Chapter 4

Results and Discussion

4.1 Chlorine Decomposition Results

4.1.1 Decomposition without Agitation

The chlorinated water used in this experiment containing 5 ppm maximum of chlorine was prepared by diluting 10 percent liquid chlorine with distillation water . The experimental period after chlorine preparation was about 3 to 4 hours. In order to investigate the decomposition of low chlorine concentration, chlorinated water of 1.7 ppm was prepared and was sampled to measure chlorine content at 30 minute interval for 3 hours. The results, as summarized in Table 4.1, demonstrated that although chlorine was able to decompose, only 40 % of the initial content decomposed within 3 hours. The system needed a certain period for decomposing chlorine to the desired value.

Table 4.1 Chlorine decomposition results

Time(Hr.)	Chlorine Conc.(ppm)	Percent Decomposition
0	1.70	
0.5	1.32	22
1	1.22	28
1.5	1.16	32
3	1.01	41

4.1.2 Decomposition with Agitation

Agitation effect to chlorine decomposition was investigated by dividing the chlorinated water into 2 portions. One was agitated with magnetic stirrer steadily for 30 minutes. While the other was left without agitation for the same period. The chlorine contents of both portions were measured and were compared, as summarized in Table 4.2.

Table 4.2 Agitation effect of chlorine decomposition

Sample No.	Chlorine Conc.(ppm)		
	0 Hr	0.5 Hour	
		Agitation	No Agitation
1	0.07	0.05	0.04
2	0.31	0.24	0.23
3	0.31	-	0.26

Although chlorine was able to decompose, it was assumed that only small amount of chlorine decomposed in comparison with the adsorbed amount of chlorine at the same condition. Consequently, the amount adsorbed was determined from the

difference in the amounts of chlorine content between at the beginning and at a given period of batch adsorption.

4.2 Batch Adsorption

4.2.1 Batch Adsorption using ORP for Chlorine Analysis

4.2.1a pH-ORP Calibration Curve

Since the ORP value could vary with the concentration of chlorine and the pH of the solution, both ORP and pH values had to be measured for a given chlorine concentration in order to establish pH-ORP calibration curve. The resulted calibration curves in Figure 4.1 were compared with that obtained from literatures, as shown in Figure 4.2[7].

For convenience, the calibration curves were divided into several parts according to a range of pH values, as shown in Figure 4.3 A-D.

