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Appendices

Appendix A

Measurement method

Appendix A

Principle

This process measures only hexavalent chromium. It is determined colorimetrically by reaction with diphenylcarbazide in acid solution. The complex red-violet color was produced that can be measured with 540 nm.

Special reagents

Diphenylcarbazide solution: dissolve 250 mg 1,5-diphenylcarbazide in 50 ml of acetone. Then, store diphenylcarbazide solution in a brown bottle. Discard when solution becomes discolored.

A.1 Calibration curve determination

1. Prepare synthetic wastewater samples whose initial concentrations of chromium (VI) are 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 ppm.
2. Take sample 5 ml.
3. Add 0.25 ml conc. H_3PO_4 and adjust to $\text{pH } 1 \pm 0.3$ with sulfuric acid and sodium hydroxide.
4. Dilute with distilled water until get 100 ml.
5. Add diphenyl-carbazide 2 ml to color.
6. Shake and wait to color for 15 minutes.
7. Measure the absorbance at 540 nm with the UV-VIS spectrophotometer.
8. Bring the result to make standard curve.

A.2 Measurement method

1. Take sample 5 ml (at higher concentration need to dilute before).
2. Add 0.25 ml conc.H₃PO₄ and adjust to pH 1 ± 0.3 with sulfuric acid and sodium hydroxide.
3. Dilute with distilled water until get 100 ml.
4. Add diphenyl-carbazide 2 ml to color.
5. Shake and wait to color for 15 minutes.
6. Measure the concentration with the UV-VIS spectrophotometer.

Appendix B
Experimental data

Appendix B

Table B.1 Experimental data of effect of pH of wastewaters

Sample	Residual chromium (VI) concentration, (ppm)								
	pH 3			pH 7			pH 11		
	1	2	Average	1	2	Average	1	2	Average
Initial chromium	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
Adsorption for 15 minutes	20.77	20.19	20.48	24.96	24.33	24.64	25.03	24.62	24.83
Irradiation for 10 minutes	15.84	15.78	15.81	24.86	24.23	24.54	24.93	24.83	24.88
Irradiation for 20 minutes	12.16	11.95	12.06	24.72	24.09	24.41	24.83	24.61	24.72
Irradiation for 30 minutes	9.29	9.35	9.32	24.37	23.76	24.06	24.76	24.61	24.69
Irradiation for 45 minutes	5.32	5.59	5.46	24.19	23.59	23.89	24.47	24.72	24.60
Irradiation for 60 minutes	0.00	0.00	0.00	23.89	23.29	23.59	24.71	24.78	24.74
Irradiation for 90 minutes	-	-	-	23.44	22.85	23.15	25.05	24.78	24.91
Irradiation for 120 minutes	-	-	-	22.93	22.36	22.65	24.48	24.82	24.65
Irradiation for 150 minutes	-	-	-	22.56	21.99	22.27	24.69	24.84	24.76
Irradiation for 180 minutes	-	-	-	22.13	21.57	21.85	24.44	24.66	24.55

Table B.2 Experimental data of effect of flow rate of wastewaters

Sample	Residual chromium (VI) concentration, (ppm)											
	Flow rate 20 mL/sec			Flow rate 40 mL/sec			Flow rate 60 mL/sec			Flow rate 80 mL/sec		
	1	2	Average	1	2	Average	1	2	Average	1	2	Average
Initial chromium	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
Adsorption for 15 minutes	23.88	23.35	23.61	22.12	21.99	22.05	20.60	20.40	20.50	20.35	20.41	20.38
Irradiation for 10 minutes	22.62	22.59	22.60	20.47	20.04	20.25	17.68	17.70	17.69	17.77	17.26	17.51
Irradiation for 20 minutes	21.47	20.41	20.94	17.42	18.10	17.76	14.91	14.89	14.90	14.25	13.54	13.89
Irradiation for 30 minutes	19.52	18.88	19.20	14.99	15.45	15.22	11.51	10.58	11.04	10.15	9.62	9.88
Irradiation for 45 minutes	17.69	17.49	17.59	12.72	12.29	12.51	6.96	7.17	7.07	5.97	5.31	5.64
Irradiation for 60 minutes	15.83	15.79	15.81	9.98	9.18	9.58	2.39	3.59	2.99	2.51	2.59	2.55
Irradiation for 90 minutes	11.53	10.45	10.99	3.89	3.82	3.85	0.00	0.00	0.00	0.00	0.00	0.00
Irradiation for 120 minutes	6.87	6.62	6.75	0.00	0.00	0.00	-	-	-	-	-	-
Irradiation for 150 minutes	3.11	1.99	2.55	-	-	-	-	-	-	-	-	-
Irradiation for 180 minutes	0.00	0.00	0.00	-	-	-	-	-	-	-	-	-

