

## CHAPTER IV

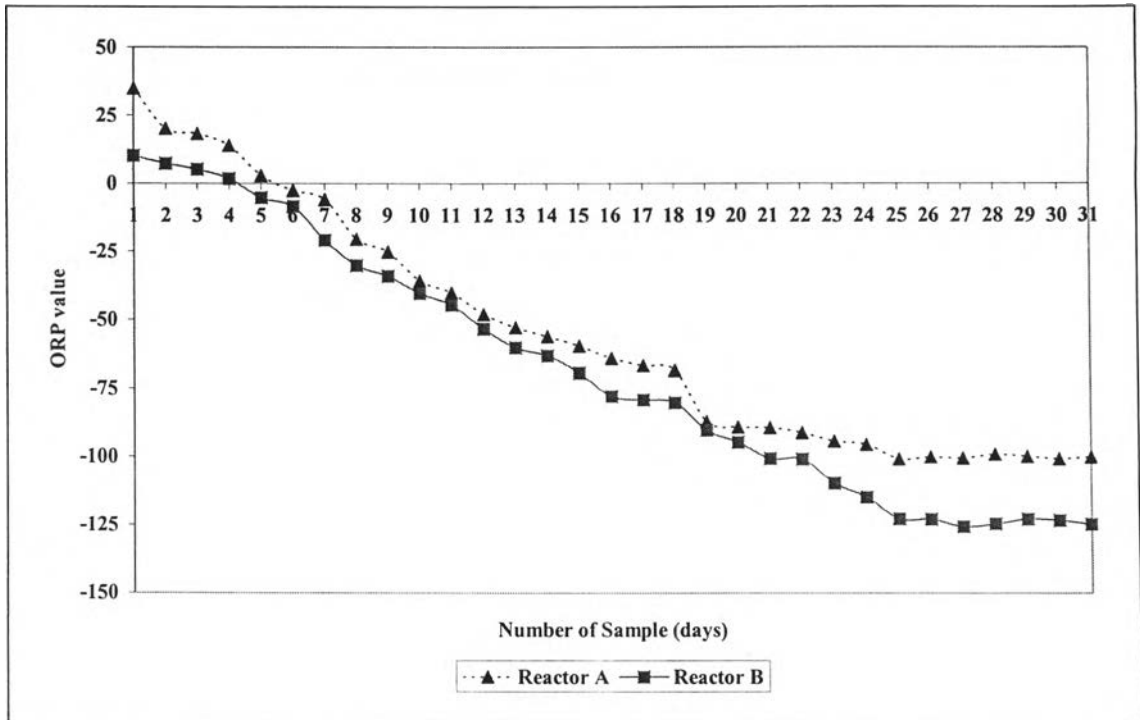
### RESULTS AND DISCUSSIONS



#### 4.1 Experiment startup and operation

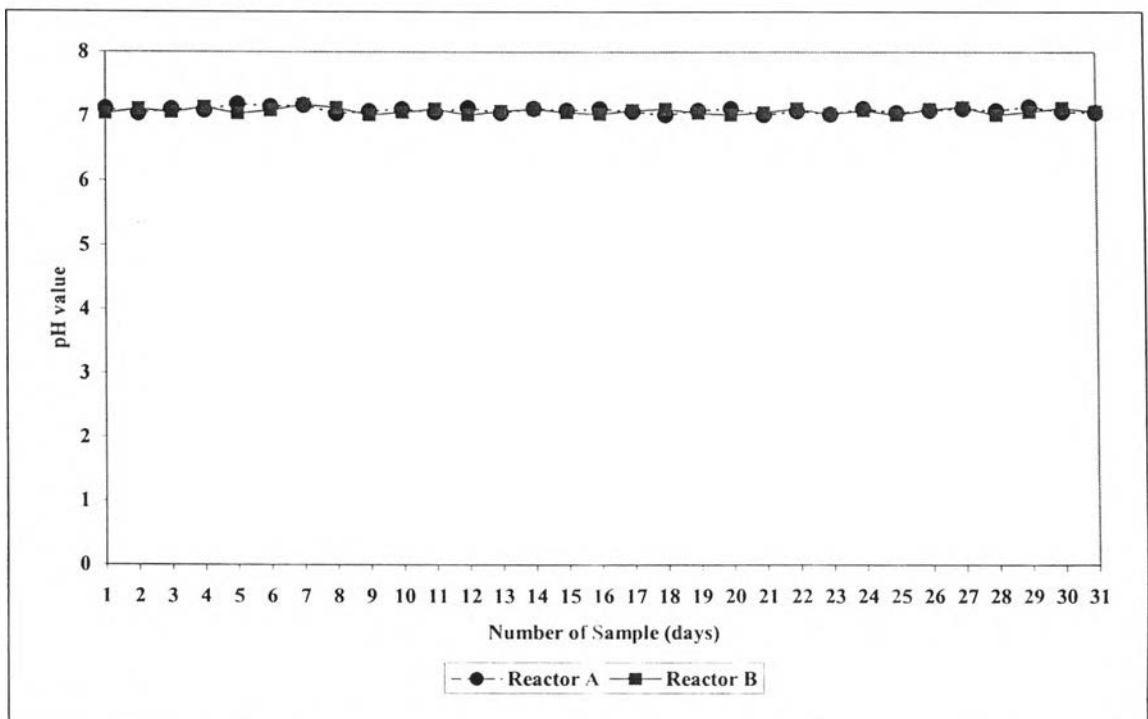
The main purpose of this experiment was to find the suitable condition of the system that provided the ability for precipitation by SRB. The suitable parameters that required to indicate the steady state of the reactors were the ORP,  $S^{2-}$ ,  $SO_4^{2-}$ , and COD.