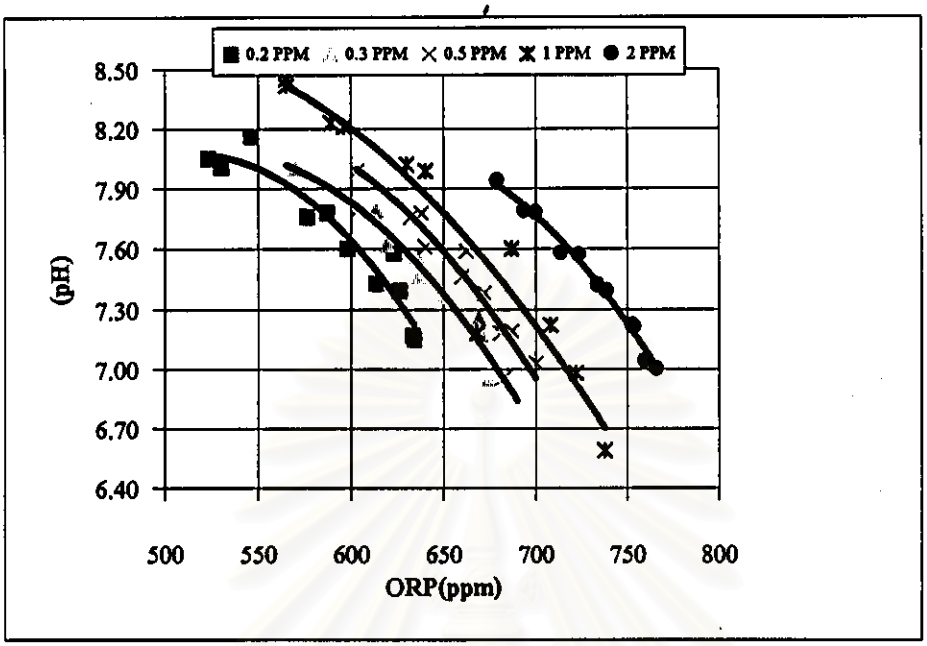

Figure 4.1 pH -ORP calibration curves in pH range of 7 to 8

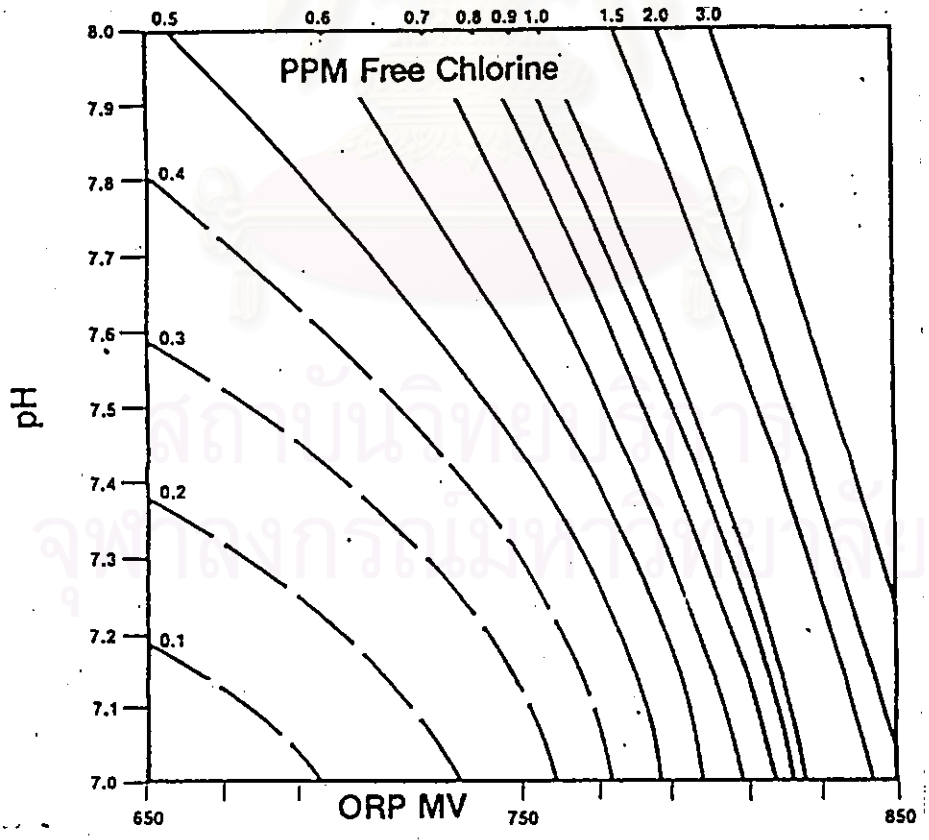

Figure 4.2 Variation of ORP for free chlorine as a function of pH

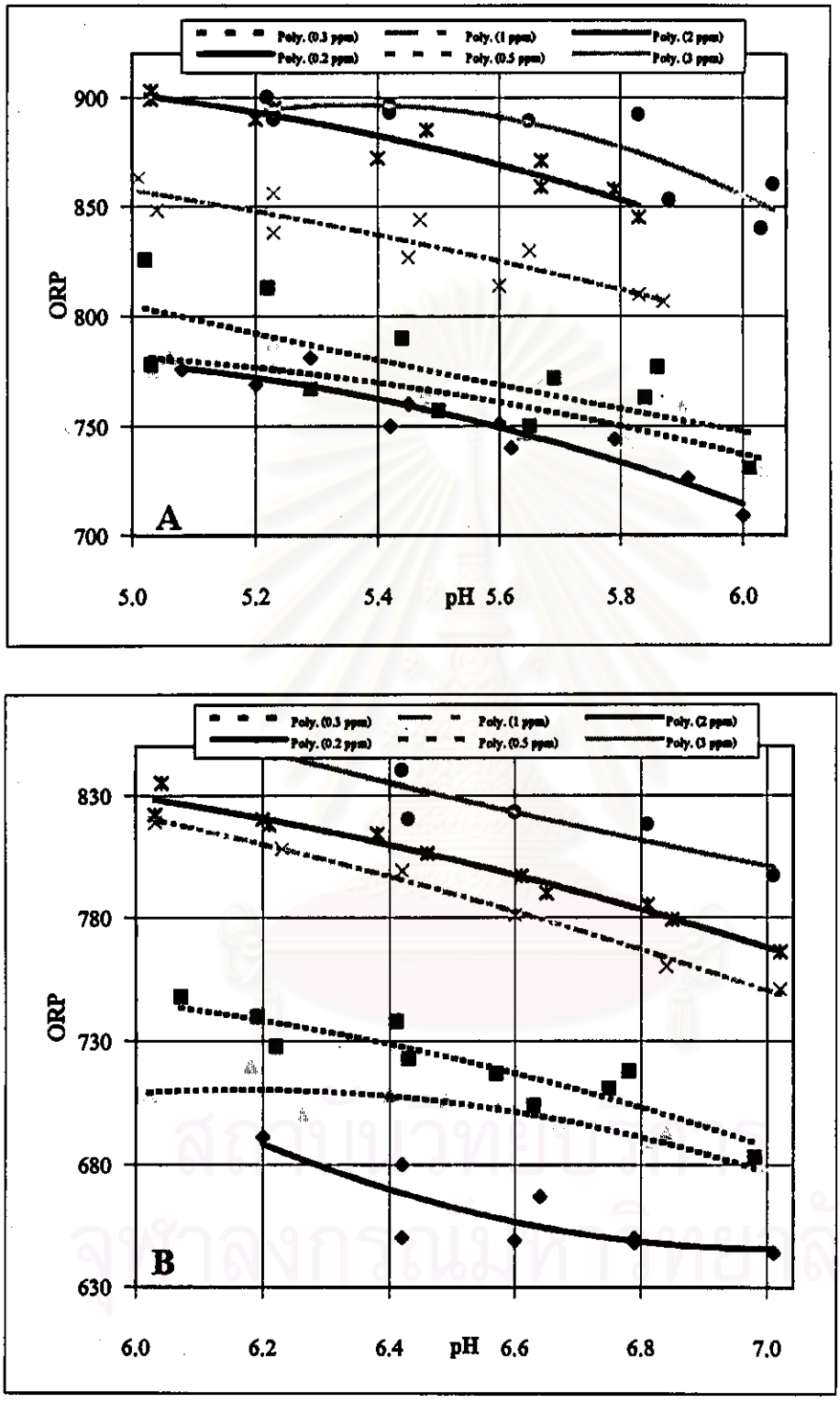

Figure 4.3 A-B pH-ORP calibration curve

A: pH 5-6, B: pH 6-7

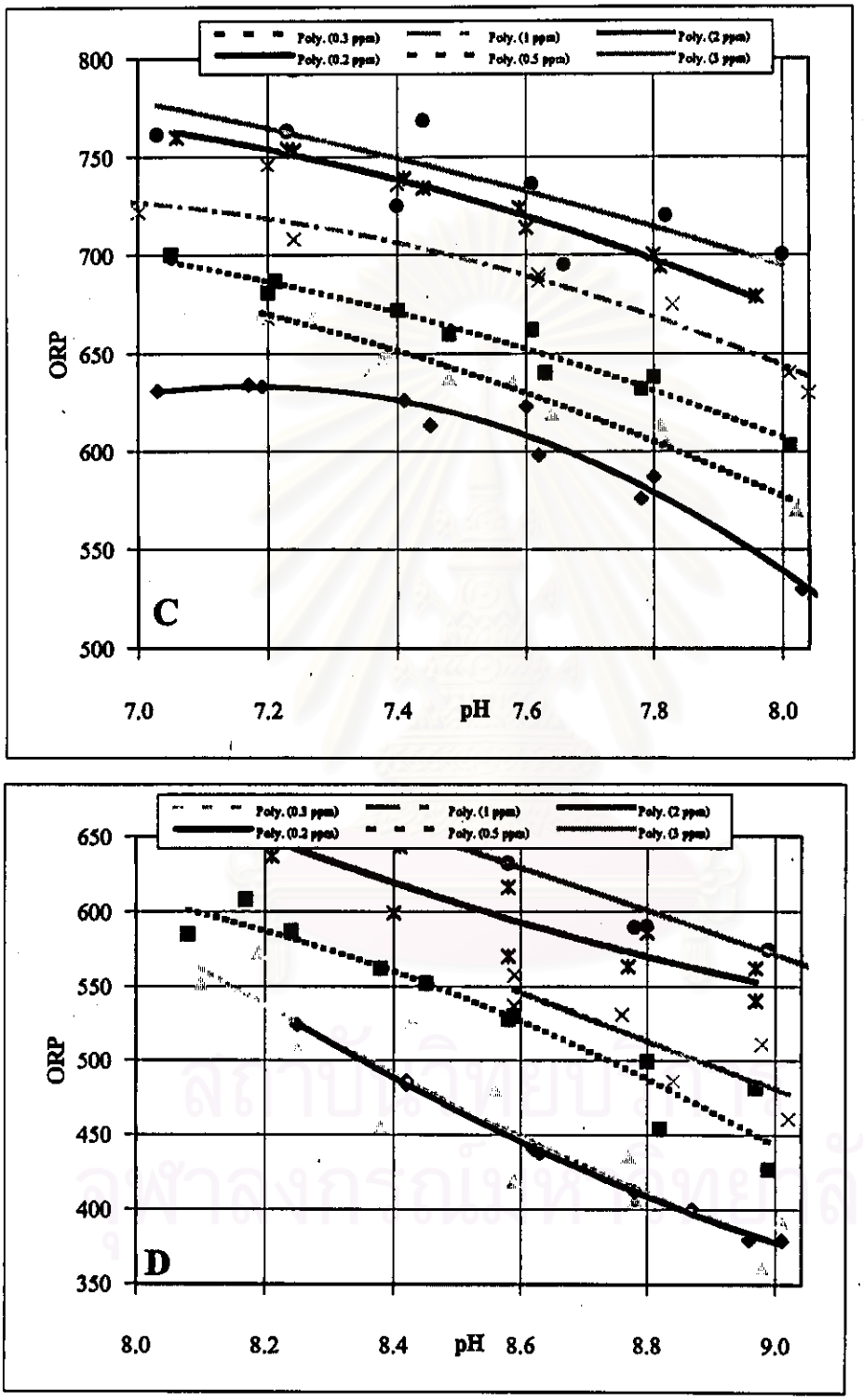

Figure 4.3 C-D pH-ORP calibration curve

C: pH 7-8, D: pH 8-9

4.2.1b Adsorption Isotherm on PHO 8/30

Batch adsorption results for a given amount of carbons in Figure 4.4 showed the amount of chlorine in water decreased from the initial concentration, 3 ppm, rapidly. Therefore the adsorption equilibrium of chlorine concentrations was evaluated from the average data of the chlorine content remaining in water within the period of 10 to 180 minutes. The adsorption isotherm, shown in Figure 4.5 corresponded with a linear isotherm. The equilibrium constant of chlorine on activated carbon PHO 8/30 was 0.0016, as expressed below

$$x/m = .0016C \quad \text{.....(4.1)}$$

Where x/m was the amount adsorbed per unit mass of carbon and C was the concentration in water which was in equilibrium with the amount adsorbed.

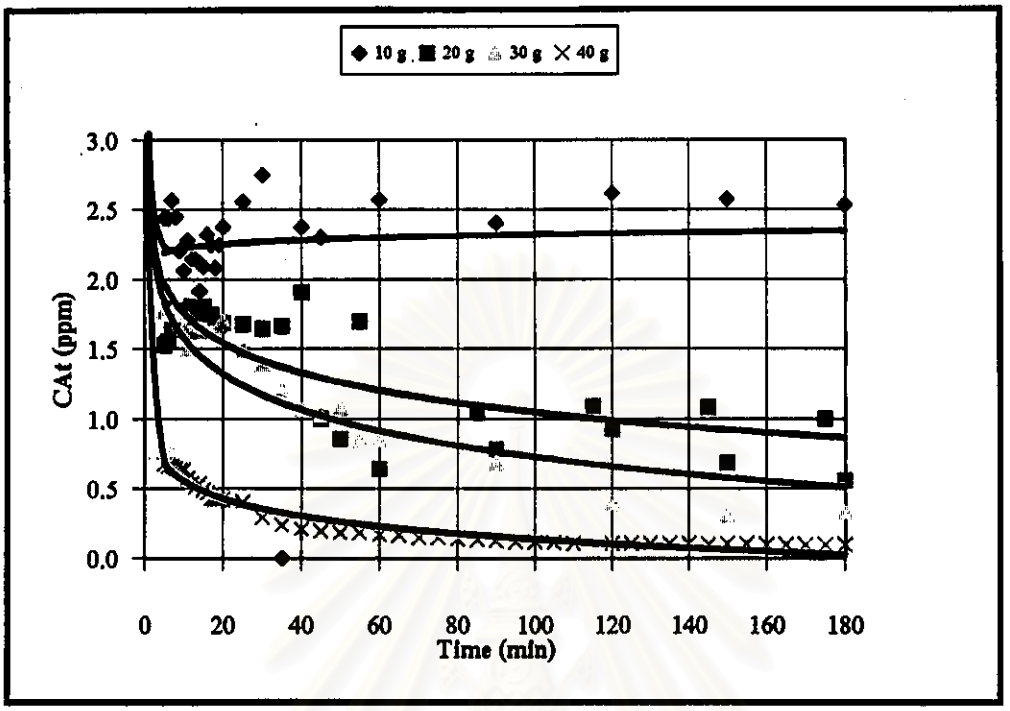

Figure 4.4 Batch adsorption on PHO 8/30 analyzed with ORP

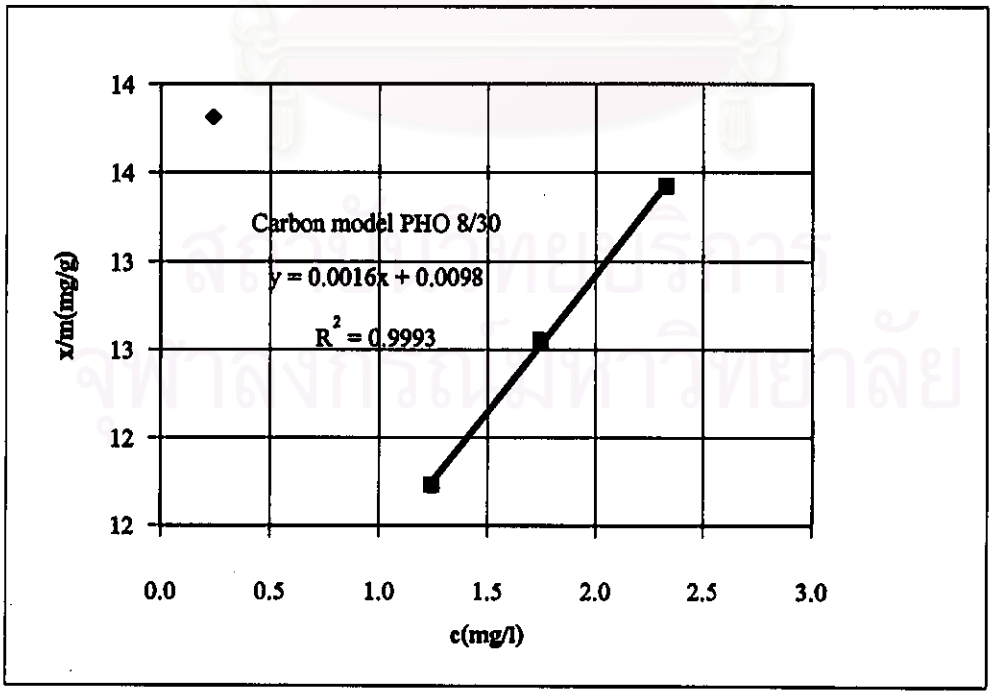

Figure 4.5 Adsorption isotherm

4.2.2 Batch Adsorption Using Spectrophotometer for Chlorine Analysis

250 mg. of activated carbon DEO 8/30, which was manufactured for dechlorination, was used to adsorb chlorine in water containing less than 5 ppm. At each 30 minute interval, the remaining chlorine was analyzed by reacting with DPD total chlorine reagent as shown in Figure 4.6. It was found that the adsorption on DEO 8/30 approached the equilibrium within a period of 3 hours, approximately as summarized in table 4.3. The adsorption isotherm also corresponded with the linear isotherm, as shown in Figure 4.7. In addition, the adsorption equilibrium constant was 0.785 as expressed in equation 4.2.

