CHAPTER III

METHODOLOGY

3.1 Chemicals

Aniline and nitrobenzene were purchased from the Merck Company. Hydrogen peroxide 35% and ferrous sulfate heptahydrate were purchased from the Merck Company. All other reagents used in this study were reagent grade.

3.2 Reactor

A 1.3 litre batch reactor (Figure 3.1) was used in all experiments. The reactor diameter is 5 inch and 12 inch height. The temperature was kept constant at 30°C by cooling water system. The sample solution was agitated with a magnetic stirrer bar.
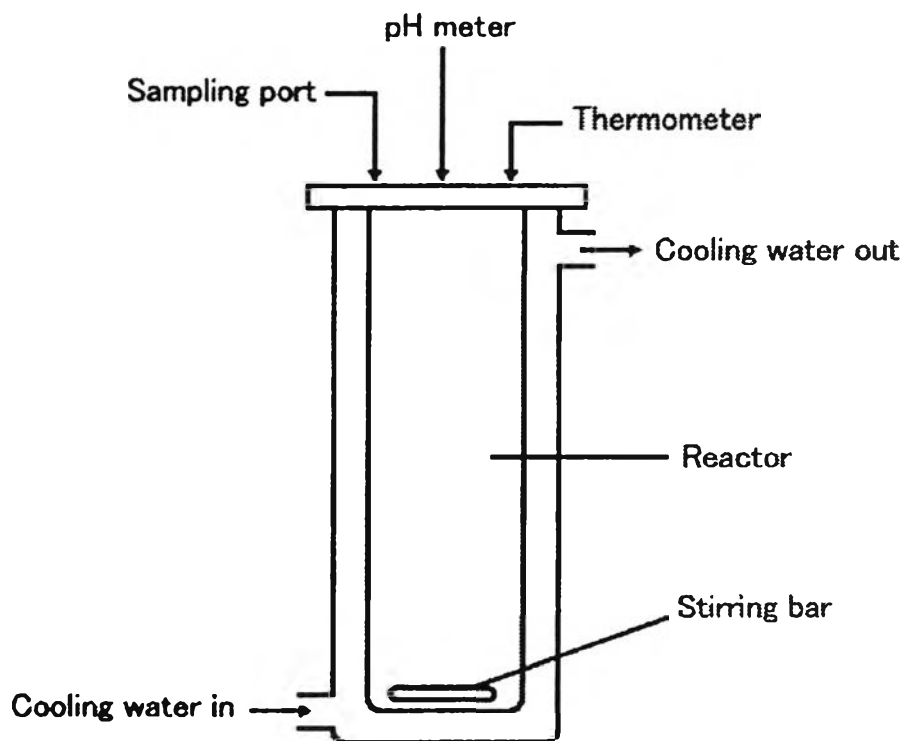

Figure 3.1 Fenton reactor used in all experiments

3.3 Experimental procedure

The experiments were divided into 3 sections:

3.3.1. Effect of initial condition on the decomposition of aniline and nitrobenzene. The studied initial conditions include:

1. Effect of initial hydrogen peroxide concentration.

2. Effect of initial ferrous ion concentration.

3. Effect of initial pH.

The experiments were started with low concentration of aniline and nitrobenzene (1 mM). Then the experiments with high concentration of aniline and nitrobenzene (10 mM) were performed. To study the effect of hydrogen peroxide dosage on the degradation of aniline and nitrobenzene, H_2O_2 concentrations were varied as free H_2O_2, 5 mM, 7.5 mM, 15 mM, 20 mM and 25 mM for 1 mM of aniline and nitrobenzene, and 50 mM, 60 mM, 75 mM, 100 mM and 150 mM for 10 mM of aniline and nitrobenzene. To investigate the effect of ferrous ion on pollutant removal, amounts of ferrous ion were varied as free Fe^{2+}, 0.1 mM, 0.25 mM, 0.5 mM, 1 mM and 2.5 mM for 1 mM of aniline and nitrobenzene concentration. And for 10 mM of aniline and nitrobenzene, ferrous ion were varied as 0.5 mM, 0.6667 mM, 1 mM, 1.25 mM, 1.875 mM and 2.5 mM. The pH values were varied as 2.7, 3, 3.5 and 4 while 1 mM of aniline and nitrobenzene was used as initial concentration, in evaluating the effect of initial pH value. From these studies, the optimum condition for treating aniline and nitrobenzene were obtained.