Table B.3 Experimental data of effect of flow rate of wastewaters

Sample	Residual chromium (VI) concentration, (ppm)								
	Flow rate 100 mL/sec			Flow rate 120 mL/sec			Flow rate 140 mL/sec		
	1	2	Average	1	2	Average	1	2	Average
Initial chromium	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
Adsorption for 15 minutes	21.16	21.49	21.32	21.43	20.76	21.09	21.55	20.75	21.15
Irradiation for 10 minutes	17.27	16.73	17.00	19.46	18.49	18.98	18.78	18.65	18.71
Irradiation for 20 minutes	13.84	14.57	14.20	16.99	17.26	17.12	17.18	16.63	16.91
Irradiation for 30 minutes	10.85	10.52	10.68	13.95	14.31	14.13	14.90	14.33	14.61
Irradiation for 45 minutes	6.92	6.22	6.57	10.00	9.92	9.96	11.56	11.39	11.48
Irradiation for 60 minutes	2.64	2.71	2.67	5.16	5.15	5.15	7.95	9.39	8.67
Irradiation for 90 minutes	0.00	0.00	0.00	0.00	0.00	0.00	4.60	4.21	4.41
Irradiation for 120 minutes	-	-	-	-	-	-	0.00	0.00	0.00
Irradiation for 150 minutes	-	-	-	-	-	-	-	-	-
Irradiation for 180 minutes	-	-	-	-	-	-	-	-	-

Table B.4 Experimental data of effect of water level of wastewaters

Sample	Residual chromium (VI) concentration, (ppm)								
	Water level 2 cm			Water level 3 cm			Water level 4 cm		
	1	2	Average	1	2	Average	1	2	Average
Initial chromium	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
Adsorption for 15 minutes	21.17	21.70	21.44	20.70	21.15	20.92	20.77	20.19	20.48
Irradiation for 10 minutes	18.21	18.80	18.50	17.95	17.47	17.71	15.84	15.78	15.81
Irradiation for 20 minutes	16.45	16.92	16.68	15.73	15.78	15.76	12.16	11.95	12.06
Irradiation for 30 minutes	14.53	15.95	15.24	13.08	14.14	13.61	9.29	9.35	9.32
Irradiation for 45 minutes	12.06	11.39	11.73	9.83	11.95	10.89	5.32	5.59	5.46
Irradiation for 60 minutes	8.67	8.44	8.55	6.07	7.44	6.75	0.00	0.00	0.00
Irradiation for 90 minutes	5.34	3.64	4.49	1.03	1.77	1.40	-	-	-
Irradiation for 120 minutes	0.00	0.00	0.00	0.00	0.00	0.00	-	-	-
Irradiation for 150 minutes	-	-	-	-	-	-	-	-	-
Irradiation for 180 minutes	-	-	-	-	-	-	-	-	-

Table B.5 Experimental data of effect of water level of wastewaters

Sample	Residual chromium (VI) concentration, (ppm)					
	Water level 5 cm			Water level 6 cm		
	1	2	Average	1	2	Average
Initial chromium	25.00	25.00	25.00	25.00	25.00	25.00
Adsorption for 15 minutes	20.61	20.49	20.55	20.09	20.40	20.24
Irradiation for 10 minutes	16.85	16.56	16.71	17.21	17.26	17.23
Irradiation for 20 minutes	13.76	13.27	13.52	15.37	15.50	15.43
Irradiation for 30 minutes	10.82	9.88	10.35	12.26	13.54	12.90
Irradiation for 45 minutes	4.80	5.24	5.02	9.06	9.03	9.05
Irradiation for 60 minutes	1.04	1.38	1.21	4.57	4.35	4.46
Irradiation for 90 minutes	0.00	0.00	0.00	0.00	0.00	0.00
Irradiation for 120 minutes	-	-	-	-	-	-
Irradiation for 150 minutes	-	-	-	-	-	-
Irradiation for 180 minutes	-	-	-	-	-	-