$$x/m = 0.7849C \quad \text{.....(4.2)}$$

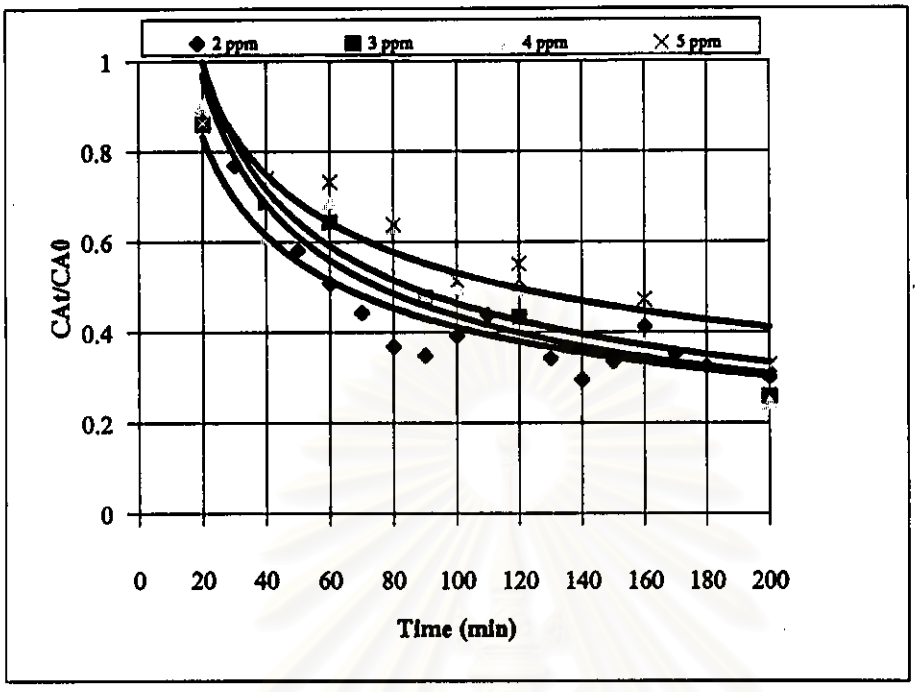

Figure 4.6 Batch adsorption on DEO 8/30 analyzed with spectrophotometer

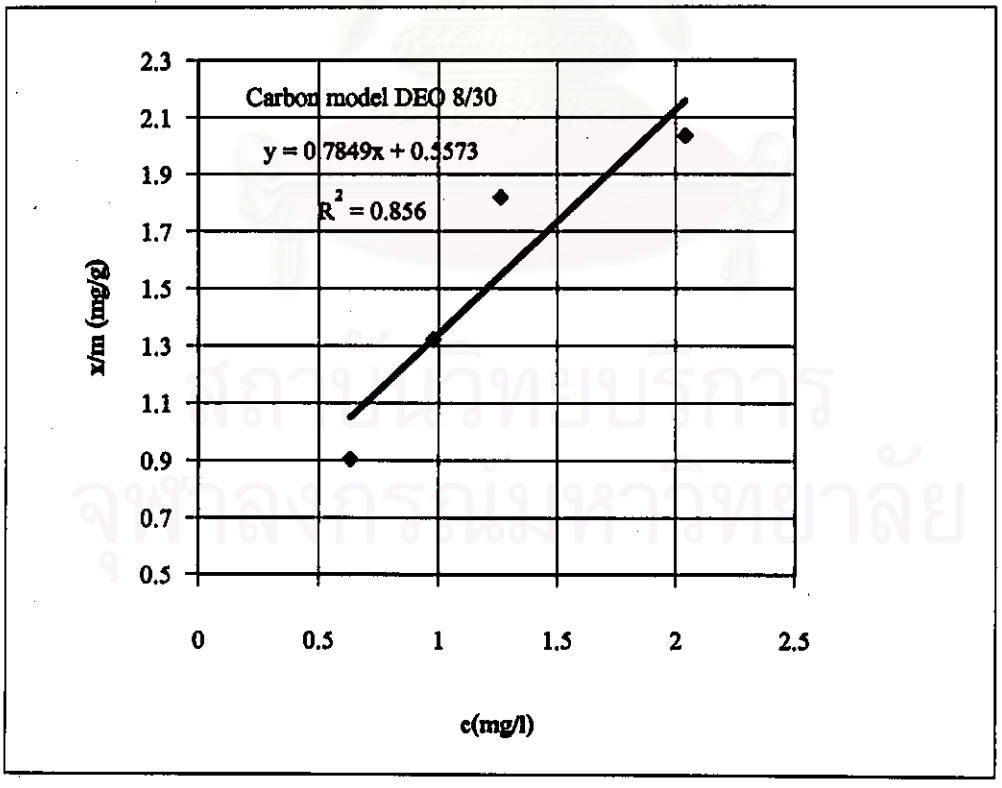

Figure 4.7 Adsorption isotherm

Table 4.3 Approximated slope of the variation of chlorine content with time

Time (min)	% slope $[C_{At}/C_{Ao}]/[C_{Atn+1}/C_{Ao}]$							
	C_{A0}=2 ppm		C_{A0}=3 ppm		C_{A0}=4 ppm		C_{A0}=5 ppm	
	First	Second	First	Second	First	Second	First	Second
40	38	39	37	36	37	36	38	39
60	57	58	56	55	56	55	57	57
80	67	68	66	65	67	65	67	67
100	73	74	73	72	73	72	73	74
120	78	78	77	76	77	76	79	78
140	81	81	80	79	80	80	81	81
160	83	84	83	82	83	82	83	83
180	85	85	84	84	85	84	85	85
200	86	87	86	85	86	86	86	87

4.3 Continuous Adsorption Column

Besides the adsorption isotherm, the rate of adsorption was essential for determination the appropriate size of an adsorber. Breakthrough data of chlorine in water had to be investigated. In this investigation, the breakthrough amount of chlorine was measured with respect to time for a certain period, i.e. 3 hours. Effects of flow rates and bed depths on the breakthrough of chlorine were studied.

4.3.1 Effects of Service Flow Rates

For a column of a selected carbons with 1 in. bed depth, the breakthroughed amount of chlorine increased with time, as shown in Figure 4.8 A-C for activated carbons DEO 8/30, PHO 8/30 and HRO 8/30, respectively. However, the breakthroughed amounts were reduced. The results demonstrate that the rate of adsorption on each carbon was so slow that the adsorption hardly reached the equilibrium. In addition, the breakthroughed amounts the longest resident time were higher than the desired value, 0.1 ppm. This indicated that the mass transfer zones of chlorine in all adsorption isotherms were longer than the bed depths. In other words, such adsorbers were not able to be used for dechlorination by increasing only residence time. Consequently, the bed depth had to be increased over the corresponding mass transfer zone.

