\AA	-	Armstrong
A_{cs}	-	The molecular cross-sectional area of the adsorbate molecule
C	-	BET constant
d	-	Distance
k	-	Reaction rate constant
MW	-	Molecular weight
N	-	The Avogadro's number (6.023×10^{23} molecules/mole) or total number of species in the system or the total number of observation
n	-	Total number of moles
P	-	Pressure
P_o	-	Saturation vapor pressure
pH_{PZC}	-	pH at which the surface charge of an oxide is neutral or zero
t	-	pore radius
t	-	time
W	-	Weight of gas adsorbate
W_m	-	Weight of adsorbate constituting a monolayer of surface coverage
wt.	-	Weight
X	-	Fraction of metal in zeolite
β	-	Beta
λ	-	Wave number
ρ	-	Density
θ	-	Angle
ΔH_f	-	Heat of formation

LIST OF ABBREVIATIONS

AOPs	-	Advanced oxidation processes
BET	-	Brunauer, Emmett and Teller
BOD	-	Biochemical oxygen demand
COD	-	Chemical oxygen demand
DO	-	Dissolved oxygen
DOE	-	department of Environment
FT-IR	-	Fourier transform infrared spectra
GAC	-	Granular activated carbon
LTA	-	Linde type A
PCB	-	Polychlorinated biphenyls
SEM	-	Scanning electron microscopy
TCD	-	Thermal conductivity detector
TPD	-	Temperature programmed desorption
TPR	-	Temperature programmed reduction
USY	-	Ultra stable Y
UV	-	Ultraviolet
XRD	-	X-Ray diffraction
ZSM-5	-	Zeolite Socony Mobil Five

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CHAPTER 1

INTRODUCTION

1.1 Introduction: Water and Its Scenario

Water is an essential living source. It is worth more than gold and necessary for survival above all other resources on earth. Without water, crops and livestock wither and die. People go hungry and become weak and weakness allows disease to run its course.

In natural ecosystems, nature prevents water pollution by recycling materials at approximately the same rate at which they are produced. In the past, our streams, lakes and oceans were a convenient place to intentionally dispose of undesirable materials produced by humans such as industrial wastes and human excrement. It was originally thought that these waters would magically eliminate these undesirables via the process of dilution. Unfortunately, the result of dumping these untreated wastes into our aquatic ecosystems has increased the risk of human disease and death of aquatic life.

In Malaysia, the water quality status of river basins indicated that 50% were clean, 39% were slightly polluted and 11% were polluted (DOE, 2001). The status of groundwater quality was also benchmarked against the National Guidelines for Drinking Water. Components such as iron, phenol, manganese, arsenic, chloride, nitrate and selenium were found to exceed the guideline's values (Chen, 2001). Figure 1.1 shows the river basin water quality of Malaysia from the year 1990 to

2000. According to the figure, the number of slightly polluted and polluted rivers in Malaysia has increased within the 10 years, although there have been some years where the water quality improved.

