CHAPTER 3

METHODOLOGY

3.1 Materials

3.1.1 Adsorbent

The different activated carbons, made from bituminous coal, coconut shell and palm shell were used in the experiment. The characteristics of the activated carbons are described in table 3.1. They were sieved with US standard screens to obtain 8-16 mesh fraction (2.36-1.18 mm). The granules were washed with reverse osmosis water (RO), then dried at 105 °C for 12 hours and stored in dessiccator at room temperature.

Table 3.1 Characteristics of activated carbons from Carbokarn co, Ltd.

Parameter	Bituminous coal	Coconut shell	Palm shell
1.Moisture %	4.20	4.1	3.3
2.Iodine number (mg/g)	983	995	971
3.BET surface area (m^2/g)	1195	1230	1087
4.Total pore volume (cm^3/g)	0.74	0.60	0.52
5.Pore diameter (Å)	18.38	14.75	14.59

3.1.2 Chemicals

4-Nitrophenol ($C_6H_5NO_3$) was purchased from Carlo erba chemical. Ferrous sulfate ($FeSO_4.7H_2O$), Hydrogen peroxide (H_2O_2) (30% w/w), Sodium Sulfite (Na_2SO_3), Sulfuric acid (H_2SO_4) and Sodium hydroxide (NaOH) were purchased from Merck chemical.

3.2 Experimental

The experiment is divided into 3 parts :

1. Adsorption and desorption of 4-Nitrophenol by GAC.
2. Regeneration of spent GAC by Fenton's reaction (in adiabatic condition).
3. Reuse of GAC after regeneration.

3.2.1 Adsorption and desorption of 4-NP by GAC

3.2.1.1 Adsorption Isotherm

Three types of GAC will be tested by the same procedure as follows.

3.2.1.1.1 Adsorption Kinetics

Adsorption kinetics of 4-nitrophenol by GAC was studied in batch experiments by varying GAC mass. The GAC mass of 0.01, 0.1 and 0.4 g were used in this experiment. 4-nitrophenol of 1 mmol/l (139.11 mg/l) was spiked in RO water and transferred to the 250 ml flask. The pH of water was neutral. GAC was added to each flask containing 150 ml of sample. Immediately the flasks were sealed with parafilm and protected from the light. The flasks were covered to avoid loss of 4-nitrophenol due to vaporization. The samples were shaken by orbital shaker at 200 rpm and room temperature (30±1°C). The sample from each flask was analyzed for 4-nitrophenol concentration by spectrophotometer at a wavelength of 455 nm. Samples were collected at 0, 1, 2, 4, 6, 10, 15, 20, 25, 30, 36, 42, 48, 60 and 72 hrs in order to determine the equilibrium time required for the maximum adsorption of 4-nitrophenol by the adsorbents.

3.2.1.1.2 Equilibrium Isotherm

The RO water was spiked with approximately 1 mmol/l (139.11 mg/l) of 4-nitrophenol, using the stock solution. The pH of wastewater was neutral. Various amounts of GAC (0.01, 0.02, 0.05, 0.1, 0.2 and 0.4 g) were added into the 250 ml flasks containing 150 ml of synthetic watersample. Immediately the flasks were

sealed with parafilm and protected from the sunlight. The flasks were covered to avoid losses of 4-nitrophenol due to vaporization. The samples were shaken at 200 rpm at room temperature (30±1°C) to reach the equilibrium state. The 4-nitrophenol remained in solution was analyzed by spectrophotometer with a wavelength of 455 nm after equilibrium was reached.

3.2.1.2 Desorption test

Two sets of desorption test were conducted with different temperatures, which were 30°C and 45°C, and the pH was varied as 3, 5, 7. Preliminary tests of desorption at pH 7 and 45°C for all types of GAC were performed and the best desorption efficiency of GAC was selected for the subsequent tests. The desorption test was performed by using 0.1g of selected GAC, which has already adsorbed 1 mmol/l of 4-NP from isotherm test. After that, this GAC was added into flask containing 150 ml of water and shaken in waterbath shaker to control temperature for each set. The flasks were sealed with parafilm and protect from sunlight. The samples were collected after 0, 0.5, 1, 2 hr. The 4-NP from each flask was analyzed by spectrophotometer with a wavelength of 455 nm.

3.2.2 Regeneration of spent GAC by Fenton's reaction

The Fenton's reaction were divided into 2 major steps. The first step was Fenton's reaction in 4-NP adsorbed GAC, and the second step was Fenton's reaction in 4-NP solution. This reaction was conducted under adiabatic condition by using vacuum bottle to prevent heat loss from reactor.

3.2.2.1 Optimal ratio for Fenton's reaction in 4-NP adsorbed GAC

Every set of experiment in this part was done by using GAC, which has already adsorbed 0.0325 M of 4-NP. The experiments were done as in the following steps.