Experimental procedures - All the solutions with the same amount of aniline and nitrobenzene were prepared in the reactor. Then, ferrous sulfate heptahydrate was completely mixed with the prepared solution in the reactor. The initial pH was adjusted to the desire pH with sulfuric acid and sodium hydroxide. The reaction was initiated by adding the hydrogen peroxide. The procedures were shown in the Figure 3.2. For all experiments, 5 ml samples were withdrawn at selected time and the Fenton reaction was stopped by adding 5 ml of 0.1 M NaOH. After adding NaOH, the solutions were filtered by 0.45 μm syringe microfilters before analysis. The samples

were taken at 0, 2, 5, 10, 20, 40, 60 and 80 min while pH and temperature were recorded. Besides, 1 ml samples were taken for residual hydrogen peroxide analysing.

Mixture of same molar of aniline and nitrobenzene

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Add the desired amount $FeSO_4$ and adjust pH

⬇

Add the desired amount of H_2O_2 to initiate the reaction

⬇

The samples were taken at 0, 2, 5, 10, 20, 40, 60 and 80 min while pH and temperature were recorded.

⬇

The samples were filtered before analysis
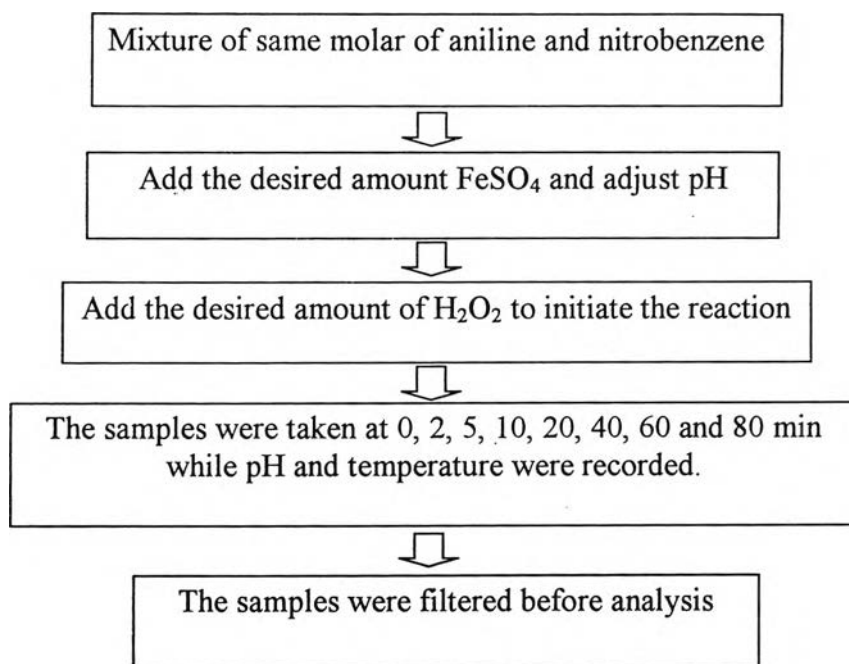
Figure 3.2 Effect of initial condition study procedures

3.3.2. Competitive degradation behavior between aniline and nitrobenzene.

This experiment set was established under the hypothesis that aniline and nitrobenzene may compete to react with hydroxyl radicals. To evaluate the competitive behavior between aniline and nitrobenzene, the experiment was conducted with the different molar ratios of aniline and nitrobenzene as 10/1, 5/1, 2/1, 1/1, 1/2, 1/5, 1/10. The control experiments for individual aniline degradation and for individual nitrobenzene degradation were also performed for comparison purpose. The competitive degradations were determined by comparing initial rates of aniline and nitrobenzene.

