

DEGRADATION OF PHENOL BY A CATALYTIC OZONATION

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To my beloved mother and father

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ABSTRACT

Screening on the catalytic ozonation of phenol over zeolite-based catalyst i.e Beta and ZSM-5 was investigated under room temperature condition using a semi continuous system. The degree of degradation of 100ppm of phenol was measured on the treated samples. The results showed that the performance of Beta was better than ZSM-5 with the degradation of phenol of 67.4 and 49.0%, respectively after 90 minutes of reaction time. In addition, the degradation of phenol was higher in the presence of both catalysts compared to without any catalyst. Further screening of beta catalyst impregnated with ferum and titanium showed that the degradation of phenol was slightly increased with the presence of Fe-beta compared to Ti-beta catalyst. Thus, Fe-beta was furthered subjected to different experimental variables such as ozone gas flow rate, temperature and pH of phenol solution, mass and metal weight percent impregnated in the catalyst, concentration and the volume of phenol to be treated. It was observed that a smaller percentage of metal loading catalyst resulted a higher degradation compared to those with higher metal loading catalyst. As expected, the degradation of phenol increases with ozone flow rates and mass of catalyst. Interestingly, the degradation of phenol was significantly high under basic condition where the degradation was almost complete i.e 98.1% at initial pH 11. On the contrary, the degradation of phenol decreases with increasing temperature, concentration and volume of phenol solution.

ABSTRAK

Proses pengozonan telah dilakukan ke atas air sisa fenol dengan menggunakan mangkin zeolite i.e Beta dan ZSM-5 pada keadaan suhu bilik dan 'semi-continuous reactor'. Kadar degradasi fenol yang berkepekatan 100ppm telah dikaji ke atas sampel yang telah dirawat. Mangkin Beta menunjukkan keputusan yang terbaik berbanding ZSM-5 dengan mencapai degradasi fenol sebanyak masing-masing 67.4 dan 49.0% selepas tindak balas selama 90 minit. Tambahan pula, degradasi fenol adalah tinggi dengan kehadiran kedua-dua mangkin tersebut berbanding dengan pengozonan tanpa mangkin. Seterusnya, pengubahsuaian mangkin Beta dengan logam ferum dan titanium menunjukkan degradasi fenol meningkat dengan kehadiran mangkin Fe-Beta berbanding dengan mangkin Ti-Beta. Oleh yang demikian, mangkin Fe-Beta telah dipilih untuk eksperimen seterusnya yang menguji kecekapannya dari segi beberapa parameter seperti kadaralir ozon, suhu dan pH air fenol, jisim mangkin dan kandungan ferum dalam mangkin, kepekatan dan isipadu fenol yang diuji. Keputusan, mendapati hanya sedikit amaun ferum sahaja yang diperlukan bagi meningkatkan degradasi fenol berbanding dengan peratus kandungan ferum yang lebih tinggi. Seperti yang dijangkakan, degradasi fenol meningkat dengan kadaralir ozon dan jisim mangkin yang digunakan dalam process pengozonan. Degradasi fenol meningkat secara mendadak dalam keadaan bes dimana degradasi fenol mencapai sebanyak 98.1% pada pH 11. Sebaliknya, degradasi fenol menurun dengan meninggikan suhu, kepekatan dan isipadu air fenol.

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CHAPTER 1

INTRODUCTION AND OVERVIEW

1.1 Introduction

Water is an essential ingredient to a healthy lifestyle. Doctors recommend we drink 6-8 glasses of water per day for optimum health, but this is often difficult when you don't like the taste or odor of your water, or are concerned about the quality of your drinking water.

Next to air, water is the substance most necessary for human existence. Practically every living cell in the body depends on water to carry out essential functions. Sufficient amounts of water in the body can increase energy and endurance, help in body weight control, aid digestion and elimination, lubricate joints, and encourage a feeling of well being. It is not difficult to understand why drinking enough water is so extremely important when we realize that nearly 70% of the body's weight is made up of water.

Water is so important that a minute reduction of body water (4-5%) will result in a decline of 20-30% in work performance. Breathing, digestion, elimination,

glandular activities and heat dissipation can be performed only in the presence of water. This combined with the role of water in dissolving the body's waste products and flushing out toxins explains why we cannot survive very long without adequate amounts of water.

It makes common sense that with all the important functions that water has in the body, the quality of water you drink can radically affect your health and well being. That is why it is vitally important that you drink only pure water.

Water pollution occurs when a body of water is adversely affected due to the addition of large amounts of material to the water. When it is unfit for its intended use, water is considered polluted. Two type water pollutants exists ie point source and non point source. Point source of pollution occurs when harmful substances are emitted directly into a body of water. A non point source delivers pollutants indirectly through environmental changes. An example of this type of water pollution is when fertilizer from a field is carried out into a stream by rain, in the form of run-off, which in turn affects aquatic life.

