CHAPTER IV

RESULTS AND DISCUSSIONS

In this chapter, experimental results are presented. The results are divided into five parts: experimental procedure and preliminary results (described in Section 4.1), experimental results (described in Section 4.2), the effects of pH, temperatures and degree of deacetylation on adsorption of mercury compounds (described in Sections 4.3 to 4.5).

Three types of chitosan are produced in Thailand. Their properties depend on sources and companies. Chitosan used in this study is commercial grade. Appendix B shows specification of chitosan produced by Seafresh Chitosan (Lab) Co., Ltd. and BET results are shown in Table 4.1. Surface area of chitosan (87% degree of deacetylation) is approximately 9 m^2/g, which is considered to be very low compared with other materials normally used as adsorbent.

Table 4.1 Comparison of BET surface area, pore diameter and total pore volume in many types of adsorbent.

Types of Adsorbent	Surface Area (m^2/g)	Average Pore Diameter (A)	Total Pore Volume (cc/g)
Chitosan Flakes	9	68	0.02
Chitosan Beads	93	170	–
Activated Carbon	1000	15	0.47
Alumina	170	55	0.23
Silica - Alumina	550	58	0.80

4.1 Experimental Procedure and Preliminary Results

This section is divided into three parts. The first part describes the adsorption experiment. The second part is the discussion of adsorption behavior at low mercury concentration. The third part shows the results from determination of adsorption period of mercury solution containing 10 ppm.

4.1.1 Adsorption Experiment

Mercury removal experiment by adsorption is conducted in batch system. Mercuric chloride ($HgCl_2$) and phenylmercuric acetate (PMA) are used as model compounds for inorganic and organic mercury compounds, respectively. After adsorption experiments, spent adsorbents are separated from aqueous samples. The pH of aqueous samples is measured and the results are shown in Appendix A.

Mercury content in aqueous phase was not directly measured by an atomic absorption spectroscopy technique. All mercury in aqueous samples is converted to mercuric ion by chemical oxidation. Chemical oxidation procedure is the method that changes the mercury compounds to mercury ion (Hg^{2+}). Mercury content in aqueous phase can be measured using cold vapor atomic absorption technique.

Selected spent adsorbent is digested to measure mercury content, which is adsorbed on the adsorbents. ASTM 1977-91 is used as a guideline for determination of mercury content. Desorption study of selected spent adsorbents is conducted to determine the desorption capability of adsorbed mercury on adsorbents. The spent adsorbent is stirred in acid solution to allow mercury on the surface to desorbed. All mercury in the solution is converted to mercuric ion by chemical oxidation (described previously). The results in desorption and adsorbent digestion are described in Section 4.2.

In each experiment, mercury concentration of the feed is analyzed and it was found that mercury concentration is not equal to the desired value. Therefore the results of adsorption experiments in this chapter are reported in term of fraction of mercury compound which has been removed from the solution, as percent removal, instead of the

mercury content in the solution. All operating conditions of this study are summarized in Table 4.2.1.

The percent removal is calculated from Equation 4.1. The amount of adsorbed mercury per amount of chitosan is calculated from Equation 4.2. As shown in Chapter III, summation of errors which caused by chemical oxidation procedure, instrumental analysis and the experiment are less than 6 %

$$\text{Percent removal (\%)} = \frac{(C_f - C_r)}{C_f} \times 100 \quad \ldots\ldots\ldots(4.1)$$

C_f = the concentration of feedstock (ppm).

C_r = the concentration of remaining mercury (ppm).

4.1.2 Adsorption Behavior at Low Mercury Concentration

A set of preliminary experiment is conducted at various conditions (described in Table 4.1.1). The experiment at each condition was conducted at least 2 times and the results are shown in Appendix A. Table 4.1.2 shows the results calculated in percent removal of mercury compound using Equation 4.1.

Table 4.1.1 Operating conditions in adsorption of $HgCl_2$ in solution containing 1 ppm.

Feed weight (g)	100
Feed concentration (ppm)	1
Pressure (atm)	1
Temperature (^{o}C)	30
Mercury compound	$HgCl_2$
Initial pH of feed	7.0
Degree of deacetylation (%)	87
Adsorbent weight (mg)	5
	10
	15
	50
Time (hour)	1
	2
	3
	6
	9

The results in Table 4.1.2 show large deviation between each experiment. When the results are averaged and percent deviations are calculated, the deviation between each experiment are as high as 146%. It is found later that our analysis method of mercury content can not be used effectively at low mercury content. Since initial concentration of mercury is low, 1 ppm, mercury content after adsorption should be much lower than 1 ppm. Analysis of mercury content at very low concentration especially when the concentration is close to the detection limit of the instrument can cause error in the result. Therefore another set of the preliminary experiment was conducted at initial

Table 4.1.2 Percent removal and percent deviation in adsorption of $HgCl_2$ in solution containing 1 ppm

Samples		% Removal										Avg. of %	Max.of %
Conditions	Time (hrs)	1	2	3	4	5	6	7	8	9	10	Removal	Deviation
CTS 5 mg	3	30.49	78.41	–	–	–	–	–	–	–	–	54.45	119.79
	6	61.47	77.59	–	–	–	–	–	–	–	–	69.53	40.29
pH 7	9	34.71	84.36	–	–	–	–	–	–	–	–	59.53	124.13
30°C	12	64.07	77.67	–	–	–	–	–	–	–	–	70.87	33.99
CTS 10 mg	3	90.92	67.01	77.81	74.57	80.11	86.67	87.59	77.36	86.58	78.15	80.68	16.94
	6	84.99	85.65	87.14	82.41	93.24	92.46	87.53	98.39	–	–	88.98	10.58
pH 7	9	92.21	95.94	85.89	80.53	99.97	94.54	91.56	–	–	–	91.52	12.01
30°C	12	80.59	97.24	89.82	85.61	95.35	–	–	–	–	–	89.72	10.18
CTS 15 mg	3	77.13	46.21	–	–	–	–	–	–	–	–	61.67	77.29
	6	79.65	84.09	–	–	–	–	–	–	–	–	81.87	11.11
pH 7	9	34.56	92.94	–	–	–	–	–	–	–	–	63.75	145.94
30°C	12	67.70	94.45	–	–	–	–	–	–	–	–	81.07	66.87
CTS 50 mg	3	64.02	67.12	–	–	–	–	–	–	–	–	65.57	7.76
	6	75.17	96.60	–	–	–	–	–	–	–	–	85.88	53.57
pH 7	9	80.63	60.75	–	–	–	–	–	–	–	–	70.69	49.70
30°C	12	81.93	62.17	–	–	–	–	–	–	–	–	72.05	49.41

mercury content of 10 ppm and the results are shown in Table 4.1.5. The deviation of each experiment is less than 6%, which is considered to be within an acceptable value.

