CHAPTER IV

RESULTS AND DISCUSSION

4.1 Start up reactor analysis

4.1.1 pH

Both the first and the second reactor, the pH during the 1st day to the 8th day was quite stable. It changed in a very narrow range from 7.13 to 7.28. The stablility of pH showed the balance of organic acid generation and organic acid digestion in the reactors.

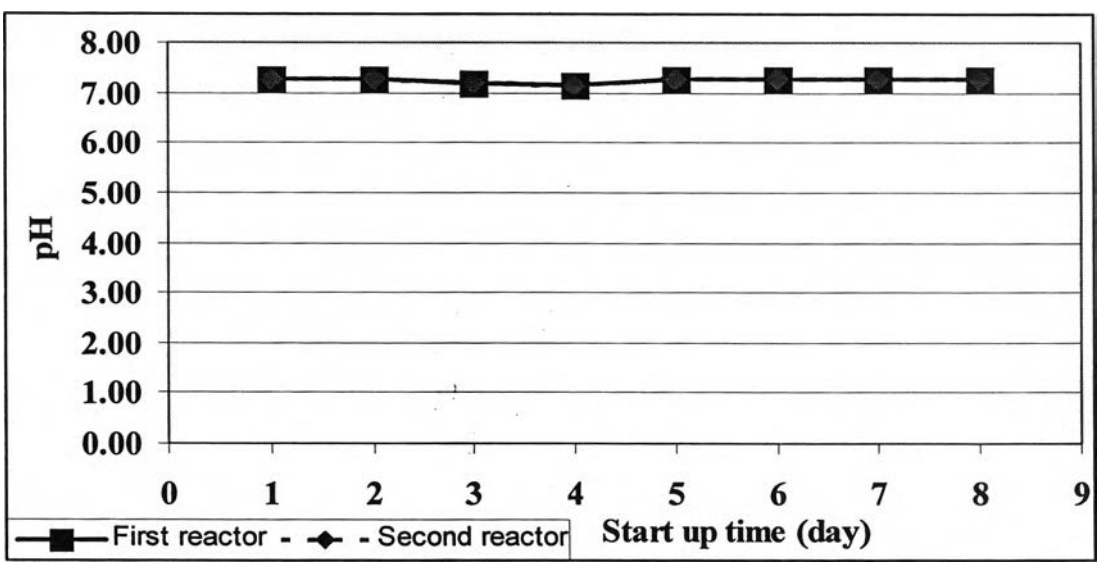

Figure 4.1 Daily pH in completely-mixed anaerobic reactors before adding Zinc.

4.1.2 Temperature

Both the first and the second reactor, the temperature in the reactors were dependent on ambient temperature. Figure 4.2 showed that the temperatures in the two reactors were changed in the range between 30 and 32 degree Celsius which were suitable for the mesophillic bacteria growth (between 25-35 °C). So, SRB could grew and established anaerobic condition in the reactors

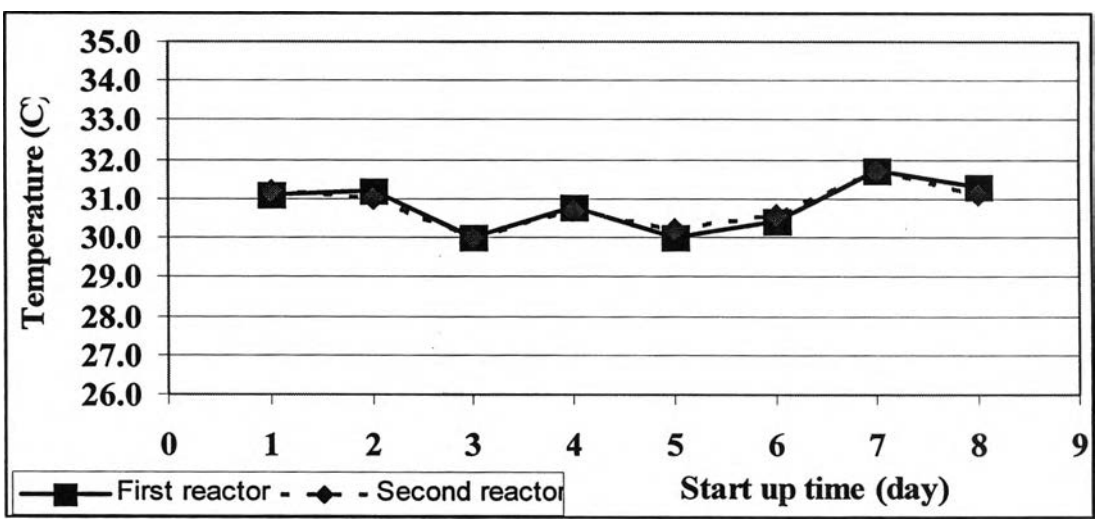

Figure 4.2 Daily temperature in completely-mixed anaerobic reactors before adding Zinc.

4.1.3 Oxidation reduction potential (ORP)

At the beginning the reactor mixture in the first and the second reactor mixed with many compositions. Then ORP increased from the sludge seeding (-195 mV). In Figure 4.3, ORP dropped from -49 mV at the beginning to -146 mV at the 8^{th} day. They showed that the anaerobic bacteria grew and was established anaerobic condition.

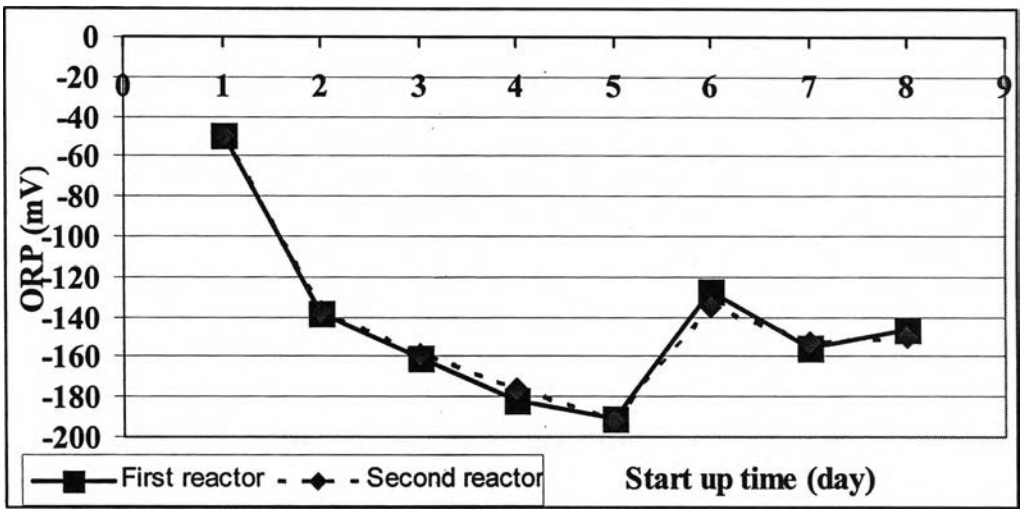

Figure 4.3 Daily oxidation reduction potential in completely-mixed anaerobic reactors before adding zinc.

4.2.4 Chemical oxygen demand (COD)

In the start up process total COD and dissolved COD would be changed in the same trend that was anaerobic bacteria using COD for their growth (Figures 4.4 and 4.5). From figure 4.4, the total the COD was decreased from the 1st to the 6th day. From the 6th to the 8th day, total COD in the reactor become stable.

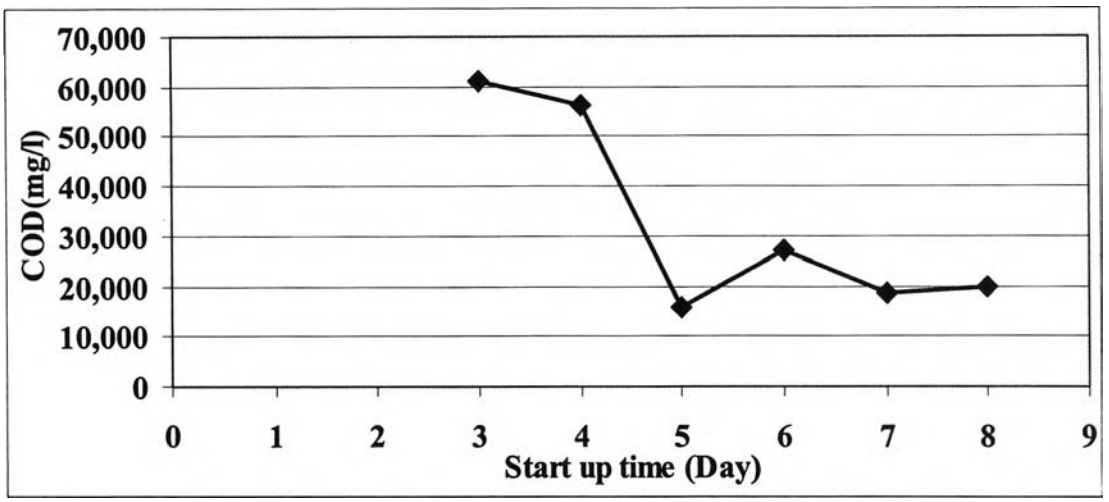

Figure 4.4 Daily total COD of the reactor mixture in completely-mixed anaerobic reactor before adding Zinc.

From figures 4.5, dissolved COD was decreased from the 1st to the 6th day. From the 6th to the 8th day, dissolved COD in the reactor become stable.

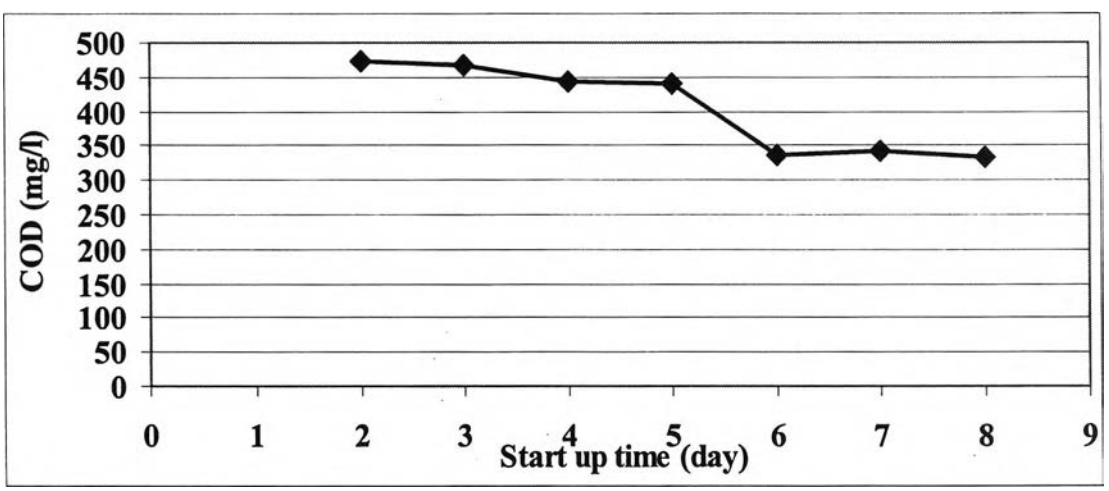

Figure 4.5 Daily dissolved COD of the reactor mixture in completely-mixed anaerobic reactor before adding zinc.

4.1.5 Sulfate

Sulfate decreased slowly at the first 2 days so the sulfate reduction was quite low. After the 3rd day, the sulfate decreased faster than the first 2 days. After the 6th day, sulfate reducing process was well established as can be seen from the low concentration of sulfate in the system. The sulfate concentration decreased to 25% of initial concentration within 6 days.

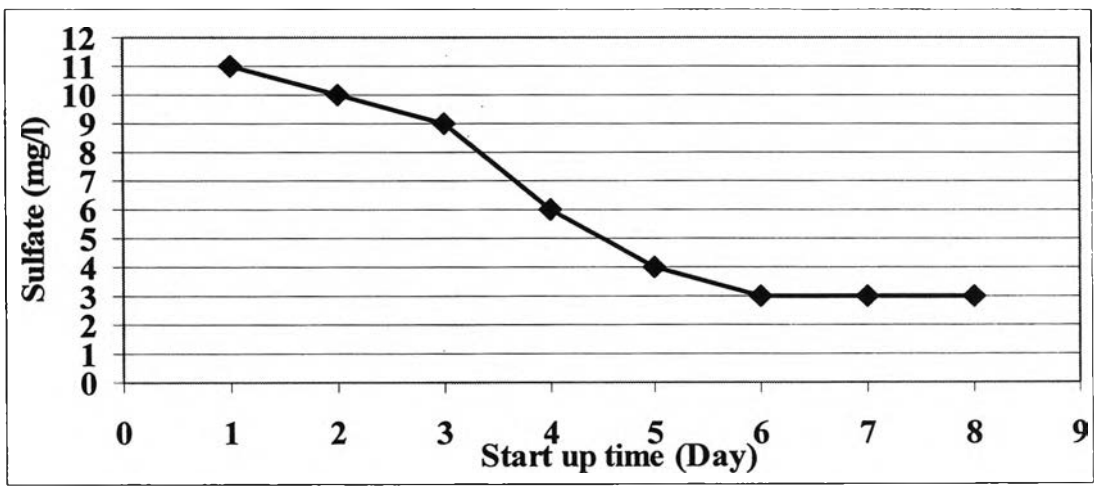

Figure 4.6 Daily sulfate in completely-mixed anaerobic reactor before adding zinc.

4.1.6 Sulfides

Sulfide increased slowly in the first 2 days and quickly from the 3rd through the 6th day. It showed the sulfate reducing bacteria can change sulfate to sulfide. The amount of decreased sulfate was equal to the amount of increased sulfide as appeared in figures 4.6 and 4.7 in term of sulfur. It showed that the increased sulfide was from decreased sulfate. From the 6th to the 8th day, the sulfide was constant at 8 mg./l. and was the indication of system readiness.

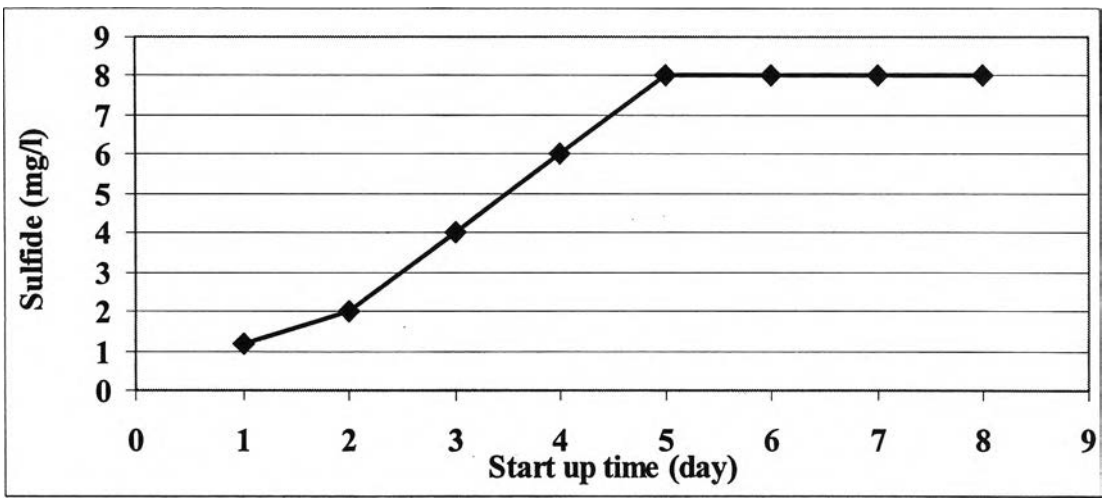

Figure 4.7 Daily sulfide in completely-mixed anaerobic reactor before adding zinc.