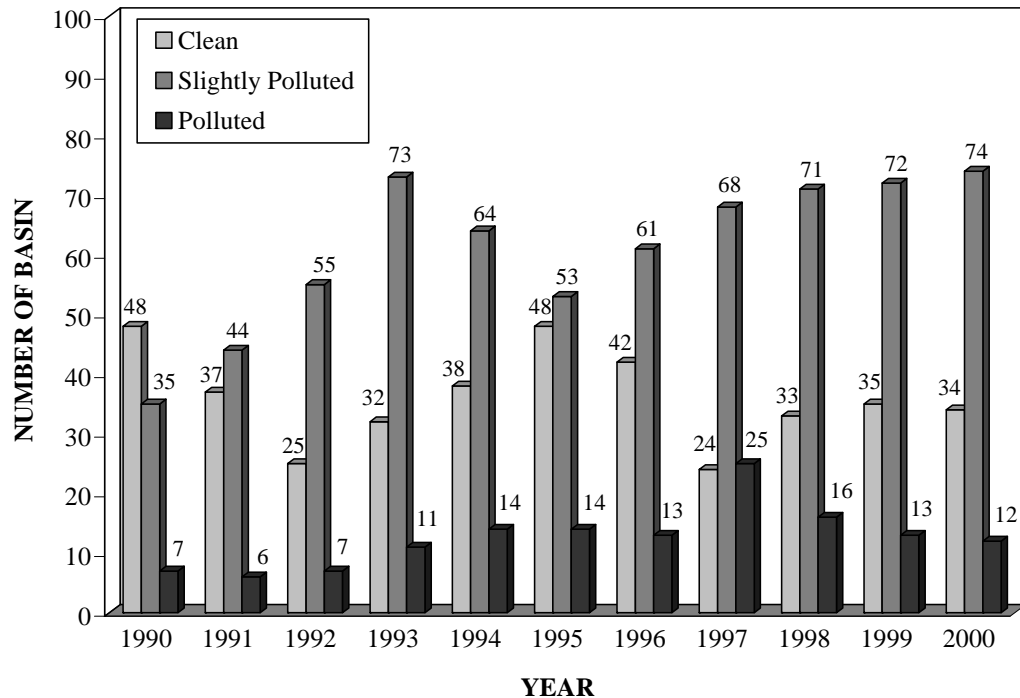


Figure 1.1 Malaysia river basin water quality for the year 1990 – 2000 (Zulkifli, 2002)

A drastic population growth and an increase in industrial and farming activities have led to an elevated demand for safe and clean water. According to the year 2000 census, the total population growth in Malaysia was 23.27 million compared to 18.38 million in 1991, thus giving an average annual population growth rate of 2.6% over the 1991-2000 periods. However, safe and clean water is more difficult to obtain due to limited natural water resources and continuous water pollution phenomena caused by natural and human activities.

Figure 1.2 shows the sources of water pollution in Malaysia. Domestic sewage and pig farms contribute to the largest percentage of water pollution which is 81.7% and 15.7% respectively, followed by the manufacturing and agro-based industries.

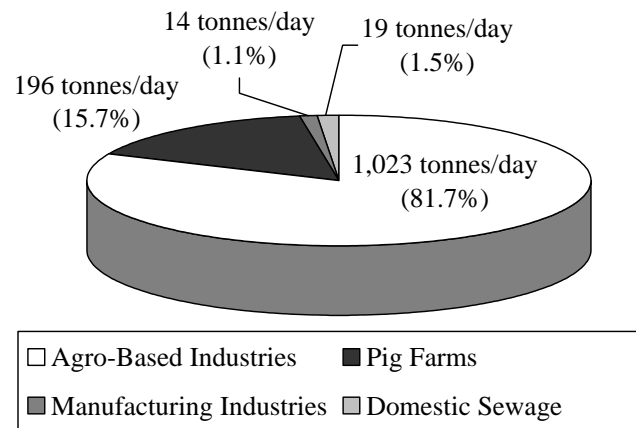


Figure 1.2 Sources of water pollution in Malaysia (Zulkifli, 2002)

Besides, the presence of toxic and non-biodegradable long or heavy chain organic components in the industrial effluent stream, especially in the chemical based industry has resulted to serious water pollution problem. The major toxic organic chemicals of concern are herbicides, pesticides, phenolic compounds and polychlorinated biphenyls (PCB) (Mustafa, 1999; Manahan 2001). They do not only endanger aquatic life by lowering the oxygen demand but also cause acute problems to human health. Thereby, urban citizens are more prone to diseases caused by water than citizens in rural areas. Table 1.1 summarizes the organic pollutants formed by different industrial processes.

Table 1.1 : Types of pollutants generated based on industry (Shineldecker, 1992)

Potential Pollutants	Type of Industry												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Proteins	■	■	■	■									■
Carbohydrates	■	■	■		■	■							■
Fats and Oils	■	■	■	■			■		■	■	■	■	■
Dyestuff			■	■	■	■							
Organic Acids						■							■
Phenols			■			■	■	■	■	■	■		
Detergents	■		■									■	■
Organo-pesticides		■											■

* Types are as follow:

- | | | |
|--------------------|--------------------------------|------------------------|
| 1. Dairying | 6. General chemical production | 11. Metallurgy |
| 2. Food processing | 7. Petrochemical production | 12. Laundry processing |
| 3. Textiles | 8. Coking ovens | 13. Agriculture |
| 4. Tanning | 9. Industrial oil production | |
| 5. Paper making | 10. Engineering | |

Realizing the hazards of water pollution to earth and mankind, regulations concerning waste disposal have been enforced worldwide. These regulations are reviewed within a certain time frame for updates on numerous types of pollutants. Increase concern over waterborne diseases caused by water pollution have led the governments in all countries to enforce much more strict and stringent regulations that cover a much broader range of contaminants for wastewater discharge.