Reactor A and B had shown a success on the establishment to the startup system as shown in Appendix C. Reactors A and B slowly produced anaerobic conditions, as this could be confirm from the reduction in the Oxidation-Reduction Potential (ORP) values. The pH values of both reactors had shown that throughout the experiment there were small fluctuations. The ORP results and the pH values as shown in Figure 4.1 and Figure 4.2 respectively were in the suitable conditions according to Lyew et al., 1994, and Garcia et al., 2001 on the specific environmental required for sulfate reducing bacteria (SRB); an anaerobic environment with a redox potential lower than - 100 mV and a pH of higher than 5.5. The ORP value gradually remained unchanged toward day 25 to day 31, as the system has progressed toward steady-state.

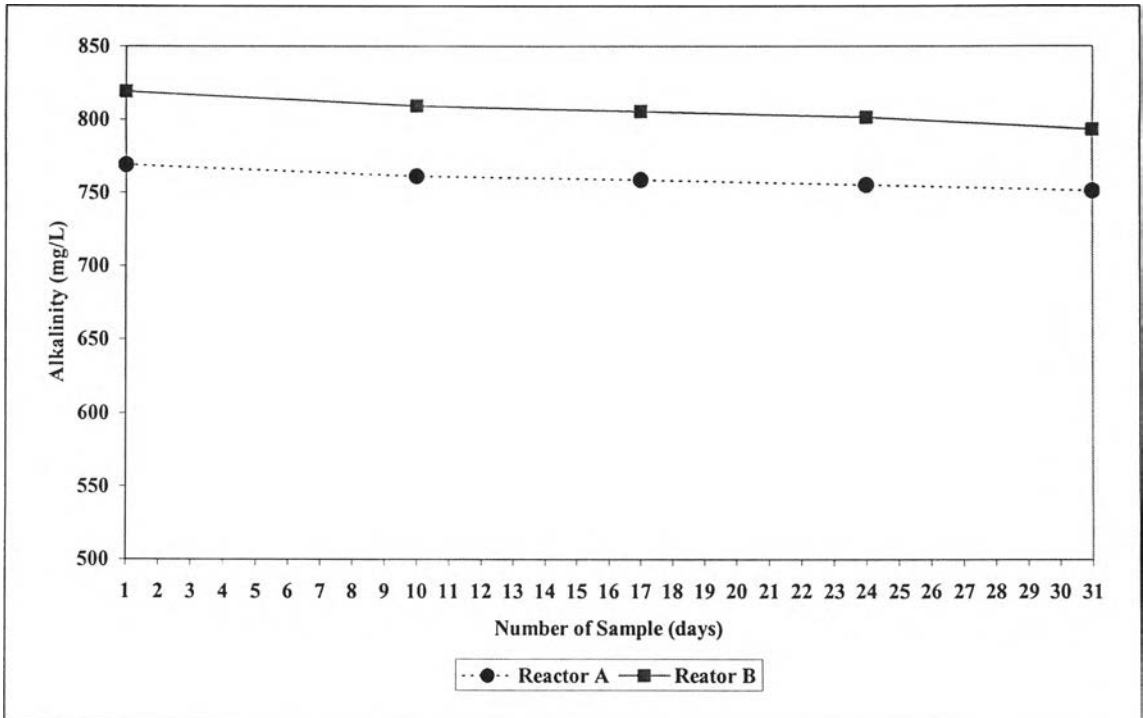


**Figure 4.1** Oxidation-Reduction Potential (ORP) value during the startup of the system.

For leachate from both reactors, total alkalinity measurement reflected the relative presence of acids and bases such as  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , TVA, phosphorus and ammonia. The total alkalinity of reactor leachate slightly decreased due to the sulfide formation.



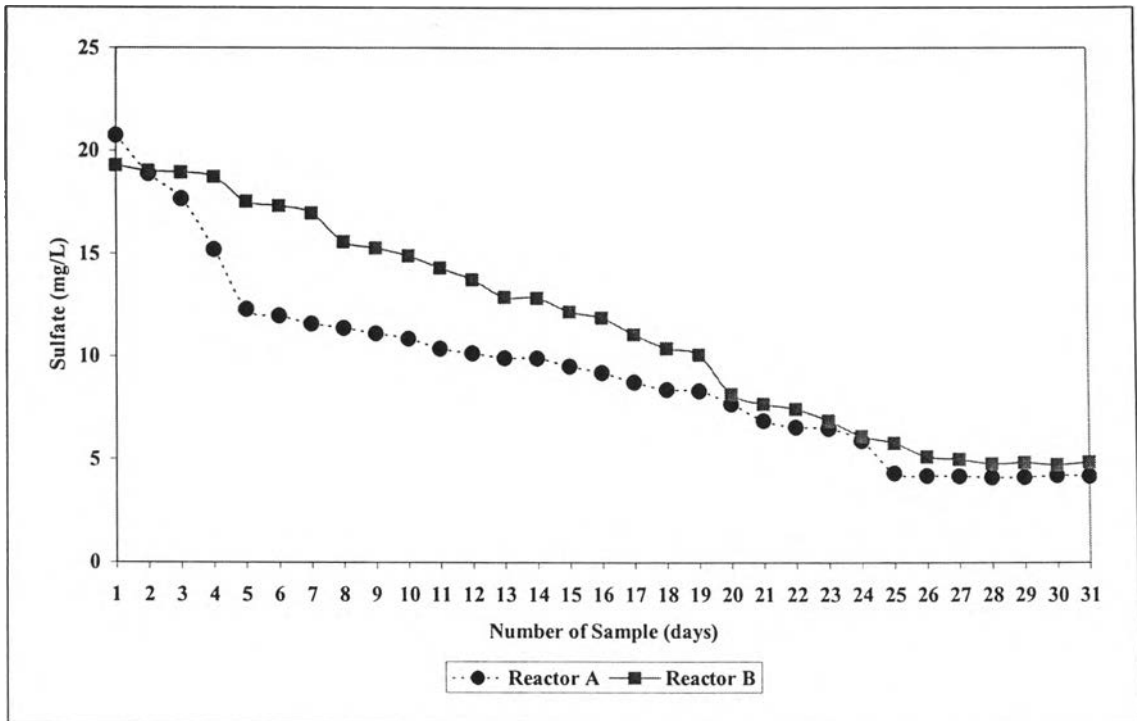
**Figure 4.2** pH values during the startup of the system.