Because of the problem in analysis method, the initial mercury content was then changed to 10 ppm.

4.1.3 Determination of Adsorption Period

Table 4.1.3 shows the conditions used in the experiments to determine suitable adsorption period. Experimental results are shown in Appendix A and summarized in Table 4.1.4. Figure 4.1.1 shows the plot of percent removed of mercury compound as a function of time.

Table 4.1.3 Operating conditions in study of effect of contact time

Feed weight (g)	100
Feed concentration (ppm)	10
Pressure (atm)	1
Temperature ($^{\circ}$C)	30
Mercury compound	$HgCl_2$ PMA
Initial pH of feed	7.0
Degree of deacetylation (%)	87
Adsorbent weight (mg)	10
Time (hour)	1 2 3 6 9

Figure 4.1.1 shows that the percent removal curve can be divided into two parts. In first period, 0 – 3 hours, percent removal of mercury compounds increases rapidly and maintains at the constant value in the second period, 3 – 9 hours. In the first period, concentration of mercury compounds in bulk solution is high. Mercury in the bulk solution can easily transfer through the surface of the adsorbent. In the second period, concentration of mercury compounds in the bulk solution is lower than the first period, thus mercury can slowly and slightly transfer to the adsorbent and the deposited mercury may be retards transferring of mercury from the bulk solution to the adsorbent surface. Thus, rate of mercury deposition on adsorbent is very slow. From this set of

experiments, the suitable contact time is considered. It indicates that the suitable time should be 3 hours.

Table 4.1.4 The results of adsorption of mercury compounds in solution containing 10 ppm

Mercury Compounds	Contact Time (Hrs)	% Removal of Mercury Compounds			Average of % Removal	Max. of % Deviation
		1	2	3		
HgCl₂	1	20.10	27.28	25.24	24.21	5.42
	2	32.99	33.01	37.49	34.50	4.87
	3	42.13	41.51	40.73	41.37	1.15
	6	47.07	42.65	41.77	43.83	5.76
	9	43.82	43.08	44.36	43.86	1.20
PMA	1	17.36	18.79	–	18.08	3.97
	2	25.61	25.05	–	25.33	1.11
	3	27.34	26.74	–	27.04	1.12
	6	26.62	28.53	–	27.58	3.47
	9	27.26	28.48	–	27.87	2.20
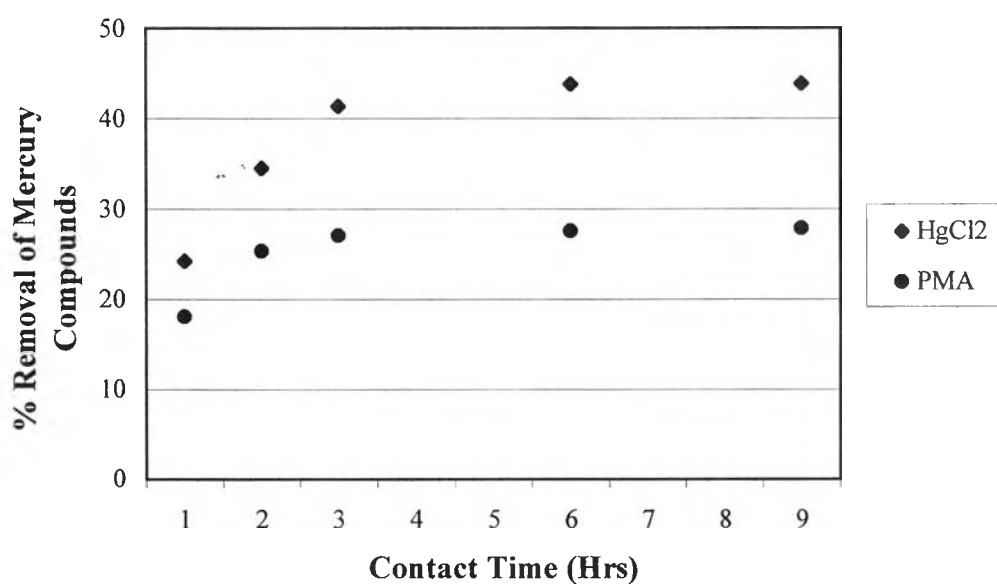
Figure 4.1.1 Effect of contact time on adsorption of mercury compounds in solution containing 10 ppm.

4.2 Experimental Results

Table 4.2.1 shows operating conditions of adsorption of mercury compound. Effects of pH, temperature and degree of deacetylation on adsorption ability of chitosan are studied.

Table 4.2.1 Operating conditions of all experiments.

Feed weight (g)	100
Adsorbent weight (mg)	10
Feed concentration (ppm)	10
Pressure (atm)	1
Time (hour)	3
Mercury compound	Mercuric Chloride Phenylmercuric Acetate
Initial pH of feed	5.0 6.0 7.0
Temperature (^{o}C)	10 30 50
Degree of deacetylation (%)	79 87 95

The results of these experiments are shown in Appendix A. Table 4.2.2 shows the percent removal of mercury compounds. Spent adsorbents are analyzed by XRD method to find crystalline substance on adsorbent. Figures 4.2.1 and 4.2.2 show the XRD patterns of spent adsorbents used in adsorption studies of mercuric chloride and phenylmercuric acetate, respectively.