Experimental procedures - All solutions with the designated amounts of aniline and nitrobenzene and 1.25 mM of ferrous ion were completely mixed together in the reactor. The initial pH was adjusted to 3.0 ± 0.1 with sulfuric acid and sodium hydroxide. The reaction was initiated by adding 67.5 mM of hydrogen peroxide. The experiment procedures were shown in Figure 3.3. For all experiments, 5 ml samples

were withdrawn at selected time and the reaction was stopped by adding 5 ml of 0.1 M NaOH. After adding NaOH, the solutions were filtered by 0.45 μm syringe microfilters before analysis. The samples were taken at 0, 2, 5, 10, 20, 40, 60 and 80 min while pH and temperature were recorded. Besides, 1 ml samples were taken for residual hydrogen peroxide analysing.
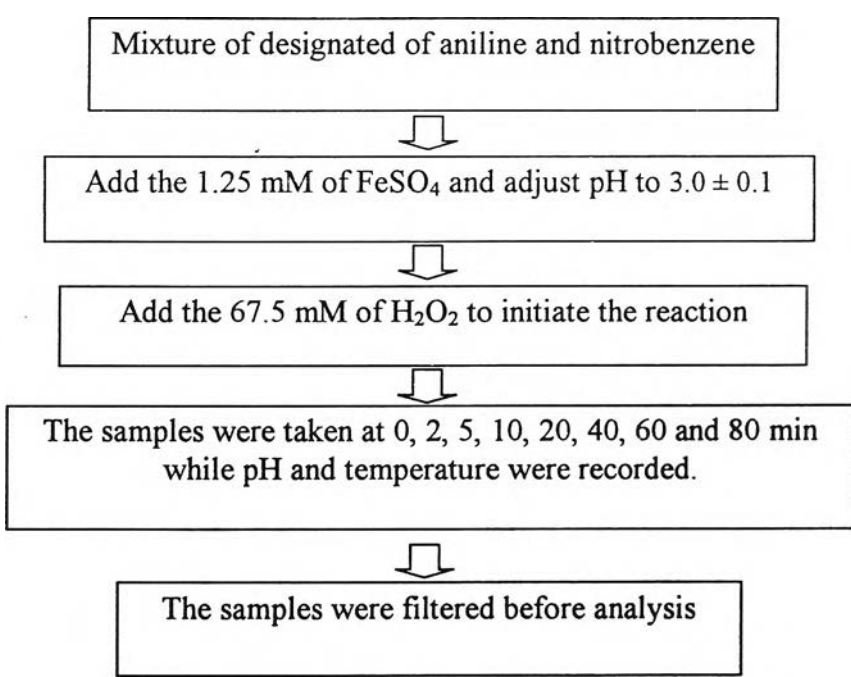
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│   Mixture of designated of aniline and nitrobenzene  │
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┌─────────────────────────────────────────────────────┐
│   Add the 1.25 mM of FeSO₄ and adjust pH to 3.0 ± 0.1│
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│   Add the 67.5 mM of H₂O₂ to initiate the reaction   │
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│  The samples were taken at 0, 2, 5, 10, 20, 40, 60   │
│     and 80 min while pH and temperature were recorded.│
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│       The samples were filtered before analysis      │
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Figure 3.3 Competitive behavior study procedures

3.3.3. Mineralization of aniline and nitrobenzene.

To study the mineralization of aniline and nitrobenzene, the decreasing of total organic carbon (TOC) was measured to represent the mineralization of aniline and nitrobenzene. The conditions obtaining from the first part (1.1 – 1.3) were used as initial condition in this part.