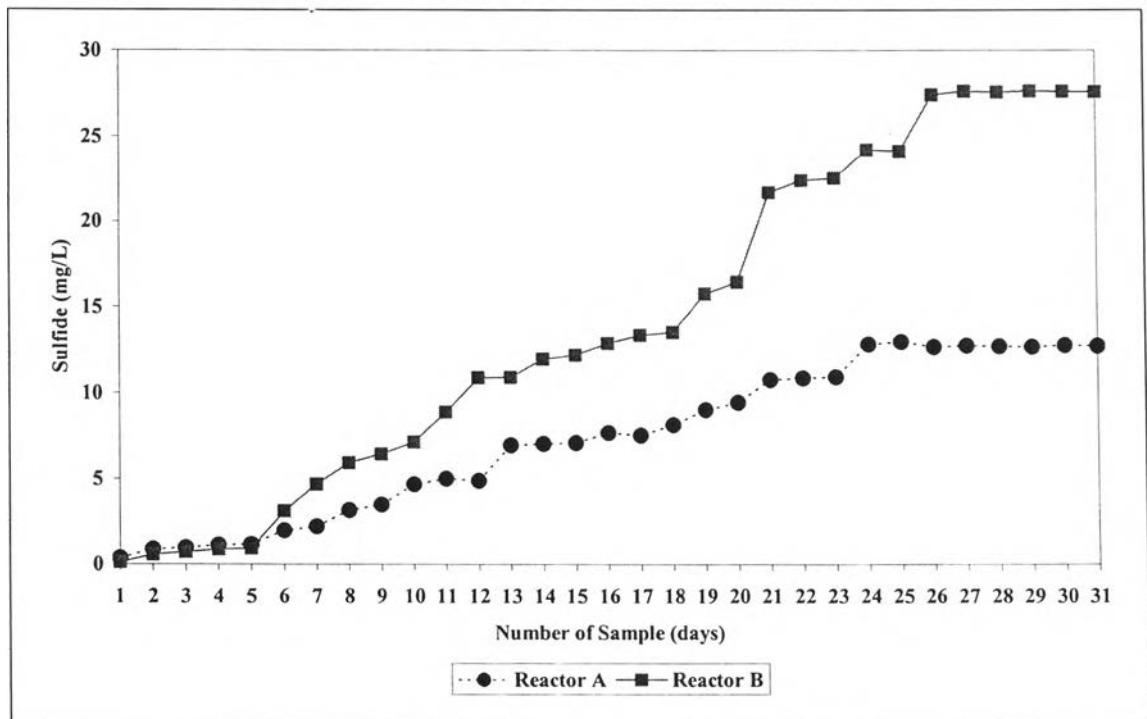
**Figure 4.3** Alkalinity value during the startup of the system.

Sulfide is another indicator of the presence of reducing conditions within the landfill environment and wastewater. Sulfide is produced during anaerobic decomposition specifically from the reduction of sulfate and other sulfur-containing inorganic compounds as well as from anaerobic protein degradation. In the  $S^{2-}$  form, sulfide is a powerful precipitating agent, even at low pH values and very low sulfide concentrations. Most of the sulfide generated is bound to heavy metals as metal sulfides in anaerobic system (Pohland, 1993).

The production of the sulfide and sulfate were shown in Figure 4.4 and 4.5. Sulfates were slowly reduced by the SRB, reduction of sulfate produce the increased in sulfide. The maximum production of sulfide for both reactors A and B were approximately 12.7 mg/L and 27.6 mg/L, respectively toward day 25 to day 31.