The XRD results indicate that $HgCl_2$ adsorbed on chitosan is in the form of $HgCl^+$ and $HgCl_2$ while PMA is in the form of $C_4H_6HgO_4$. Kawamura et al. (1993) studied the adsorption of Hg(II) on chitosan and suggested that adsorption of Hg(II) on

chitosan is not an ion exchange mechanism. They proposed an adsorption mechanism as a complex reaction formation, as indicated in Equation 4.3.

$$R\text{-}\underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{N}} + HgCl_2 \rightleftharpoons R\text{-}\underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{N}}\text{-}HgCl_2 \quad\text{.............................(4.3)}$$
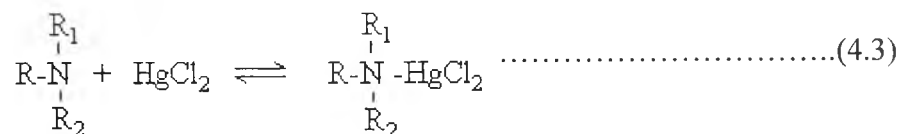
R_1 and R_2 are hydrogen or cross-linking reagent. Chitosan is called the multidentate ligands or chelating substance. Multidentate ligands have more than one atom, which has lone pair electron. Amino group on chitosan can make coordinate-covalent bond between N atom with Hg atom. In the case of $HgCl^+$, the adsorption of $HgCl^+$ on chitosan may be ligand adsorption on amino group fixed in the chitosan particle. The reaction is shown by Equation 4.4.

$$R\text{-}NH_2 + HgCl^+ \rightleftharpoons R\text{-}NH_2\text{-}HgCl^+ \quad\text{..........................(4.4)}$$
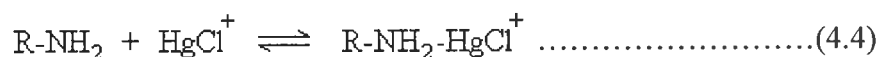
Table 4.2.2 Percent removal in adsorption of mercury compounds

Degree of deacetylation (%)	Temperatures ($^\circ$C)	% Removal of Mercury Compounds					
		HgCl$_2$			PMA		
		pH 5	pH 6	pH 7	pH 5	pH 6	pH 7
79	10	23.68	21.25	18.61	28.88	24.17	19.99
	30	51.52	34.87	27.57	28.79	23.98	20.29
	50	42.66	30.06	21.06	28.97	28.30	21.87
87	10	30.55	29.33	26.73	30.21	26.92	25.65
	30	51.82	39.63	35.46	32.38	30.12	27.04
	50	44.47	29.66	25.07	34.61	34.00	29.87
95	10	35.73	29.56	26.85	30.03	27.00	25.05
	30	54.08	44.60	36.24	33.27	31.10	28.29
	50	47.38	33.46	24.41	35.95	34.58	30.40

The XRD result indicates that PMA adsorbed on chitosan in the form of $C_4H_6HgO_4$. The most possible compound having this formula is mercury(II) acetate (Chemical Properties Handbook). The adsorption of PMA on chitosan may be ligand adsorption on amino group fixed in chitosan particle, according to Equation 4.5.

$$R–NH_2 \; + \; Hg(COOCH_3)_2 \quad \rightleftharpoons \quad R–NH_2–Hg(COOCH_3)_2 \quad \text{.................(4.5)}$$