4.2 Operation reactor analysis

After the ORP, Total COD, Dissolved COD, sulfate and sulfide had become steady at the 8th day and the synthesized wastewater was injected, the results appear as follows:

4.2.1 The first injection

On the 9th day, 2 ml of the synthesized wastewater containing 10,000 mg/l of zinc was injected to bring concentration of the zinc in the reactor to be 10 ppm (Zinc 20 mg. for 2 liters in the reactor, 10 mg/l or 10 ppm). Sulfide and Zinc in reactor were observed every 30 minutes for the first 2 hours. Sulfide decreased rapidly because some was used to precipitate the zinc so the figure 4.8 showed the sulfide decreased instantly from 8 mg/l to 2 mg/l in the first 30 minutes for zinc precipitation. However, the amount of sulfide increased slowly in the next 2 hours to showed the recovery of sulfide in the system by sulfate reducing bacteria to change sulfate in synthesized wastewater to sulfide. The sulfide recovery can be made to the same level within 900 minutes (15 hours). After 900 minutes (15 hours) of the injection of synthesized wastewater, the sulfide recovery would be at the same level as it was before injection. It showed 10 ppm of zinc in the reactor did not have effect on sulfide recovery process.

Figure 4.9 showed that zinc precipitated very quickly. Zinc precipitated to nearly 0 mg/l (0.17 ppm or 0.17 mg/l) in the first 30 minutes. So after the first 30 minutes, concentration of zinc did not change (or changes less than 0.1 ppm).

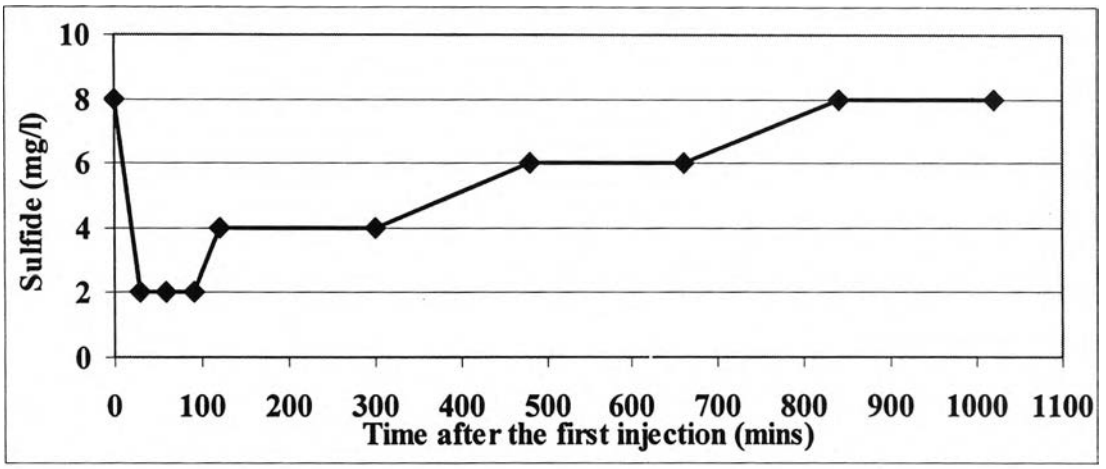

Figure 4.8 Sulfide in completely-mixed anaerobic reactor after the first injection.

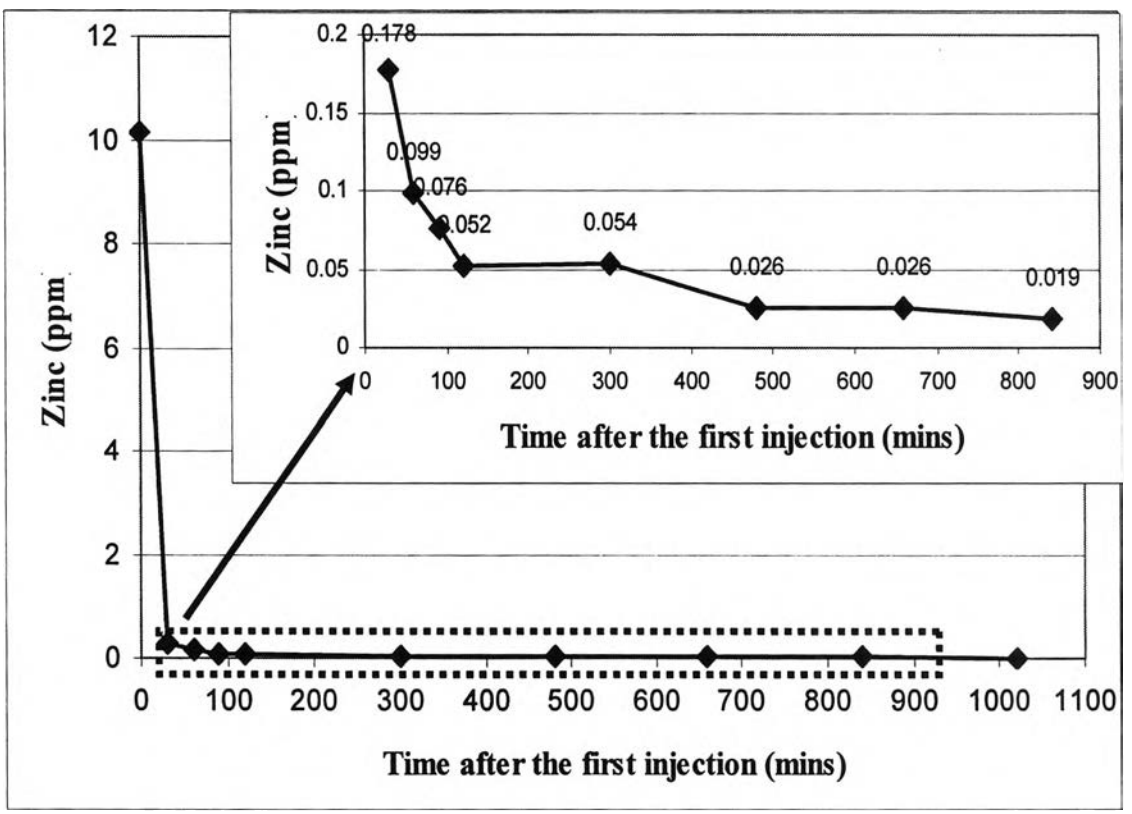

Figure 4.9 Zinc in completely-mixed anaerobic reactor after the first injection.

4.2.2 The second injection

50 mg/l of additional sulfur ($MgSO_47H_2O$) was filled on the 12th day. The additional sulfur was filled to increase sulfate level in the system. This additional sulfur calculated from sulfur 50 mg/l was sufficient to precipitate zinc 100 ppm. The sulfate and sulfide were observed every day. Sulfide increased very fast on the 13th day (from 8 mg/l to 36 mg/l) and would increase slowly at the 14th day until the 22nd day.

On the 23rd day, 4 ml of the synthesized wastewater contain 10,000 mg/l of zinc was injected into the reactor to increase the concentration of zinc (Zinc 40 mg for 2 liters in the reactor, 20 mg/l or 20 ppm). Sulfide and Zinc in the reactor were observed for every 10 minutes for 1 hour. Sulfide decreased rapidly because some was used to precipitate the zinc. So the figure 4.10 showed sulfide decreases instantly from 52 mg/l to 42 mg/l in the first 10 minutes for zinc precipitation.

Figure 4.11 showed zinc precipitated very quickly. Zinc precipitated to 0.34 mg/l (0.34 ppm) in the first 10 minutes. So after the first 10 minutes, concentration of zinc did not change (or changes less than 0.1 ppm). 1hr. after the injection, the concentration of zinc was decrease to 0.19 mg/l (0.19 ppm).

This injection showed the precipitation process happened very fast. The rate of zinc precipitation and sulfide recovery did not have effect from the increase of zinc concentration injection from 10 ppm to 20 ppm. Figure 4.26 showed sulfide at the 23rd day before the second injection was equal to sulfide at the 24th day. It showed the recovery of sulfide could bring sulfide back to 50 mg/l in the next day.

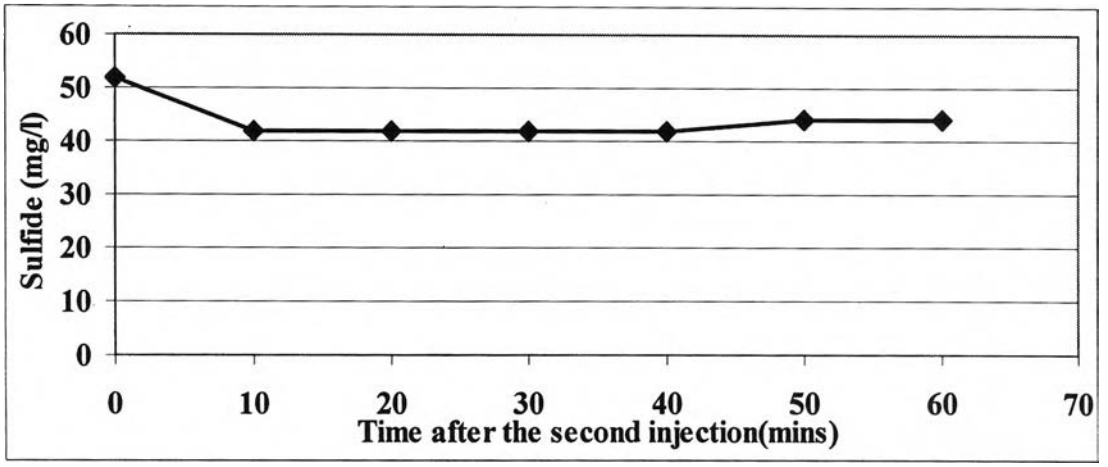

Figure 4.10 Sulfide in completely-mixed anaerobic reactor after the second injection.

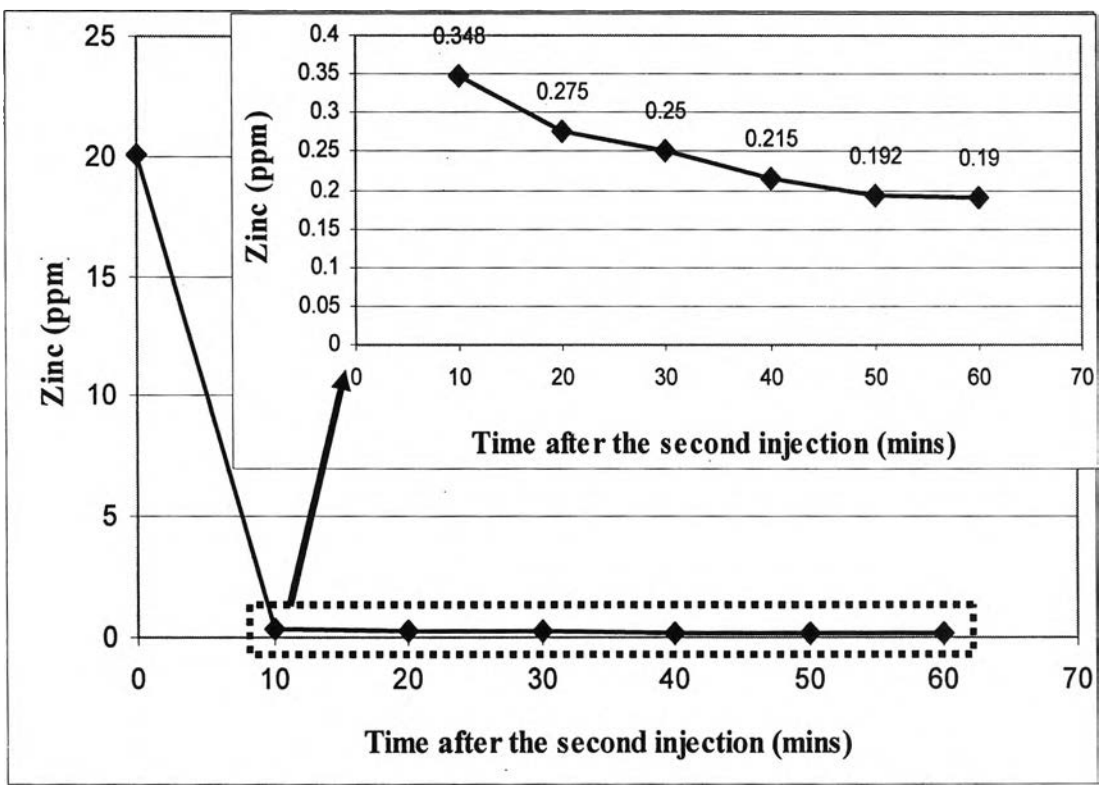

Figure 4.11 Zinc in completely-mixed anaerobic reactor after the second injection.

4.2.3 The third injection

On the 25th day, 4 ml of the synthesized wastewater contain 10,000 mg/l of zinc was injected into the reactor to increased the concentration of zinc (Zinc 40 mg for 2 liters in the reactor, 20 mg/l or 20 ppm). Sulfide and Zinc in the reactor were observed every 10 minutes for 1 hour. Sulfide decreased rapidly because some was used to precipitate the zinc. So figure 4.12 showed that sulfide decreases instantly from 52 mg/l to 42 mg/l in the first 10 minutes for zinc precipitation.

Figure 4.13 showed zinc precipitated very quickly. Zinc precipitated to 0.46 mg/l (0.46 ppm) in the first 10 minutes. After the first 10 minutes, the concentration of the zinc did not change (or changes less than 0.1 ppm). 1hr. after the injection, the concentration of zinc was decrease to 0.20 mg/l (0.20 ppm)

This injection showed the precipitation process happened very fast. Figure 4.26 showed sulfide on the 25th day before the third injection was equal to sulfide on the 26th day. It showed the recovery of sulfide could bring sulfide back to 52 mg/l in the next day and injection 20 ppm of zinc into the reactor did not have effect on sulfide recovery process.

