CHAPTER III

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

The preparations of experiment and analysis techniques are described in this chapter. It is divided into three sections. The first section concerns with the adsorbent preparation. Vacuum procedure is described in this section. The second part describes the experimental apparatus and adsorption procedures. The third section refers to analysis techniques and errors of the experiments.

3.1 Adsorbent Preparation

Adsorbent was composed of chitosan flake degree of deacetylation 79% 87% and 95% that was obtained from the factory in Thailand (Seafresh Chitosan Lab.). Specifications of chitosan see in Appendix B.

Vacuum Procedure

Vacuum was the procedure that injects deionized water into pore of chitosan for better mass transfer and wet chitosan easy to use. Approximately 10 grams of chitosan in a round-bottom flask was vacuum by a vacuum pump under pressure at 10 mmHg for 15 minutes. Deionized water 0.5 ml. was dropped in the flask under vacuum pressure. The flask was slowly shake for well mixed between chitosan and deionized water.
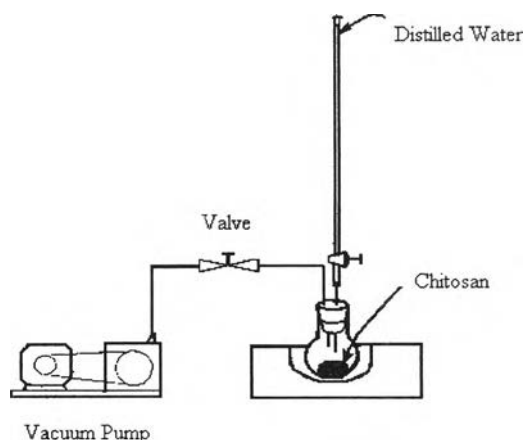

Figure 3.1 Schematic diagrams of vacuum apparatus.

3.2 Experimental Apparatus and Adsorption Procedures

3.2.1 Experimental Apparatus

Figure 3.2 shows the apparatus of adsorption experiment. The apparatus was comprised of a 250-ml. flask, which was connected with a propeller and motor. Figure 3.2 a, the flask was immersed in an oil bath, which was heated by a heater. The temperature of the oil bath was controlled with the temperature controller for constant temperature at $30^{\circ}C$ and $50^{\circ}C$. Figure 3.2 b, the flask was immersed in a water bath, which was cooled by a cooler tank. The temperature of the water bath was controlled by thermometer and cooler tank at temperature of $10^{\circ}C$. Table 3.1 showed variables of this experiment. The adsorption procedures are described below.

Table 3.1 Variables of the adsorption experiment.

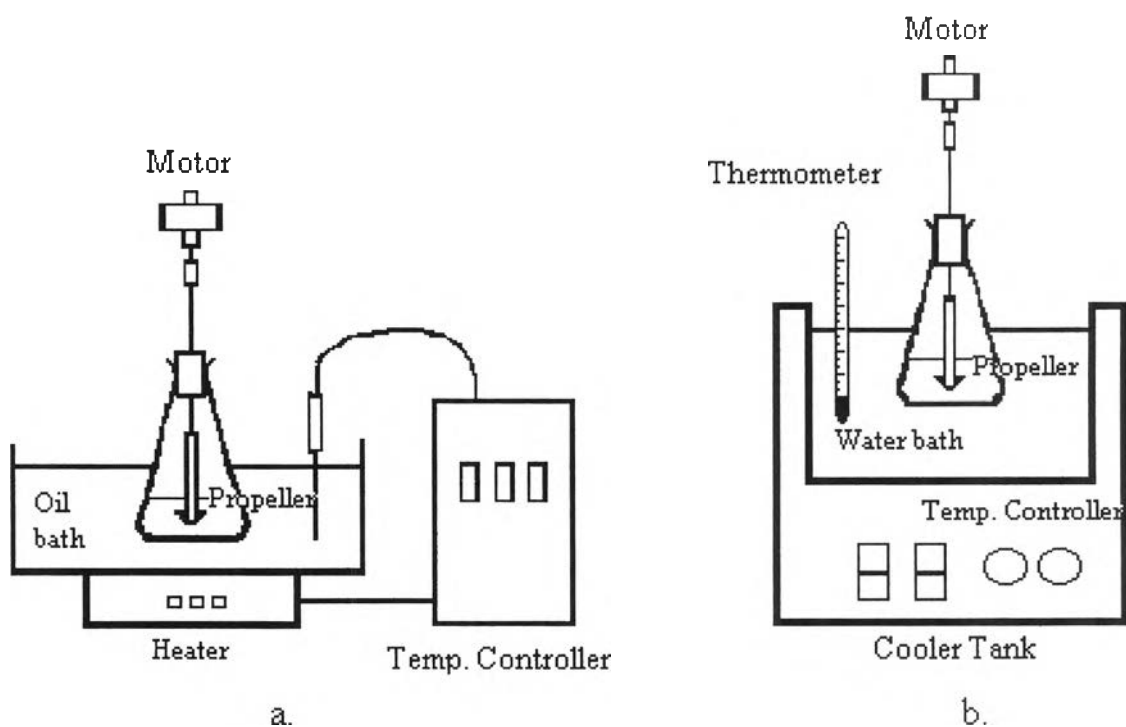| Compound	Mercuric chloride ($HgCl_2$)
	Phenylmercuric acetate (PMA)
Type of chitosan	Chitosan 79 % DD
	Chitosan 87 % DD
	Chitosan 95 % DD
Initial pH of solution	5
	6
	7
Temperature (°C)	10
	30
	50