Table B.6 Experimental data of effect of TiO₂ coating surface area

Sample	Residual chromium (VI) concentration, (ppm)								
	6 plates			9 plates			12 plates		
	1	2	Average	1	2	Average	1	2	Average
Initial chromium	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00
Adsorption for 15 minutes	46.89	47.78	47.34	47.74	48.43	48.09	48.17	47.73	47.95
Irradiation for 30 minutes	44.06	44.15	44.10	45.91	45.35	45.63	45.47	45.43	45.45
Irradiation for 60 minutes	40.12	39.74	39.93	43.27	41.39	42.33	40.05	39.59	39.82
Irradiation for 90 minutes	35.86	37.26	36.56	40.10	38.60	39.35	37.47	36.13	36.80
Irradiation for 120 minutes	34.14	35.21	34.67	37.32	36.02	36.67	33.05	33.04	33.05
Irradiation for 150 minutes	32.60	31.09	31.85	32.56	31.63	32.10	28.81	29.20	29.00
Irradiation for 180 minutes	28.90	29.03	28.97	28.51	27.84	28.17	23.01	24.84	23.93
Irradiation for 210 minutes	26.63	26.00	26.31	22.60	23.08	22.84	20.51	20.54	20.53
Irradiation for 240 minutes	22.96	23.13	23.05	20.70	20.56	20.63	15.20	13.90	14.55
Irradiation for 270 minutes	18.92	19.86	19.39	16.55	18.01	17.28	11.53	11.90	11.71
Irradiation for 300 minutes	15.20	16.10	15.65	11.09	11.54	11.32	8.19	7.92	8.05
Irradiation for 330 minutes	10.82	11.26	11.04	6.97	5.86	6.41	4.81	4.43	4.62
Irradiation for 360 minutes	6.99	6.58	6.78	3.02	3.56	3.29	0.00	0.00	0.00
Irradiation for 390 minutes	3.01	3.40	3.21	0.00	0.00	0.00	-	-	-
Irradiation for 420 minutes	0.00	0.00	0.00	-	-	-	-	-	-

Table B.7 Experimental data of effect of TiO₂ coating surface area

Sample	Residual chromium (VI) concentration, (ppm)					
	15 plates			18 plates		
	1	2	Average	1	2	Average
Initial chromium	50.00	50.00	50.00	50.00	50.00	50.00
Adsorption for 15 minutes	48.73	48.12	48.43	47.20	46.80	47.00
Irradiation for 30 minutes	43.83	44.94	44.39	41.83	43.70	42.77
Irradiation for 60 minutes	41.39	42.65	42.02	36.49	35.80	36.15
Irradiation for 90 minutes	37.23	38.71	37.97	29.71	31.09	30.40
Irradiation for 120 minutes	33.16	33.84	33.50	23.41	24.24	23.82
Irradiation for 150 minutes	29.07	28.41	28.74	17.01	17.32	17.16
Irradiation for 180 minutes	25.25	25.03	25.14	10.47	9.80	10.14
Irradiation for 210 minutes	20.14	20.28	20.21	4.80	3.91	4.35
Irradiation for 240 minutes	14.03	12.94	13.48	0.63	0.00	0.31
Irradiation for 270 minutes	10.60	7.95	9.27	0.00	0.00	0.00
Irradiation for 300 minutes	4.95	3.13	4.04	-	-	-
Irradiation for 330 minutes	0.15	0.09	0.12	-	-	-
Irradiation for 360 minutes	0.00	0.00	0.00	-	-	-