The first set of experiment in this part was done by varying Fe^{2+} concentration in the range of 16-65 mM and a constant of 0.325 M H_2O_2. The initial concentration of 4-NP was constant and initial pH was controlled at 3. Thus, 4-NP: H_2O_2: Fe^{2+} molar ratio was 1: 20 : (0.5-2). The second set of experiment was done by varying the pH values (3, 5, 7), while the ratio of 4-NP: H_2O_2: Fe^{2+} obtained from first set of experiment was fixed. Concentration of Fe^{2+} varied with a constant pH, which was derived from the second set of experiment. The last set of experiment, concentration of H_2O_2 varied with a constant pH derived from the second set of experiment, in which concentration of Fe^{2+} was obtained from the third set of experiment. Hence, the optimal ratio for GAC regeneration was obtained.

Experimental preparation: 15 g of 4-NP adsorbed GAC was filled into 500 ml vacuum bottle. Ferrous solution from stock solution was added. The samples were adjusted to the designated pH, using 0.1 and 1 N solution of H_2SO_4 or 0.1 and 1 N NaOH. H_2O_2 was then added into bottle based on the studied ratio. The entire volume of solution in the vacuum bottle was 300 ml for every single set. The bottles were then shaken at 200 rpm in orbital shaker. Samples were collected at 0.5, 1, 1.5 and 2 hr. Temperature and pH were monitered continuously. The H_2O_2 residue was measured by the iodometric tritration method [47]. At each interval of sampling, 10 ml of solution was taken from vacuum bottle and filled into a beaker containing 2 ml of 6 N NaOH and 2 ml of 10% Na_2SO_3, and diluted into a volume of 100 ml. Sodium hydroxide (NaOH) was added to stop the reaction, due to precipitation of catalyst at pH > 10 [36]. The sodiumsulfite (Na_2SO_3) removes the remaining H_2O_2 very quickly [48].This diluted sample was analyzed for 4-NP by spectrophotometer with a wavelength of 455 nm. The organic carbon was analyzed by TOC analyzer. GAC sample was taken and washed by water of pH 3. The washed GAC was prepared for analyzing residual adsorbate of 4-NP. The 4-NP adsorbed onto GAC was extracted by sonicfication with 150 ml of 10% NaOH and analyzed at a wavelength of 462 nm.

3.2.2.2 Fenton's reaction in 4-nitrophenol solution

Fenton's reaction in solution was done to investigate the degradation of 4-NP comparing with reaction in GAC. The concentration of 4-NP in solution based on system volume is the same as in the set of experiment of Fenton's reaction in GAC.

Experimental preparation: 200 ml of 4-NP from stock solution was added into 500 ml vacuum bottle. Ferrous solution from stock solution was added and adjusted to designated pH value by using 0.1 and 1 N solution of H_2SO_4 or 0.1 and 1 N NaOH. H_2O_2 was then added into bottle based on studied ratio. The entire volume of solution in vacuum bottle was 300 ml for every single set. The bottles were then shaken at 200 rpm in orbital shaker. Samples were collected at 0.5, 1, 1.5 and 2 hr. Temperature and pH were monitored continuously. The H_2O_2 residue was checked by iodometric tritration. At each interval of sampling 10 ml of solution was taken from vacuum bottle and fill in beaker containing 2 ml of 6 N NaOH and 2 ml of 10% Na_2SO_3, then adjusted to 100 ml as dilution. This dilution sample was analyzed for 4-NP by spectrophotometer and organic carbon by TOC analyzer.

3.2.2.3 The role of Fenton's reaction to GAC

To study the role of Fenton's reaction to GAC, 2 sets of experiment were conducted. One is Fenton's reaction in regenerated GAC and another in fresh GAC respectively with the same quantity of adsorbed 4-NP. Regenerated GAC sample would be taken to analyze total Fe by X-ray fluorescence (XRF) spectroscopy.

Both sets were done by adding 5g of GAC into reactor. 98 ml of water was added into reactor. This reaction was done in pH 7. After that, 2 ml of 30% H_2O_2 was filled and the total solution volume was 100 ml. Then, reactors were shaken in orbital shaker at 200 rpm. GAC from both sets of experiment of experiment was taken out for extraction of 4-NP.