**Figure 4.4** Sulfates reduction during the startup of the system.

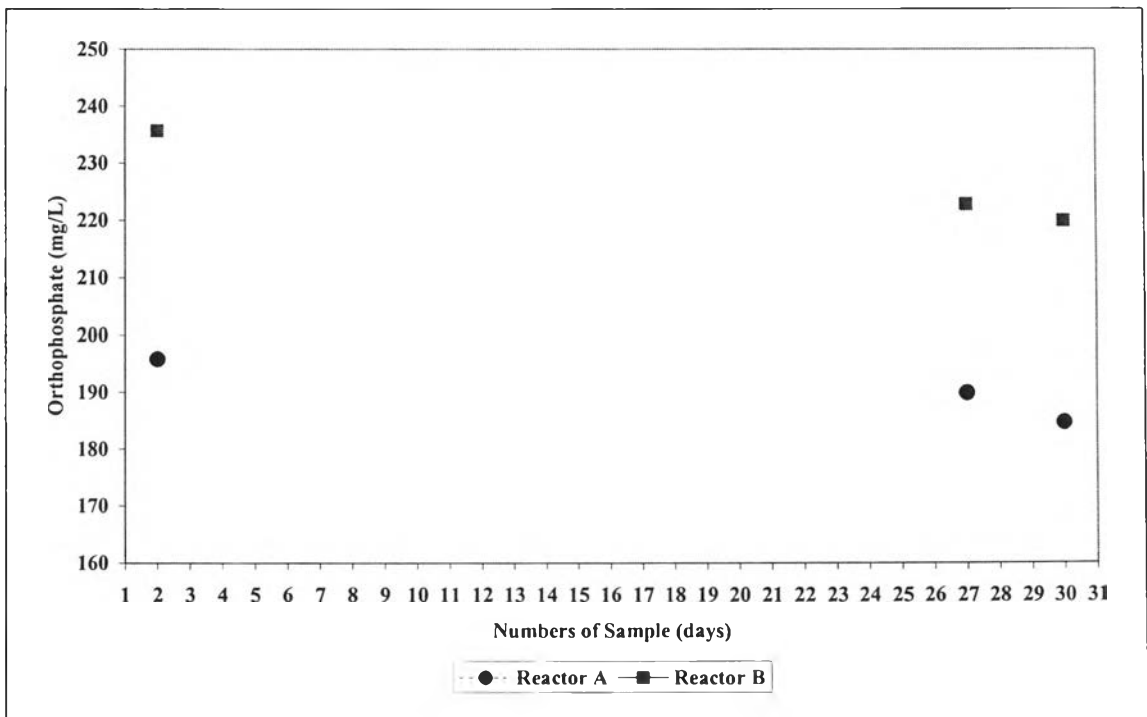


**Figure 4.5** Sulfides production during the startup of the system.

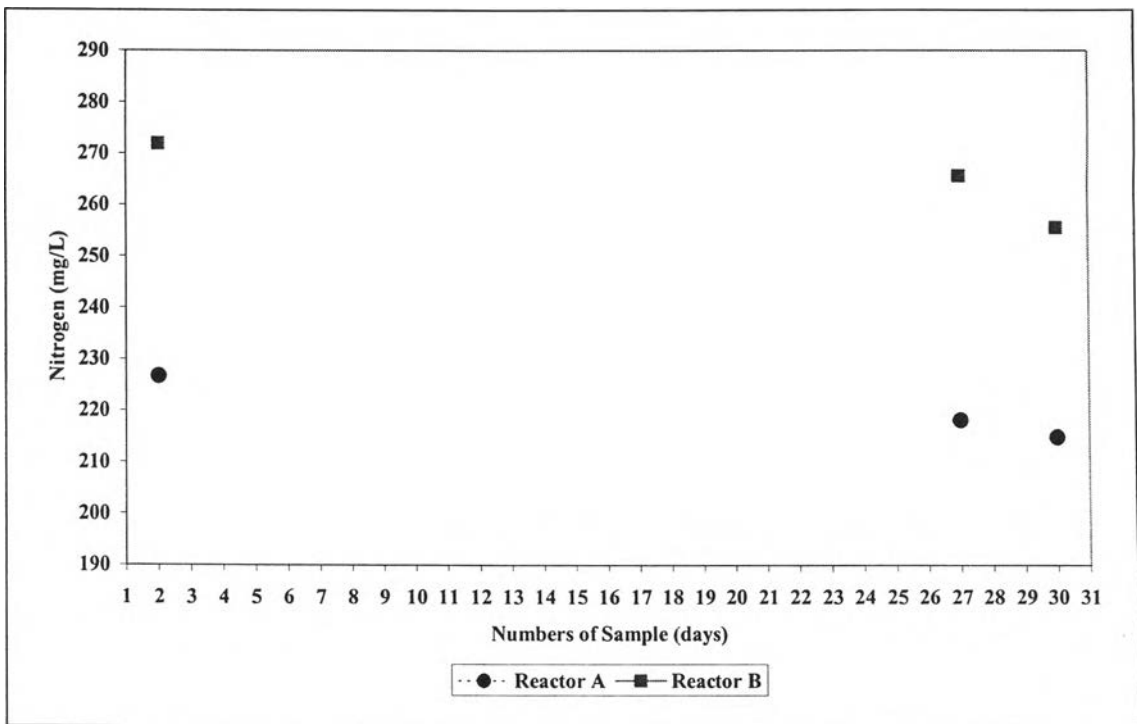
The availability of nutrients and carbon sources were essential to the microbial during the oxidation of sulfate by SRB. In order to ensure that adequate nutrients and carbon were available for microbial, orthophosphate, ammonia nitrogen and COD concentrations were periodically measured as indicated in Figure 4.6 and 4.7.

The initial concentrations of orthophosphate in two reactors (A and B) were 195.8 mg/L and 235.7 mg/L respectively. However, orthophosphate concentrations began to decrease as a result of orthophosphate assimilation by microorganisms. The orthophosphate concentrations in both reactors A and B slowly decreased throughout the 31 days of setup period. This was attributed to microbial utilization, washout (dilution) and possible complexation reactions.

The ammonia nitrogen in both simulated reactors A and B were found to be similar in the trend of concentrations, with an initial concentration of 226.7 mg/l and 271.9 mg/l respectively. The result also suggesting that the uniformity in decreasing in ammonia nitrogen in both reactors was used up by the SRB during the oxidation of sulfate to sulfide.

