CHAPTER 3
MATERIAL AND METHODS

3.1 Sample Sources and Preparation

Two types of water samples were used in this study: surface and synthetic water samples. Surface water samples were collected from a storage reservoir, which is a water source for the Khon Kaen University Water Treatment Plant. This treatment plant supplies water for the whole campus. The plant relies on conventional treatment processes: coagulation, flocculation, sedimentation, rapid sand filtration, and chlorination. The samples were collected three times per week for 4 weeks. They were stored under 4°C for no longer than 48 hours prior to Fenton's experiments.

For the synthetic water samples, 2,4-dichlorophenol (2,4-DCP) was chosen in this study because of its refractory nature. It is a good representative of chlorinated compounds because it has long been regarded as a main intermediate in the synthesis of herbicide particularly ones associated with chlorine-based. Productions of some pesticides and wood preservatives were reported having 2,4-DCP as one of their constituents. Moreover, it is usually found as a main degradation by-product of other hazardous compounds such as 2,4-dichlorophenoxyacetic (2,4-D) (Ureta-Zañartu et al., 2002 and Benitez et al., 2000).

The 5 mg/L of 2,4-DCP solution was prepared by diluting a standard solution (Merck, analytical grade) with deionized water at the ratio of $5{:}10^6$ (vol./vol.). After that, the samples were immediately used in Fenton's experiment. The concentration of 5 mg/L was chosen because DOC in raw water generally does not exceed 10 mg/L.

3.2 Experimental Set-up and Procedure

Fenton's reaction was performed in a 10-L fermentator (Biostat ® B, IOB. Braun Biotech International, Germany). All experiments were conducted at a room temperature of approximately 25°C. DOC and AOC of water samples were measured before performing each run of Fenton's experiments. Each experiment was begun with adjusting pH to a desired level (2, 3, or 4) by H_2SO_4 (Merck) or NaOH (Merck).

Next, 0.36 M of Fe^{2+} solution (prepared by dissolving 20 grams of $FeSO_4.7H_2O_2$ in 200 mL deionized water) was introduced to the tested sample. Immediately after, H_2O_2 (Merck, 35%, reagent grade) was added to initiate Fenton's reaction. Once the reaction was started, 200 mL of the tested sample was withdrawn at 1, 3, 6, 10, 25, and 40 minutes and placed in a 250-mL glass bottle.

To stop the oxidation at the prescribed oxidation time, 1-2 mL of sodium thiosulfate solution ($Na_2S_2O_3$) was added to the sample. The solution was prepared by dissolving 10 g of sodium thiosulfate in 100 mL deionized water to make a concentration of 0.63 M. This dose is based on the fact that 0.1 mL of this concentration is capable of destroying 5 mg residual chlorine (APHA, 1998). Therefore, using 1-2 mL should be an adequate dose for quenching OH• from Fenton's reaction. After the reaction was quenched, approximately 20 mL of the sample was used for DOC measurement whereas the remaining portion was taken for pH and AOC_{P17} and AOC_{NOX} measurements.

3.3 Experimental Design

Experiments were classified mainly into two groups based on the type of samples (surface and synthetic water samples). Three pHs, 2, 3, 4, were examined. To investigate the effects of H_2O_2 and Fe^{2+} concentrations, 3 different ratios of H_2O_2:DOC (mass basis) combined with 3 different ratios of Fe^{2+}:H_2O_2 (mass basis) resulting in 9 different matrices of Fe^{2+}:H_2O_2:DOC, 0.025:0.5:1, 0.05:0.5:1, 0.25:0.5:1, 0.1:2:1, 0.2:2:1, 1:2:1, 0.5:10:1, 1:10:1, and 5:10:1, were employed. All tested parameters are summarized in Table 3.1. To ensure statistical accuracy, each batch run was duplicated.

3.4 Analytical Methods

DOC was analyzed using a TOC analyzer (Shimadzu, Model 5000A) after the samples were filtered through 0.7 μm glass fiber filter (GF/F, Whatman) (APHA, 1998). pH was measured using a pH meter (Accumet, Model 10). AOC measurement was performed following the Standard Methods (APHA, 1998).

Table 3.1 Experimental Design for Surface and Synthetic Water Samples.

$[Fe^{2+}]/[H_2O_2]/[DOC]$																	
pH 2						pH 3						pH 4					
Time (min.)						Time (min.)						Time (min.)					
1	3	6	10	25	40	1	3	6	10	25	40	1	3	6	10	25	40
*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
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Where * = 0.025:0.5:1, *** = 0.25:0.5:1, ♦♦ = 0.2:2:1, ♠ = 0.5:10:1, ♠♠♠ = 5:10:1
** = 0.05:0.5:1, ♦ = 0.1:2:1, ♦♦♦ = 1:2:1, ♠♠ = 1:10:1,