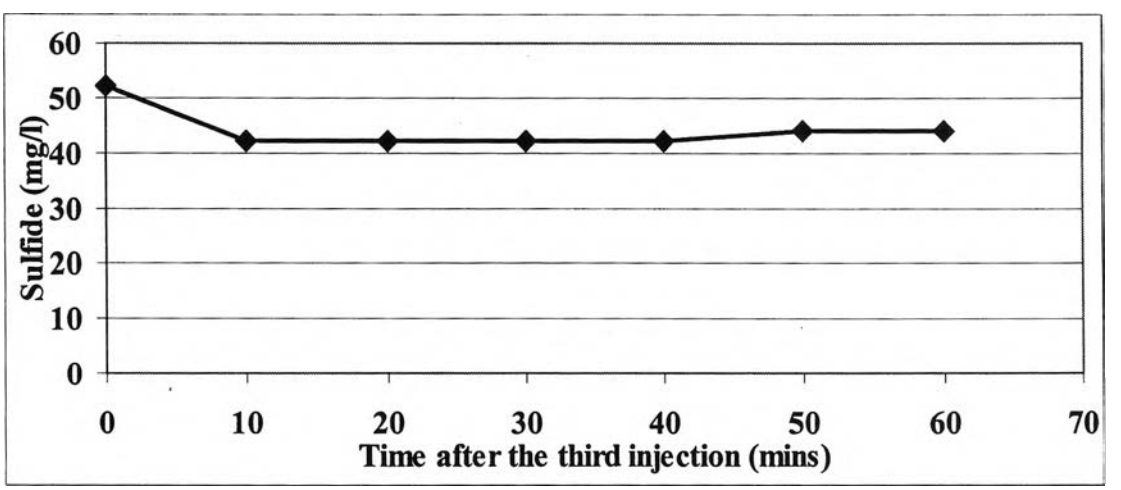

Figure 4.12 Sulfide in completely-mixed anaerobic reactor after the third injection.

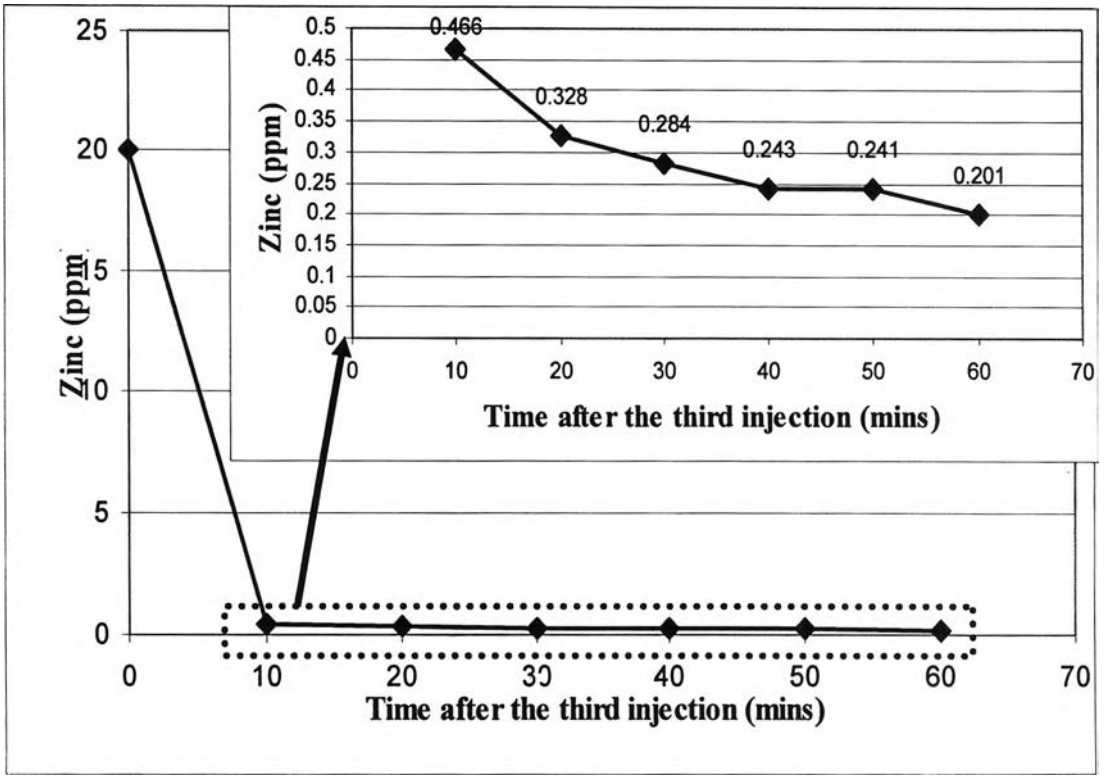

Figure 4.13 Zinc in completely-mixed anaerobic reactor after the third injection.

4.2.4 The forth injection

On the 28th day, 4 ml of the synthesized wastewater contain 10,000 mg/l of zinc was injected into the reactor to increase the concentration of zinc (Zinc 40 mg for 2 liters in the reactor, 20mg/l or 20 ppm). Sulfide and Zinc in the reactor were observed every 10 minutes for 1 hour. Sulfide decreased rapidly because some was used to precipitate the zinc. The figure 4.14 showed that sulfide decreases instantly from 52 mg/l to 42 mg/l in the first 10 minutes for zinc precipitation.

Figure 4.15 showed zinc precipitated very quickly. Zinc precipitated to 0.42 mg/l (0.42 ppm) in the first 10 minutes. After the first 10 minutes, the concentration of the zinc did not change (or changes less than 0.1 ppm). 1hr. after the injection, the concentration of zinc was decrease to 0.36 mg/l (0.36 ppm).

This injection showed the precipitation process happened very fast. Figure 4.26 showed sulfide on the 28th day before the fourth injection was equal to sulfide on the 29th day. It showed the recovery of sulfide could bring sulfide back to 52 mg/l in the next day and injection 20 ppm of zinc into the reactor did not have effect on sulfide recovery process.

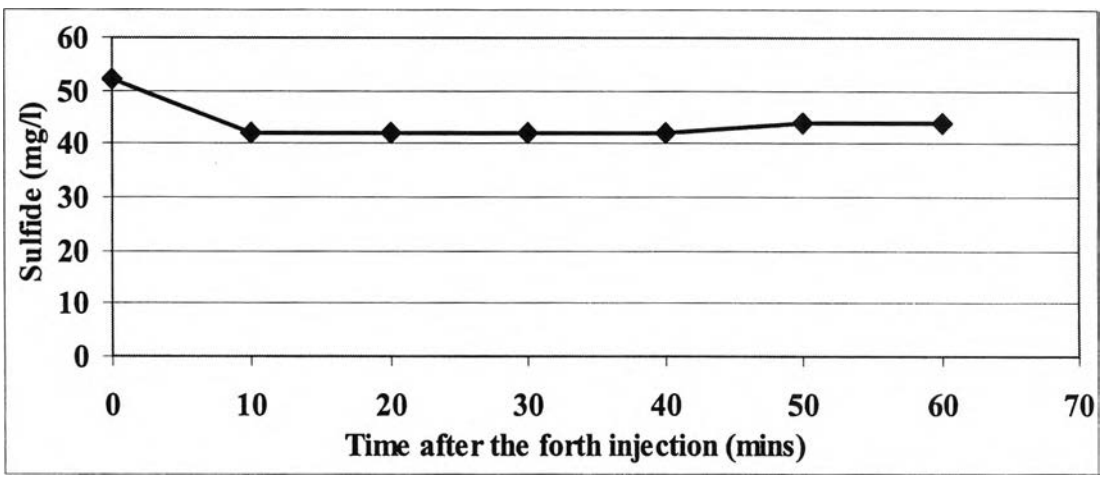

Figure 4.14 Sulfide in completely-mixed anaerobic reactor after the forth injection.

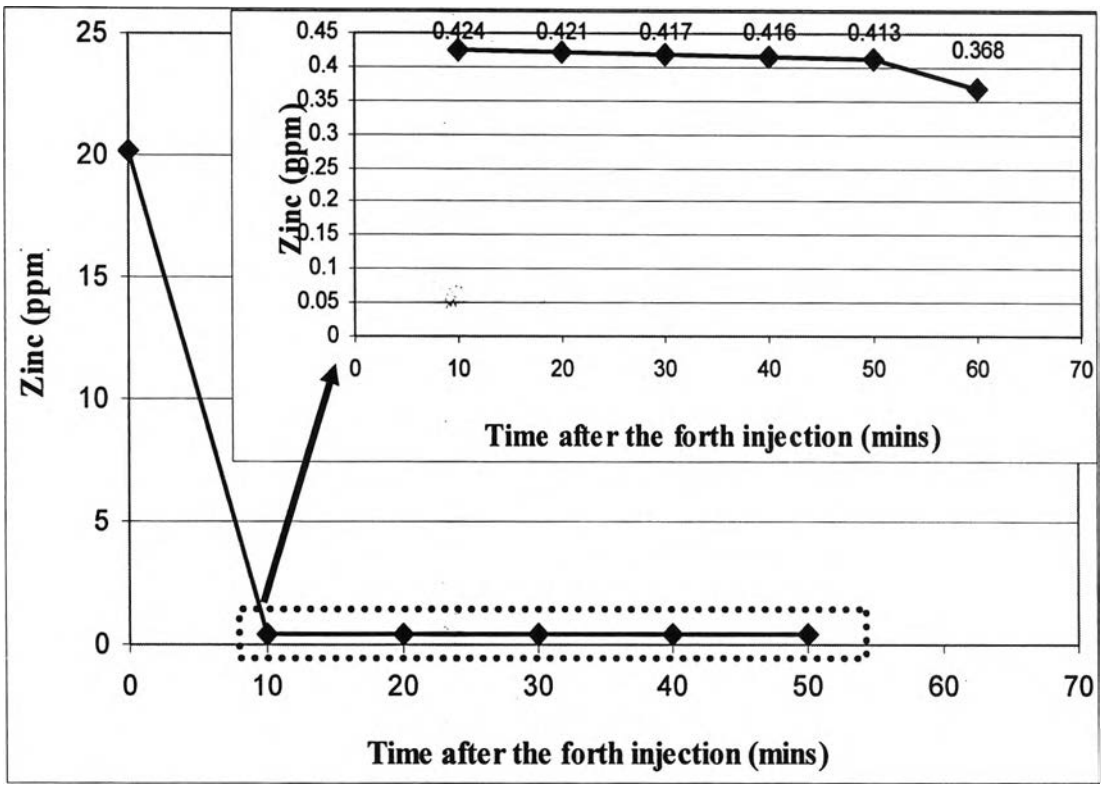

Figure 4.15 Zinc in completely-mixed anaerobic reactor after the forth injection.

4.2.5 The fifth injection

On the 29th day, 4 ml of the synthesized wastewater contain 10,000 mg/l of zinc was injected into the reactor to increase the concentration of zinc (Zinc 40 mg for 2 liters in the reactor, 20 mg/l or 20 ppm) in the reactor. Sulfide and Zinc in the reactor were observed for every 10 minutes for 1 hour. Sulfide decreased rapidly because some was used to precipitate the zinc. The figure 4.16 showed that sulfide decreased instantly from 52 mg/l to 42 mg/l in the first 10 minutes for zinc precipitation.

Figure 4.17 showed zinc precipitated very quickly. Zinc precipitated to 0.43 mg/l (0.43 ppm) in the first 10 minutes. After the first 10 minutes, the concentration of the zinc did not change (or changes less than 0.1 ppm). The concentration of zinc was decreased to 0.28 mg/l (0.28 ppm) in one hour after the injection.

This injection showed the precipitation process happened very fast. Figure 4.26 showed sulfide on the 29th day before the fifth injection was equal sulfide at the 30th day. It showed the recovery of sulfide could bring sulfide back to 52 mg/l in the next day and injection 20 ppm of zinc into the reactor did not have effect on sulfide recovery process.

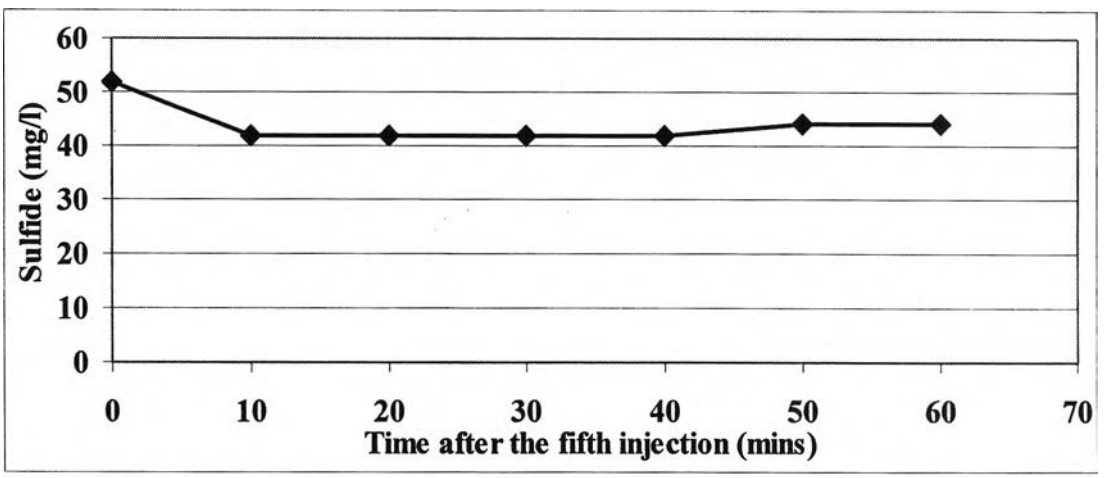

Figure 4.16 Sulfide in completely-mixed anaerobic reactor after the fifth injection.