Figure 3.2 Schematic diagram of the experimental apparatus. a. for temperature controlled at 30°C and 50°C. b. for temperature controlled at 10°C

3.2.2 Feed Preparation

In this study, mercuric chloride and phenylmercuric acetate was selected as model of inorganic and organic mercury compound respectively. The initial concentration of mercury compound in solutions was prepared at 10 ppm. Mercury compound was weight and put in 2-liter Erlenmeyer flask. 1500 g and 1300 g of deionized water was poured to the flask. A magnetic stirrer stirred the solutions for at least 2 hours for mercuric chloride and 5 hours for phenylmercuric acetate. The solution used as feedstock and kept this feedstock in refrigerator.

3.2.3 Adsorption Procedures

1. Chitosan flakes was weighed out approximately 10 gram and put to a 250-ml. Erlenmeyer flask.

2. The flask was vacuumed by vacuum pump. Approximately 0.5 ml. of deionized water was dropped in the sample flask to fill pore of the adsorbent. Slowly shake the flask for well mixed between deionized water and the adsorbent.

3. Approximately 100 grams of feedstock was poured into the sample flask.

4. The sample flask was placed in the oil bath or water bath that was controlled temperature. It was stirred at constant temperature for 3 hours.

5. The solution was filtered with filter paper to separate a spent adsorbent from liquid product.

6. The spent adsorbent was kept in a plastic bag. It was analyze the properties after adsorbed mercury compounds. All mercury in liquid product was converted to mercuric ion by chemical oxidation before to determine the mercury remaining.

3.3 Analysis technique and Errors of Experiments

This section is described analytical techniques and errors of experiments. In each experiment, fresh adsorbents and spent adsorbents were analyzed characteristics such as surface area and pore volume of adsorbents, mercury content. Analytical procedures are described below. Analytical results are shown in the Chapter IV

3.3.1 Adsorbent Characterizations

Surface and Pore Volume

A micrometrics model ASAP 2000 is an instrument to measure surface area, pore volume and pore size distribution of the adsorbents. The instrument detects the volume of adsorbed nitrogen gas on surface at various relative pressures. There are two

operating steps i.e. the degassing step and analysis step. Firstly, the adsorbent was heated and placed under vacuum to remove the moisture and other contaminants. The condition of degassing was operated at 150 °C and vacuum until pressure to 10 mmHg. After that, the sample cell was transferred the sample cell from a degas port to an analyze port.

At the analyze port, the sample was analyzed at various relative pressures and liquid nitrogen was used as coolant. Nitrogen gas was used as an analysis gas. The volume of adsorbed nitrogen on sample will relate with the relative pressure (P/P_o). The volumes of adsorbed nitrogen gas and relative pressures were plotted the graph. The Y-intercept and slope of the graph was calculated BET surface area of sample. The other results of the instrument were BJH cumulative pore volume and average pore diameter. In each experiment, this instrument analyzed adsorbents in order to study the variation of properties.

Adsorbent Digestion

The determination of mercury content in the adsorbent followed the standard test method ASTM D1977-91. The procedure of digestion in standard test used concentrated acids to decompose mercury from the adsorbent. The procedures are described below.