Table B.8 Experimental data of effect of initial concentrations

Sample	Residual chromium (VI) concentration, (ppm)					
	25 ppm			30 ppm		
	1	2	Average	1	2	Average
Initial chromium	25.00	25.00	25.00	30.00	30.00	30.00
Adsorption for 15 minutes	20.77	20.19	20.48	25.63	26.98	26.31
Irradiation for 10 minutes	15.84	15.78	15.81	23.79	25.15	24.47
Irradiation for 20 minutes	12.16	11.95	12.06	20.87	21.71	21.29
Irradiation for 30 minutes	9.29	9.35	9.32	19.47	19.95	19.71
Irradiation for 45 minutes	5.32	5.59	5.46	15.58	15.93	15.75
Irradiation for 60 minutes	0.00	0.00	0.00	10.44	10.07	10.25
Irradiation for 90 minutes	-	-	-	2.51	4.28	3.39
Irradiation for 120 minutes	-	-	-	0.00	0.00	0.00

Table B.9 Experimental data of effect of initial concentrations

Sample	Residual chromium (VI) concentration, (ppm)								
	50 ppm			100 ppm			150 ppm		
	1	2	Average	1	2	Average	1	2	Average
Initial chromium	50.00	50.00	50.00	100.00	100.00	100.00	150.00	150.00	150.00
Adsorption for 15 minutes	47.20	46.80	47.00	94.18	95.61	94.89	145.52	145.45	145.48
Irradiation for 30 minutes	41.83	43.70	42.77	86.57	87.65	87.11	136.90	137.37	137.14
Irradiation for 60 minutes	36.49	35.80	36.15	72.95	75.28	74.12	128.48	129.58	129.03
Irradiation for 90 minutes	29.71	31.09	30.40	64.18	64.92	64.55	120.90	122.47	122.68
Irradiation for 120 minutes	23.41	24.24	23.82	54.27	56.76	55.52	115.04	117.67	116.35
Irradiation for 150 minutes	17.01	17.32	17.16	44.27	44.24	44.25	108.29	106.69	107.49
Irradiation for 180 minutes	10.47	9.80	10.14	35.21	37.53	36.37	101.59	100.08	100.84
Irradiation for 210 minutes	4.80	3.91	4.35	26.00	26.64	26.32	89.38	90.15	89.76
Irradiation for 240 minutes	0.63	0.00	0.31	16.33	17.05	16.69	79.28	80.12	79.70
Irradiation for 270 minutes	0.00	0.00	0.00	9.10	10.09	9.59	74.02	72.81	73.42
Irradiation for 300 minutes	-	-	-	1.16	3.73	2.44	68.55	63.92	66.24
Irradiation for 330 minutes	-	-	-	0.00	0.00	0.00	59.31	57.17	58.24
Irradiation for 360 minutes	-	-	-	-	-	-	49.74	50.17	49.95
Irradiation for 390 minutes	-	-	-	-	-	-	45.50	44.03	44.76
Irradiation for 420 minutes	-	-	-	-	-	-	41.43	42.40	41.92
Irradiation for 450 minutes	-	-	-	-	-	-	41.51	42.66	42.08
Irradiation for 480 minutes	-	-	-	-	-	-	41.15	41.94	41.54
Irradiation for 510 minutes	-	-	-	-	-	-	41.40	42.72	42.06
Irradiation for 540 minutes	-	-	-	-	-	-	41.47	42.27	41.87