Consequently, wastewater reuse has become an attractive option for protecting the environment and extending available water resources (Xu *et al.*, 2002). This is to help minimize water pollution caused by the industries and other activities to safeguard other fresh water supply. The safe operation of water reuse systems however depends on the reliability of wastewater treatment and disinfection techniques. This is particularly important for public health protection.

The conventional water and wastewater treatment processes consist of biological or physical-chemical processes which include activated sludge, filtration, coagulation or flocculation and adsorption. These are the most common technologies employed to remove natural or synthetic organic pollutants from water (Guzella *et al.*, 2002).

Biological treatment is the prime unit in wastewater treatment facilities. Here, the removal of organic pollutants takes place. Experiences from the industries highlight that biological treatment currently used is ineffective for the removals of biorefractory organic pollutants (Pillay and Mohd. Zaharon, 2003) resulting into a discharge quality that does not comply with the regulation standards. Furthermore, use of chlorine as a disinfectant in water has extended the problem by generating highly toxic and harmful organochlorinated byproducts such as trihalomethanes (THM) (Legube and Leitner, 1999; Gracia *et al.*, 2000; Buleandra *et. al.*, 2001; Xu *et al.*, 2002).

Therefore, in recent years, new technologies emerge for use not only in the areas at risk, such as the industrial wastewater, but also for safe drinking water production. Some of the emerging technologies that hold great promise to provide alternatives for better protection of public health and the environment are membrane

filtration, advanced oxidation processes (AOPs) and UV irradiation (Zhou and Smith, 2002).

Ozonation of water or wastewater is a well-known technology in water treatment for the removal of organic pollutants and disinfection. Its strong oxidative properties have been well documented. The first use of ozone for water sterilization was in 1893, when Schnelllar, Vander Sleen and Tindal constructed an industrial apparatus at Oudshoorn in Holland for the sterilization of Rhine water after sedimentation and filtration (Evans III, 1972).

The oxidation processes involving hydroxyl radical have also shown their potential to destroy toxic organic compounds in wastewater. These processes are called the advanced oxidation processes (AOPs). They are the combination of ozone with other oxidant agents such as hydrogen peroxide (H_2O_2), ultraviolet (UV) radiation and also various types of catalysts (Esplugas *et al.*, 2002). They allow oxidation of dissolved organic compounds that are commonly refractory to the direct attack of ozone (Kusakabe *et al.*, 1990).

Lately, AOPs have gained researchers great attention due to its non-selective characteristics. Many researches have been conducted to study the effect and feasibility of these processes on different types of wastewaters (Beltrán *et al.*, 1999a,b; Legube and Leitner, 1999; Gracia *et al.*, 2000; Guzzella *et al.*, 2002). These researches have shown overwhelming results, thus they are being developed to achieve remarkable acceptance in various industries.

Investigation of catalytic ozonation processes, which are most commonly catalysed by transition metals have received tremendous attention for organic degradation. Catalytic ozonation may take place homogeneously or heterogeneously. Numerous metals (Fe, Mn, Ni, Co, Mn, Ag, Cr) under various forms (salts, solid oxide and deposited metal on support) were reported to enhance the efficiency of ozone towards the removal of different organic compounds in aqueous solution through oxidation (Legube and Leitner, 1999).

Compared to the homogeneous catalysis, the heterogeneous catalysis provides a better alternative in terms of catalyst recovery. Heterogeneous catalysts used may be metal oxides such as titanium dioxide (TiO_2) or manganese dioxide (MnO_2) (Villaseñor *et al.*, 2002). In addition, supports may also be used to increase the treatment efficiency (Cooper and Burch, 1999b; Beltrán *et al.*, 2004) and accommodate some transition metals such as copper (Cu) (Qu *et al.*, 2004). The most commonly used support in this process is alumina (Al_2O_3) (Legube and Leitner, 1999; Beltrán *et al.*, 2004; Qu *et al.*, 2004). Besides, molecular sieves such as silica and natural or synthetic zeolites are also believed to have reasonable catalytic and adsorptivity effect in organic removal from aqueous solution (Marcus and Cormier, 1999).