Tezuka and Tonomura (1976) studied the dissociation of PMA in underwater and proposed that PMA dissociated by enzyme catalyst in water, as shown in Figure 4.2.1. PMA in water reacted with organomercurial lyase and dissociated in three groups, Hg^{2+}, phenyl group and acetate group. It is possible in this study that PMA can dissociate and Hg^{2+} and acetate groups are adsorbed on chitosan. The presence of phenyl groups, which should remain in water phase, can not be determined because of its low concentration.
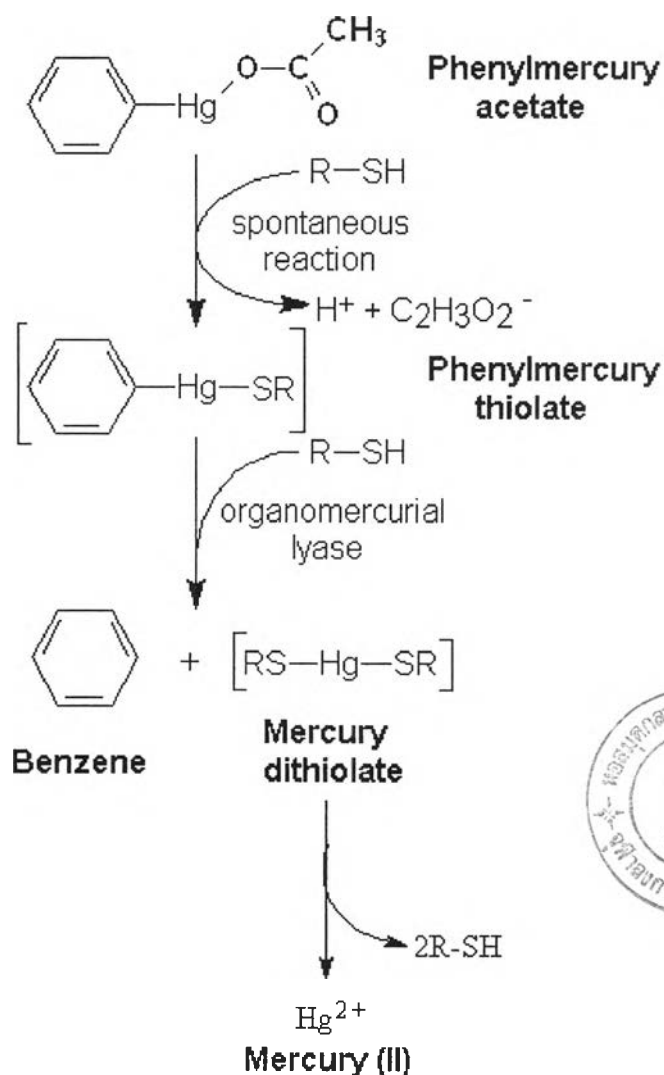
Figure 4.2.1 Solubility of PMA in underwater.
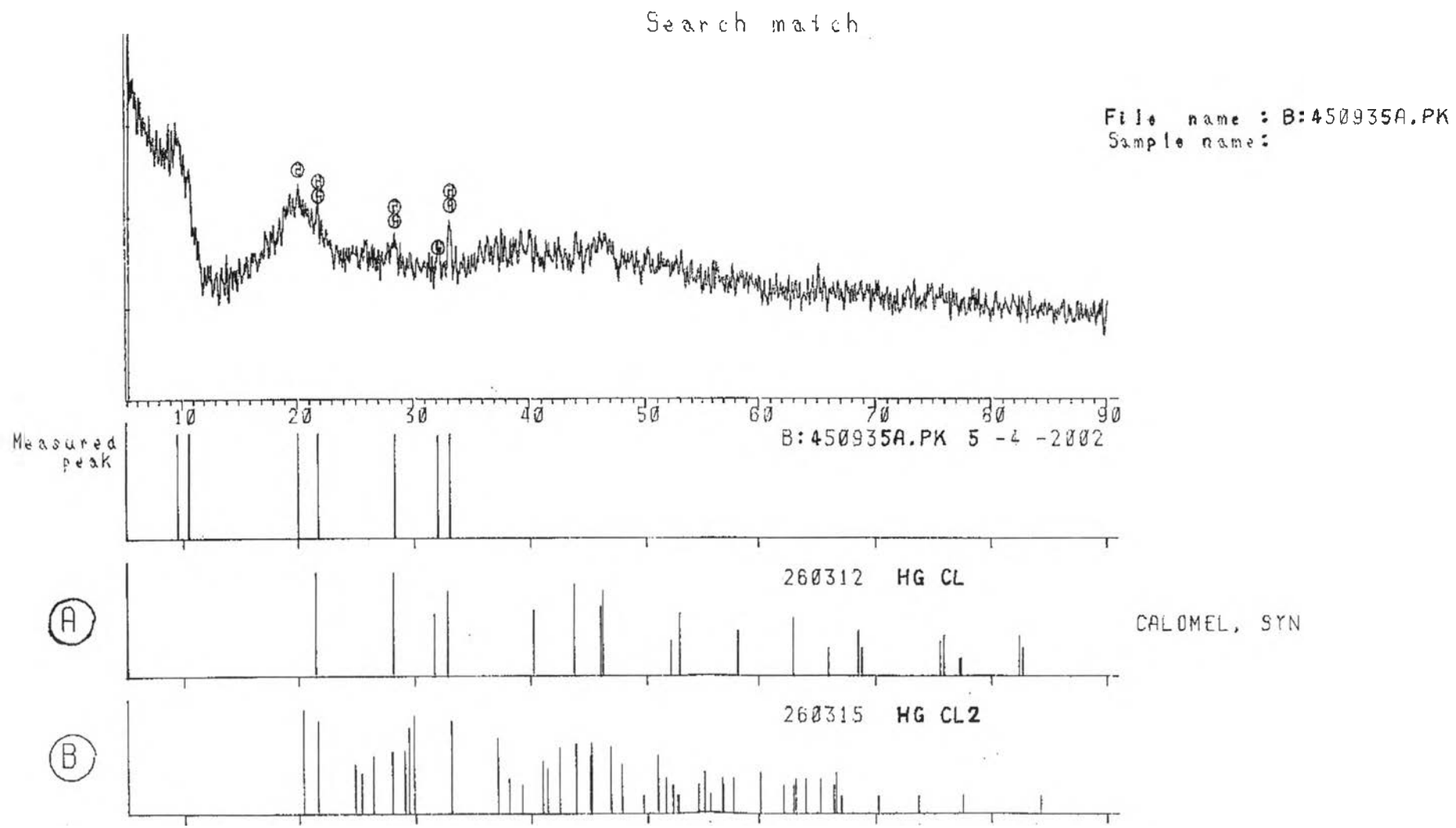
Figure 4.2.2 XRD pattern of mercuric chloride on spent adsorbent
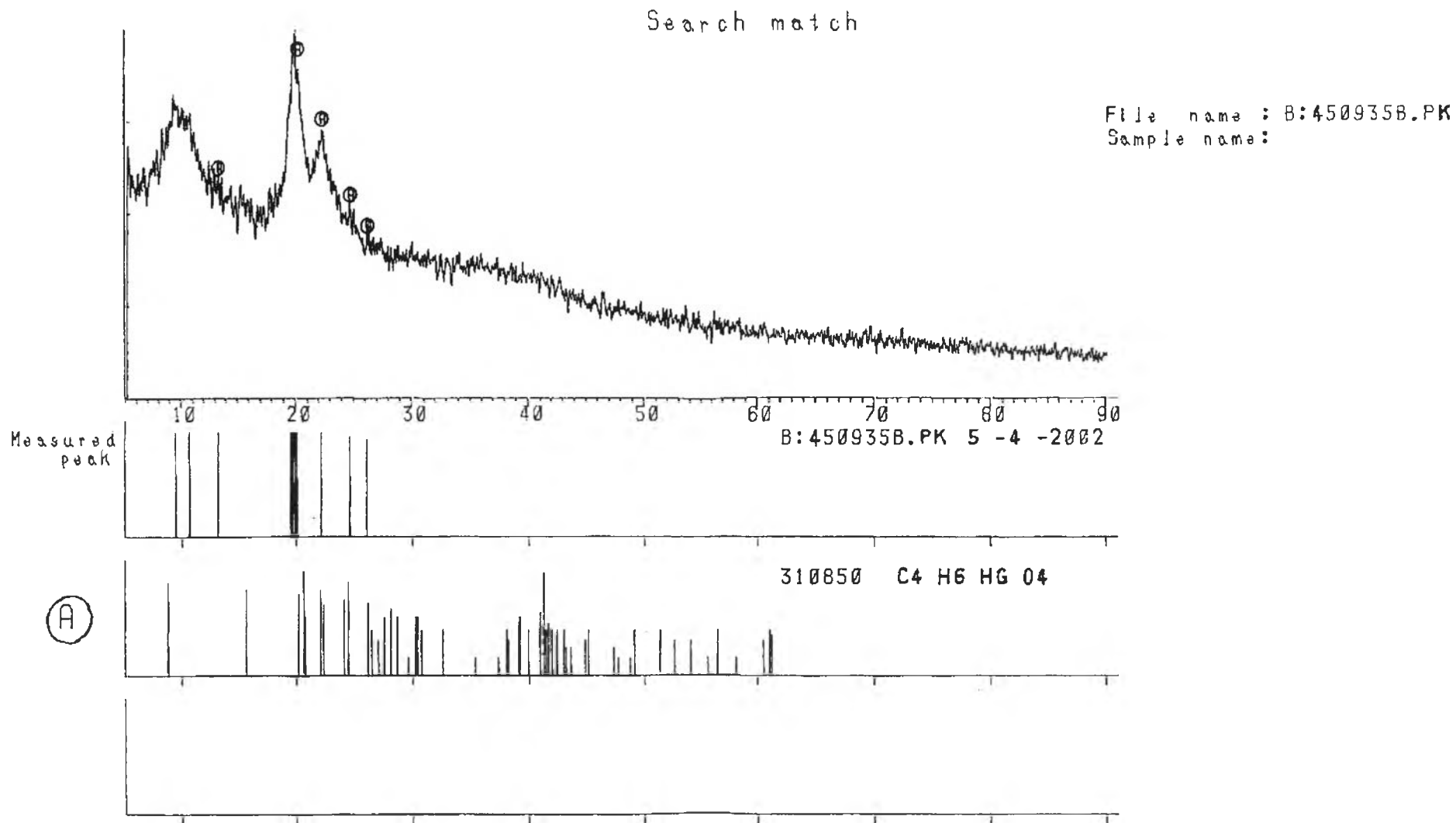
Figure 4.2.3 XRD pattern of phenylmercuric acetate on spent adsorbent

The pH of the feed is measured by pH meter, it is found that pH of deionized water is approximately 6.4. After $HgCl_2$ or PMA was dissolved, the pH of the solution was approximately 4.8. The pH of the solution was then adjusted to 5, 6 and 7 using NaOH solution. After each experiment, the pH of the solution was measure again. Table 4.1.1 shows examples of pH of the solution before and after adsorption at temperature of $30^{\circ}C$.