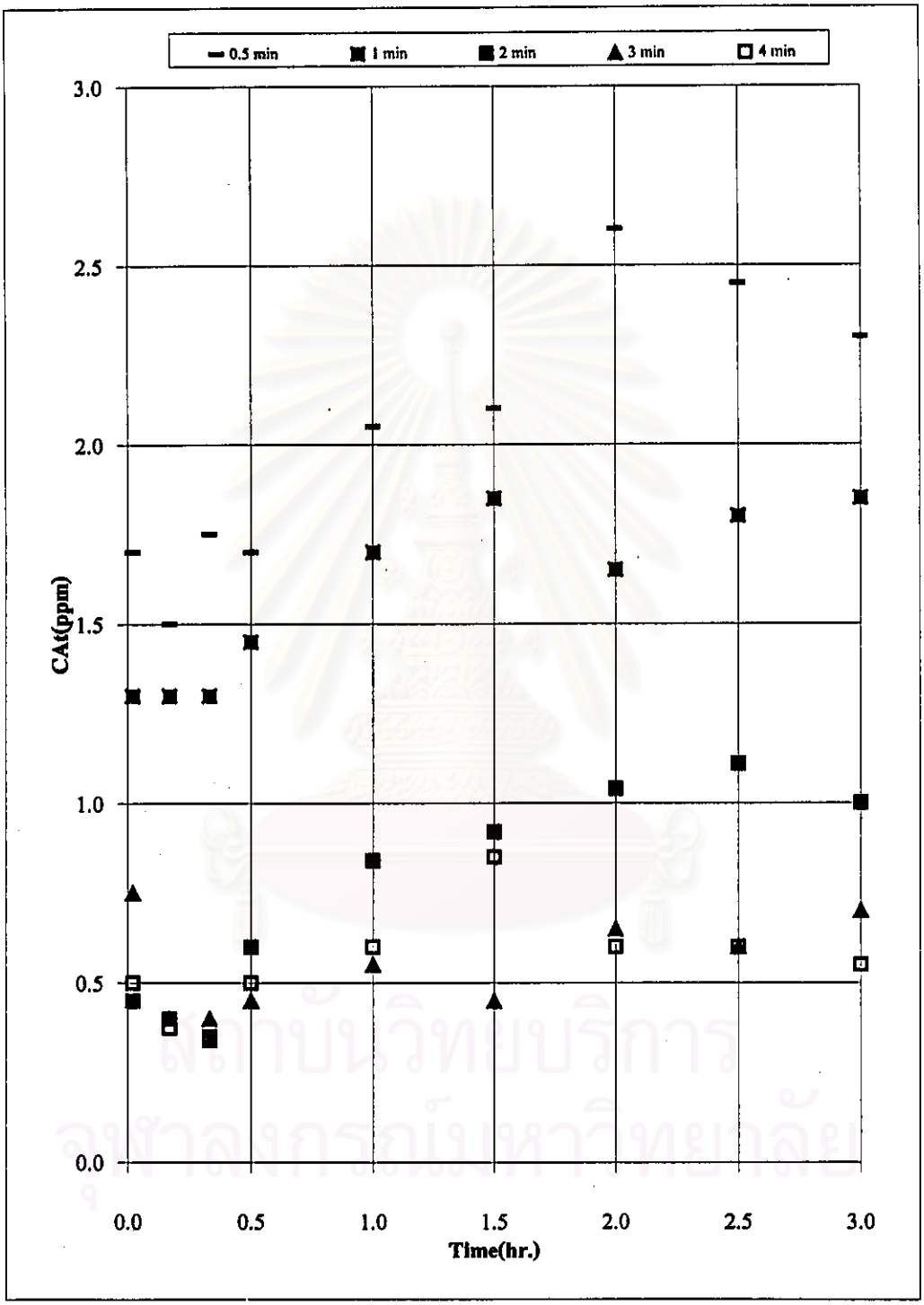

Figure 4.8A Effluent chlorine concentration

from 1" bed depth of activated carbon model DEO 8/30

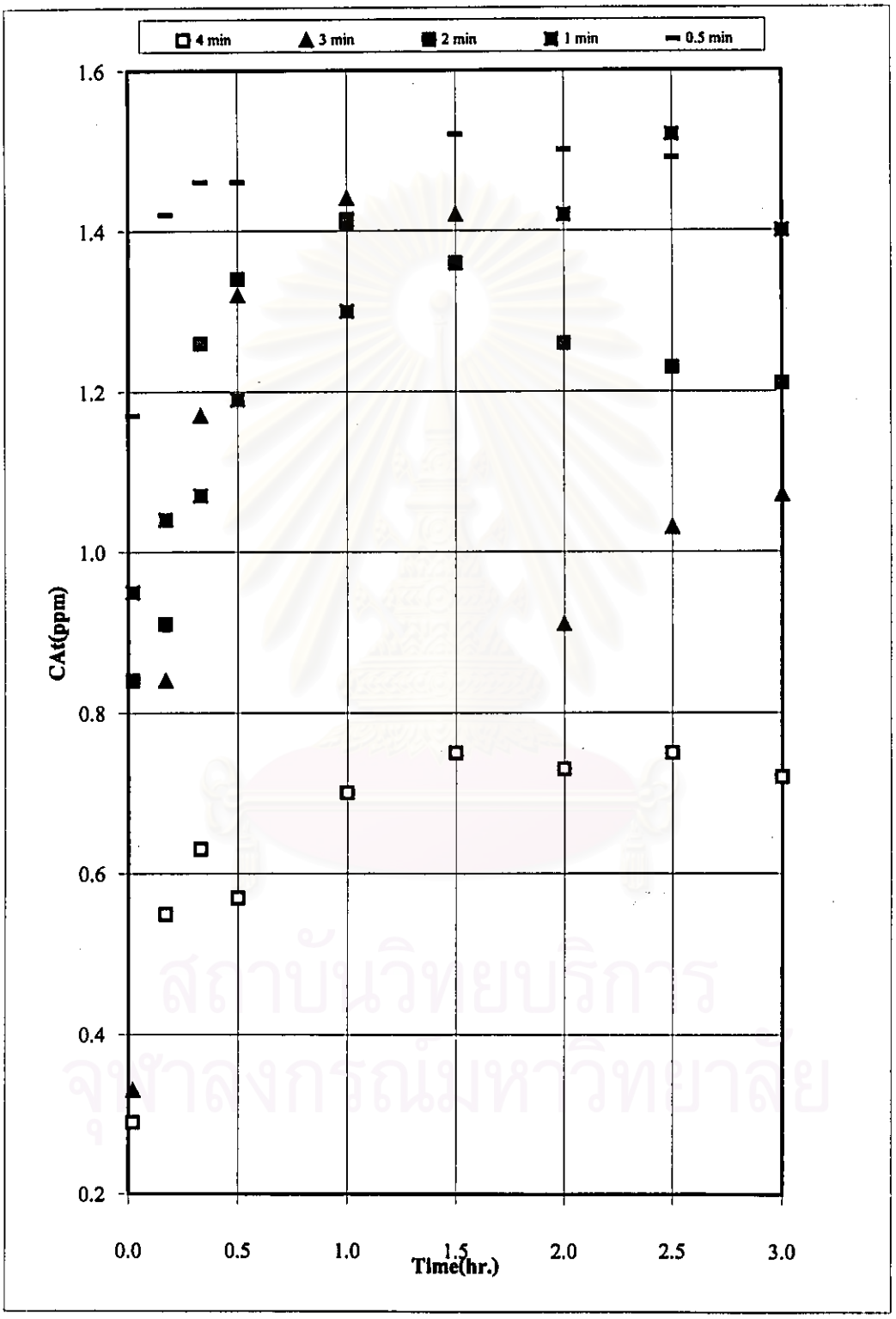

Figure 4.8B Effluent chlorine concentration

from 1" bed depth of activated carbon model PHO 8/30

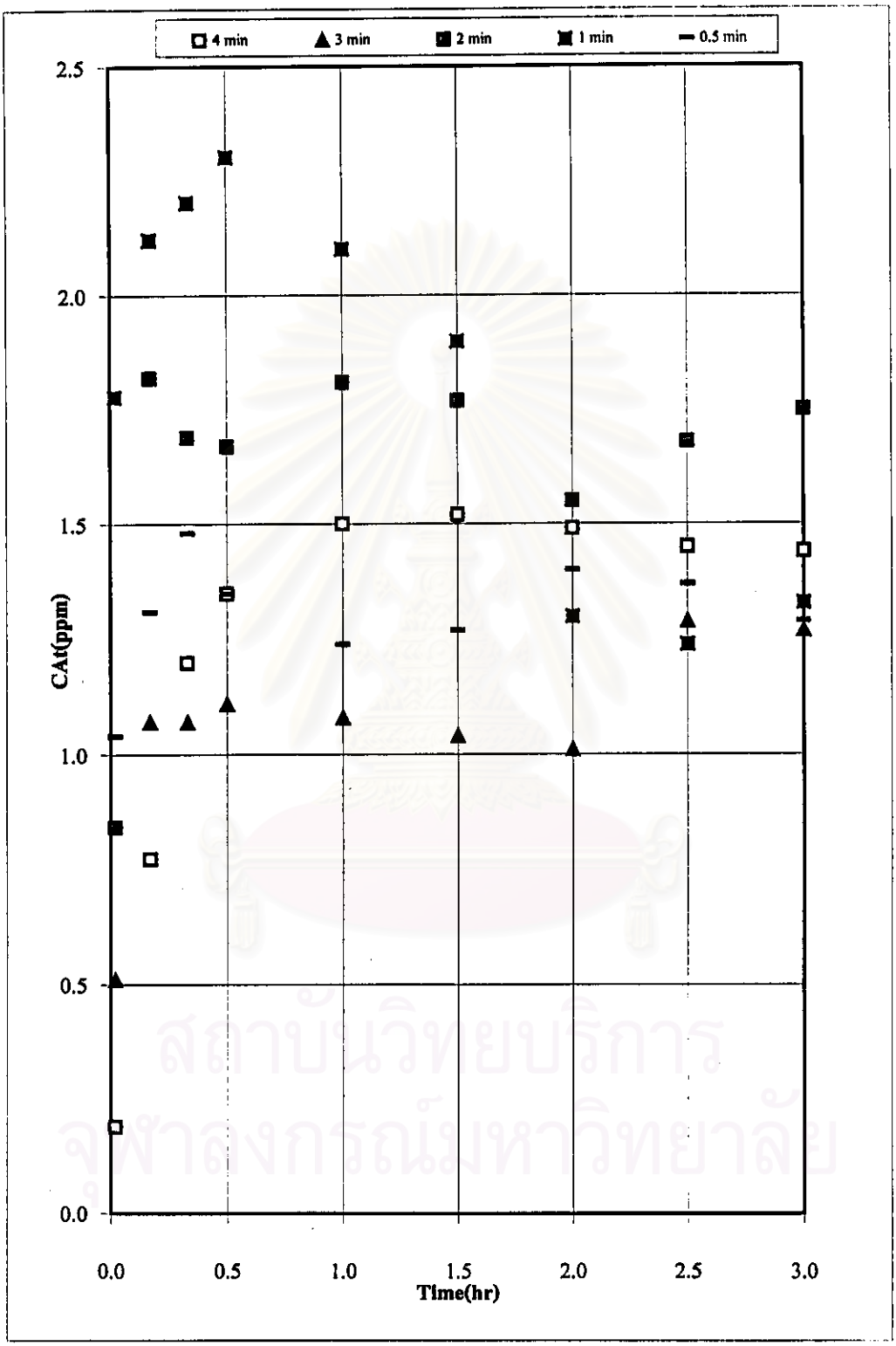

Figure 4.8C Effluent chlorine concentration

from 1" bed depth of activated carbon model HRO 8/30

4.3.2 Effects of Bed Depths

The resulted effect of an increase in bed depth at a given service flow rate according to conditions of the previous experiments were shown in Figure 4.9A-C for DEO 8/30, PHO 8/30 and HRO 8/30, respectively. These varying bed depths yielded residence time of 1 to 5 minutes. With an increase in bed depth, the chlorine contents in the effluent were reduced to below 0.5 ppm. With the bed depth 4 in. or longer than 4 in., the chlorine content became below 0.2 ppm and were almost constant after an hour of continuous flows. This demonstrated that the bed depth became relatively longer than the mass transfer zone of adsorption for the given flow rate. The results suggested that all selected activated carbons could be used for dechlorination water under an appropriate bed depth and operating condition, especially the flow rate of chlorinated water.