Experimental procedures - All solutions are the mixture solution with the same molar concentration of aniline and nitrobenzene as 1 mM. Then, the 0.5 mM of ferrous ion was completely mixed with the prepared solution in the reactor. The initial pH was adjusted to 3.0 ± 0.1 with sulfuric acid and sodium hydroxide. The reaction was initiated by adding the 20 mM of hydrogen peroxide to the reactor. The procedures were shown in Figure 3.4. For all experiments, 5 ml samples were

withdrawn at selected time and the reaction was stopped by adding 5 ml of 0.1 M NaOH. After adding NaOH, the solutions were filtered by 0.45 μm syringe microfilters before analysis. The samples were taken at 0, 2, 5, 10, 20, 40, 60, 80, 100, 140, 180 and 240 min while pH and temperature were recorded. Besides, 1 ml samples were taken for residual hydrogen peroxide analysing.
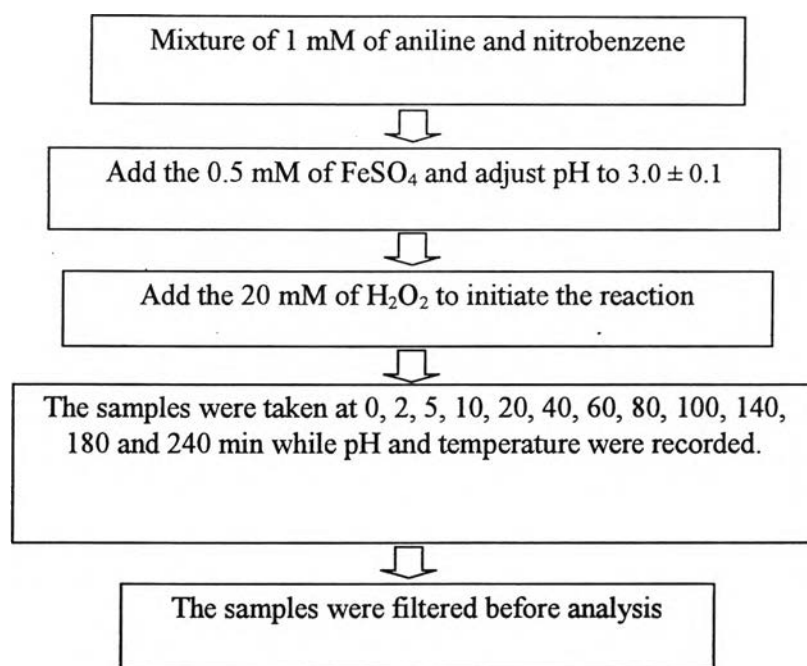
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│        Mixture of 1 mM of aniline and nitrobenzene     │
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┌──────────────────────────────────────────────────────┐
│    Add the 0.5 mM of FeSO₄ and adjust pH to 3.0 ± 0.1  │
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┌──────────────────────────────────────────────────────┐
│     Add the 20 mM of H₂O₂ to initiate the reaction     │
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┌──────────────────────────────────────────────────────┐
│  The samples were taken at 0, 2, 5, 10, 20, 40, 60, 80, 100, 140, │
│   180 and 240 min while pH and temperature were recorded. │
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┌──────────────────────────────────────────────────────┐
│        The samples were filtered before analysis       │
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Figure 3.4 Mineralization study procedures

3.4 Analytical methods

Aniline and nitrobenzene were analyzed by a gas chromatograph equipped with a flame ionization detector (HP4890). After that, a capillary column (SUPLCO 18165-U) with the following dimension, 15 m, and 1.5 μm, was used. And, the temperature program during the GC analysis was used as follows: 85 °C, rate 40 °C·min^{-1} until 200 °C. Injector temperature was 250 °C and detector temperature was 250 °C. TOC was analyzed by TOC analyzer. The concentrations of hydrogen peroxide were determined by standard iodometric method (Kingzett, C.T., 1880). The pH values were determined by pH meter.