Table 4.2.3 pH values before and after adsorption of $HgCl_2$ at temperature of $30^{\circ}C$.

Types of Chitosan	pH of Solution	
(DD)	Initial	Final
79%	5.0	5.6
	6.0	6.2
	7.0	6.3
87%	5.0	6.0
	6.0	6.3
	7.0	6.4
95%	5.0	6.2
	6.0	6.3
	7.0	6.6

The results in Table 4.2.3 indicate that after each experiment the pH of the solution changes and tends toward a value of approximately 6.0 to 6.3. Wu and Tseng (1999) described the behavior of chitosan in aqueous solution that the amino groups of chitosan react with H^+ according to

$$R\text{-}NH_2 + H^+ \rightleftharpoons R\text{-}NH_3^+, \quad K_p \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots(4.6)$$
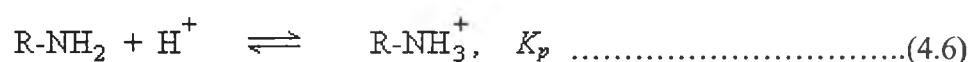
Because the protonation constant is $\log K_p = 6.3$, then behavior of chitosan is the same as buffer. When the pH of feed is less than 6.3, equilibrium of Equation 4.1 shift to the right while when the pH of feed is more than 6.3, equilibrium of Equation 4.6 shift to the left. The results indicate an agreement with Equation 4.6.

4.3 Effects of pH on Adsorption of Mercury Compounds

A set of experiments is conducted to study the effect of pH on adsorption of mercury compounds. The initial pH of the solution in this study is 5, 6 and 7. The results of mercury compounds removal by chitosan at various initial pH of solution are shown in Table 4.2.2 and are plotted in Figures 4.3.1 and 4.3.2 for $HgCl_2$ and PMA.
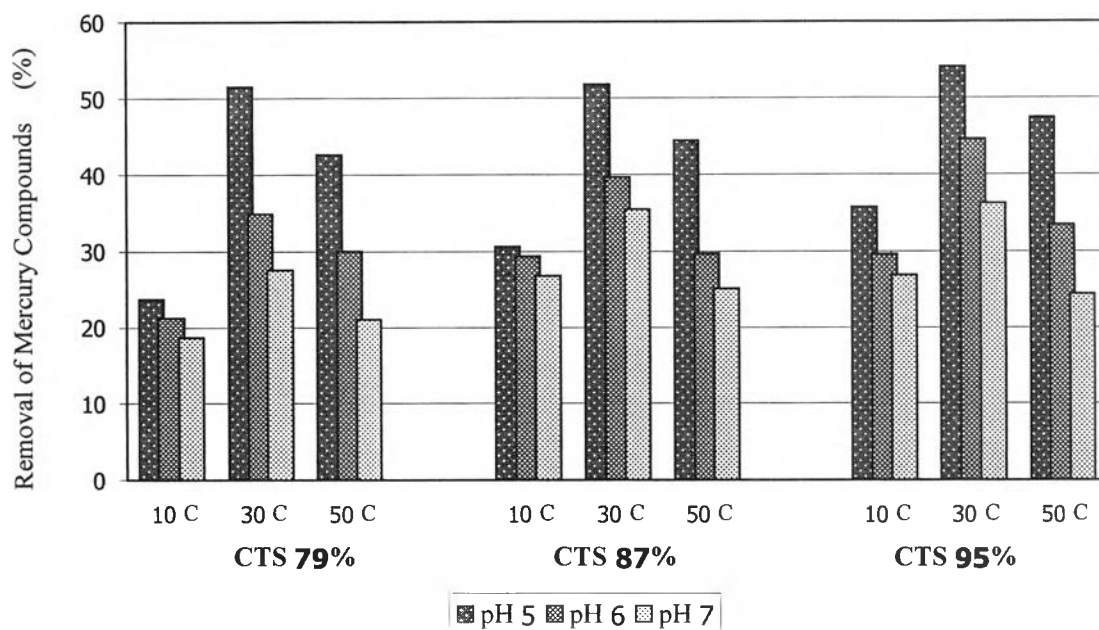

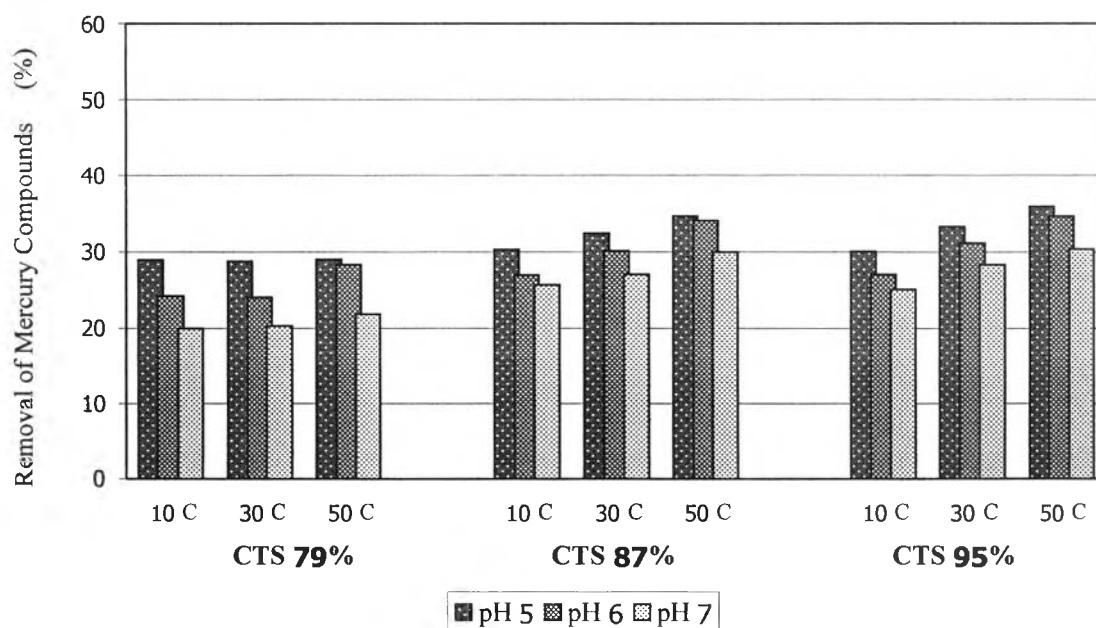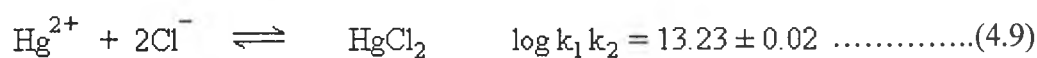**Figure 4.3.1** The comparison of initial pH of feed in adsorption of $HgCl_2$
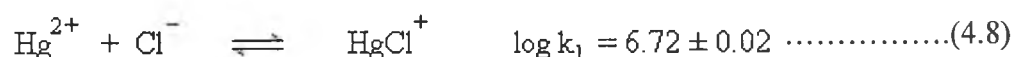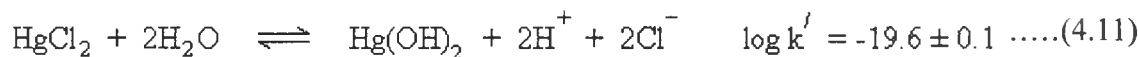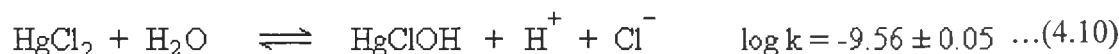