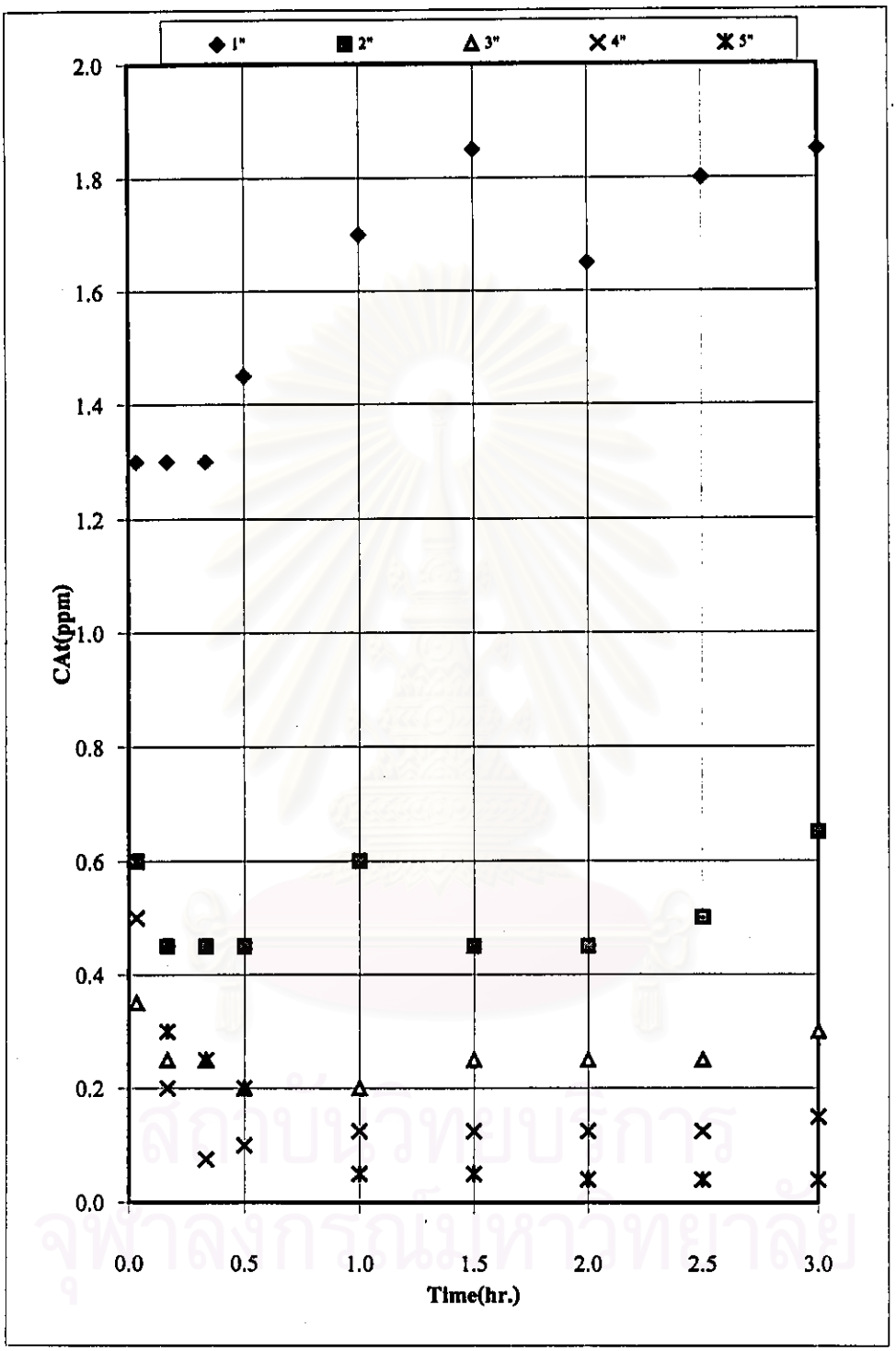

Figure 4.9A Effluent chlorine concentration from activated carbon model DEO 8/30 for service flow rate .622 gal/min/ft^2

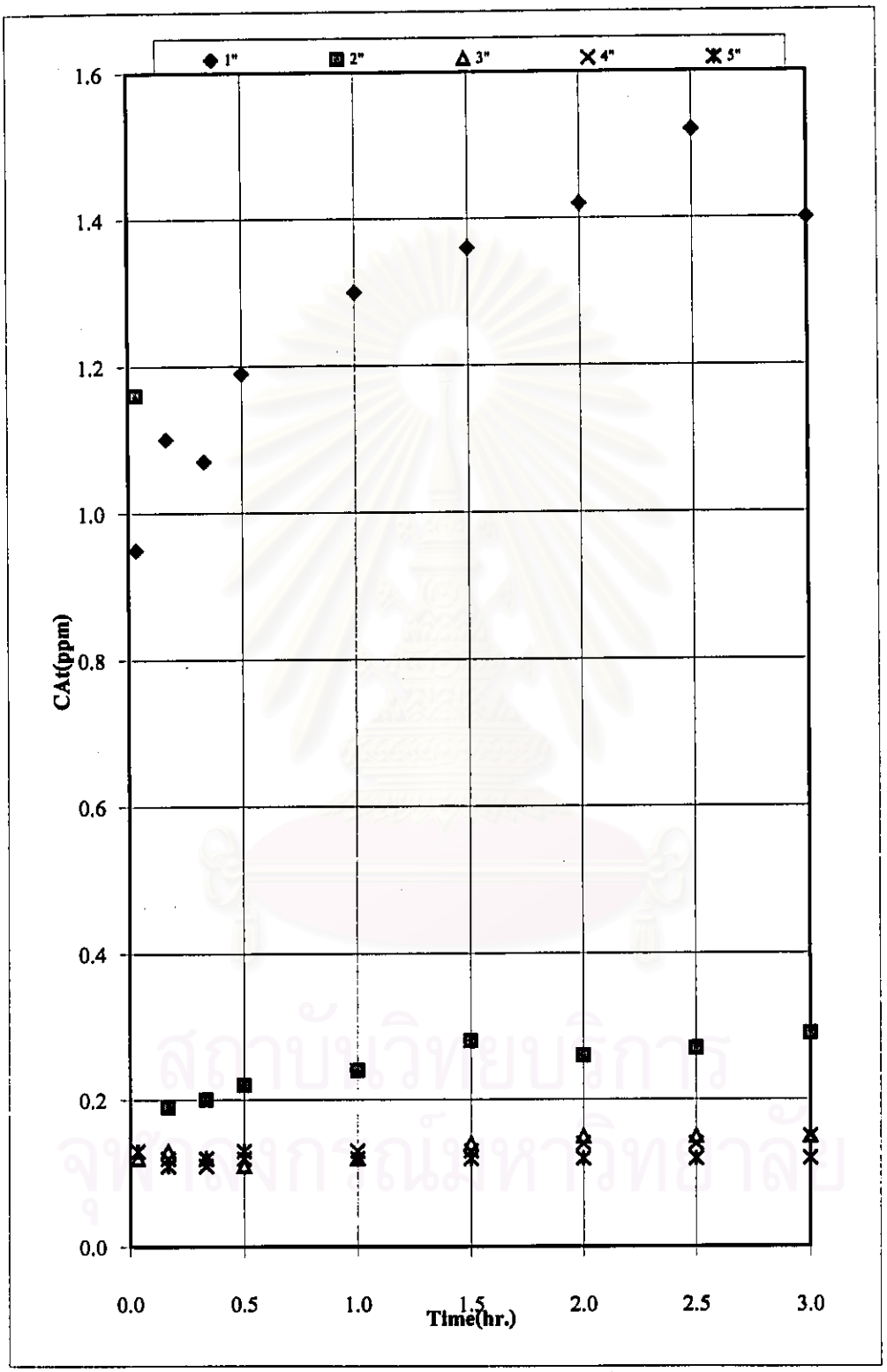

Figure 4.9B Effluent chlorine concentration of activated carbon model PHO 8/30 for service flow rate .622 gal/min/ft^2

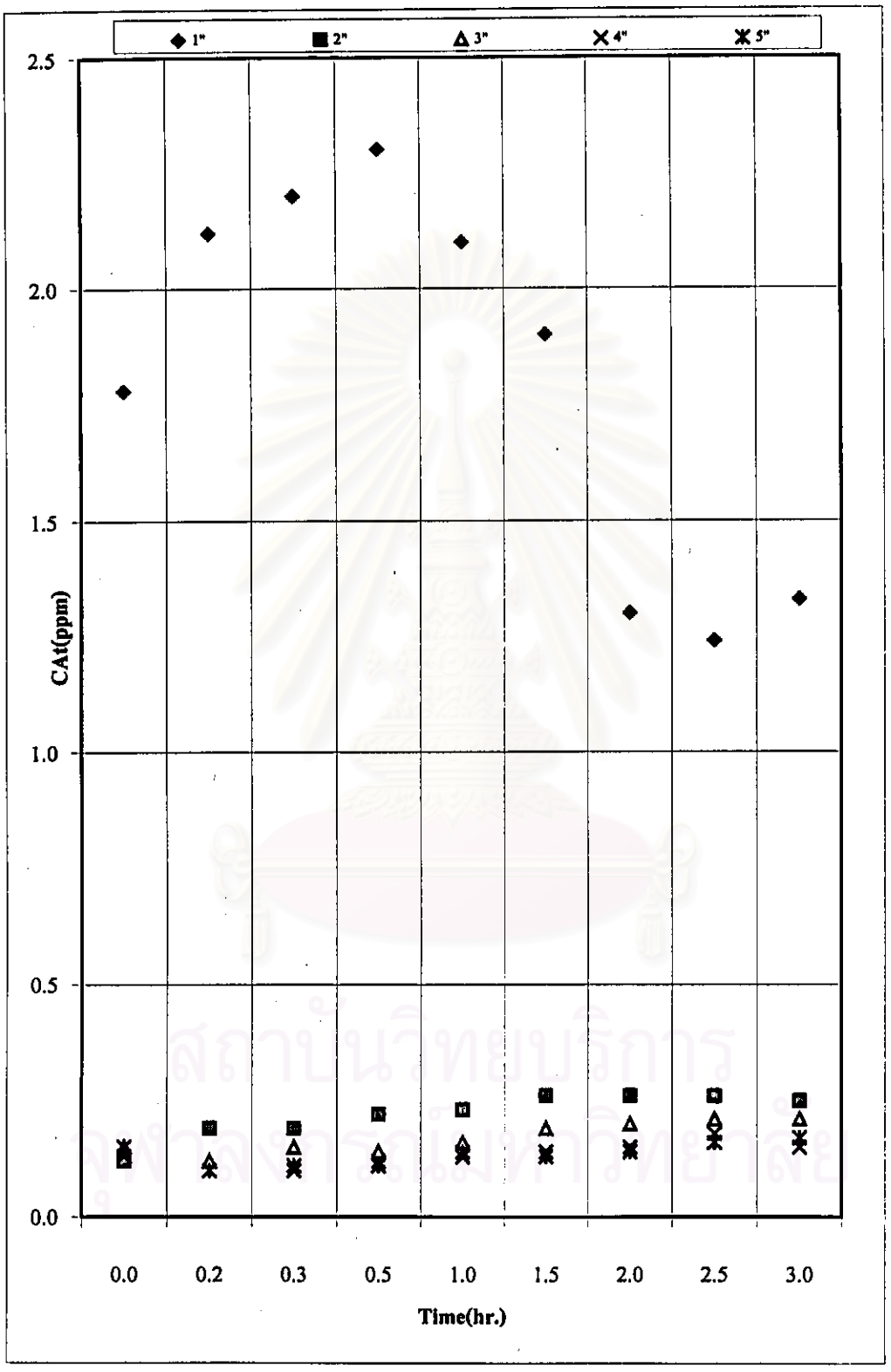

Figure 4.9C Effluent chlorine concentration from activated carbon model HRO 8/30 for service flow rate .622 gal/min/ft^2

For each type of activated carbon, the concentration of chlorine in the effluent did not depend on the residence time only, as shown in Figure 4.10. With the same residence time, the chlorine content in the effluent was reduced drastically as increasing the bed depth to 2 in. except the bed of DEO 8/30. The chlorine content in the effluent was reduced further slightly as an increase in the bed depth which was proportional to the residence time. With a sufficient bed depth, i.e. 3 in. at least for PHO 8/30 and 4 in. at least for both DEO 8/30 and HRO 8/30, the chlorine content became constant as and increase in the residence time as the bed depth. This demonstrated that the mass transfer zone for chlorine was shorter than the bed depth. Consequently, the results provided basic information of the appropriate bed depth for achievement of desired dechlorination performance.