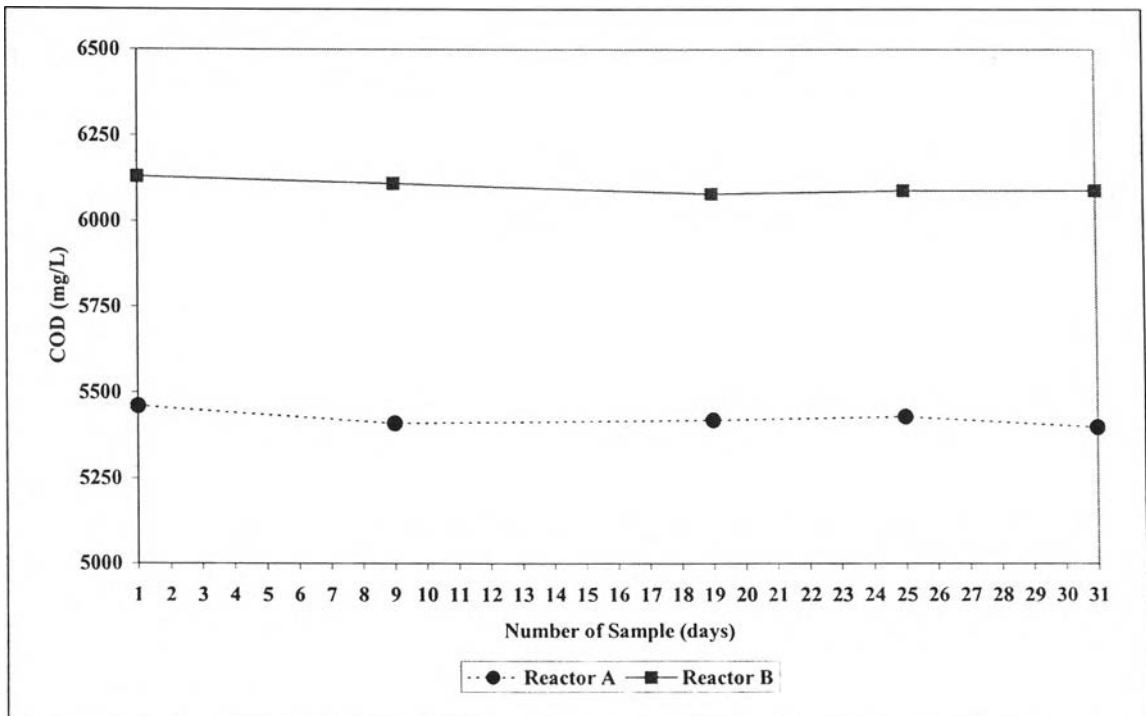


**Figure 4.6** Orthophosphate values during the startup of the system.



**Figure 4.7** Ammonia Nitrogen values during the startup of the system.

The sources of carbon of both reactors A and B were slightly decreased as shown by the values of COD. The carbon source was slightly consumed over the startup period of 31 days by the SRB during the reduction of sulfate to sulfide.



**Figure 4.8** COD values during the startup of the system.

## 4.2 Zinc Addition

### 4.2.1 First addition of Zinc (10 mg/L)

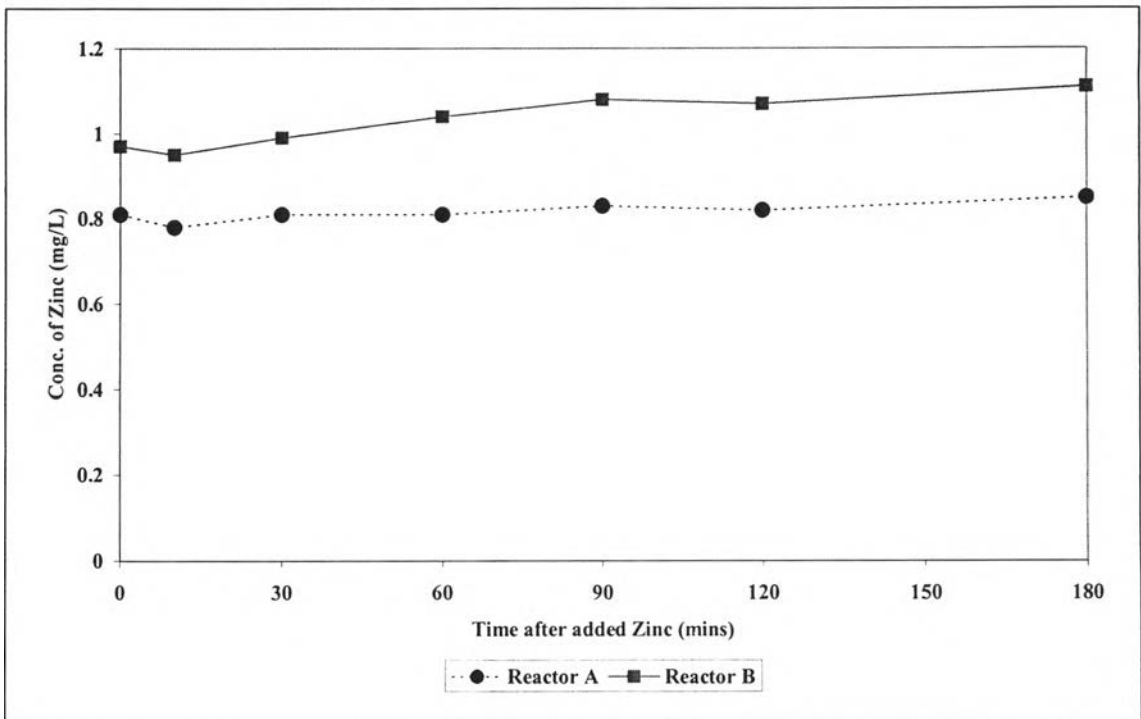


Figure 4.9 (a) Values of zinc concentration after the first addition of zinc (10mg/L) first 180 minutes.