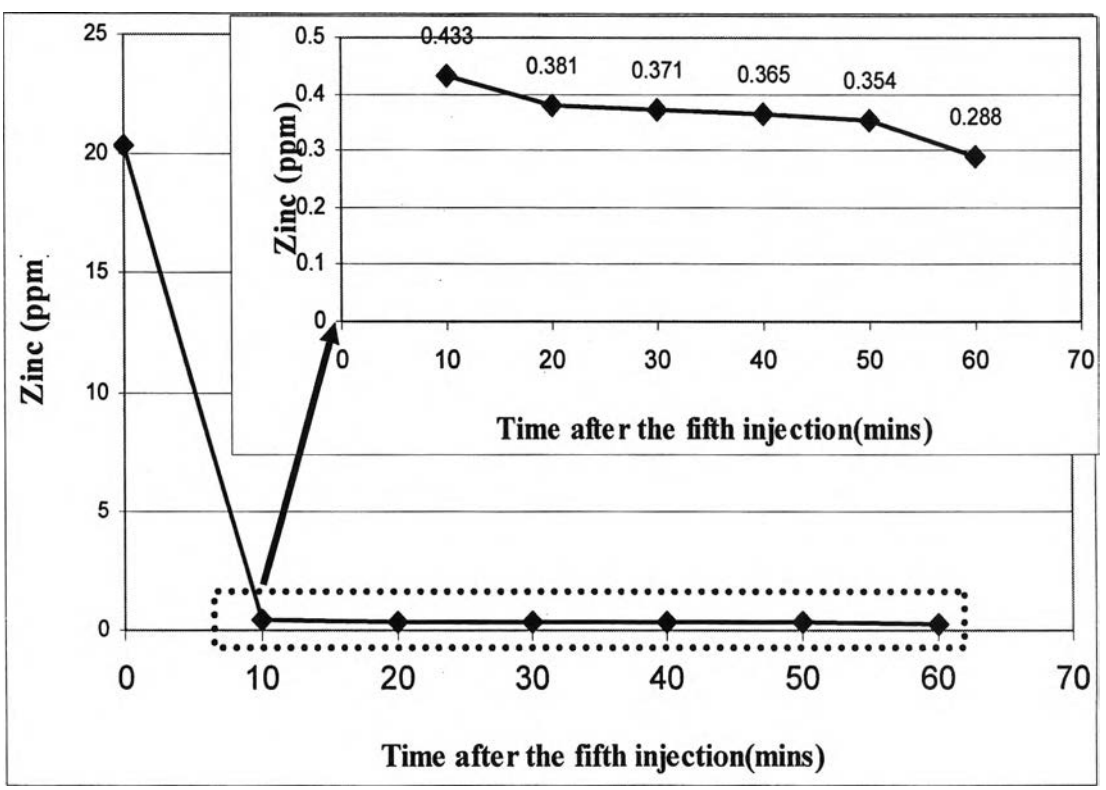

Figure 4.17 Zinc in completely-mixed anaerobic reactor after the fifth injection.

4.2.6 The sixth injection

On the 31st day, 10 ml of the synthesized wastewater contain 10,000 mg/l of zinc was injected into the reactor to increase the concentration of zinc (Zinc 100 mg for 2 liters in the reactor, 50 mg/l or 50 ppm) in the reactor. Sulfide and Zinc in the reactor were observed for every 10 minutes for 1 hour. Sulfide decreased rapidly because some was used to precipitate the zinc. The figure 4.18 showed that sulfide decreases instantly from 52 mg/l to 24 mg/l in the first 10 minutes for zinc precipitation.

Figure 4.19 showed zinc precipitated very quickly. Zinc precipitated to 0.81 mg/l (0.81 ppm) in the first 10 minutes. After the first 10 minutes, concentration of zinc decreased slowly from 0.8 ppm at the 10th minute to 0.6 ppm at the 60th minute.

This injection showed the precipitation process happens very fast in the first 10 minutes. The 49.4 ppm of zinc was precipitated in first 10 minutes. The zinc did not precipitate to near 0 at the first 10 minutes. A small amount of zinc (0.8 ppm) was available in the reactor. After the first 10 minutes the zinc precipitation continues slowly until zinc concentration lower than 0.5 ppm in the next day (the 32nd day). Figure 4.26 showed sulfide on the 31st day before the sixth injection was not equal to sulfide on the 32nd day. It showed the recovery of sulfide had an effect from the increased concentration of zinc from 20 ppm to 50 ppm. The sulfide recovery could not bring sulfide to the beginning level with the same time.

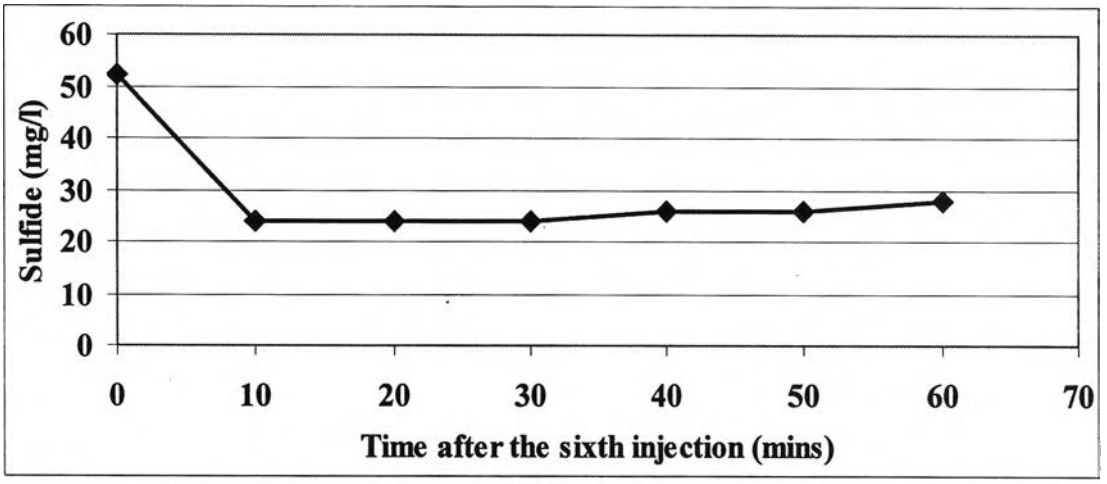

Figure 4.18 Sulfide in completely-mixed anaerobic reactor after the sixth injection.

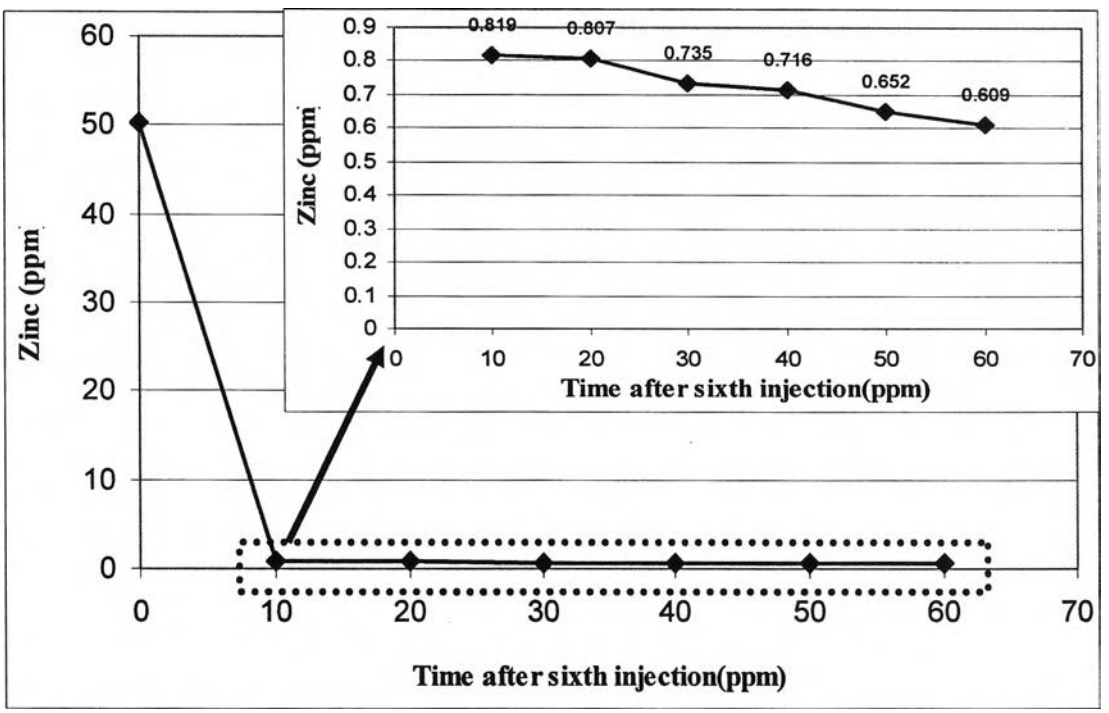

Figure 4.19 Zinc in completely-mixed anaerobic reactor after the sixth injection.

4.2.7 The seventh injection

On the 32nd day, 10 ml of the synthesized wastewater contain 10,000 mg/l of zinc was injected into the reactor to increase the concentration of zinc (Zinc 100 mg for 2 liters in the reactor, 50 mg/l or 50 ppm) in the reactor. Sulfide and Zinc in the reactor were observed every 10 minutes for 1 hour. Sulfide decreased rapidly because some was used to precipitate the zinc. So, the figure 4.20 showed that sulfide decreased instantly from 44 mg/l to 20 mg/l in the first 10 minutes for the zinc precipitation.

Figure 4.21 showed the zinc precipitated very quickly. The zinc precipitated to 1.06 mg/l in the first 10 minutes. After the first 10 minutes, concentration of zinc decreased slowly from 1.06 ppm at the 10th minute to 0.79 ppm at the 60th minute.

This injection showed that the precipitation process happened very fast in the first 10 minutes. The 49.39 ppm of zinc was precipitated in the first 10 minutes. The zinc did not precipitate to near 0 at the first 10 minutes. A small amount of zinc (1.06 ppm) was available in the reactor. After the first 10 minutes, the zinc precipitation continues slowly until its concentration to 0.52 ppm in the next day (the 33rd day). Figure 4.26 showed sulfide on the 32nd day before the seventh injection was equal to sulfide on the 33rd day. It showed the recovery of sulfide could bring sulfide back to 44 mg/l in the next day. And injection 50 ppm of zinc into the reactor did not have effect on sulfide recovery process.

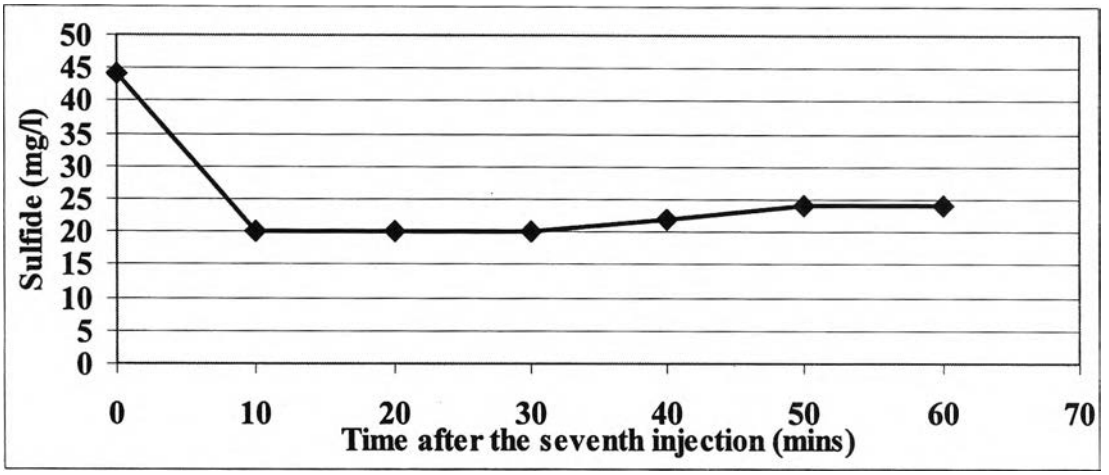

Figure 4.20 Sulfide in completely-mixed anaerobic reactor after the seventh injection.

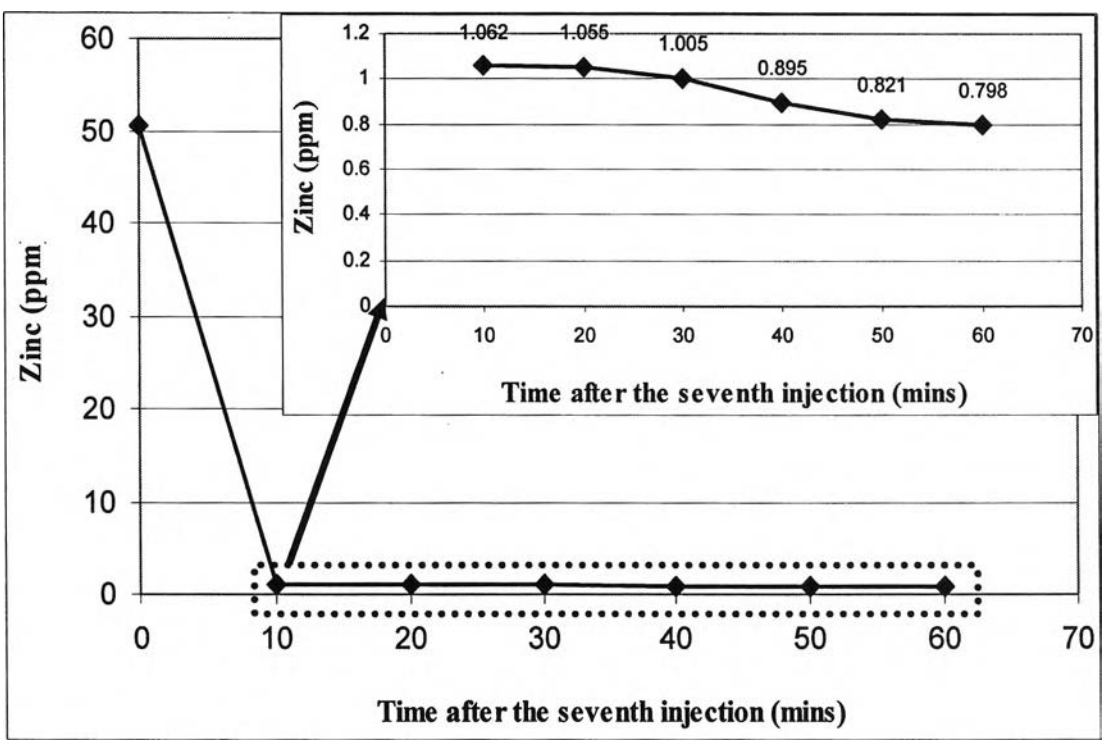

Figure 4.21 Zinc in completely-mixed anaerobic reactor after the seventh injection.

4.2.8 The eighth injection

On the 33rd day, 20 ml of the synthesized wastewater contain 10,000 mg/l of zinc was injected into the reactor to increase the concentration of zinc (Zinc 200 mg for 2 liters in the reactor,100mg/l or 100 ppm) in the reactor. Sulfide and Zinc in the reactor were observed for every 10 minutes for 1 hour. Sulfide decreased rapidly because some was used to precipitate the zinc. So, the figure 4.22 showed sulfide decreased instantly from 44 mg/l to 6 mg/l in the first 10 minutes for zinc precipitation.

Figure 4.23 showed zinc precipitated very quickly. Three-fourths of the zinc concentration would precipitate in the first 10 minutes. After the first 10 minutes concentration of the zinc would decrease slowly from 24 ppm at the 10th minute to 19 ppm at the 60th minute.