Figure 4.3.2 The comparison of initial pH of feed in adsorption of PMA

The results indicate that the ability of chitosan on adsorption of $HgCl_2$ decreases significantly with increasing of pH at operating temperature of $30^{\circ}C$ and $50^{\circ}C$. The effect of pH can not be clearly identified at a temperature of $10^{\circ}C$ eventhough the same trend is also observed.

Ciavatta and Grimaldi (1968a) described the ionization mechanism of $HgCl_2$ in the liquid phase as shown in Equations 4.8 and 4.9. They also calculated the formation constants $(k_1, k_1 k_2)$ as below.

$$Hg^{2+} + Cl^{-} \rightleftharpoons HgCl^{+} \qquad \log k_1 = 6.72 \pm 0.02 \quad \cdots\cdots\cdots\cdots(4.8)$$

$$Hg^{2+} + 2Cl^{-} \rightleftharpoons HgCl_2 \qquad \log k_1 k_2 = 13.23 \pm 0.02 \quad \cdots\cdots\cdots\cdots(4.9)$$
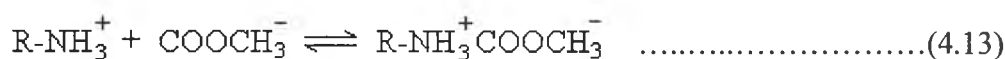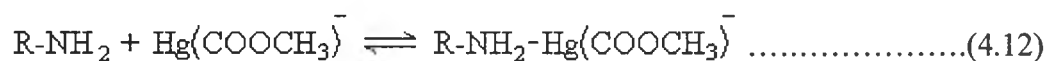
The formation constants show that the concentration of Hg^{2+} is negligibly small. Ciavatta and Grimaldi (1968b) also showed that $HgCl_2$ can dissociate in water with the formation of $HgClOH$ and $Hg(OH)_2$, as shown in Equations 4.10 and 4.11.

$$HgCl_2 + H_2O \rightleftharpoons HgClOH + H^{+} + Cl^{-} \qquad \log k = -9.56 \pm 0.05 \quad \cdots(4.10)$$

$$HgCl_2 + 2H_2O \rightleftharpoons Hg(OH)_2 + 2H^{+} + 2Cl^{-} \qquad \log k' = -19.6 \pm 0.1 \quad \cdots\cdots(4.11)$$

In the case of the single-solute system of $HgCl_2$, the dissociation constants (k, k') denote that $HgCl_2$ does not dissociate at all in the liquid phase. The concentration of any ionized or dissociated species from $HgCl_2$ was negligibly small and only $HgCl_2$ can be assume to be existed in the experimental solution.

However, Michelsen et al. (1975) studied the dissociation of $HgCl_2$ in water and suggested that around pH 4 the prevalent mercury species in the single-solute system of $HgCl_2$ were Hg^{2+}, $HgCl^{+}$ and $HgCl_2$ and the molar ratio of chloride to mercury was two. When pH of the solution rises, the neutral species $Hg(OH)_2$ become more prevalent and species Hg^{2+}, $HgCl^{+}$ and $HgCl_2$ decreased. Therefore, $HgCl_2$ and $HgCl^{+}$ adsorbed by Equations 4.3 and 4.4 decreases with increasing pH of the solution. Furthermore, the results show that percent removal of mercury compounds decreases between initial pH of 5 and 6 more than between initial pH of 6 and 7. It indicates that when pH of the solution rises, the amount of species $HgCl^{+}$ and $HgCl_2$ decreases rapidly. Therefore pH is very effect to $HgCl_2$ removal.

In adsorption of PMA experiments, the results indicate that removal ability of chitosan at some operating conditions are slightly decreases with increasing initial pH of the solution. At other conditions, the effect of pH can not be concluded because the differences in percent removal of PMA are lower than the error limit of the experiment. As discuss earlier in this chapter, PMA can dissociate when it is soluble in water. Upon its dissociation, Hg^{2+}, phenyl group and acetate group may form. Acetate group and Hg^{2+} may adsorb on chitosan easier than phenyl group. Mercury (II) acetate can adsorb on chitosan (as described previously). However, PMA may adsorb on chitosan in the other forms such as mercury (I) acetate adsorb on chitosan by ligand adsorption, as indicated in Equation 4.12. When pH of the solution is low, chitosan may react with H^+ according to Equation 4.6. Acetate anion can adsorb by electrostatic attraction, as indicated in Equation 4.13.

$$R\text{-}NH_2 + Hg(COOCH_3)^- \rightleftharpoons R\text{-}NH_2\text{-}Hg(COOCH_3)^- \quad \dots\dots\dots\dots\dots\dots(4.12)$$

$$R\text{-}NH_3^+ + COOCH_3^- \rightleftharpoons R\text{-}NH_3^+COOCH_3^- \quad \dots\dots\dots\dots\dots\dots\dots(4.13)$$