Fajerweg and Debellefontaine (1996), Phu *et al.* (2001) and Durgakumari *et al.* (2002) from their research concluded that ZSM-5, which is a zeolite, can be used with another oxidizing agent such as hydrogen peroxide or UV to degrade organics as an adsorbent or support without losing its activity after several treatments. Other zeolites such as β , Y, A, Mordenite and Clinoptilolite can also be used for treatment.

Therefore, this study is carried out realizing the significant improvement this new technology can bring to the environment and also due to the urgent demand from industries for clean, efficient and economical wastewater treatment.

1.2 Problem Statement

The use of conventional water and wastewater treatment processes has become increasingly challenged with the identification of more and more contaminants, rapid growth in population and industrial activities and the diminishing availability of water resources (Zhou and Smith, 2002).

The contaminants in the wastewater, organics and inorganics, are many and continuously vary (Kirk *et al.*, 1972). Lately, concerns are raised regarding the presence of phenolic compounds in industrial waste streams. Phenols are toxic

organic compounds that may cause harmful effects to water consumers if present at high level. Regulations have set a discharge quality of 0.001 and 1.0 mg/l for Standard A and Standard B type of industry respectively (MDC, 2000). However, Chen (2001) reported that presence of phenol in water exceeds the guideline's value.

From various researches carried out, the catalytic ozonation process is potentially a promising treatment technique to remove persistent organic pollutants in wastewater (Hordern *et al.*, 2003). The catalysts used can be of many types of nature such as various transition metal salt and oxides, activated carbons, silica or alumina. Transition metal salts such as Fe and Cu or their oxides such as MnO₂ and TiO₂ are the most commonly used catalyst (shown later in Tables 2.6 and 2.7). However, many findings focus either one catalyst or organic compound and the reaction conditions greatly differ from one another.

Currently, supported catalysts are employed to advance the process efficiency. Focus is drawn into zeolite based supports, particularly high silica zeolites. This is due to their unique properties compared to other materials (Marcus and Cormier, 1999) and their capability to act as an adsorbent for additional cleavage (Hordern *et al.*, 2003).

At present, Fujita and co-workers (2004a,b) have evaluated the effectiveness of zeolite ZSM-5, Mordenite and USY, with different sets of SiO₂/Al₂O₃ ratios for each of the zeolite, to adsorb ozone and treat trichloroethene (TCE). In their study, they demonstrated that high silica zeolite (ZSM-5) is the most promising material for adsorption of water-dissolved ozone and decomposition of TCE. Nevertheless, the types of zeolite material and the relevant operating conditions for treatment of various other organic compounds are still not well established.

Therefore, this study is undertaken to study the effects of various types of potential transition metal catalytic materials loaded onto zeolite based support to enhance the ozonation of phenol. Types of zeolitic supports are many. Therefore, screening of a suitable zeolite support is initially required.

1.3 Objectives of the Study

Ozonation of water for organic removal and disinfection is a well established technology for better water quality overseas. Combination of another material such as an additional oxidising agent or adsorbent can assist in higher persistent organic removal in wastewaters through the generation of highly reactive hydroxyl radicals.

Transition metals are good catalytic materials in organic oxidation reactions due to their presence in oxidation states. Zeolites, whereas, are large surface area inorganic material that inherit good adsorption capability. Besides, from the experiences in other processes, it is discovered that variables such as temperature, pH, ozonated gas flow rate and amount of metal content in the catalyst may have significant effects to a certain extent in the process (Andreozzi *et al.*, 1992,1996; Beltrán *et al.*, 2002).

Therefore, this study is undertaken with the following objectives:

- i. To compare the reducibility of aqueous phenol in a non-catalytic and catalytic ozonation system.
- ii. To compare the effectiveness of high silica zeolite (HZSM-5) against other zeolites (H- β , H-Mordenite and H-USY) in the ozonation of phenol and screen for the best zeolite.
- iii. To screen for the best transition metal catalysts among Ti, Mn, Fe and Cu), which are loaded on the best zeolite.
- iv. To investigate and compare the effectiveness of ozonation of phenol treatment using GAC and alumina as catalyst against zeolites and metal/zeolite.

1.4 Scopes of the Study

Firstly, the development of an appropriate experimental rig and procedures for the process are decided.

Then, the screening tests of zeolites are conducted at different levels of phenol concentration, temperature, ozonated air flow rate and pH with other variables kept constant during the tests. Phenol adsorption tests are also carried out. The effectiveness of all the ozonation tests is compared based on phenol and COD removals achieved after each test. Then, the best zeolite is determined. The zeolites used in this process are also characterized with XRD, FT-IR and N₂ adsorption to determine their properties and to study the significance of these properties in the ozonation of phenol.