After this injection percentage of zinc removal in the first 10 minutes was lower than previous injection. For the previous injections, the percentage of zinc removal was 97 to 98 percent in the first 10 minutes but this injection was 75 percent (table 4.1 and table 4.2). Then, this injection showed that the increase of zinc concentration from 50 ppm to 100 ppm had an effect on the precipitation rate. The precipitation process still happened very fast in the first 10 minutes. The 76.32 ppm of zinc was precipitate in the first 10 minutes. But some of the zinc did not precipitated at the first 10 minutes. One-fourth of the zinc concentration (25 ppm) was available in the reactor. After the first 10 minutes, the zinc precipitation continues slowly. Zinc concentration 15 ppm was available in the next day. Figure 4.26 showed sulfide on the 33rd day before the eighth injection was not equal to sulfide on the 34th day. It showed the recovery of sulfide was affected from the increased concentration of zinc from 50 ppm to 100 ppm. Because some of sulfide produced must be used to precipitate available zinc in the reactor. And the sulfate reducing bacteria was inhibited by the available zinc in the reactor. However, sulfate reducing can bring sulfide back to 40 mg/l on the next day (the 34th day).

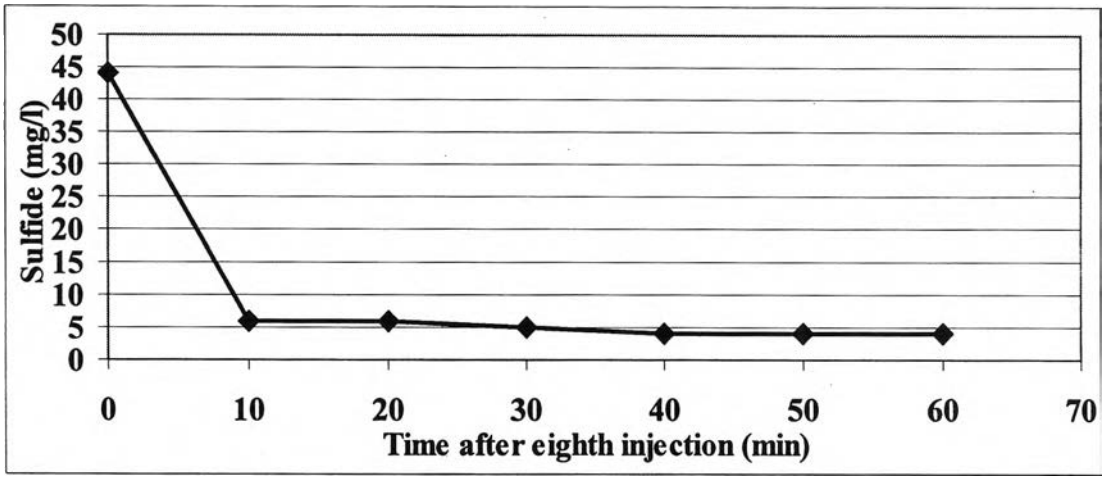

Figure 4.22 Sulfide in completely-mixed anaerobic reactor after the eighth injection.

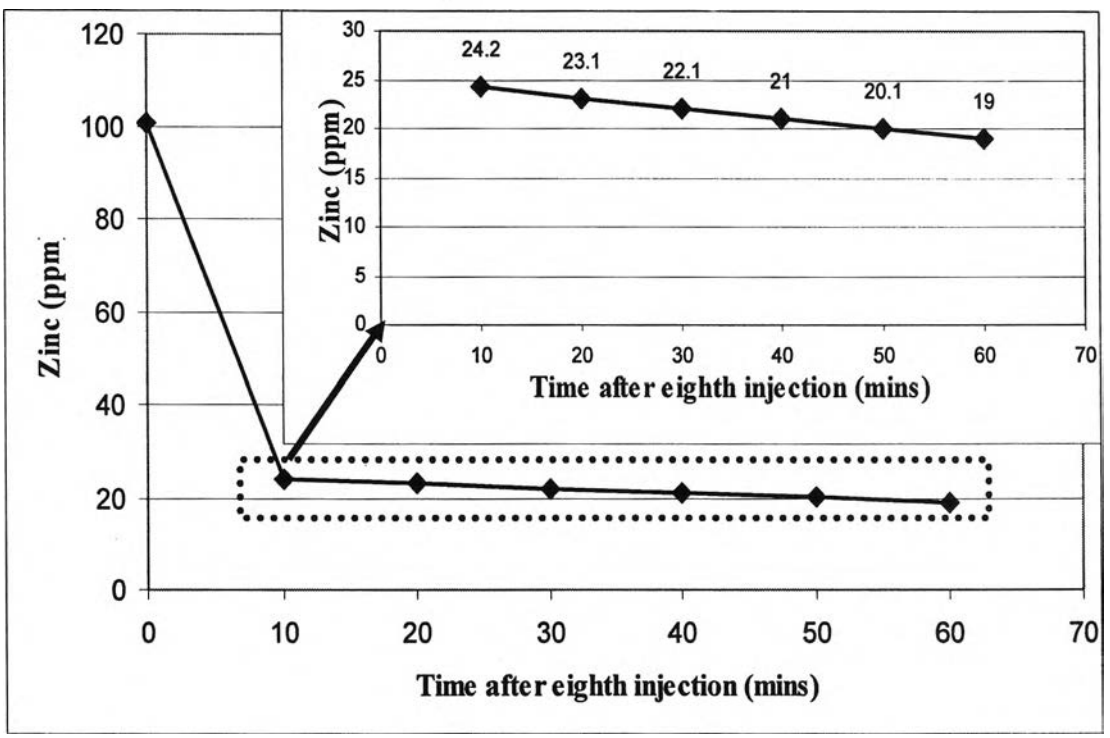

Figure 4.23 Zinc in completely-mixed anaerobic reactor after the eighth injection.

4.2.9 The ninth injection

On the 34th day, 20 ml of the synthesized wastewater contain 10,000 mg/l of zinc was injected into the reactor to increase the concentration of zinc (Zinc 200 mg for 2 liters in the reactor,100 mg/l or 100 ppm) in the reactor. Sulfide and Zinc in the reactor were observed for every 10 minutes for 1 hour. Sulfide has decreased rapidly because some has to be used to precipitate the zinc. So the figure 4.24 showed sulfide decreased instantly from 40 mg/l to 0 mg/l in first 10 minutes for zinc precipitation.

Figure 4.25 showed the zinc precipitated very quickly. A lot of zinc would precipitate in the first 10 minutes. After the first 10 minutes, concentration of zinc would decrease slowly from 35 ppm at the 10th minute to 29 ppm at the 60th minute.

After this injection, percentage of zinc removal in the first 10 minutes was lower than previous injection. The percentage of zinc concentration was 97 to 98 percent in the first 10 minutes for the first 7 injections and 75 percent in the first 10 minutes for the eighth injection (Table 4.4). But the percentage of zinc removal for this injection was 69 percent in the first 10 minutes. Then, this injection showed that the second 100 ppm injection of the zinc has an effect on the precipitation rate. The precipitation process happened very fast in the first 10 minutes. The 79.8 ppm of zinc was precipitate in the first 10 minutes. But some of the zinc did not precipitate at the first 10 minutes because sulfide was not sufficient for zinc precipitation. Much zinc (35 ppm) was available in the reactor. Figure 4.26 showed sulfide was not present on the 35th. It showed the recovery of sulfide caused by 100 ppm concentration of zinc. Because some of sulfide produced must be used to precipitate the available zinc in the reactor. And sulfate reducing bacteria was inhibited by zinc toxicity. Then sulfate reducing process cannot convert sulfate to sulfide to sufficient for precipitating the zinc in the reactor. Sulfide decreases to 0 mg/l on the next day (the 35th day) because available sulfide used to precipitate zinc. And SRB cannot change sulfate to sulfide.

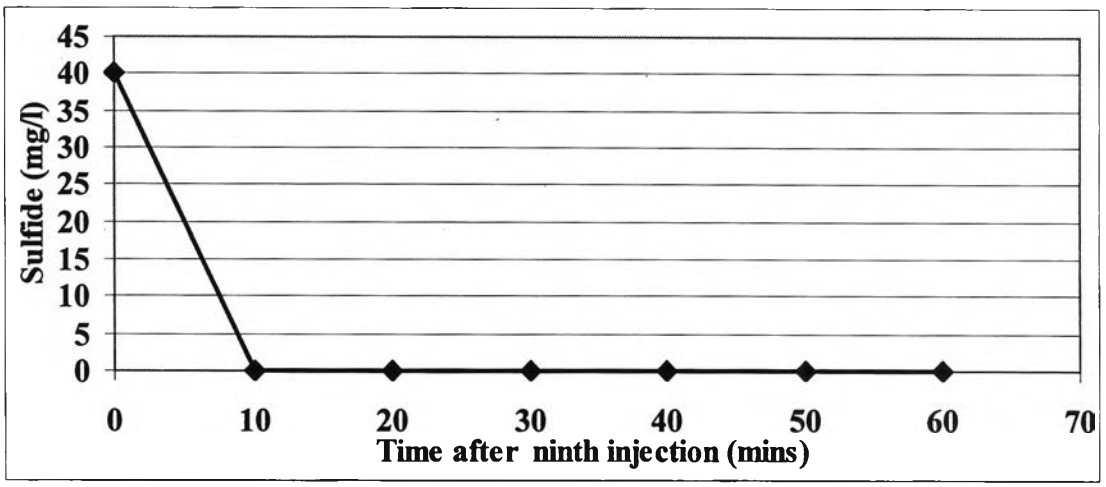

Figure 4.24 Sulfide in completely-mixed anaerobic reactor after the ninth injection.

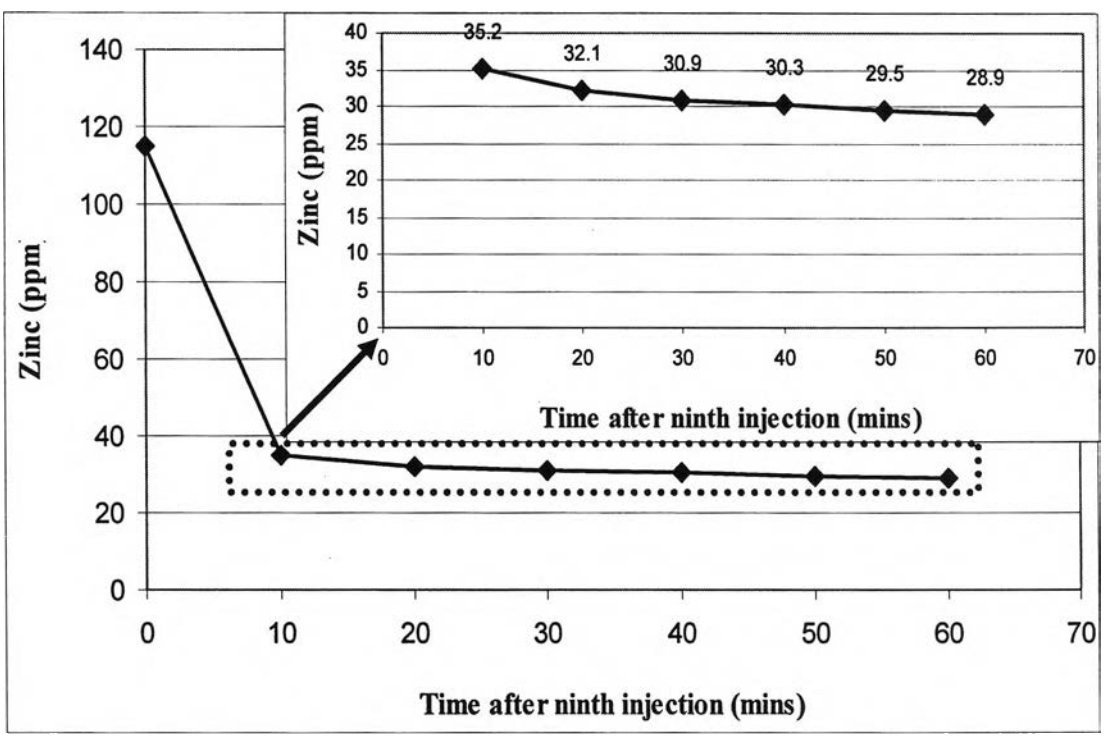

Figure 4.25 Zinc in completely-mixed anaerobic reactor after the ninth injection.

4.2.10 Relationship of Sulfate, Sulfide, Total Sulfur and zinc from the 9th day to the 35th day

The total dissolved sulfur in the reactors was not changed its level without adding sulfur ($MgSO_47H_2O$) and the added synthesized wastewater was containing the amount of sulfur equal to the amount of sulfide used for completely zinc precipitation. But in this experiment, the total dissolved sulfur was increased twice. The first increase was on the 13th day by adding 50 mg/l sulfur ($MgSO_47H_2O$). And the second increase was from the 34th day to the 35th day by the accumulation of sulfate. For the second time, the total dissolved sulfur was increased because the added sulfate was more than sulfide precipitated. 50 mg/l of sulfate was added for the 34th day and the 35th day. But 42 mg/l of sulfide was precipitated on the 34th day and 48 mg/l was precipitated on the 35th day. So, 8 mg/l of dissolved sulfur from the 34th day and 2 mg/l from the 35th day were accumulated in the reactor (Sulfur balance Appendix K).

In this experiment, the sulfate was transformed to sulfide and all the decreased sulfate was transformed to sulfide. Most of zinc could completely precipitation with residual sulfide in the reactor. But not for the 8th injection and the 9th injection, all sulfide has been used to precipitate zinc on the 34th day and 35th day but was still not enough. The zinc was accumulated in the reactor as shown in figures 4.26

From the residual sulfide, the amount of precipitated zinc in the reactor can be calculate. From the precipitation equation, 65 g of zinc precipitate completely with 32 g sulfide. From sulfur balance Appendix K, sulfide in the reactor was precipitated 185 mg/l or 185 x 2 = 370 mg. The 370 mg of sulfide can precipitate zinc 370 x 65/32 = 751.56 mg And from zinc balance Appendix N, total precipitated zinc in the reactor is 371.54 mg/l or 743.09 mg. The zinc was precipitated lower than the calculation from sulfur balances a little bit (743.09 mg and 751.56 mg). It showed the efficiency of precipitation by sulfide was 743.09/751.56 = 98.87%.