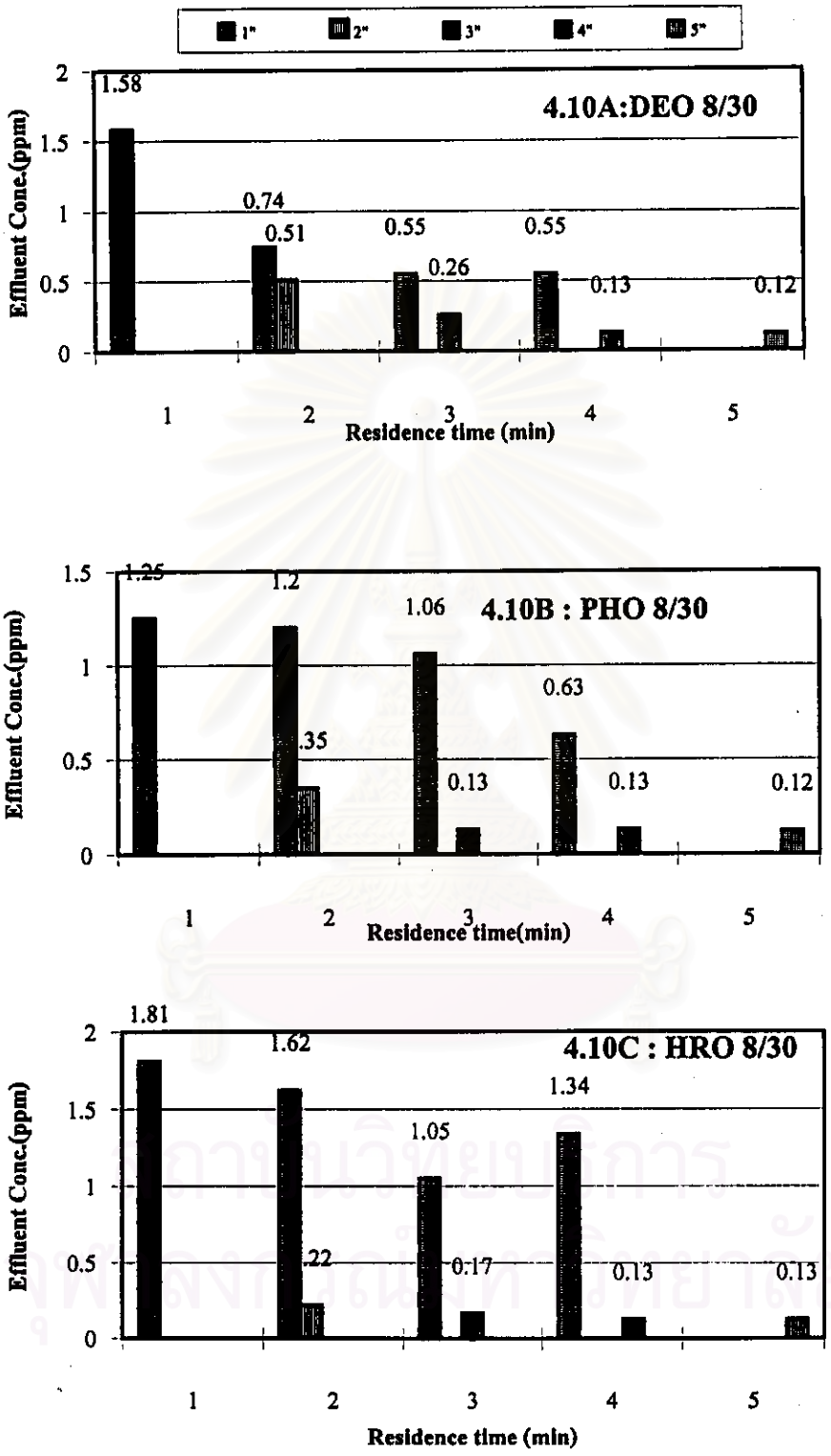

Figure 4.10A- C Comparison of effluent concentration with same residence time but different bed depth A:DEO8/30, B: PHO 8/30, C: HRO 8/30

According to the previous results, both DEO 8/30 and PHO 8/30 performed dechlorination consistently with the bed depth of 4 in., while the dechlorination performance of HRO 8/30 was unchanging as reducing the residence time to a half of the previous condition, as shown in Figure 4.11

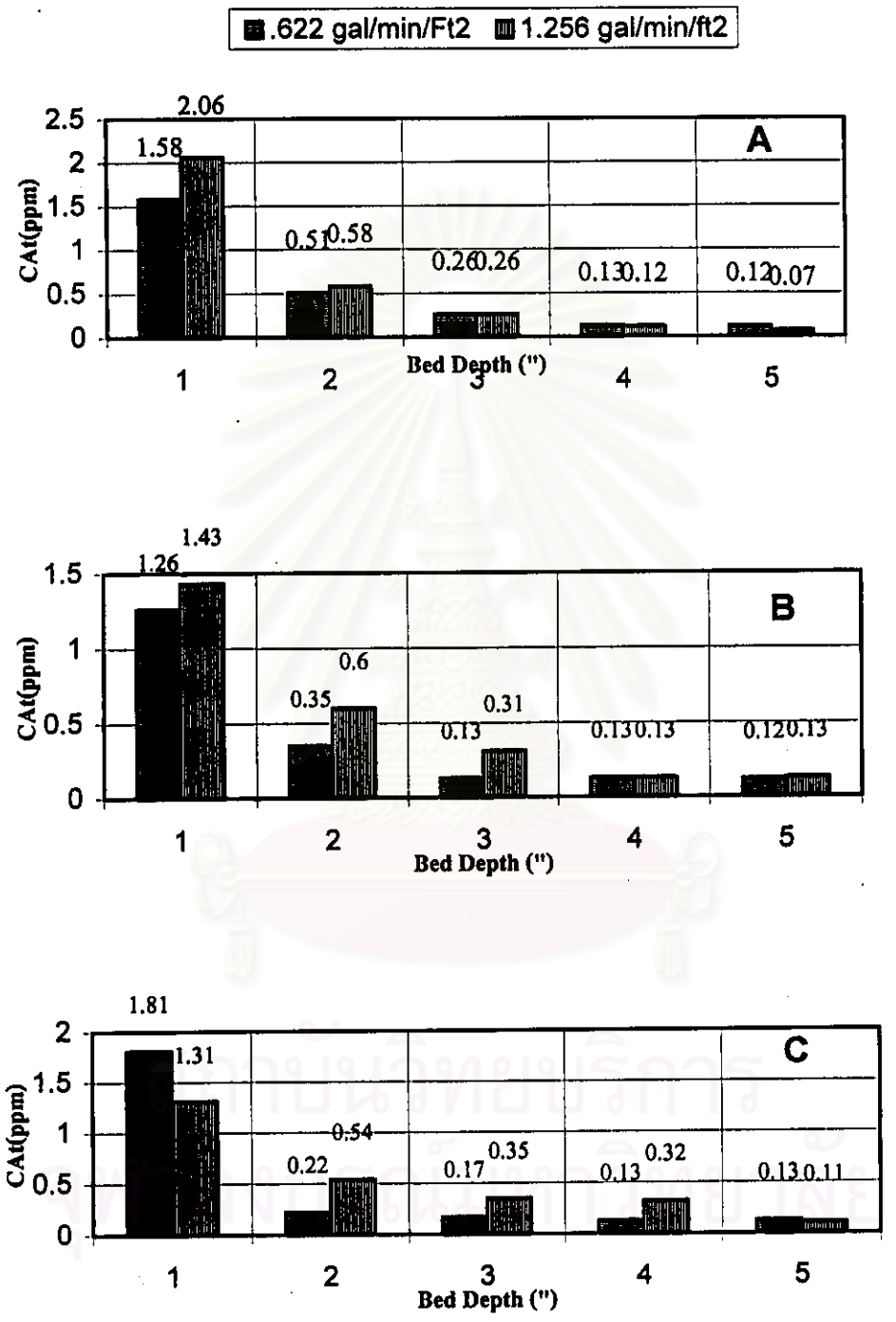

Figure 4.11A-C Comparison of average effluent chlorine concentration at each bed depth of activated carbon using 2 service flow rates A:DEO 8/30, B:PHO 8/30, C:HRO 8/30

With a further increase in the service flow rate, the dechlorination performance of all selected carbons decreased to an unacceptable level, i.e. the chlorine content in the effluent was greater than 0.1 ppm, as shown in Figure 4.12A-B and 4.13. This demonstrated that although the bed depth was longer than the mass transfer zone for a certain condition, the performance was limited by the residence time. In other words, the performance depended on both the bed depth and the residence time which interacted each other. Subsequently, the appropriate residence time for a given bed depth of each carbon for 2 in. column in diameter was able to be determined as summarized in Table 4.4