1. Approximately 0.5 gram of the adsorbent was put in a crucible.

2. The sample was added with 10 ml. of concentrated sulfuric acid, 10 ml. of concentrated nitric acid, 5 ml. of concentrated hydrofluoric acid, and 10 ml. of deionized water.

3. The mixture was placed on a hot plate and slowly stirred. The adsorbent was first dissolved in acid solution and precipitated again after the acid was evaporated. The solution was evaporated to near dryness.

4. The crucible was removed from the hot plate and cooled to room temperature.

5. The sample was again added 20 ml. of 19 % hydrochloric acid and 30 ml. of 3% hydrogen peroxide. The crucible was covered with a watch glass and returned to the hot plate.

6. The solution was heated and kept boiling until the adsorbent dissolved. The crucible was cooled to room temperature.

7. The solution was made volume to 100 ml. with deionized water. The finished solution was kept in refrigerator.

Forms of Mercury on Adsorbent Surface

In this study, the form of adsorbents was verified by using X-ray diffraction spectroscopy. The principle of X-ray diffraction technique was the scatter of X-ray through the crystalline sample to give the characteristic pattern of intensities. This pattern can be interpreted in terms of the location of atom in the molecules and give information about molecular structure.

3.3.2 Standard Test Method for Total Mercury in Water

The determination of total mercury in the water followed the standard test method ASTM D3223-91. The test method consists of a wet chemical oxidation and cold vapor atomic absorption analysis. Chemical oxidation converts all mercury to the mercuric ion and reduction of mercuric ions to metallic mercury, followed by a cold vapor atomic absorption analysis. Because total mercury in aqueous phase cannot be directly measured by an atomic absorption spectroscopy technique, chemical oxidation is the method that is using strong acids and high temperature to change all mercury species to mercury II ion (Hg^{2+}). Figure 3.3 shows the apparatus for converts all mercury to the mercuric ion. It was comprised of a round bottom flask that was connected with a condenser. The flask was immersed in the oil bath and heat at 95°C for 2 hours. The procedure of digestion is described below.
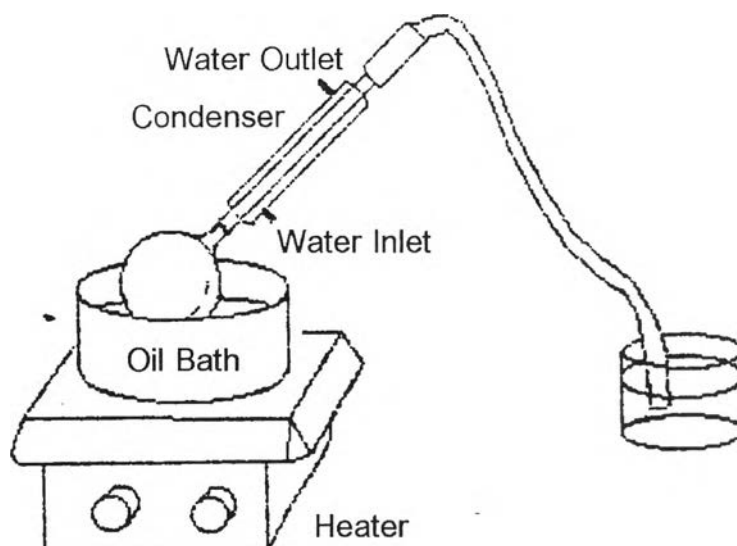
Figure 3.3 Schematic diagram of apparatus for converts all mercury to the mercury ions

Procedure

1. Approximately 10 grams of the sample was transferred to a 250 ml. flat round flask.

2. The sample was added with 5 ml. of concentrated sulfuric acid, 5 ml. of concentrated nitric acid and 15 ml. of 5% potassium permanganate solution.

3. The sample was stirred at 600 rpm for 15 minutes. After that, 8 ml. of 5% potassium persulfate was added to the flask.

4. The flask at the top was equipped with a reflux condenser and subsequently heated the oil bath at 95 °C for approximately 2 hours.

5. After that, the flask was removed from the oil bath and cool to the ambient temperature.

6. The sample was added 6 ml. of sodium chloride-hydroxylamine hydrochloride to reduce the excess permanganate. Slowly shake approximately 10 minutes. The sample was transferred into a polyethylene bottles.

