CHAPTER 1

INTRODUCTION

1.1 Research Motivation

The degradation of formaldehyde has attracted considerable attention due to the worldwide concern about the toxicity of this compound. Formaldehyde is frequently encountered in industrial waste-streams (pharmacy, perfumery and cosmetics, organic synthesis, manufacture of resin and colours, etc.); its concentration in wastewaters from chemical industries can be as high as 5-10 g/l (Grushko Y., 1982). Besides, it is also used in the hospital as an embalming solution at approximately 1.9 % concentration. Due to its mutagenic and carcinogenic effects (Grafstrom et al., 1985), direct discharges of those streams threaten life in the receiving water. The biological processes, which are preferably applied to treat wastewater containing organic compounds, do not always give satisfactory results, since many organic substances are resistant to biological treatment (Christoskova and Stoyanova, 2002; Mantzavinos et al., 1999). According to King Mongkut's University of Technology Thonburi's studies (Charuratana and Voranisarakul, 1993; Cheawchanthanakit and Sangphromma, 1997), it is recommended that the major factor causing the problem to wastewater treatment plants in many hospitals in Thailand, normally biological processes, is the batch discharging of chemical substances that causes the shock load of toxic chemicals of the wastewater treatment plant. Due to a large volume of discharged formaldehyde; it becomes the significant pollutant in a hospital wastewater.

The preliminary study in our research group on biodegradability of formaldehyde was conducted using sequencing batch reactor (SBR) biological treatment process (see Appendix B). The results showed that with the initial concentration of formaldehyde of 0.333 M, the SBR system has an inability in COD removal. Results also indicated that there was an accumulation of COD occurred in the system. With lower concentration of formaldehyde, 3.33×10^{-4} - 1.65×10^{-2} M, COD can be removed at the first period after the treatment had begun. Then COD was accumulated to a higher value and eventually the system had no longer capability to remove COD. While the control experiment yielded 98% in COD removal. Another parameter, suspended solid, was monitored to observe the effect of formaldehyde on the amount of microorganisms in the system. The reactors used in the experiment contained about 3,000 mg/l of suspended solid each. It is found that the suspended solid decreased rapidly if a high amount of formaldehyde was applied in the system. This finding points out the fact that formaldehyde toxicity affected the population of microorganism, which leaded to lower the efficiency of the biological system on formaldehyde removal.

Recently, chemical treatment methods known as advanced oxidation processes (AOPs) have been used for pollutant abatement due to the high oxidative power of the hydroxyl radicals ($OH^{\bullet}$), the main reactive species generated by such processes. Hydroxyl radical is a powerful oxidant and a short lived, highly reactive, and non-selective reagent that is easy to produce (Oppenländer T., 2002). The most widely know AOPs include: heterogeneous photocatalytic oxidation, H_2O_2/UV systems, Fenton, and photo-Fenton type reactions. Fenton's reagent, a mixture of hydrogen peroxide and ferrous ion, is able to destroy organic pollutants in the dark, although it may not able to mineralize organic pollutants in a short time (Kuo and Lo, 1999; Ruppert et al., 1993; Murphy et al., 1992; Pignatello J. J., 1992). Recent reports indicate that the illumination of the Fenton system (H_2O_2/Fe^{2+}/UV) can significantly enhance the mineralization of many organic compounds (Goi and Trapido, 2002).

In this study, therefore, Fenton and photo-Fenton processes were applied to investigate the oxidation of formaldehyde in aqueous phase. In addition, approximately 10 % of methanol is also added in the commercial product of formaldehyde, which to limit the extent of polymerization, most commonly sold as a 37% solution in water is called by trade names such as formalin or formol. Since methanol always exists in formaldehyde solution and may compete hydroxyl radical with formaldehyde during the oxidation reaction, methanol oxidation, as well as the competition between itself and formaldehyde, was also evaluated. Three parameters, namely initial pH, [H_2O_2], and [Fe^{2+}] were used to explore their effect on the oxidation reaction. The oxidation of formaldehyde in the presence of different methanol concentrations was also studied. Furthermore, mineralization and toxicity of the solution mixture were evaluated.

1.2 Research Objectives

The major objective of this research was to investigate the removal efficiency of formaldehyde and methanol by Fenton and photo-Fenton processes. The specific objectives are as follows.

1. To study the effect of initial pH, H_2O_2, Fe^{2+}, and CH_3OH concentrations on photodecomposition of formaldehyde and methanol.

2. To compare the oxidation efficiency of formaldehyde and methanol treated by Fenton and photo-Fenton processes.
3. To study the competition behavior between formaldehyde and methanol
4. To evaluate the mineralization of formaldehyde and methanol by Fenton and photo-Fenton processes.
5. To study the toxicity reduction of formaldehyde by Fenton and photo-Fenton processes.

1.3 Hypotheses

1. The efficiency of photo-Fenton process depends upon an initial pH and the concentrations of H_2O_2, Fe^{2+}, and CH_3OH.
2. UV-light can promote the efficiency of the Fenton process for oxidizing formaldehyde and methanol.
3. Methanol may compete with formaldehyde to consume hydroxyl radicals resulting in the retardation of the oxidation reactions.

4. Fenton and photo-Fenton processes could achieve the mineralization of formaldehyde and methanol.
5. All of the toxicity could be removed by Fenton and photo-Fenton processes.

1.4 Scopes of Work

Scopes of this work were as follows:

1. Synthetic formaldehyde wastewater with a concentration of 0.333 M, corresponding to the real wastewater, was used for all experiments.
2. Initial pH, [H_2O_2], and [Fe^{2+}] were used to explore their effect on the oxidation reaction.
3. Measured parameters were residual concentration of CH_2O, residual concentration of CH_3OH, residual concentration of H_2O_2, pH, total organic carbon and toxicity.

1.5 Advantages of This Work

Results obtained from this research can be beneficial for a treatment of medical wastewater containing formaldehyde and methanol. Fenton and photo-Fenton technologies can be transferred to a bigger scale and use as a pretreatment method for formalin solution as well.