4.4 Effect of Temperatures

A set of experiment is conducted to study the effect of operating temperatures on adsorption of mercury compounds. The operating temperatures in this study are 10°C, 30°C and 50°C. The results are shown in Table 4.2.2 and are plotted in Figures 4.4.1 and 4.4.2 for $HgCl_2$ and PMA.
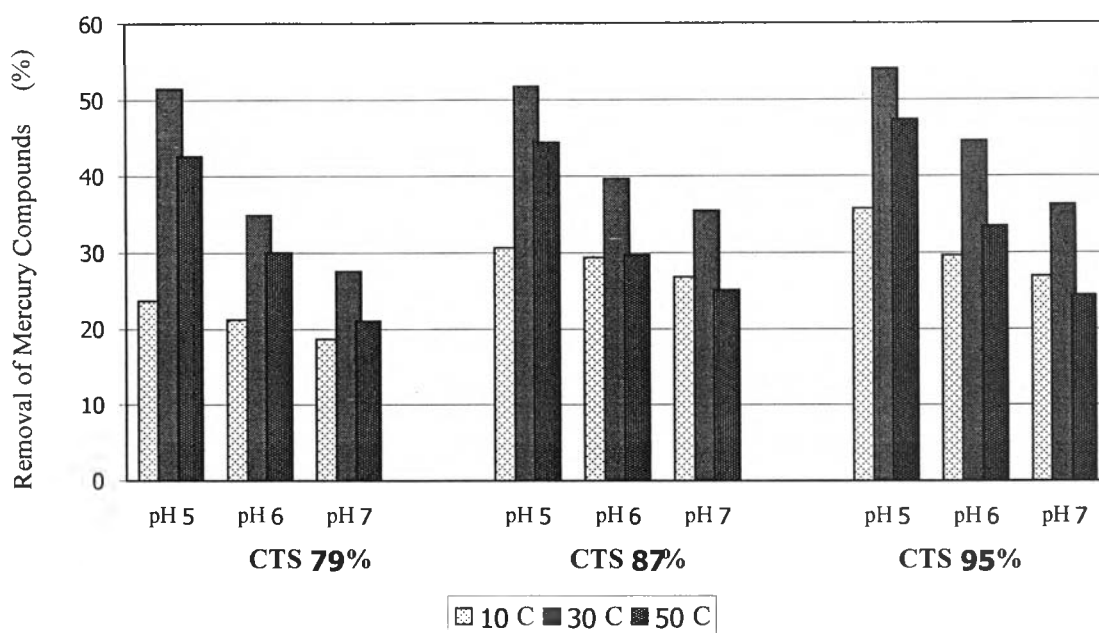

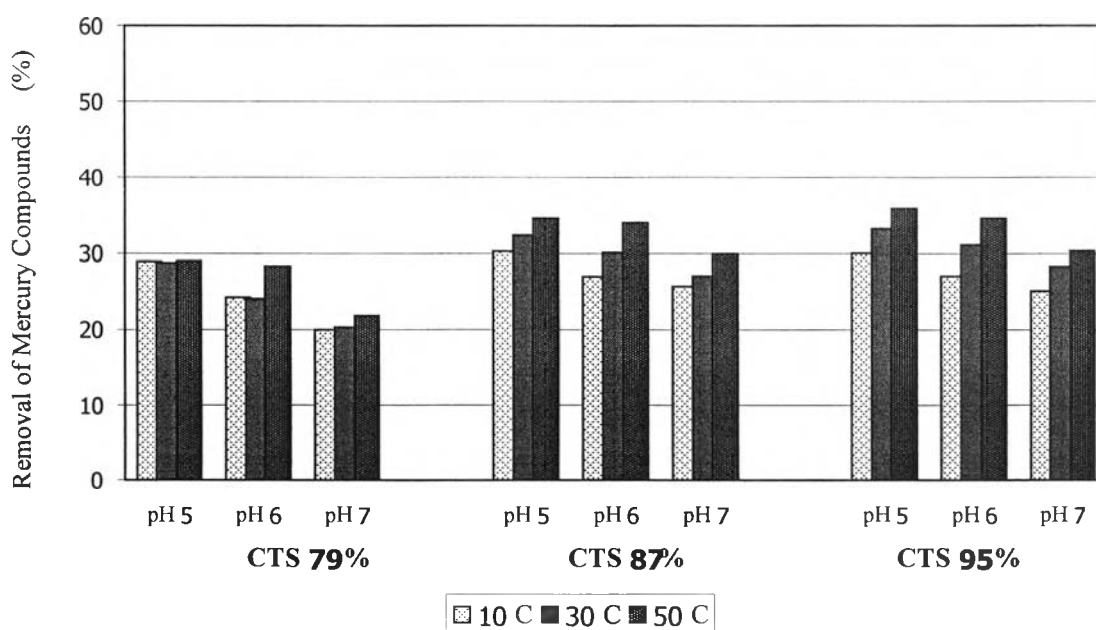**Figure 4.4.1** The comparison of operating temperature in adsorption of $HgCl_2$

Figure 4.4.2 The comparison of operating temperature in adsorption of PMA

For $HgCl_2$ experiments. the results show that percent removal of $HgCl_2$ increases significantly with operating temperature increasing between $10^{o}C$ and $30^{o}C$ but percent removal of $HgCl_2$ decreases significantly with operating temperature increasing between $30^{o}C$ and $50^{o}C$. At temperature of $50^{o}C$ structure of chitosan may be changing because it is organic substance. Juang et al. (1997) studied effect of pH in removal of copper compound using polyaminated chitosan beads. The results showed that percent removal of copper compound increased with increasing of temperatures between $15^{o}C$ to $45^{o}C$. They suggested that the equilibrium constant and number of layer decreased with increasing of temperature. The results in other studies also indicated that temperature affected the adsorption of $HgCl_2$.

For adsorption of PMA experiments, the results indicate that removal ability of chitosan at some conditions slightly increased with increasing operating temperature. At other conditions, the effect of operating temperature can not be concluded because the differences of percent removal of PMA are lower than the error limit of the experiment. Comparison of percent removal of mercury compound indicated that $HgCl_2$ could be removed more effectively than PMA. This may be the result of polarity and complication of the molecule of mercury compounds. $HgCl_2$ is an ionic compound and it has more polar than PMA that is an organic compound. In contrast, PMA has one benzene ring that is stable because of its high resonance energy of π electron in molecular. The results indicate that type of mercury compounds affects the removal of mercury compounds.

