

## CHAPTER II BACKGROUND AND LITERATURE REVIEW

## 2.1 Background

Wastewater is a major problem in industries. It affects the environment, and it is toxic to human, living organisms, and aquatic animals. Moreover, the cost of wastewater treatment is extremely high. There are many kinds of wastewater in the industries. Ethanol and isopropanol are considered as contaminants because they are toxic, hazardous, and have foul-smelling generally found a lot in many industries. For example, polyethelene production process generates high quantity of ethanol and isopropanol in the wastewater.

Wastewater treatment is, therefore, important in industries in order to eliminate toxic organic and inorganic compounds. Advanced oxidation process (AOP) is one of the method to destroy the organic compounds and to reduce color presented in polluted water. Biological processes are not able to efficiently treat organic compounds and chemically toxic water, compared to AOPs. AOP is based on the utilization of highly reactive hydroxyl radicals (OH<sup>•</sup>) generated by oxidants such as hydrogen peroxide, ozone, etc. Hydroxyl radicals help to oxidize organic compounds to carbon dioxide and water.

A polyethylene plant in Thailand generates wastewater commonly composed of 1 %wt ethanol and 0.2 %wt isopropanol. This wastewater is suitable for using AOP in the treatment because it contains organic compounds in the suitable range of AOP applications as shown in Figure 2.1.



Figure 2.1 The suitable range of wastewater treatment

## 2.1 Literature Review

Tock *et al.* (1993) studied advanced oxidation process with hydrogen peroxide as an oxidant, platinum gauze as a catalyst, and air as a feed with varied temperatures. At high temperatures, COD removal was higher than at low temperatures. The mathematical model was proposed as follows:

For evaporation

$$\frac{-d[CC_i]}{dt} = \left(\frac{Q}{22.4}\right) \left(\frac{M_w}{m_w}\right) \left(\frac{P_i^{vap}}{P}\right) [CC_i] \gamma$$
(2.1)

For chemical oxidation

$$\frac{-d[CC_i]}{dt} = k[CC_i] \tag{2.2}$$

where

Q

= air flow rate(STP), L/min,

- M<sub>w</sub> = molecular weight of water, grams/mol
- $m_w = mass of water, grams,$
- [CC<sub>i</sub>] = concentration of organic component i in the liquid phase, mole/l.

P <sub>i</sub> <sup>vap</sup>	=	vapor	pressure	of	componen	ıt i,	atm,
			1			,	····,

 $\gamma_i$  = activity coefficient of component i, and

P = total pressure, atm.

COD removal was calculated by the summation of the solutions solved from these two equations. The results from the model were compared with experimental data, but there still were some errors. Therefore, this model was further developed in this research work.

There are various AOP techniques such as Fenton process using reagents, photo assisted fenton processes, photocatalysis, ozone water system, and AOP reactor (Andreozzi *et al.*, 1999).

Alnaizy and Akgerman (2000) studied phenol degradation using a UV/ $H_2O_2$  advanced oxidation process in a completely mixed, batch photolytic reactor. They found that hydrogen peroxide dosage, initial phenol concentration,  $H_2O_2$ /phenol molar ratio, pH, and temperature affected the results of AOP. The reaction mechanism was proposed. A kinetic model which assumed pseudo-steady state can well predict hydroxyl radical concentration.

Ghaly *et al.* (2001) investigated the oxidation of p-chlorophenol by  $UV/H_2O_2$  and photo-fenton process. The photo-fenton process produced the highest rate of degradation of p-chlorophenol. The reaction was influenced by pH, input concentration of  $H_2O_2$ , amount of iron catalyst, and types of iron salt. The optimum conditions were obtained at the pH value of 3.0, the Fe(II) concentration of about 1 mmol/l and the  $H_2O_2$  concentration of about 0.3 mol/l for UV/ $H_2O_2/Fe(II)$  system, and the Fe(III) concentration of about 0.4 mmol/l, and the  $H_2O_2$  concentration of about 0.01 mol/l for UV/ $H_2O_2/Fe(III)$  system.

Dye can be oxidized using ozonation, Fenton's reagent, and photo-fenton reagent. The initial dye concentration, pH, and NaCl concentration affected each process. Ozonation was effective with high dye concentration and high pH, but photo-fenton process was effective with low dye concentration and low pH (Aplin and Waite, 2000).

Critttenden *et.al* (1998) modified a model for advanced oxidation process using hydrogen peroxide and UV (UV/H<sub>2</sub>O<sub>2</sub>) in a completely mixed batch reactor. The photochemical parameters and rate constants were considered in this model. Pseudo-steady state assumption and constant pH were not employed, however good prediction was still attained. 1,2-dibromo-3-chloropropane (DBCP) in distilled water was examined for its removal, and the results were compared with those from the model. The modified model predicted closely with the concentration of H<sub>2</sub>O<sub>2</sub> and DBCP from experiments. The presence of carbonate ions decreased the efficiency of UV/H<sub>2</sub>O<sub>2</sub> process.

Kang *et al.* (1999) investigated the removal of COD and color from a dye manufacturing wastewater plant. Removal of COD and color of approximately 80% and 90%, respectively, can be achieved by  $H_2O_2/UV/Fe^{2+}$  processes. For the removal of COD and color in  $H_2O_2/UV/Fe^{2+}$  processes,  $H_2O_2/UV$ , approximately accounted for 80%,  $H_2O_2/UV$  for 10% and  $UV/Fe^{3+}$  for the remaining 10%. The effect of Fe<sup>2+</sup> at higher dosage resulted in the higher rate of COD removal, but not color removal. The UV irradiation appeared to be favorable in color removal more than in COD removal. There were some benefits gained by multi-step addition of Fe<sup>2+</sup>, but not  $H_2O_2$ .

Andreozzi *et al.* (1999b) studied advanced oxidation process of  $O_3/UV$  and  $O_3/H_2O_2$  which have been adopted for mineral oil-contaminated wastewater treatment.  $O_3/UV$  system was capable of achieving high level of COD removal of about 80-90%, which was higher than the ability of  $O_3/H_2O_2$ . A model was proposed to evaluate the rate parameters involved in some reactions and calculate COD. The COD was compared between the model and experiment values, which were closely fitted.

Beltran *et al.* (1999) proposed the kinetic model for advanced oxidation process (ozonation only, ozone-hydrogen peroxide, UV radiation only, and UV radiation-hydrogen peroxide for aromatic hydrocarbons). The experiments were performed on oxidation of nitrobenzene and phenanthrene. The accurate results were obtained on all models of every processes, except on ozone-UV system.

From the literature survey, Fenton method  $(Fe^{2+}/H_2O_2)$  with air was studied on the treatment of wastewater from the polyethylene plant by varing the parameters: the concentration of hydrogen peroxide, air flow rate, and ferrous ion. Samples were collected to examine the concentration of each components, COD, and TOC. A mathematical model was proposed to compare the theoretical results and the experimental results.