Generally, there was compiled ten categories have been defined by EPA as major contributors of water pollution:

- 1 Industrial, including pulp and paper mills, chemical manufactures and food processing plants
- 2 Municipal, including publicly owned sewage treatment works that may receive indirect discharges from small factories or businesses
- 3 Combined sewers, including storm and sanitary sewers that, when combined, may discharged untreated wastes during storms
- 4 Storm sewers and runoff, including runoff from streets, paved area and lawns that enters a sewer, pipe or ditch
- 5 Agricultural, including crop production, pastures, rangeland or feedlots
- 6 Silvicultural, including forest management, harvesting and road contraction

- 7 Construction, including highway building and land development
- 8 Resource extraction, including mining, petroleum drilling and runoff from mine –tailing sites
- 9 Land disposal, including leach ate or discharge from septic tanks, landfills, hazardous-waste disposal sites
- 10 Hydrologic, including channelization, dredging, dam construction and stream-bank modification.

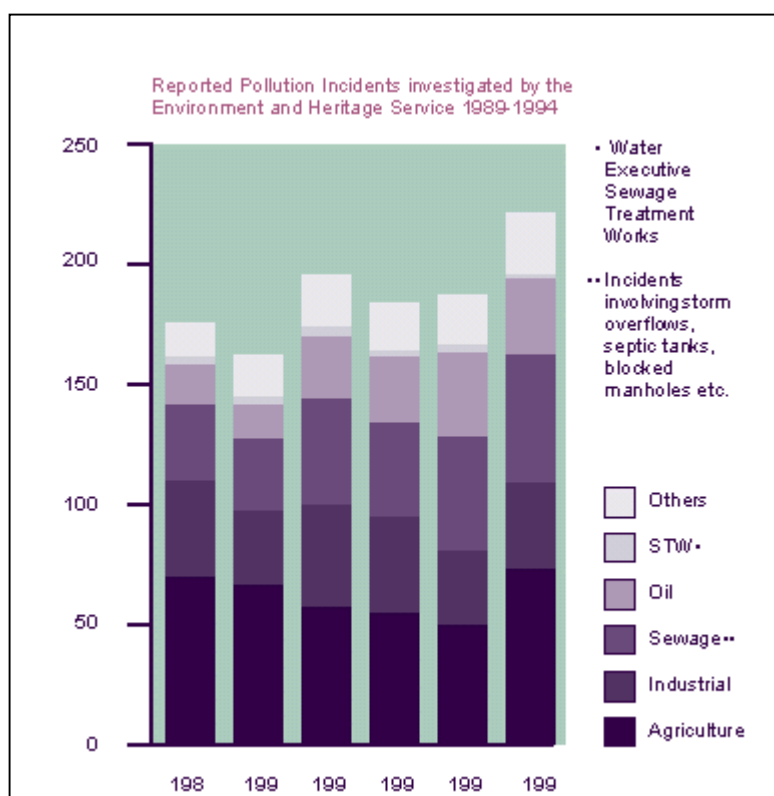


Figure 1.1: Reported pollution incidents investigation by the Environment and heritage service 1989 – 1994.

Figure 1.1 shows that the agriculture, industry and sewage are contributed a large amount of pollutants. Many causes of pollution including sewage, fertilizer, textile, oleo chemicals contain nutrients such as nitrates, phenol, phosphates. In excess levels, nutrients over stimulate the growth of aquatic plants and algae. Excessive growth of this type of organisms consequently clogs the waterways, use up dissolved oxygen as they decompose, and block light deeper waters. This, in turn, proves very harmful to aquatic organisms as it affects the respiration ability of fish

and other invertebrates that reside in water. The major sources of water pollution can be classified as municipal, industrial and agricultural (Figure 1). Municipal water pollution consists of waste from homes and commercial establishments. For many years, the main goal of treating municipal wastewater was simply to reduce its content of suspended solids, oxygen demanding materials, dissolved inorganic compounds, and harmful bacteria. The basic method of treating municipal wastewater fall into three stages and they are primary, secondary and tertiary treatment

In primary treatment some process are carried out including grit removal, screening, grinding and sedimentation. Secondary treatment, which entails oxidation of dissolved organic matter by means of biologically active sludge, which is then filtered off and tertiary treatment, in which advanced biological methods such as granular filtration and activated carbon adsorption are employed.

In recent year, the application of oxidizing chemicals in the treatment of drinking water and wastewater continues to be an active topic of scientific research and an interest to water utility practitioners. Thus, considerable attention has been paid to the study of chlorine dioxide, potassium permanganate, ozone, ozone/H₂O₂ and UV/ H₂O₂. Ozone, due to its high oxidation and disinfection potential, has recently received much attention in water treatment in water treatment technology. It is applied in order to improve taste and color as well as to remove the organic and inorganic compounds in water. Ozonation has been a treatment method widely used for tackling various industrial wastewaters. Many researches have been conducted to study the effects of ozone on different type of wastewater (Esplugas *et al.*, 2002; He *et al.*, unknown; Wu *et al.*, 2000; Stockinger *et al.*, 1996; Oquz *et al.*, 2005).