4.5 Effect of Degrees of Deacetylation

A set of experiments is conducted to study the effect of degree of deacetylation of chitosan on adsorption of mercury compounds. Chitosan are classified on the basis of their degree of deacetylation (DD). Degree of deacetylation determines the content of free amino groups (as described in Chapter II). Degree of deacetylation in this study is 79%, 87% and 95%. The results are shown in Table 4.2.2 and are plotted in Figures 4.5.1 and 4.5.2 for $HgCl_2$ and PMA.
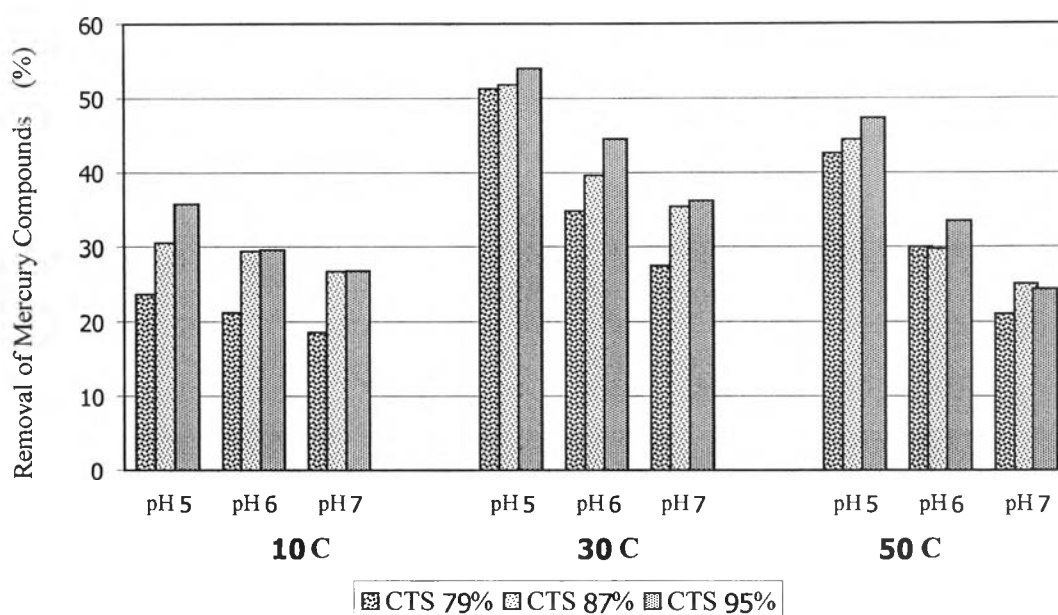

Figure 4.5.1 The comparison of degree of deacetylation of chitosan on $HgCl_2$ removal at various pH of feed and temperatures.

Figures 4.5.1 and 4.5.2 shows that the differences of percent removal of mercury compounds at all condition are lower than the error limit of the experiment except at one operating condition which $HgCl_2$ is in the feed and at temperature of $10^\circ C$ and pH of 5. Thus, the effect of degree of deacetylation can not be concluded. However, similar results were observed by Cha Young Kim et al. (1996) who showed that the rate and capacity of the metal adsorption on chitin was proportional to the degree of deacetylation in chitin at each pH, and the opposite effect was shown with pH change for each deacetylated chitin. This was mainly due to the increase of $-NH_3^+$ group in chitosan with high degree of deacetylation and the low pH of the system that in accordance with description in Section 4.1.
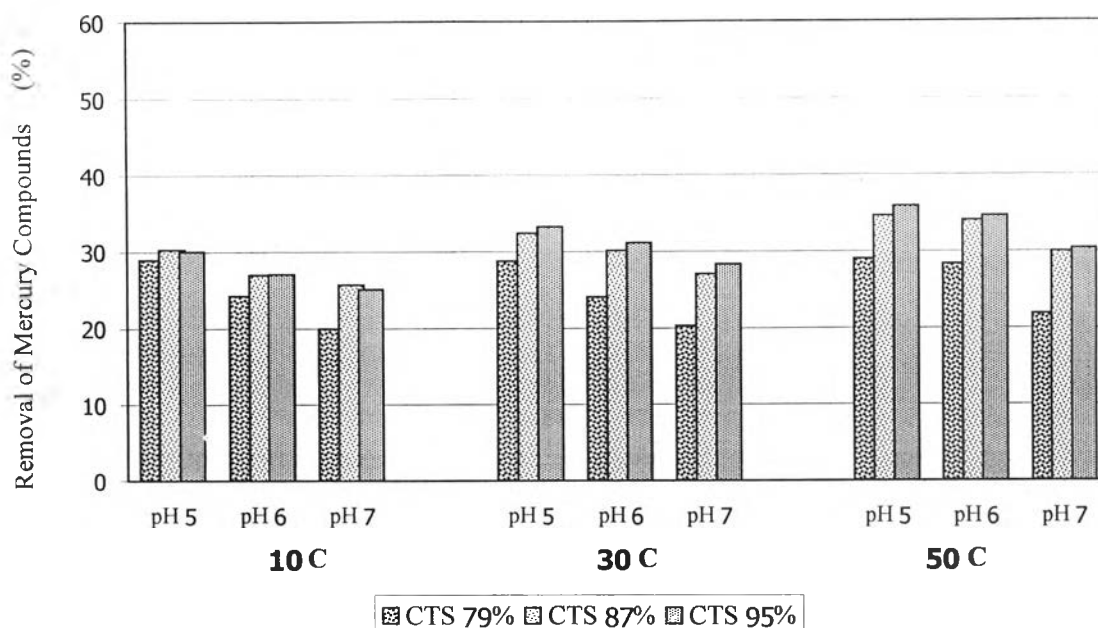
Figure 4.5.2 The comparison of degree of deacetylation of chitosan on PMA removal at various pH of feed and temperatures.

Furthermore, Bassi et al. (2000) suggested that the reaction between metal ion and chitosan was related with degree of deacetylation and the spread of $-NH_3^+$ group on polymer chain of chitosan. The $-NH_3^+$ group can be coordinated with metal ion because nitrogen atom in amino group have lone pair electron. Kaminski and Modrzejewska (1997) reported the chelating between chitosan and copper (II) ion. For $HgCl_2$ experiments, from equation (4.3), $HgCl_2$ was adsorbed on amino group ($-NH_2$). Therefore percent removal of $HgCl_2$ may depend on amount of amino group on chitosan.