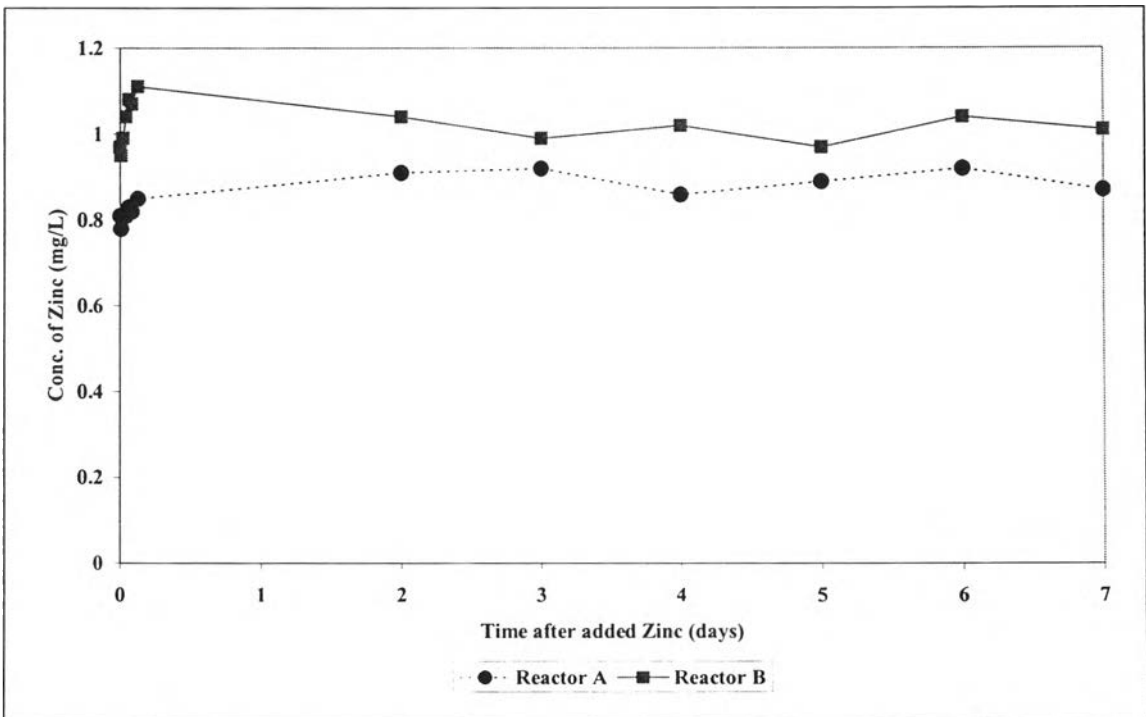


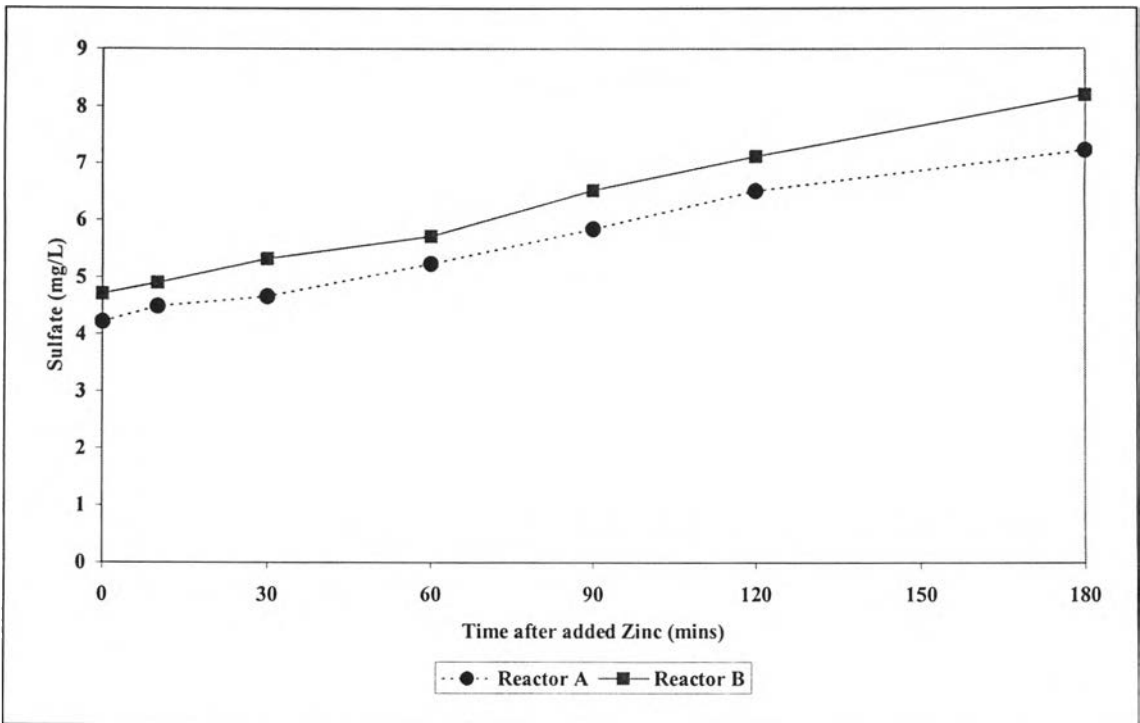
Figure 4.9 (b) Values of zinc concentration after the first addition of zinc (10mg/L) over the period of 7 days.