Table B.10 Experimental data of effect of initial concentrations

Sample	Residual chromium (VI) concentration, (ppm)								
	200 ppm			300 ppm			500 ppm		
	1	2	Average	1	2	Average	1	2	Average
Initial chromium	200.00	200.00	200.00	300.00	300.00	300.00	500.00	500.00	500.00
Adsorption for 15 minutes	195.16	194.65	194.90	297.69	288.69	293.19	498.00	494.67	496.33
Irradiation for 30 minutes	185.42	185.42	185.42	289.31	281.12	285.22	489.39	477.85	483.62
Irradiation for 60 minutes	175.67	176.42	176.05	278.73	265.68	272.21	476.53	469.16	472.84
Irradiation for 90 minutes	167.90	167.55	167.73	268.77	256.54	262.66	466.98	459.07	463.02
Irradiation for 120 minutes	159.98	160.80	160.39	258.71	246.51	252.61	455.90	451.41	453.66
Irradiation for 150 minutes	151.55	148.55	150.05	249.39	233.63	241.51	443.87	436.92	440.39
Irradiation for 180 minutes	144.13	139.13	141.63	243.00	228.02	235.51	432.31	425.32	428.82
Irradiation for 210 minutes	137.57	132.63	135.10	233.57	219.17	226.37	424.17	412.80	418.49
Irradiation for 240 minutes	131.87	122.25	127.06	225.71	210.91	218.31	414.98	404.80	409.89
Irradiation for 270 minutes	128.14	116.55	122.34	218.48	206.00	212.24	405.07	395.06	400.07
Irradiation for 300 minutes	119.91	111.41	115.66	213.24	200.10	206.67	396.93	390.31	393.62
Irradiation for 330 minutes	114.41	105.94	110.17	207.58	194.79	201.18	388.80	383.35	386.07
Irradiation for 360 minutes	109.82	103.10	106.46	203.39	190.86	197.12	380.19	378.59	379.39
Irradiation for 390 minutes	101.24	99.23	100.23	198.78	189.48	194.13	373.47	368.16	370.81
Irradiation for 420 minutes	94.27	94.13	94.20	193.01	186.23	189.62	367.33	359.58	363.46
Irradiation for 450 minutes	88.82	94.09	91.46	187.78	179.15	183.46	360.50	359.46	359.98
Irradiation for 480 minutes	88.67	94.21	91.44	183.79	174.43	179.11	354.25	359.93	357.09
Irradiation for 510 minutes	89.02	94.07	91.55	179.60	169.47	174.54	353.54	359.23	356.38
Irradiation for 540 minutes	89.12	94.14	91.63	176.25	166.67	171.46	354.36	360.04	357.20
Irradiation for 570 minutes	-	-	-	176.14	166.62	171.38	-	-	-
Irradiation for 600 minutes	-	-	-	176.88	166.96	171.92	-	-	-
Irradiation for 630 minutes	-	-	-	176.35	166.47	171.41	-	-	-



Appendix C

Calculation method

Appendix C

C.1 Contact time calculation

Example

Assign:

Length of reactor = 66 cm

Width of reactor = 33 cm

Height of reactor = 12 cm

Feed flow rate of wastewaters = 20 ml/s

Height of wastewaters in reactor = 6 cm

Reaction times = 80 min

From data we got:

Volume of wastewaters in reactor = $66 \times 33 \times 6 \text{ cm}^3$

= $13,068 \text{ cm}^3 = 13,068 \text{ ml}$

$$\text{Volume of wastewaters that flow in reactor} = 20 \times 1 \times 60 \frac{\text{ml}}{\text{sec}} \times \text{min} \times \frac{\text{sec}}{\text{min}}$$

$$\text{within 1 minutes} = 1,200 \text{ ml}$$

$$\text{So, contact time} = \frac{13,068 \frac{\text{ml}}{\text{cycle}}}{1,200 \frac{\text{ml}}{\text{min}}}$$

$$= 10.89 \frac{\text{min}}{\text{cycle}}$$

C.2 Treating cycle calculation

Example

Assign:

$$\text{Length of reactor} = 66 \text{ cm}$$

$$\text{Width of reactor} = 33 \text{ cm}$$

$$\text{Height of reactor} = 12 \text{ cm}$$

$$\text{Feed flow rate of wastewaters} = 20 \text{ ml/s}$$

$$\text{Height of wastewaters in reactor} = 6 \text{ cm}$$

$$\text{Reaction times} = 80 \text{ min}$$

From data we got:

$$\begin{aligned}\text{Volume of wastewaters in reactor} &= 66 \times 33 \times 6 \text{ cm}^3 \\ &= 13,068 \text{ cm}^3 = 13,068 \text{ ml}\end{aligned}$$

$$\text{Volume of wastewaters that flow in reactor} = 20 \times 80 \times 60 \frac{\text{ml}}{\text{sec}} \times \text{min} \times \frac{\text{sec}}{\text{min}}$$