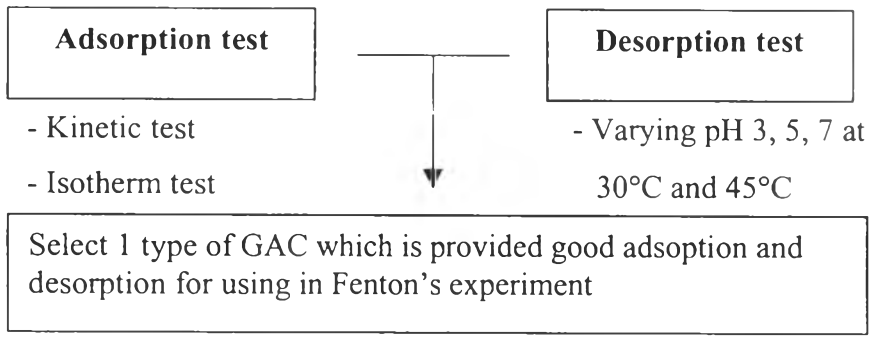
3.2.3 Reuse of GAC after regeneration

3.2.3.1 Adsorption isotherm

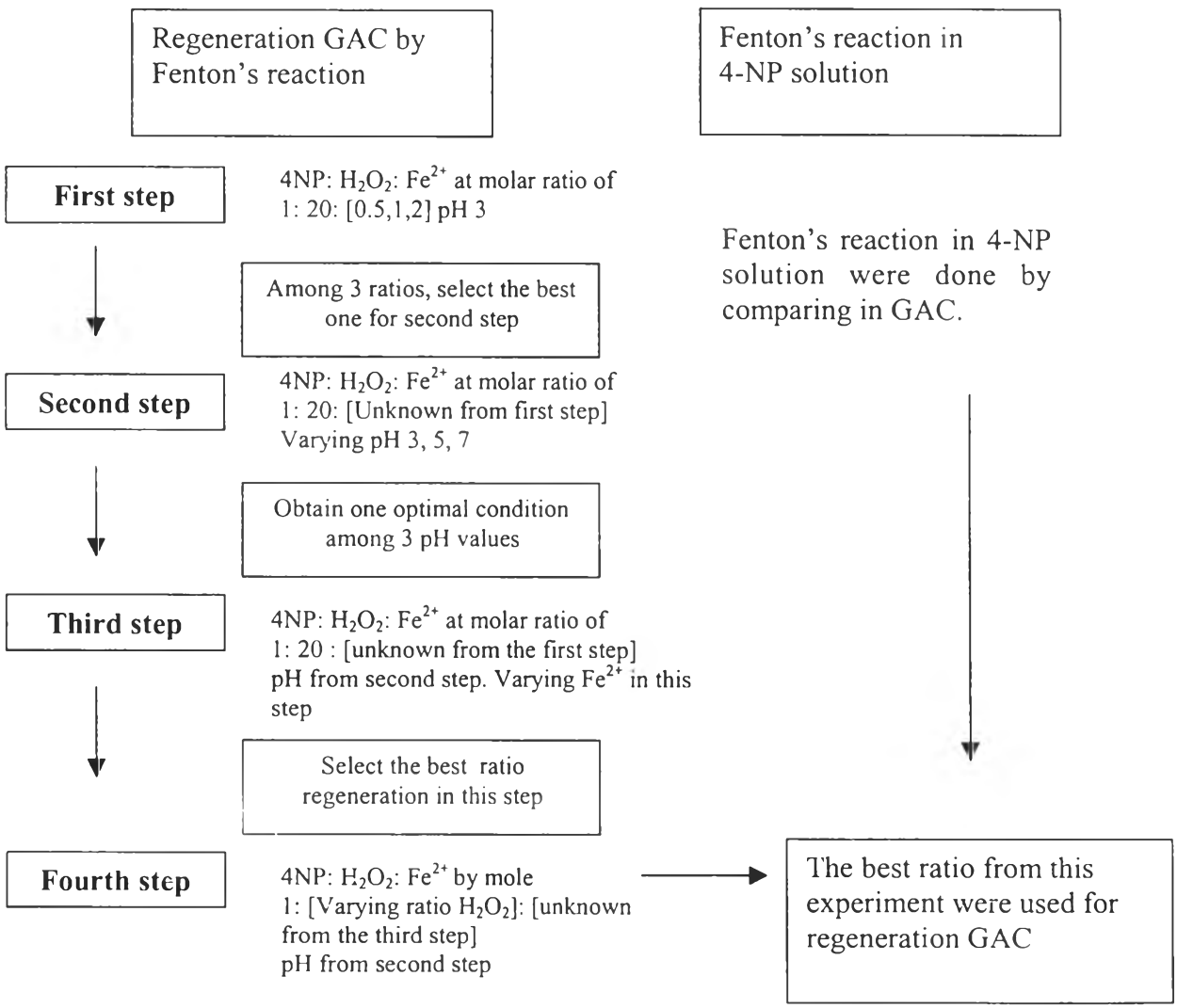
The adsorption isotherm of GAC after one cycle of regeneration was determined and compared with the fresh one.

3.3 Experimental Chart

Part 1 Adsorption and desorption of 4-NP by GAC



Part 2 Fenton's reaction in adiabatic condition



Part 3 Reuse of GAC after regeneration