Zinc (10 mg/L) with a volume of 200 ml was first added to reactor A and B on the day 32 of experiment.

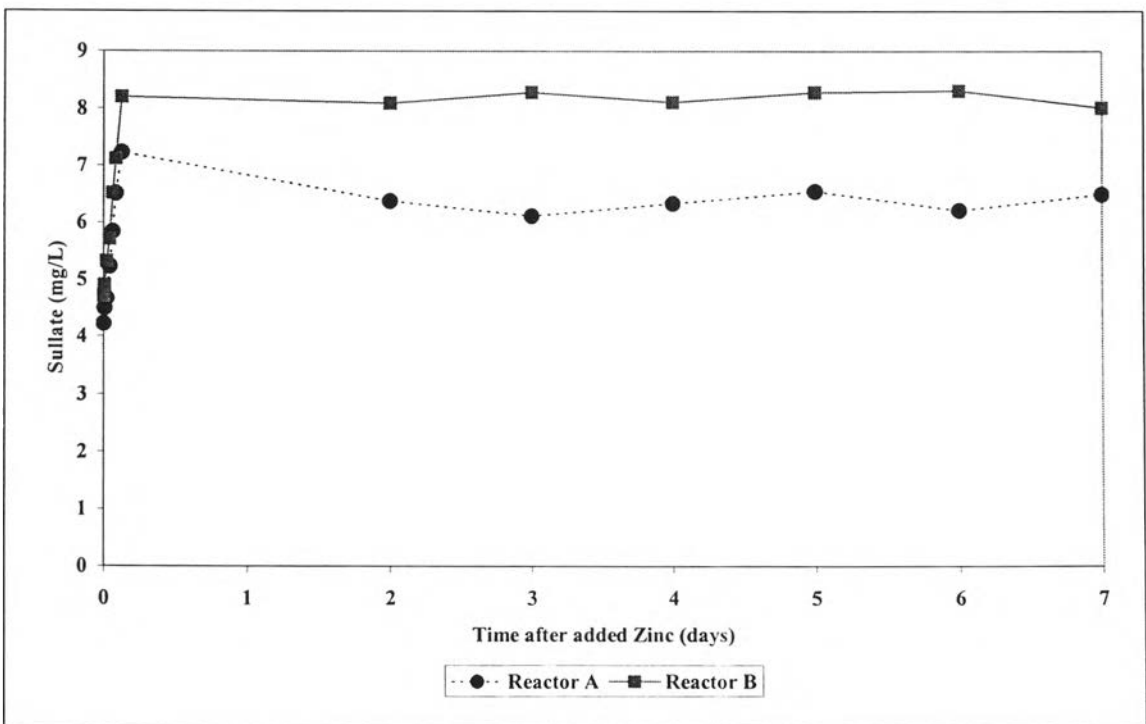
After the first addition of synthesized wastewater containing 10 mg/L of zinc, there were slightly change in the zinc concentration throughout the experiment as shown in Figure 4.9 a and b. During the first sample at 10 minutes showed a slight drop in the zinc concentration. The zinc concentration from both reactors gradually increased slowly after the 30<sup>th</sup> minutes and later it showed small fluctuation in concentration up to the 180 minutes. The zinc concentration were increases in reactor A and decreased in reactor B when reach day two, and later both of the reactor showed small fluctuation toward the end of day 7. This showed that the zinc that had added to reactor A and B were treated. As the result showed that the zinc concentration were treated by both reactors A and B was 93.43% or 2.474 mg and 92.72% or 2.574 mg of zinc, respectively.

There were changes in the sulfate and sulfide after addition of zinc, as shown in the Figure 4.10 and 4.11. There were increased in sulfate throughout the period of 7 days of after the addition. During the first day of the experiment, there were dramatically increased in the sulfate from 4.44 to 7.23 mg/L for reactor A and 4.71 to 8.20 mg/L for reactor B. The experiment from day 2 to day 7 had shown that there were slightly fluctuations in the sulfate when compared with the result from the day one. Reactor A and B was fluctuated between 6.12 to 6.49 and 8.01 to 8.31, respectively.





**Figure 4.10(a)** Values of Sulfates after the first addition of zinc (10mg/L) first 180 minutes.



**Figure 4.10(b)** Values of Sulfates after the first addition of zinc (10mg/L) over the period of 7 days.

The amounts of sulfide were reduced throughout the experiment, but the reductions of sulfide were divided into two parts. The significant decrease occurred during the first part of experiment, whereas the rest of the experiment were slightly decrease with small fluctuation. The first part of the experiment was in

precipitation of zinc with sulfide during the first 180 minutes of the experiment. After that, the amount of sulfide slightly fluctuated due to no further zinc precipitation in the reactor and slow sulfide production by the SRB.