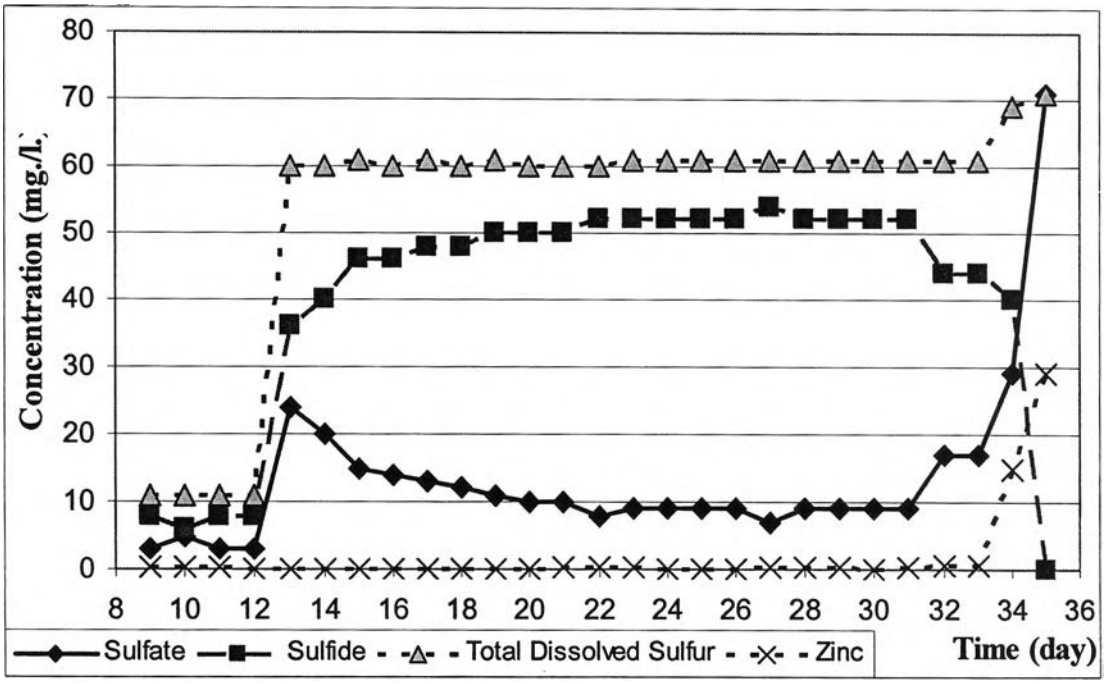

Figure 4.26 Sulfate, sulfide, total sulfur and zinc in completely-mixed anaerobic reactor from the 9th day to the 35th day

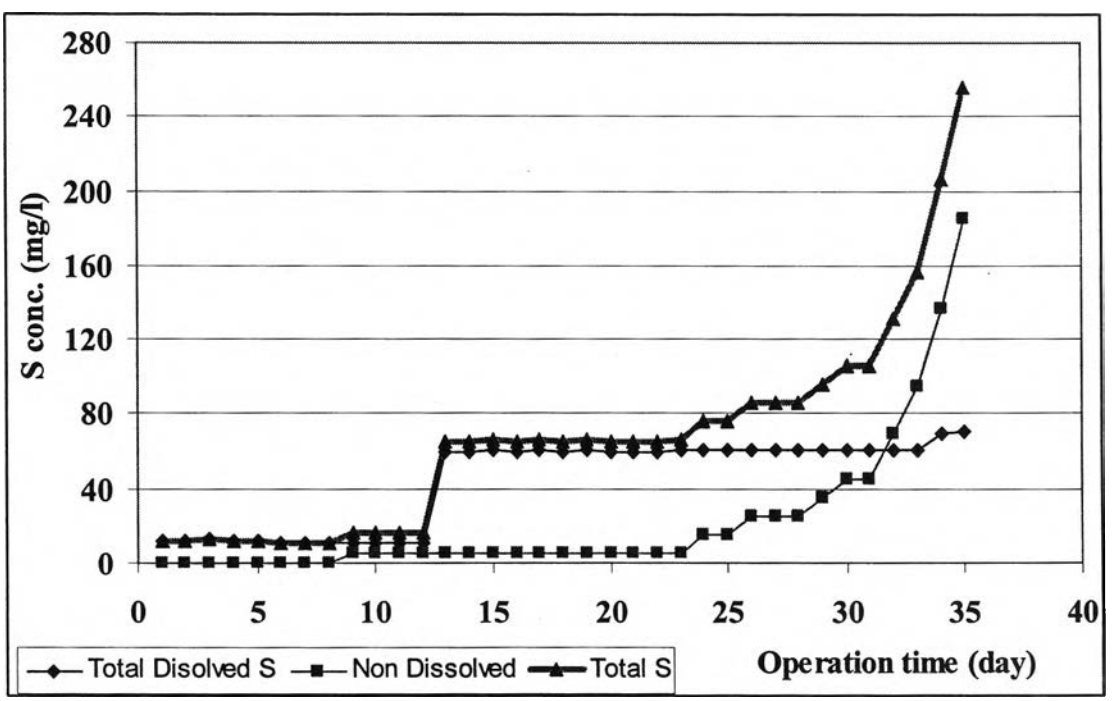

Figure 4.27 dissolved sulfur, non-dissolved sulfur, and total sulfur in completely-mixed anaerobic reactor from the 9th day to the 35th day

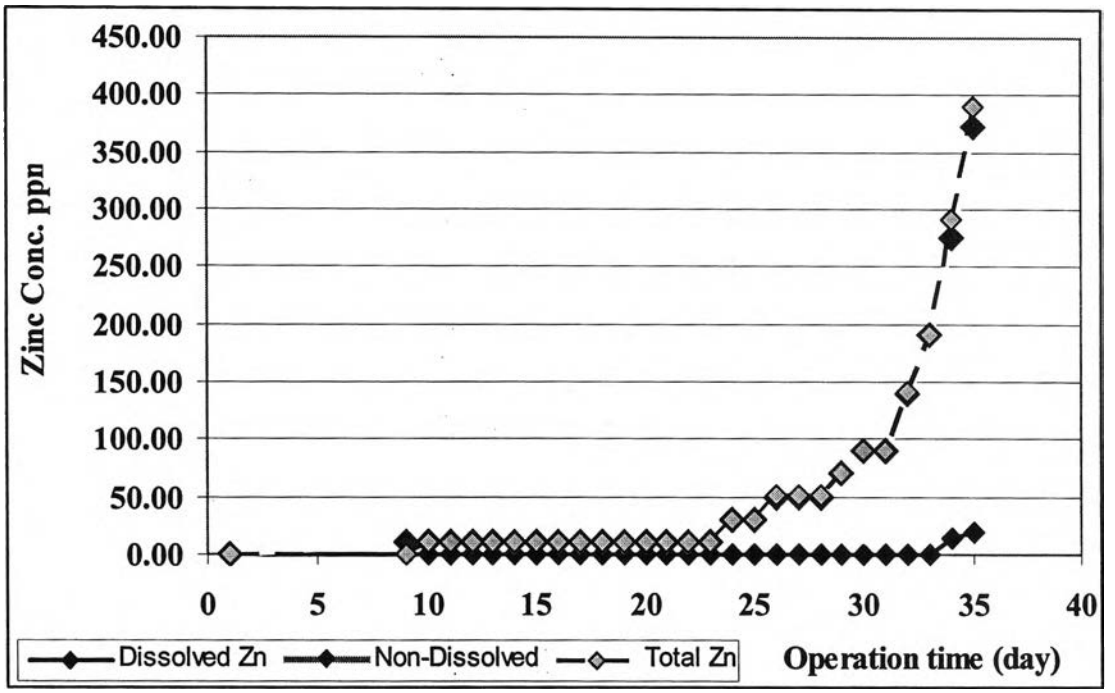

Figure 4.28 dissolved zinc, non-dissolved zinc, and total zinc in completely-mixed anaerobic reactor from the 9th day to the 35th day

4.2.11 Comparison of the 2nd, 3rd, 4th, and 5th injection

The 2nd, 3rd, 4th, and 5th injection were considered to compare because the same amount of zinc were injected. Figure 4.29 showed the concentration of zinc in the 2nd to the 5th injection. All of them (2nd to 5th injection) have same trend concentration of zinc. But at 1 hr. after the 2nd injection, the residual zinc concentration was lower than the 3rd, the 4th and 5th injection. And for 1 hr. after the 3rd injection, the residual zinc was lower than the 4th and the 5th injection. It showed the accumulation of residual zinc in the reactor. For the 4th injection, the zinc concentration was not lower than the 5th injection. It assumed zinc concentration on the 4th injection was error by instrument.

One day after the injection, they can recovery the residual sulfide to be at the same level as it was before the injection. The concentrations of zinc in the four injections were the same trend but the concentration of zinc 1 hour after the injections has a little difference. The 2nd injection, the concentration of zinc 1 hour after injection was 0.19 ppm (minimum). The third, the fourth and the fifth were 0.20 ppm, 0.36 ppm and 0.28 ppm respectively. The zinc concentration and sulfide at the other time shown in table 4.1. The concentrations of sulfate in these four injections were the same level (9 ppm) at 1day after injection.

Table 4.1 Remaining of zinc and sulfide in the 2nd injection to the 5th injection.

	Zinc (mg)				Sulfide (mg)			
Time (min)	2nd	3rd	4th	5th	2nd	3rd	4th	5th
0	40.70	40.14	40.30	40.56	104	104	104	104
10	0.68	0.92	0.84	0.86	84	84	84	84
20	0.54	0.64	0.84	0.38	84	84	84	84
30	0.50	0.56	0.82	0.37	84	84	84	84
40	0.42	0.48	0.82	0.36	84	88	84	84
50	0.38	0.48	0.82	0.35	88	88	88	88
60	0.38	0.40	0.72	0.28	88	88	88	88

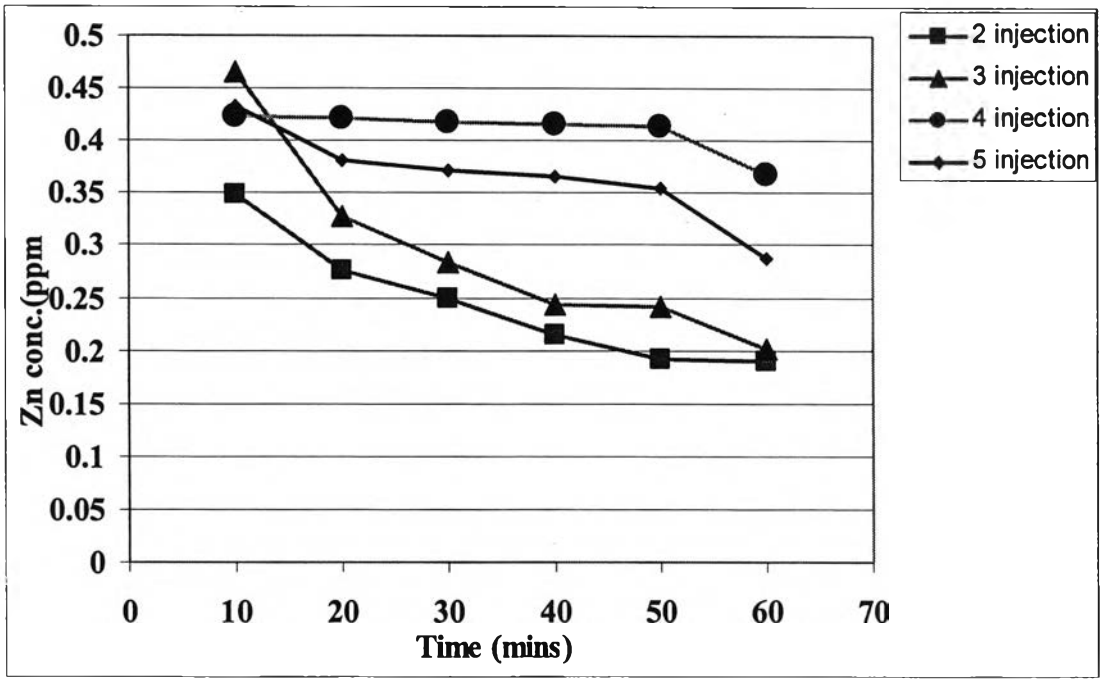

Figure 4.29 Concentration of zinc from 10 to 60 minutes after injection of synthesized wastewater for the 2nd injection to the 5th injection.

4.3 Comparison of the 1st injection to the 9th injection

From figure 4.30, zinc concentrations decreased rapidly in the first 10 minutes and decreased gradually after the first 10 minutes in all injections. But the available zinc was not same level as shown in figures 4.28 and 4.29.

4.3.1 Comparisons of available zinc after 1 hr. for each injection

One hour after injection, the 1st to the 5th injection the available zinc was the same level. The amount of available zinc in the 6th and the 7th injection were higher than the earlier injections as shown in figure 4.31. But the zinc removal efficiency of the 1st to the 7th injection in 60 minutes was between 98%-99% as shown in table 4.3. The 8th and 9th injection have removed zinc more than that of the 1st to the 7th injection. But they have available zinc in the reactor more than the earlier injection (19 ppm and 28 ppm) as shown in table 4.2 and figure 4.28. The zinc removal efficiency of the last 2 injections (85% and 78% as shown in table 4.3) was lower that of than the 1st to the 7th injection.

4.3.2 Comparisons of sulfide recovery in 24 hrs. for each injection

For the 1st to the 5th injection, the sulfide recovery could recovery 100% (the amount of recovered sulfide equal to the amount of precipitated sulfide) as shown in tables 4.2 and 4.3. They showed the sulfate reducing bacteria did not have effect from the zinc injection and could achieve sulfate reducing process. But in the 6th injection, the sulfide recovery dropped to 76.92% (20 ppm from 26 ppm) as shown in tables 4.2 and 4.3. It showed the increased concentration of zinc injection from 20ppm to 50ppm has an effect on sulfate reducing process. But for the next (the 7th) injection, the sulfide recovery can recover 100% again (24 ppm from 24 ppm). It shows the sulfate reducing bacteria adjusts to achieve sulfate reducing process under 50 ppm of zinc in the reactor. For the 8th injection, the sulfide recovery is dropped to 90% (40 ppm from 45 ppm) as shown in table 4.2 and table 4.3. It showed the increased concentration of zinc injection from 50 ppm-100 ppm has an effect on sulfate reducing process. But the last injection, sulfide recovery was not presented because too much available zinc in the reactor would inhibit sulfate reducing bacteria and all of the recovered sulfide must be used to precipitate the available zinc in the reactor.