7. Finally, deionized water was added and shaken vigorously to made the total volume to 100 ml.

Cold vapor technique

In this study, the high sensitivity measurement of mercury content is the cold vapor technique or the hydride technique. The cold vapor technique involves the reaction of acidified aqueous samples with a reducing agent such as sodium borohydride. Mercury is the only element apart from the inert gas with appreciable vapor pressure at room temperature. The reaction is shown in the following equations

$$NaBH_4 + 3H_2O + HCl \longrightarrow H_3BO_3 + NaCl + 8H \dots\dots\dots\dots(3.1)$$

$$Hg^{n+} + H \text{ (radical)} \longrightarrow Hg + H_2 \dots\dots\dots\dots(3.2)$$

Equation 3.1 shows the reaction between sodium borohydride and hydrochloric acid to generate radical hydrogen in quartz cell. In quart cell, radical hydrogen reacts with mercury (II) ion to gaseous mercury atoms as shown in Equation 3.2. Mercury atoms can absorb 253.7 nanometers of wavelength. The content of mercury is interpreted from the intensity of light that absorbed by mercury atoms. The sensitivity of this technique is approximately 10^{-9} g.

3.3.3 Experimental and Analysis Error

Experimental Error

In this section, experiments are conducted to verify repeatability, an average and a standard deviation value of the experiment. Equation 3.3 and Equation 3.4 define an average value and percent deviation.

$$\text{Average value } \overline{X} = \frac{\sum x}{n} \dots\dots\dots\dots(3.3)$$

Percent deviation from average value $= \dfrac{\sqrt{(X - \bar{X})^2}}{\bar{X}} \times 100$ ....(3.4)

After each experiment, the solution liquid, feed and spent adsorbents were analyzed for the mercury content by using atomic absorption spectroscopy techniques. The experiment was repeatedly adsorbed and converted all mercury to the mercuric ion at the same condition for 3 times. Average concentration of remaining mercury and the maximum percent deviation value were calculated and shown in Table 3.2.

Table 3.2 Average of mercury remaining and percent deviation in adsorption on chitosan repetitive study.

Chitosan (DD)	Type of Mercury	Temperature ($^{\circ}$C)	Int. pH of Solution	Average (ppm)	Maximum % Deviation
79%	HgCl$_2$	30	6	6.513	1.63
	PMA	10	5	7.112	5.17
87%	HgCl$_2$	30	6	6.037	2.34
	PMA	30	7	7.296	1.12
95%	HgCl$_2$	50	7	7.559	1.45
	PMA	30	5	7.311	1.72

Error from Chemical Oxidation Procedure.

This experiment was conducted to study the error from chemical oxidation that converts all mercury to the mercuric ion. In this experiment was repeatedly adsorbed for 3 times. Average concentration and maximum deviation of these experiments are shown in Table 3.3

Table 3.3 Average concentration and maximum deviation of mercury compound from chemical oxidation procedure.

Descriptions	1 (ppm)	2 (ppm)	3 (ppm)	Average Conc. (ppm)	Maximum (%) Deviation
CTS 87% HgCl$_2$ pH7 50°C	7.57	7.57	7.61	7.58	0.35

Instrumental Error

This experiment was conducted to verify instrumental error, average and deviation of experiments. The same sample was analyzed for 3 times by the instrument at the same condition. From analysis, the maximum percent deviations were in range of 5 % for mercuric chloride removal and phenylmercuric acetate removal.

Mercury Content in Chitosan

This experiment was to verify the mercury content that existed in chitosan. A chitosan flake was digested by the acid digest regent and measured the digested solution by cold vapor atomic absorption technique as described in previous Section. This result shows that the mercury content is not over 1 ppb.

Blank Test

The experiment in this section verified the quantity of disappearance mercury compounds during operations. No adsorbent was used in this test. Percent of mercury loss from feed are shown in Table 3.4. It was found that mercuric chloride and phenylmercuric acetate concentration in product and feed was almost identical. Then, it indicates that mercuric chloride and phenylmercuric acetate disappear by adsorption of the glassware.

Table 3.4 Percent of mercury compounds losses from feed at various

temperatures.

Component	Mercury losses from feed (%)		
	$10^{\circ}C$	$30^{\circ}C$	$50^{\circ}C$
Mercuric chloride	1.36	2.06	3
Phenylmercuric acetate	1.42	1.24	2