$$\text{within 80 minutes} = 96,000 \text{ ml}$$

$$\text{So, treating cycle} = \frac{96,000 \text{ ml}}{13,068 \text{ ml}}$$

$$= 7.34 \text{ cycle}$$

C.3 The kinetic coefficient and adsorption equilibrium constant calculation

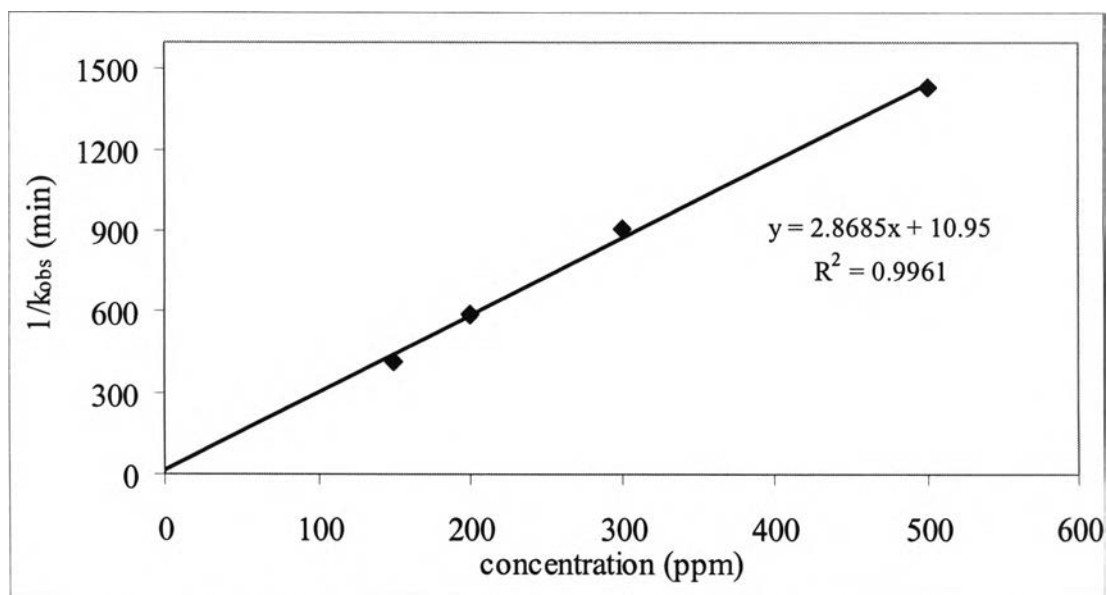


Figure 4.22 Determination of the adsorption equilibrium constants and degradation rate constants

From Langmuir-Hinshelwood equation and the figure, it get

$$\frac{1}{k_{obs}} = \frac{1}{kK} + \frac{C}{k} \quad (11)$$

$$y = 2.8685 + 10.95 \quad (12)$$

$$\frac{1}{k} = 2.8685 \quad (13)$$

$$k = 0.3486 \frac{mg}{l.min} \quad (14)$$

$$\frac{1}{kK} = 10.95 \quad (15)$$

$$K = 0.2620 \frac{l}{mg} \quad (16)$$

Then, get $k = 0.3486 \frac{mg}{l.min}$, and $K = 0.2620 \frac{l}{mg}$.

C.4 The amount of absorbed chromium (VI) calculation

Amount of absorbed chromium (VI) = (Residual chromium (VI) concentration at
initial) - (Residual chromium (VI)
concentration after adsorption)

Example

Sample	Residual chromium (VI) concentration, (ppm)					
	Flow rate 20 mL/s			Flow rate 60 mL/s		
	1	2	Average	1	2	Average
Initial chromium	25.00	25.00	25.00	25.00	25.00	25.00
Adsorption for 15 minutes	23.88	23.35	23.61	20.60	20.40	20.50

At flow rate 20 mL/s

$$\begin{aligned} \text{Amount of absorbed chromium (VI)} &= 25.00 - 23.61 \\ &= 1.39 \text{ mg/L} \end{aligned}$$

At flow rate 60 mL/s

$$\begin{aligned} \text{Amount of absorbed chromium (VI)} &= 25.00 - 20.50 \\ &= 4.50 \text{ mg/L} \end{aligned}$$

Biography

Mr. Audtapon Piyasichok was born on April 1, 1982 in Bangkok, Thailand. He graduated his Bachelor's degree in Environmental Engineering from faculty of Engineering, Chulalongkorn University in 2004. At Chulalongkorn University, he has studied in the topic of "Heavy metal removal from electroplating industrial wastewater treatment by using chelating polymer" as his senior.

After that, he pursued his Master Degree studies in the International Postgraduate Program in Environmental Management (Hazardous Waste Management), Inter-Department of Environmental Management Chulalongkorn University Bangkok Thailand on May, 2004.