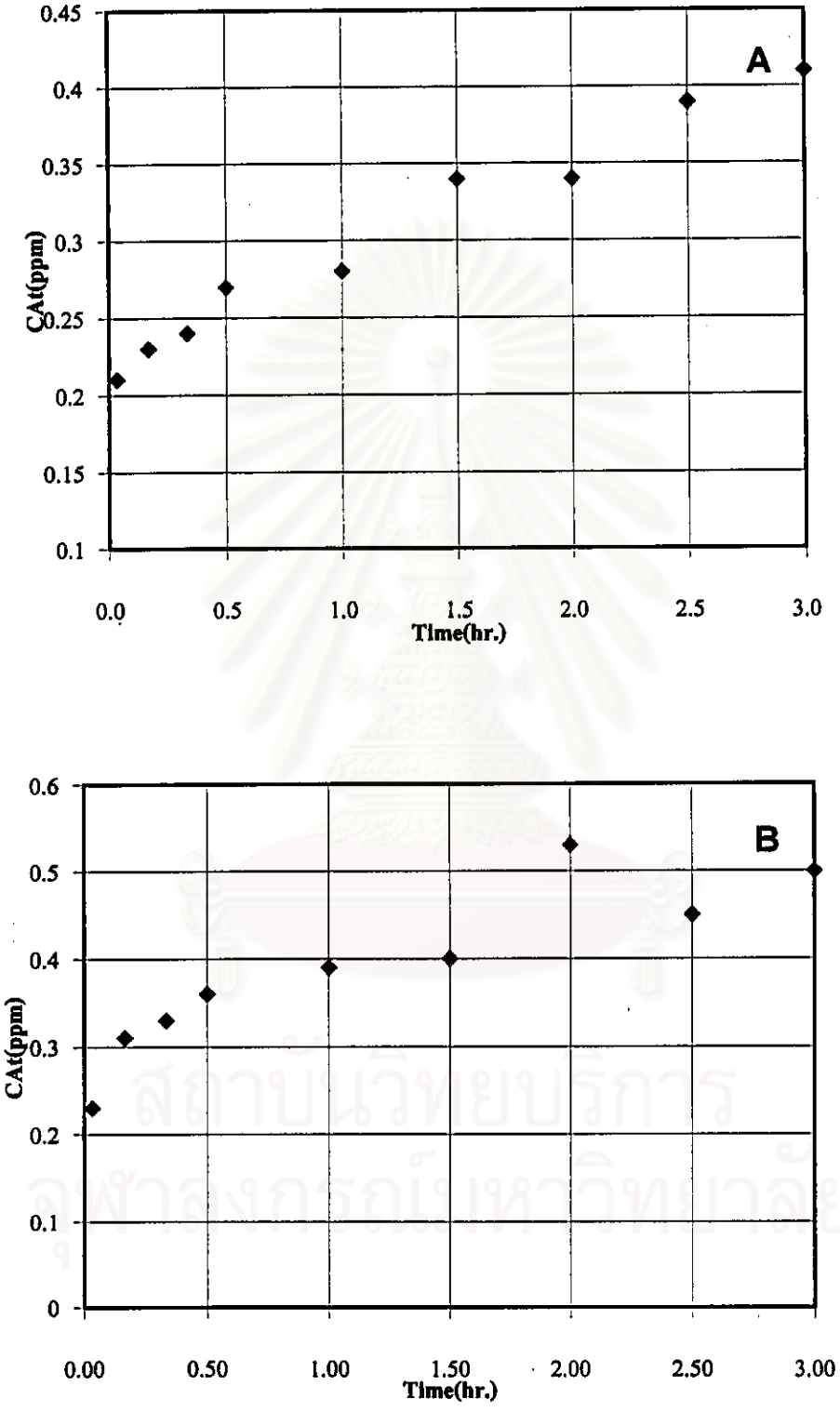

Figure 4.12A-B Effluent chlorine concentration from 4" bed depth for service flow rate 2.512 gal/min/ft2 A:PHO 8/30, B: HRO 8/30

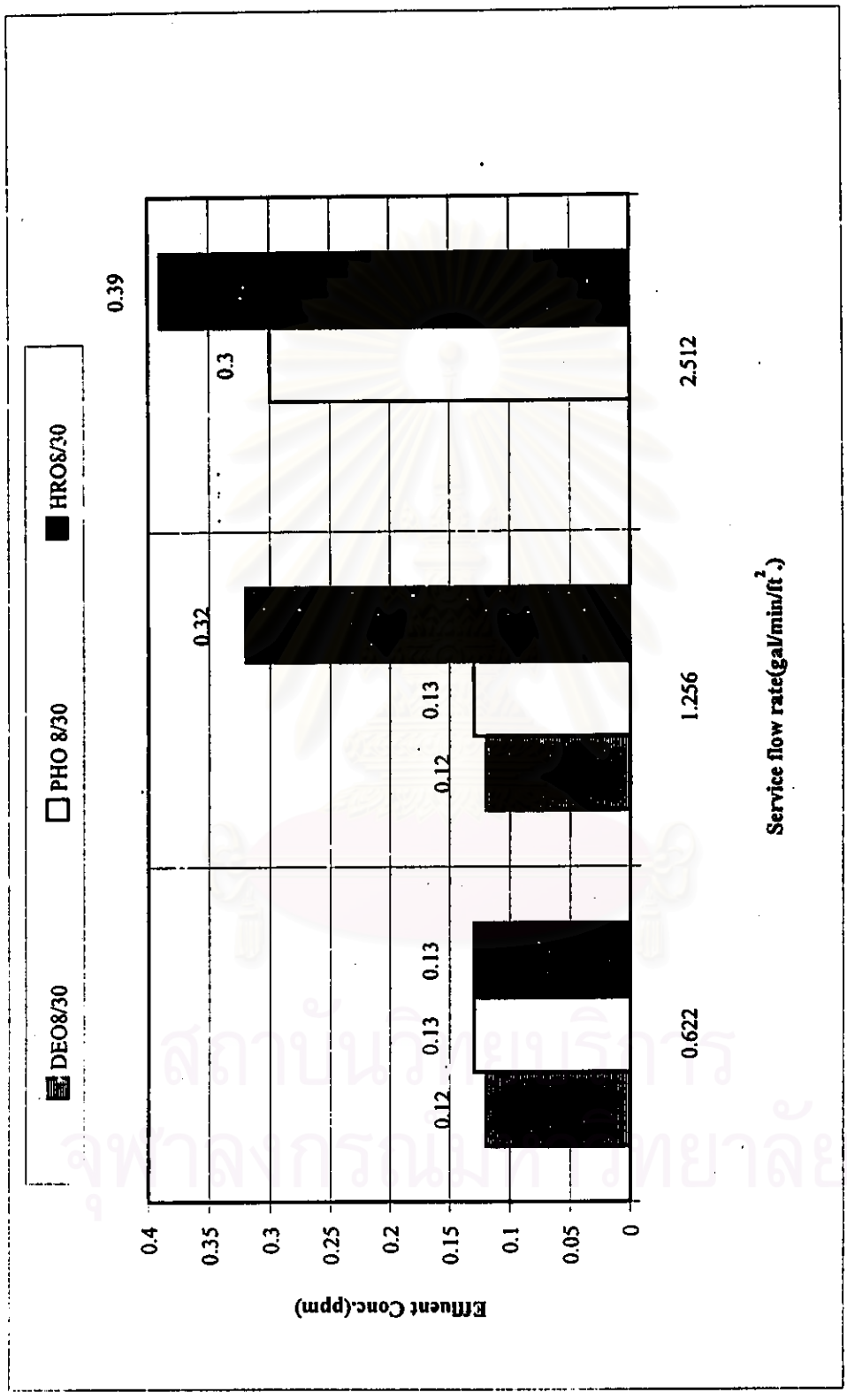

Figure 4.13 Average effluent concenttration from 4" bed depth with various service flow rates

Table 4.4 Acceptable parameters and average effluent concentration for 3 activated carbon using 2" diameter column with 4 ppm feed concentration.

Parameter	DEO 8/3	PHO 8/30	HRO 8/30
Bed depth (inch)	4	4	5
Service flow rate (gal/min/sq.ft.)	1.256	1.256	1.256
Residence time(min)	2	2	2.5
Avg. Effl. Conc. (ppm)	0.12	0.13	0.11
Percent Chlorine Removal (%)	97	97	97

At each acceptable condition, the bed depth had to be longer than mass transfer zone length and the suitable residence time might be obtained by adjusting the service flow rate corresponding to the selected bed depth. Different types of activated carbons produced differents level of effluent concentration. Activated carbon HRO 8/30 needed the longest bed depth which results in the longest residence time to yield as same effluent concentration level as the others.

Acceptable condition from experimental results of each activated carbon model was able to be used as the design parameters for tank sizing by maintaining constant residence time during scale up as shown in the example in Appendix A3. The bed length might not be the same based on the scale up principle that the length of mass transfer zone did not change with the total bed depth. Therefore, a bed depth, which was longer than the required one, could be used to achieve the similar performance.

4.4 Comparison of Experimental Results with Typical Design Parameters.

For typical design of an adsorber packed with activated carbons, the size of an adsorber has been 8 in. minimum in diameter and 24 in. bed depth for the sevice flow rate of 5 gal/min/ft^2. With an increase in flow rate, only the diameter of the adsorber has been expanded in order to maintain the service flow rate or residence time. Therefore, examples of the size of an adsorber for a given flow rate have been summarized in Table 4.5.

Table 4.5 One of typical activated carbon adsorption tank sizing design samples.

Service flow rate (gal/min/ft^2.)	5	5	5	5	5
Flow rate (gal./min.)	1.75	3	5	8	10
Tank diameter (inch.)	8	11	14	17	19
Bed depth (ft.)	2	2	2	2	2
Bed volume(cu.ft.)	0.7	1.2	2	3.2	4
Residence time(min.)	3	3	3	3	3

For comparison purposes, experimental parameters for HRO 8/30 was selected as an example.

Determination of service flow rate for the column with 2 ft. bed depth that would yield the residence time at 2.5 minutes as in the experiment results as the follows:

Required superficial velocity is 2 ft./2.5 min. = 0.8 ft./min

Service flow rate is (0.8 ft./min)(7.48 gal/cu.ft.) = 6 gal/min/sq.ft.

The results was close to the design parameters, as summarized in table 4.5. For the experimental service flow rate, the dimension of an adsorber was summarized in Table 4.6.

Table 4.6 Design of activated carbon adsorption tank sizing samples using experimental parameters of activated carbon model HRO 8/30

Service flow rate (gal/min/ft^2.)	6	6	6	6	6
Flow rate (gal./min.)	1.75	3	5	8	10
Tank diameter (".)	7	10	12	16	18
Bed depth (ft.)	2	2	2	2	2
Bed volume(cu.ft.)	0.6	1.0	1.7	2.7	3.3
Residence time(min.)	2.5	2.5	2.5	2.5	2.5

Because HRO 8/30 required shorter residence time than conventional activated carbons, the size of the adsorber packed with HRO 8/30 was smaller than that packed with conventional carbon.