Recently catalytic ozonation has been attracting the interest of the scientific community dedicated to the study of ozone processes in water treatment. Catalytic ozonation was found to be effective for the removal of several organic compounds from drinking water and wastewater (Canton *et al.*, 2003; Phu *et al.*, 2001; Gimeno

et al., 2005; Einaga *et al.*, 2004; Andreozzi *et al.*, 1998; Ma and Graham., 2000 and Qu *et al.*, 2004). Catalytic ozonation can be considered firstly as homogeneous catalytic ozonation, which is based on ozone activation by metal ions present in aqueous solution, and secondly as heterogeneous catalytic ozonation in the presence of metal oxides or metals/metal oxides on supports.

The aim of the work is to study the effectiveness of degradation of phenol using catalytic ozonation with zeolite-based catalyst. Two different types of zeolite catalysts i.e zeolite beta and ZSM-5 and ferum and titanium as transition metal were investigated in the study. As a comparison, ozonation of phenol solution without catalyst was also carried out in this study. In addition, the influences of various variables also were studied in this study.

1.2 Objectives of the Study

In general, the study is to investigate the effectiveness of catalytic ozonation on the degradation of phenol under different operating variables, such as ozone flowrate, temperature and pH of phenol solution, mass and metal weight % in the catalyst, concentration and the volume of phenol treated. The main objectives of the study were:

1. To study the performance of zeolite beta and ZSM-5 in catalytic ozonation treatment of phenol.
2. To study the performance of modified zeolite catalyst impregnated with titanium and ferum in catalytic ozonation of phenol, and
3. To identify the best operating conditions of the selected metal-based zeolite catalyst in catalytic ozonation of phenol.

1.3 Scopes of Work

The study is to investigate the performance of zeolite-based catalyst in catalytic ozonation of phenol. The catalytic ozonation of the zeolite-based catalysts was investigated under same operating conditions and the effectiveness of each of the catalyst was observed. The best performed zeolite-based catalysts either Beta or ZSM-5, was selected and modified with metals to check on its performance on the degradation of phenol in the following experiments.

The selected zeolite-based catalyst was modified with metals i.e ferum and titanium, by impregnation method. The catalytic ozonation of the metal-based zeolite catalysts was tested on 100 and 1600ppm of phenol solution and their respective performance on degradation of phenol was observed for a total period of 90 minutes. The best-performed metal-based zeolite catalyst was chosen from the study for further experiments.

The performance of the selected metal-based zeolite catalyst was further investigated under different experimental variables such as ozone flow rate, temperature and initial pH of phenol solution, mass and metal weight percent impregnated in the catalyst, concentration and the volume of phenol to be treated where finally, the best operating conditions on the degradation of phenol was identified. The degradation of phenol in the study was determined using HPLC method. In addition, the degree of degradation was also determined indirectly through Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) of the samples.

1.4 The Importance of the Study

To date, research on the application of zeolite-based catalyst on treating of organic substances in wastewater is well known. ZSM-5 and Beta are two commonly used zeolite-based catalysts in wastewater treatment. However, a comparative performance study between in these two catalysts on the degradation of phenol solution is not available in literature. Thus, it is aptly that such study be carried out to investigate their relative performance in degradation of phenolic solution, particularly under the influence of ozonation.

In addition, study on the performances of modified-metal-based zeolite catalyst using ferum and titanium on the degradation of phenolic compound under influence of ozonation is very limited. Therefore, the catalytic ozonation of titanium and ferum in zeolite catalyst was tested and their respective performance on degradation of phenol was investigated in the process of selecting the best-performed metal-based zeolite catalyst in this study. The selected metal-based zeolite catalyst was further subjected to various operating variables, in which the study hopes to find, if any, the best operating conditions that influence the degradation of phenol solution.

1.5 Overview of the Thesis

The thesis has been organized in five chapters. Chapter 1 presents the introduction and overview of the thesis. It described the objectives and scopes of the study. The importance of the study is also given in this chapter. It presents the reader the general contents of the thesis.

Chapter 2 presents the pertinent literatures on the ozonation and catalytic ozonation technique performed by other researchers. It presents an overview of the recent developments in catalytic ozonation processes, which acts as a basis for this study. The chapter also describes the characteristics of zeolite and phenolic solution, which present the background of the study.

Chapter 3 describes the methodology of the whole research activity involved in this study. The description of the experimental rig, the procedures of the experiments and method of analysis are presented in this chapter. The method of modifying zeolite catalyst impregnated with selected metals is also presents in this chapter. Others indirect methods for the determination of degradation using TOC and COD indicators, apart from using HPLC and the methods of characterization of the catalyst are also described in this chapter.

Chapter 4 presents the results and discussion on the degradation of phenol in catalytic ozonation treatment using both zeolite and modified metal-based zeolite catalyst. The performance of these zeolite catalysts on the degradation of phenol and the optimum operating conditions of the best-selected metal-based zeolite catalyst found in the study is present in this chapter. In addition and as a comparison, results on the ozonation of phenol solution without application of catalyst were also given in this chapter.

Finally, Chapter 5 gives the overall conclusion of the study. Suggestion for possible research work in future has been given in this chapter.

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