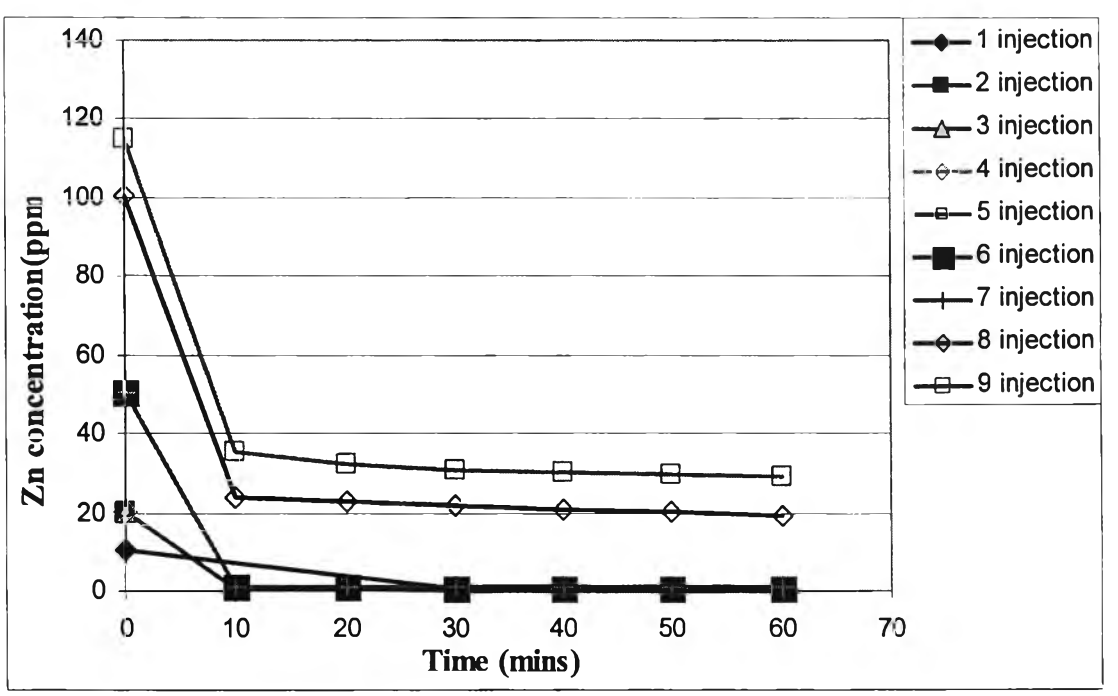

Figure 4.30 Concentration of zinc during 60 minutes after injection synthesized wastewater for every injection.

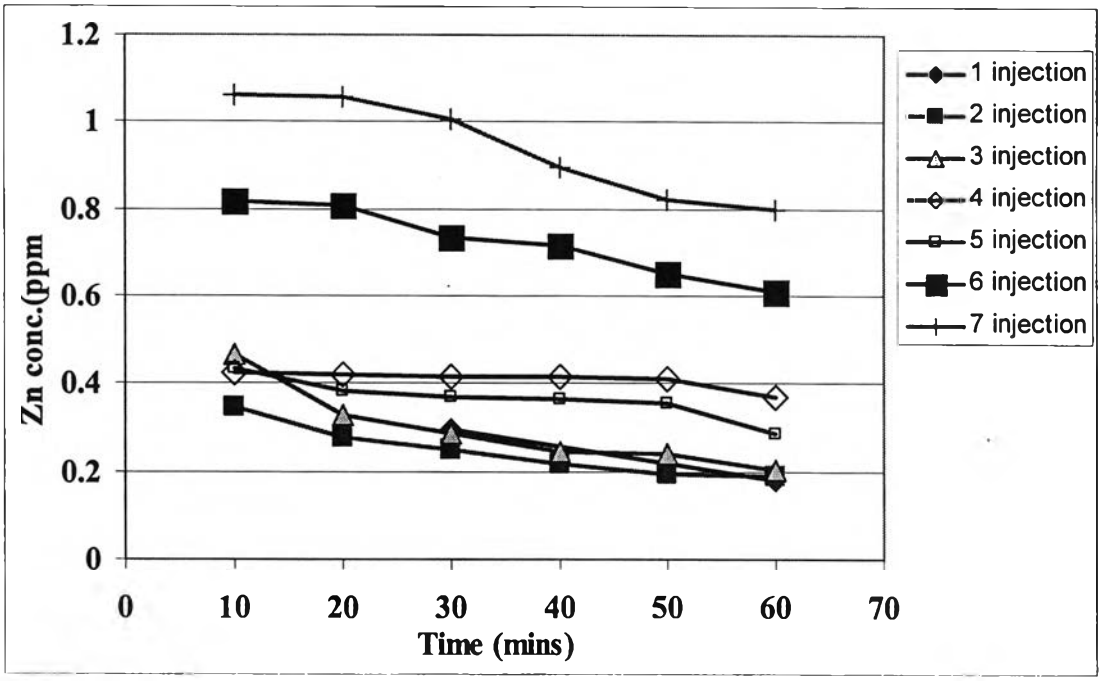

Figure 4.31 Concentration of zinc from the 10th minute to the 60th minute after injection synthesized wastewater for 1st injection to 7th injection.

Table 4.2 Sulfide recovery and amount of Zn in the 10th and the 60th minutes

Injection	S^{2-} recovery for 24hrs. (mg)	Zn at 24hrs. After injection (mg)	Zn at 10 minutes after injection (mg)	Zn at 60 minutes after injection (mg)	Add zinc (mg)
1	6	0.36	-	0.35	20
2	10	0.26	0.87	0.38	40
3	10	0.28	0.93	0.40	40
4	10	0.56	0.84	0.73	40
5	10	0.18	0.86	0.57	40
6	20	0.91	1.64	1.22	100
7	24	1.04	2.12	1.61	100
8	40	30	48.4	38.00	200
9	0	50	70.4	57.80	200

Table 4.3 The % of sulfide recovery and % of Zn removal at the 10^{th} minutes, the 60^{th} minutes and 24 hrs.

Injection	% S^{2-} recovery for 24hrs.	% of Zn removal at 24hrs. After injection	% of Zn removal at 10 minutes after injection	% of Zn removal at 60 minutes after injection
1	100	99.81	-	99.74
2	100	99.34	98.67	99.56
3	100	99.29	97.91	99.23
4	100	98.60	98.64	98.92
5	100	99.54	99.25	99.97
6	76.92	99.09	98.83	99.25
7	100	98.96	98.79	99.32
8	90	85.08	76.32	81.52
9	0	78.26	69.39	74.87

4.3.3 Environmental Condition

4.3.3.1 ORP

The ORP was quite stable. It changed in narrow range -155mV to -125mV. In Figure 4.32, ORP keeps their level lower than -100mV to establish anaerobic condition. Until the 34^{th} day and the 35^{th} day, the ORP was increased very fast. It showed that the failure of the anaerobic condition would happen. From figure 4.30, the reactor failed after the 9^{th} injection.

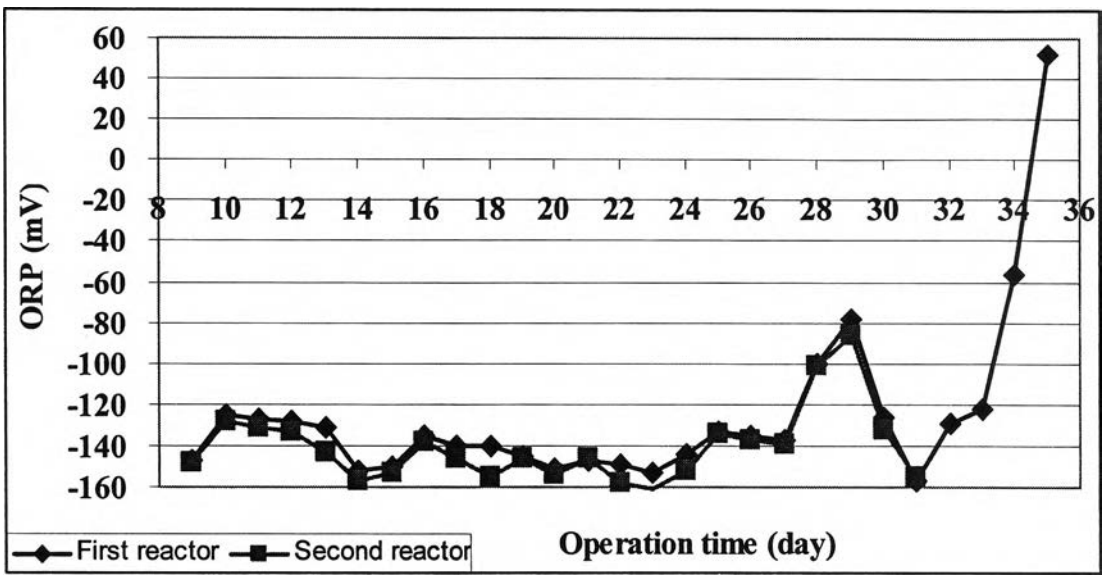

Figure 4.32 Oxidation reduction potential during operation reactors.

4.3.3.2 Volatile fatty acid/Alkalinity ratio

The VFA/Alk ratio showed the status of anaerobic system. Figure 4.33 showed that VFA/Alk was lower than 0.8 on the1st day to the 33rd day. But VFA/Alk value was higher than 0.8 (1.1) on the 35th day. It showed the failure of the anaerobic system.(Saipanich, 1987)

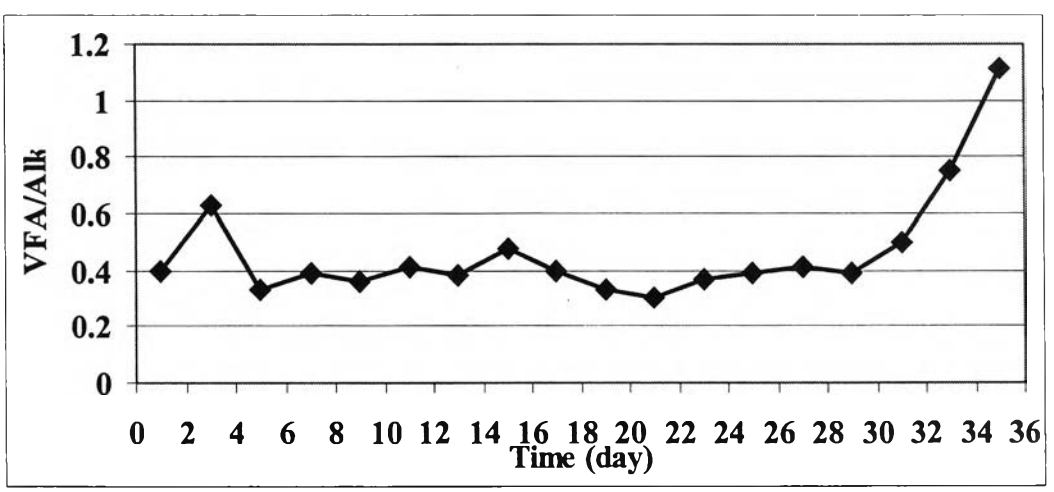

Figure 4.33 VFA/Alk ratio in completely mixed anaerobic reactor every 2 days.

4.3.3.3 Alkalinity

Alkalinity was observed every 2 days. In figure 4.34, on the 1st day, it showed that alkalinity value was not high. For the first 5 days, alkalinity would increased. The increased alkalinity on the 3rd day to the 5th day showed sulfate reducing bacteria produced bicarbonate in the reactor.

$$4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$$

$$CH_3COO^- + SO_4^{2-} \rightarrow HS^- + 2HCO_3^-$$

After the 5th day alkalinity was stable (changes in narrow range). Until the 31st day, alkalinity dropped lower than 85 mg/l It showed that sulfate reducing bacteria was inhibited. And SRB cannot produced bicarbonate equal to the previous time.

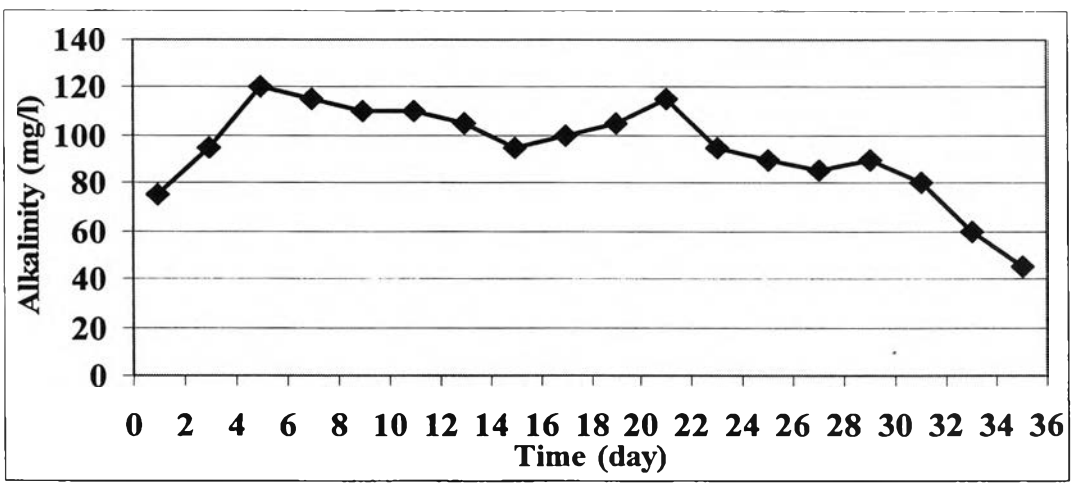

Figure 4.34 Alkalinity in completely mixed anaerobic reactor every 2 days.

4.3.3.4 Volatile Fatty Acids

Volatile fatty acid was observed every 2 days. In figure 4.35, it showed on the 1st day VFA value did not high. The large increased VFA on the 3rd day showed that acidogenic bacteria started to produce a lot of organic acid in the reactor. After the 3rd day VFA was decreased and become stable (changes in narrow range) after the 5th day. From 31st day, VFA was increased by accumulation of the organic acid. It showed that sulfate reducing bacteria was inhibited; reaction cannot be preceded as SRB cannot work as usual due to high level of Zn as in Figure 4.35

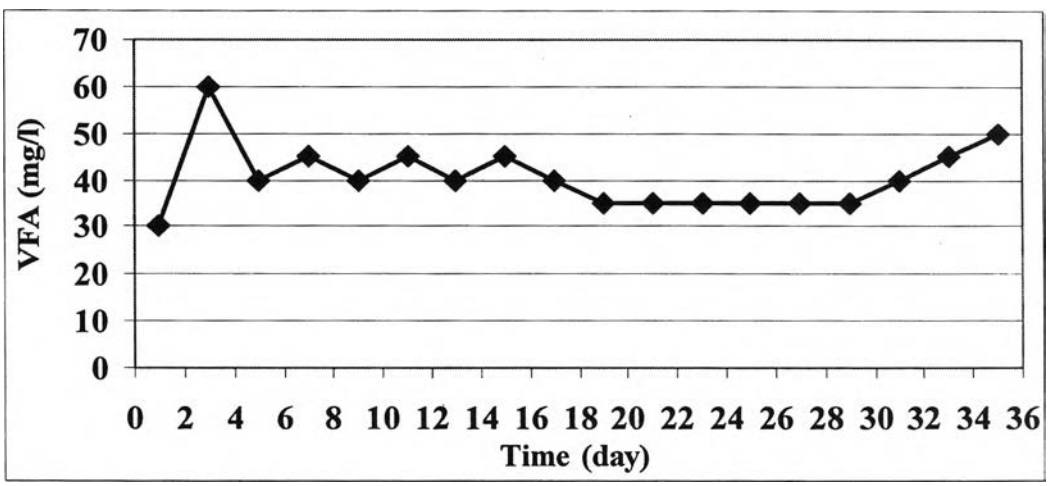

Figure 4.35 VFA in completely mixed anaerobic reactor every 2 days.