For the others carbons, i.e. DEO 8/30 and PHO 8/30, performed dechlorination similary but performed better than HRO 8/30. The size of the adsorber packed with DEO 8/30 or with PHO 8/30 became smaller than that packed with HRO 8/30. Consequently, the cost of the adsorber was reduced. The follows was an example of determination of the adsorber size for DEO 8/30 or PHO 8/30 with 2 minute residence time for scaleup at 2 ft. bed depth.

Required superficial velocity is 2 ft./2.0 min. = 1.0 ft./min

Service flow rate is (1.0 ft./min)(7.48 gal/cu.ft.) = 7.48 gal/min/sq.ft.

The results were summarized in Table 4.7

Table 4.7 Design of activated carbon adsorption tank sizing samples using experimental parameters of ctivated carbon model DEO 8/30 and PHO 8/30.

Service flow rate (gal/min/ft2.)	7.48	7.48	7.48	7.48	7.48
Flow rate (gal/min)	1.75	3	5	8	10
Tank diameter (in.)	7	9	11	14	16
Bed Depth (ft.)	2	2	2	2	2
Bed Volume (cu.ft.)	0.5	0.8	1.3	2.1	2.7
Residence time (min)	2	2	2	2	2

Beside 2 ft. bed depth, adsorption tanks might be operated at the higher bed depth by maintaining constant residence time. However, the limitation of bed depth and service flow rate selection depended on pressure drop during adsorption period and % bed expansion during backwash period. In practice, the pressure drop should be less than 10 psi. The pressure drop and bed expansion data of these activated carbon were shown in Figure 4.14 The service flow rate of 20 gal/min/ft^2 for activated carbon model 8/30 bed operated at 27 ^{o}C provided 9 in water/ft bed depth pressure drop. The % bed expansion on backwash at this service flow rate was about 56 %. Pressure drop at available bed depth and service flow rate data for adsorber sizing of activated carbon used in the experiment were summarized in Table 4.8 and Table 4.9. The former was activated carbon HRO 8/30 with 2.5 minute residence time and the later was activated carbon DEO 8/30 and PHO 8/30 with 2 minute residence time. At each selected bed depth, the service flow rate was achieved by calculation using constant residence time. Then pressure drop was read from Figure 4.14.

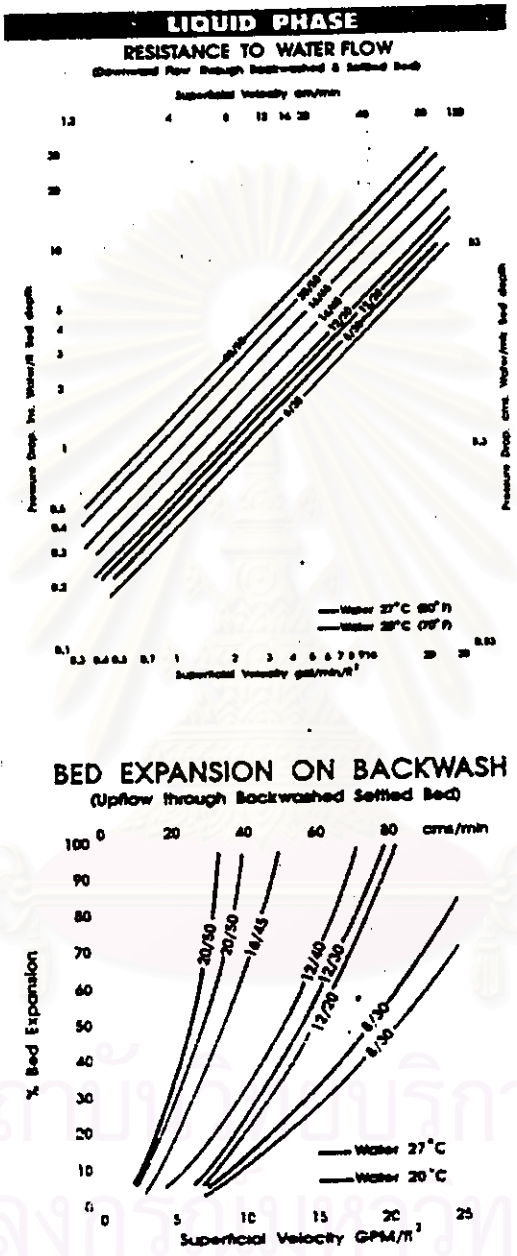

Figure 4.14 Pressure drop and bed expansion at variuos bed depth and service flow rate of activated carbon used in the experiments

Table 4.8 Pressure drop at selected bed depth and service flow rate of activated carbon model HRO 8/30 using 2.5 minute residence time for bed sizing

Bed Depth	Service flow rate	Pressure drop	
(ft)	(gal/min/ft2)	in. water/ft bed depth	psi
2.0	6	3	0.2
2.5	7	3.4	0.3
3.0	9	4	0.4
3.5	10	4.7	0.6
4.0	12	5	0.7
4.5	13	5	0.8
5.0	15	6	1.1
5.5	16	7	1.4
6.0	18	7.5	1.6
6.5	19	8	1.9
7.0	21	9	2.3
7.5	22	9.5	2.6
8.0	24	11	3.2
8.5	25	12	3.7
9.0	27	13	4.2

Table 4.9 Pressure drop at selected bed depth and service flow rate of activated carbon model DEO and PHO 8/30 using 2.0 minute residence time for tank sizing

Bed depth	Service flow rate	Pressure drop	
(ft)	(gal/min/ft2)	in. water/ft bed depth	psi
2.0	7	3.4	0.2
2.5	9	4	0.4
3.0	11	4.5	0.5
3.5	13	5	0.6
4.0	15	7	1.0
4.5	17	8	1.3
5.0	19	8.3	1.5
5.5	21	9.5	1.9
6.0	22	10	2.2
6.5	24	12	2.8
7.0	26	13	3.3
7.5	28	15	4.1

From Table 4.8 and 4.9, bed depth up to 9 ft. has still provided pressure drop at its suitable service flow rate about 4 psi. It was applicable because this pressure drop was lower than 10 psi. To use data in Table 4.8 and 4.9 for tank sizing, the procedure was as same as the example in Table 4.6 and 4.7. Table 4.10 and 4.11 were the example of tank sizing using various bed depth from Table 4.8 and 4.9, respectively.

Table 4.10 Dechlorination bed sizing examples using data from table 4.8

Bed depth	Service flow rate	Tank diameter and bed volume at each influent flow rate									
(ft.)	(gal/min/ft2)	1.75		3		5		8		10	
.		Dia.(in.)	Vol.(ft3)	Dia.(in.)	Vol.(ft3)	Dia.(in.)	Vol.(ft3)	Dia.(in.)	Vol.(ft3)	Dia.(in.)	Vol.(ft3)
2	6	7	0.6	10	1.0	12	1.7	16	2.7	18	3.3
2.5	7	7	0.6	9	1.0	11	1.7	14	2.7	16	3.3
3	9	6	0.6	8	1.0	10	1.7	13	2.7	14	3.3
3.5	10	6	0.6	7	1.0	9	1.7	12	2.7	13	3.3
4	12	5	0.6	7	1.0	9	1.7	11	2.7	12	3.3
4.5	13	5	0.6	6	1.0	8	1.7	10	2.7	12	3.3
5	15	5	0.6	6	1.0	8	1.7	10	2.7	11	3.3
5.5	16	4	0.6	6	1.0	7	1.7	9	2.7	11	3.3
6	18	4	0.6	6	1.0	7	1.7	9	2.7	10	3.3
6.5	19	4	0.6	5	1.0	7	1.7	9	2.7	10	3.3
7	21	4	0.6	5	1.0	7	1.7	8	2.7	9	3.3
7.5	22	4	0.6	5	1.0	6	1.7	8	2.7	9	3.3
8	24	4	0.6	5	1.0	6	1.7	8	2.7	9	3.3
8.5	25	4	0.6	5	1.0	6	1.7	8	2.7	8	3.3
9	27	3	0.6	5	1.0	6	1.7	7	2.7	8	3.3

Table 4.11 Dechlorination bed sizing examples using data from table 4.9

Bed depth	Service flow rate	Tank diameter and bed volume at each influent flow rate									
(ft.)	(gal/min/ft2)	1.75		3		5		8		10	
		Dia.(in.)	Vol.(ft3)	Dia.(in.)	Vol.(ft3)	Dia.(in.)	Vol.(ft3)	Dia.(in.)	Vol.(ft3)	Dia.(in.)	Vol.(ft3)
2	7	7	0.5	9	0.8	11	1.3	14	2.1	16	2.7
2.5	9	6	0.5	8	0.8	10	1.3	13	2.1	14	2.7
3	11	5	0.5	7	0.8	9	1.3	11	2.1	13	2.7
3.5	13	5	0.5	6	0.8	8	1.3	11	2.1	12	2.7
4	15	5	0.5	6	0.8	8	1.3	10	2.1	11	2.7
4.5	17	4	0.5	6	0.8	7	1.3	9	2.1	10	2.7
5	19	4	0.5	5	0.8	7	1.3	9	2.1	10	2.7
5.5	21	4	0.5	5	0.8	7	1.3	8	2.1	9	2.7
6	22	4	0.5	5	0.8	6	1.3	8	2.1	9	2.7
6.5	24	4	0.5	5	0.8	6	1.3	8	2.1	9	2.7
7	26	4	0.5	5	0.8	6	1.3	7	2.1	8	2.7
7.5	28	3	0.5	4	0.8	6	1.3	7	2.1	8	2.7
8	30	3	0.5	4	0.8	6	1.3	7	2.1	8	2.7
8.5	32	3	0.5	4	0.8	5	1.3	7	2.1	8	2.7
9	34	3	0.5	4	0.8	5	1.3	7	2.1	7	2.7

From tank sizing examples, increasing of bed depth results in decreasing of tank diameter and the volume of bed at each enfluent flow rate was constant in order to keep residence time at the desired value. With this tank sizing criteria, any bed depth should provide the same chlorine content in the effluent. The height of tank usually need 100 % bed depth free board to support bed expansion during backwash period. Bed depth to tank diameter ratio should be suitable. Bed depth could be varied from 1/3 to 3 times of tank diameter. For example, the bed depth for influent flow rate of 10 gal/min can be varied from 2.5 to 3.5 ft. providing bed depth/tank diameter ratios from 1.9 to 3.2 and pressure drop from 0.3 to 0.6 psi, respectively, by the use of data in Table 4.6 and 4.8. Furthermore, the tank size selection had to be suitable with many factors such as the available area for tank installation, access during operating and maintenance period and the costs of tank and face piping material.