After the screening of zeolites, the zeolite that gives the best results for phenol removal is utilized as a support to study the effect of different transition metals (Ti, Fe, Mn and Cu) as catalyst. The metals are loaded at 5wt.% onto the best zeolite via the dry impregnation technique and characterized with TPR-H₂. The effectiveness of ozonation of phenol with different metal/zeolite catalysts and zeolite is then compared and the best metal/zeolite catalyst is determined. Tests are also conducted to identify the most promising metal amount that can be loaded onto the zeolite before its activity falls.

Finally, ozonation tests are conducted with GAC and alumina. Then, the removals of phenol and COD achieved by the zeolitic and non-zeolitic catalytic ozonation are compared. Figure 1.3 illustrates the generalized scopes involved in this research.

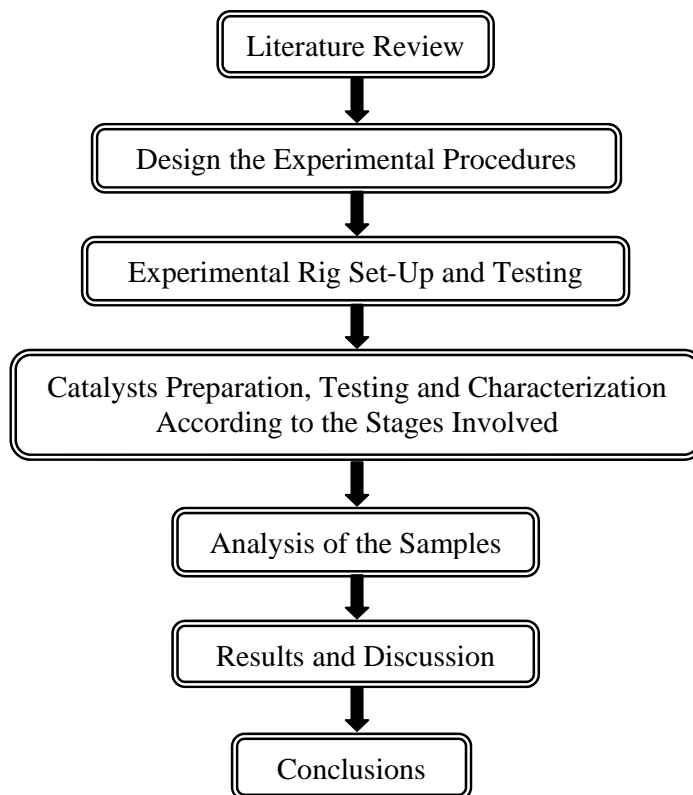


Figure 1.3 The scopes of the research

1.5 Organization of the Thesis: A Synopsis

This thesis consists of seven chapters. In Chapter 1, the research background, problem statement, objectives and scope of the study are described.

Chapter 2 gives the detailed literature survey concerning the main elements involved in this study as well as researches involved in this area.

Chapter 3 discusses the experimental procedures such as the experimental rig set-up, catalyst preparation, characterization and testing methods and the analytical procedures involved to evaluate the efficiency of the treatment in this study.

In Chapter 4, the results obtained for all zeolites in the phenol ozonation and adsorption tests are presented and discussed. The effectiveness of phenol ozonation

with different zeolites is compared and the zeolite that gives the highest phenol and COD removals in the ozonated system is identified. The possible factors that determine the activity of the best zeolite are also discussed. From the study, HZSM-5 (80), which is the best zeolite, is chosen for further study.

In Chapter 5, results obtained from ozonation of phenol with different metal/zeolites catalysts are presented. Initially, 5 wt.% metal/zeolite catalysts are screened and the catalyst that gives the highest phenol and COD removals is chosen to study the influence of different metal contents on the treatment efficiency.

Chapter 6 presents the results and their respective discussions obtained for catalytic ozonation of phenol using different groups of catalytic materials. The catalysts tested are GAC and alumina. The results obtained in this stage are then compared with the results obtained by the best zeolite and metal/zeolite. The most suitable catalyst with reasonably high phenol and COD removals is then decided.

Chapter 7 is the final chapter that answers the objectives of this research and concludes the findings of each chapter. Recommendations and suggestions for future work in assurance of successful continuation of this research are also suggested.

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