4.3.3.5 pH

The pH during the 9th day to 33rd day was quite stable. It changes very narrow range 7.00 to 7.28. But on the 34th day and the 35th pH dropped to lower than 7.00.

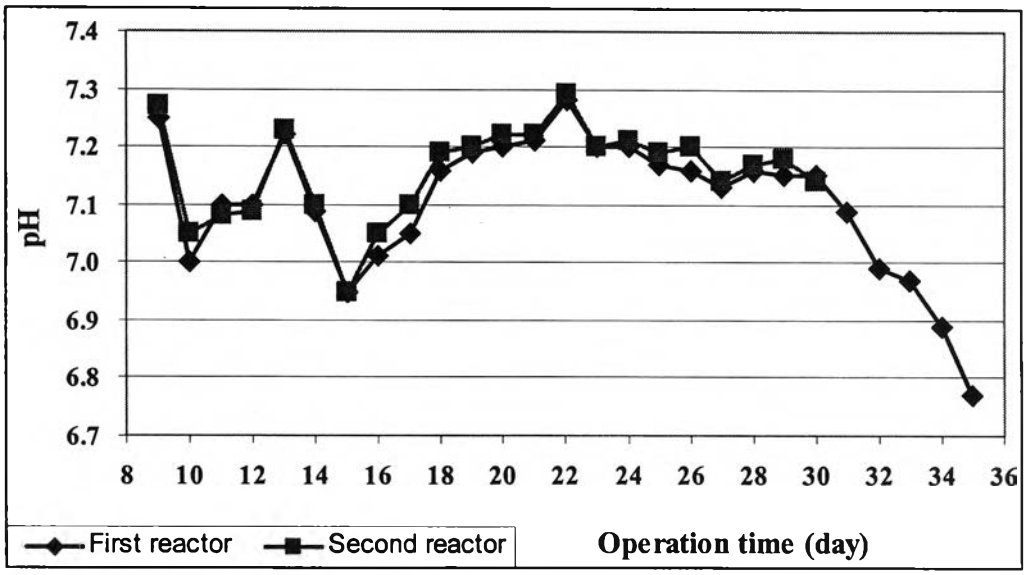

Figure 4.36 The pH during operation reactors

4.3.3.6 Temperature

The temperature in the reactor was dependant on ambient temperature. Figure 4.37 showed that the temperatures in the reactor were changed in the range between 25 and 35 degree Celsius which were suitable for the mesospheric bacteria growth (between 25-35 °C)(Saipanich, 1987).

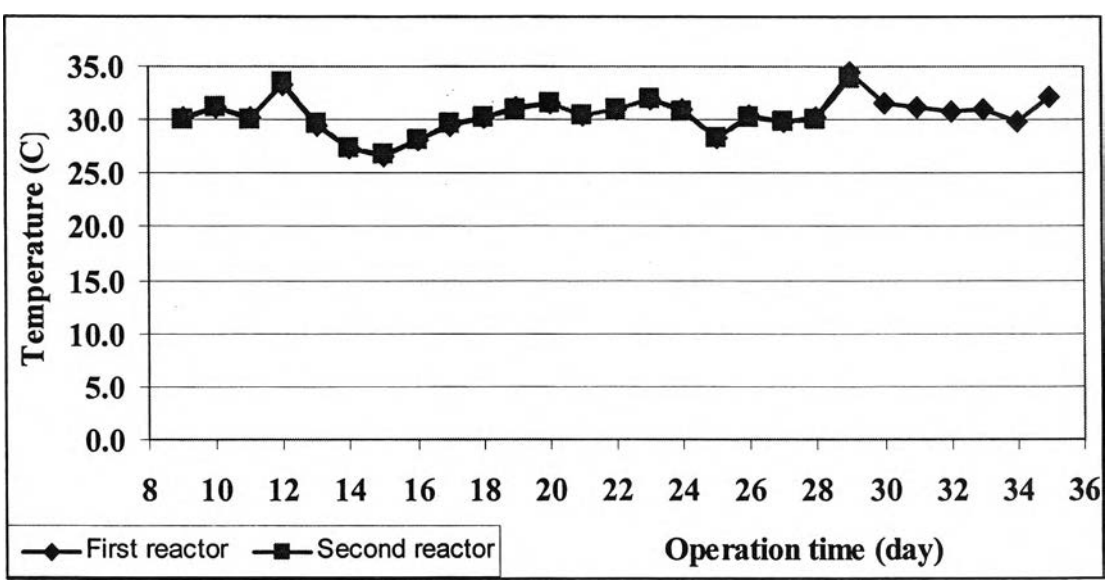

Figure 4.37 Temperature during operation reactor

4.3.3.7 Mixed Liquor Suspended Solid (MLSS)

From figure 4.38, the MLSS were changed in narrow range. It changed between 17,000 mg. and 28,000 mg. The average of MLSS was 21,611 mg./l . It showed the MLSS 21,611 mg./l can treated zinc 743 mg.

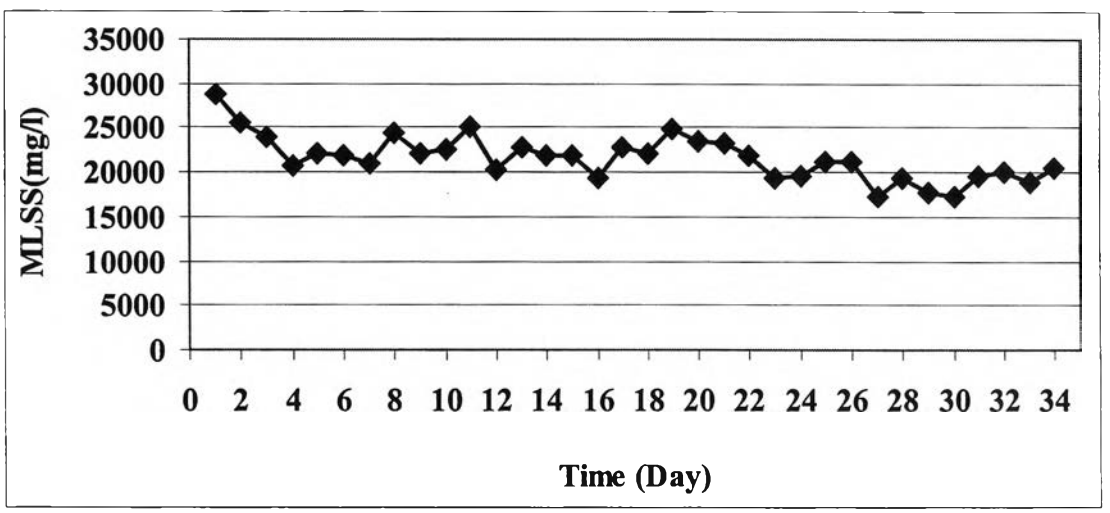

Figure 4.38 Mixed Liquor Suspended Solid during operation reactor

4.3.3.8 Total kjeldahl nitrogen

Total kjedahl nitrogen in completely mixed anaerobic reactor was changed in narrow range (89 mg./l. to 137.2 mg./l.).

Measurement of total kjedahl nitrogen was performed to assess nutrient availability in the completely mixed anaerobic reactor, and showed the sufficient of nutrient to the completely mixed anaerobic reactor. The results of analyses were expressed in mg/L of nitrogen and were presented in Figure 4.39, with corresponding data included in Table B-4 of Appendix B.

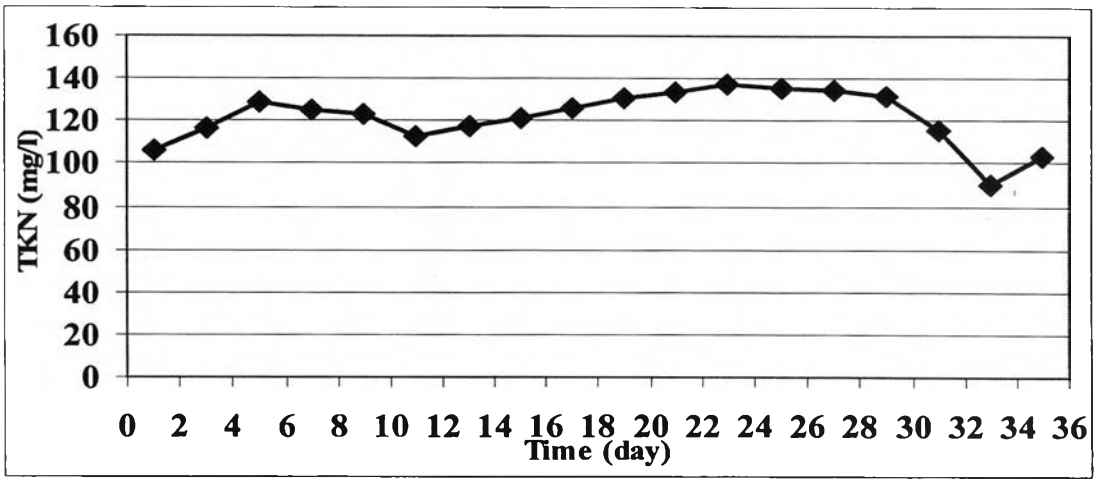

Figure 4.39 TKN in completely mixed anaerobic reactor every 2 days.

4.4 Gas production analysis

Daily gas volumes produced from completely mixed anaerobic reactor was shown in Figure 4.40 (Table D-1 in Appendix D). The daily gas volumes were continuously generated from the 1st day to the 35th day. The gas production rate changed with narrow range (1ml/day-2ml/day).

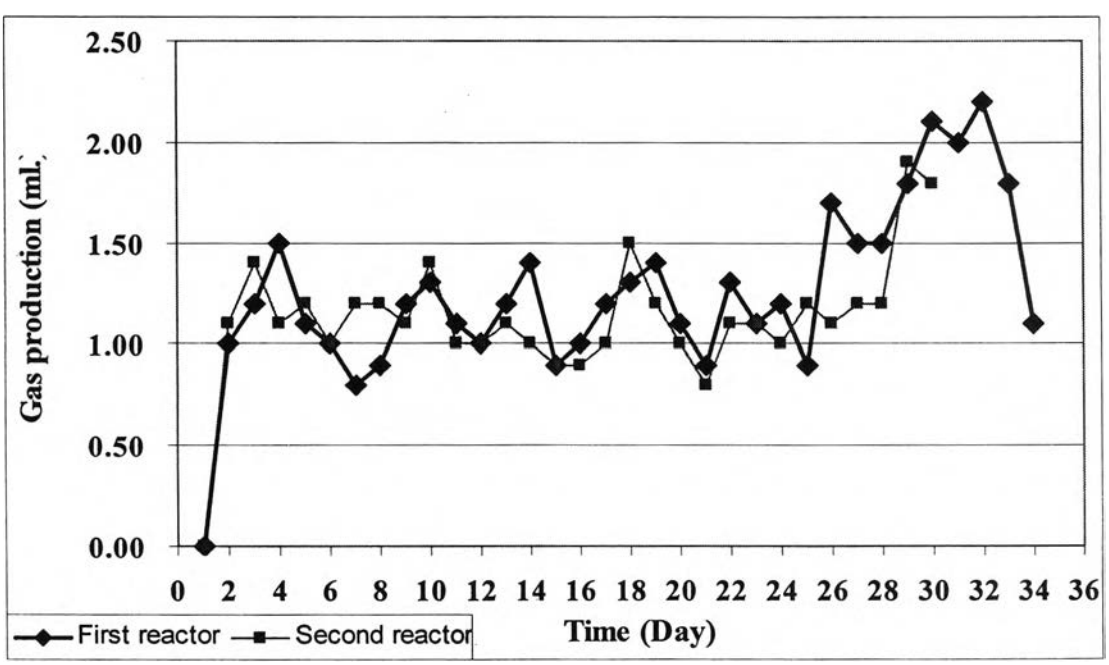

Figure 4.40 Daily gas productions in completely-mixed anaerobic reactors.

4.5 Mass balance

The total sulfur in the reactor was divided into 2 parts, dissolved sulfur and precipitated sulfur. To add the synthesized wastewater was also to add sulfate into the reactor (SO_4 in$ZnSO_4$). But the residual sulfide precipitated with zinc immediately. The amount of sulfide used for complete zinc precipitation was equal to the amount of sulfate added into the reactor together with zinc. The sulfur mass balance showed in table 4.4

Table 4.4 Sulfur mass balance

Injection	Before injection			After injection			Accumulated Precipitated Sulfide (mg.)
	Sulfide (mg.)	Sulfate (mg.)	Add SO_4 (mg.)	Sulfide (mg.)	Sulfate (mg.)	Precipitated sulfide (mg.)	
First	16	6	10	12	10	10	10
second	104	18	20	104	18	20	30
third	104	18	20	104	18	20	50
forth	104	18	20	104	18	20	70
fifth	104	18	20	104	18	20	90
sixth	104	18	50	88	34	50	140
seventh	88	34	50	88	34	50	190
eighth	88	34	100	80	58	84	274
ninth	80	58	100	0	142	96	370

The zinc in the reactor was injected and removed as shown in table 4.5. The removed zinc was precipitated with sulfide completely. From table 4.5, total of zinc removal was 371.54 ppm in 2 liters reactor. It means 743.11 mg of zinc was precipitated with sulfide. From table 4.6, total of sulfide removed was 185 ppm in 2 liters reactor. It means 370 mg of sulfide was removed. The entire removed sulfide was used for zinc precipitation. The amount of zinc precipitated by removed sulfide was 751.56 mg. But from the experiment, zinc was removed 743.11 mg. It could be calculated that the efficiency of zinc precipitation by sulfide is 98.87%.

The zinc was usually precipitate to ZnS in the reactor, because ZnS was easy to precipitate than Zn(HS)2 as showed by pK value.

$$Zn^{2+} + HS^{-} \leftrightarrow Zn(HS)^{+} \qquad pK = -6.5 \qquad (1)$$

$$Zn^{2+} + 2HS^{-} \leftrightarrow Zn(HS)_2 \qquad pK = 14.0 \qquad (2)$$

$$ZnS(s) \leftrightarrow Zn^{2+} + S^{2-} \qquad pK = -24.7 \qquad (3)$$

The $Zn(OH)_2$ can not present in the reactor. The reactors were operate under pH 7 to 7.2, $Zn(OH)_2$ can present only pH over 8.5.

Table 4.5 Zinc mass balance

	Residual before injection (mg.)	Injection (mg.)	Residual after injection (mg.)	Removed Zinc (mg.)	% of zinc removal
First	0.3	20	0.08	20.22	99.60
Second	0.7	40	0.26	40.44	99.36
Third	0.15	40	0.28	39.87	99.30
Forth	0.30	40	0.56	39.74	98.61
Fifth	0.56	40	0.18	40.38	99.55
Sixth	0.46	100	0.9	99.56	99.10
Seventh	0.90	100	1.04	99.86	98.97
Eighth	1.04	200	30	171.04	85.52
Ninth	30	200	38	192.00	83.48