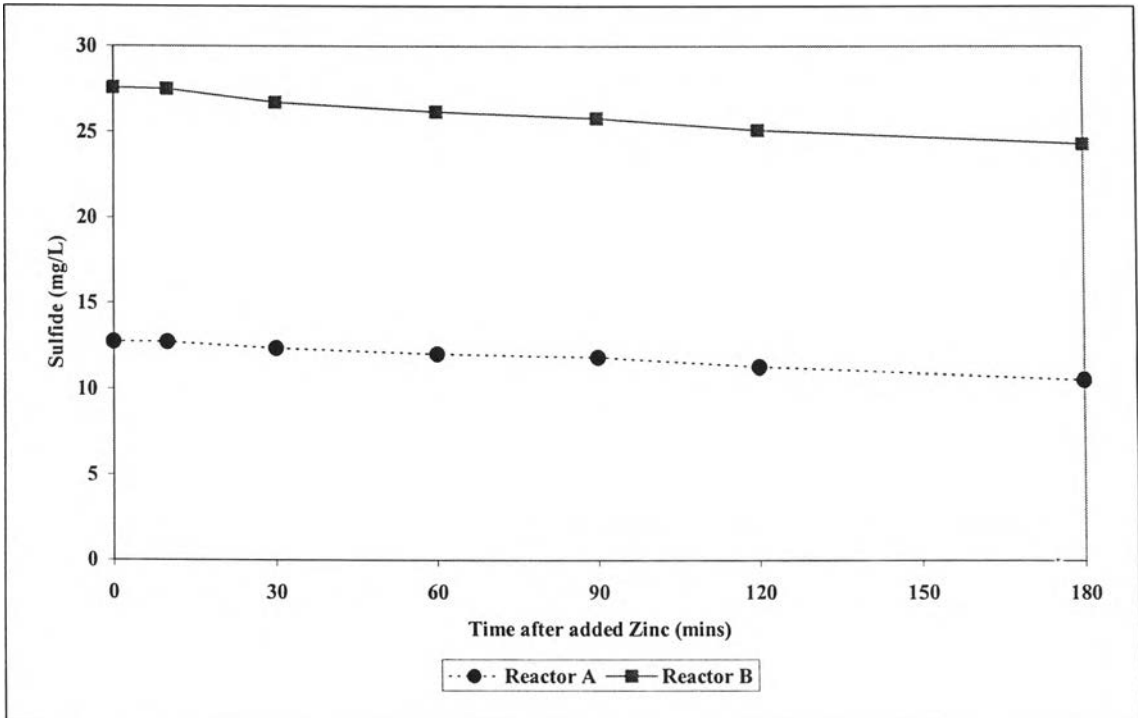


Figure 4.11(a) Values of Sulfide after the first addition of zinc (10mg/L) first 180 minutes

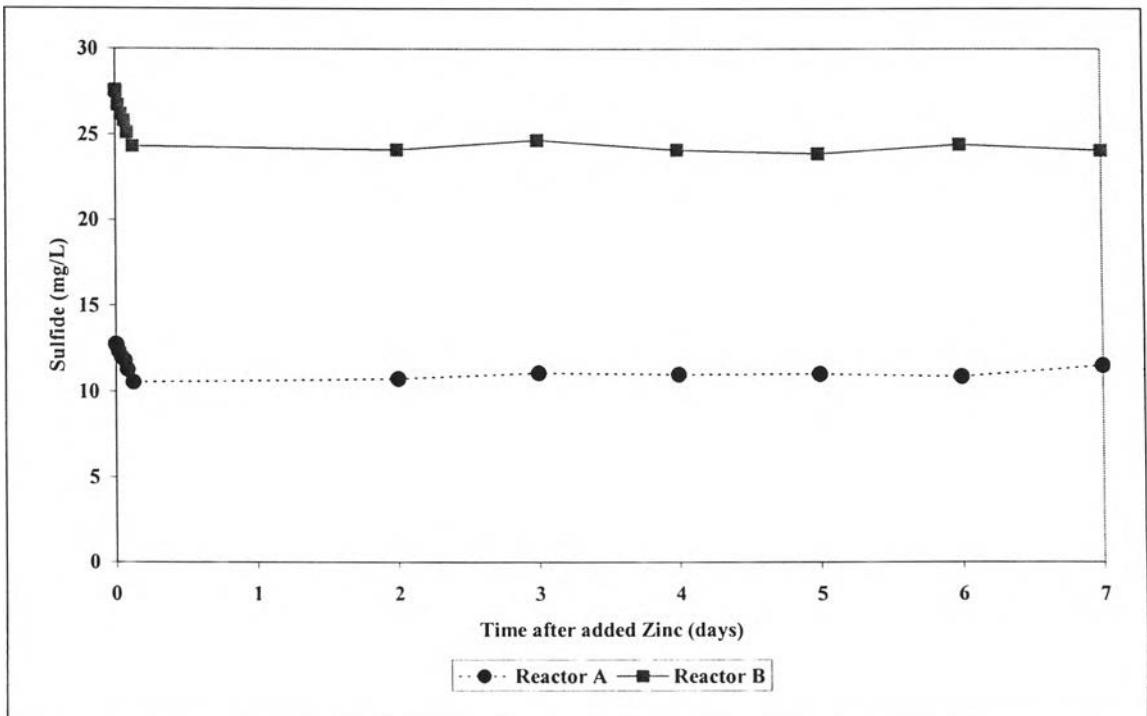


Figure 4.11(b) Values of Sulfide after the first addition of zinc (10mg/L) over the period of 7 days.

The ORP values had shown small changes over the period 7 days after the addition of zinc at the 10 mg/L for both reactors A and B as shown in Figure 4.12.

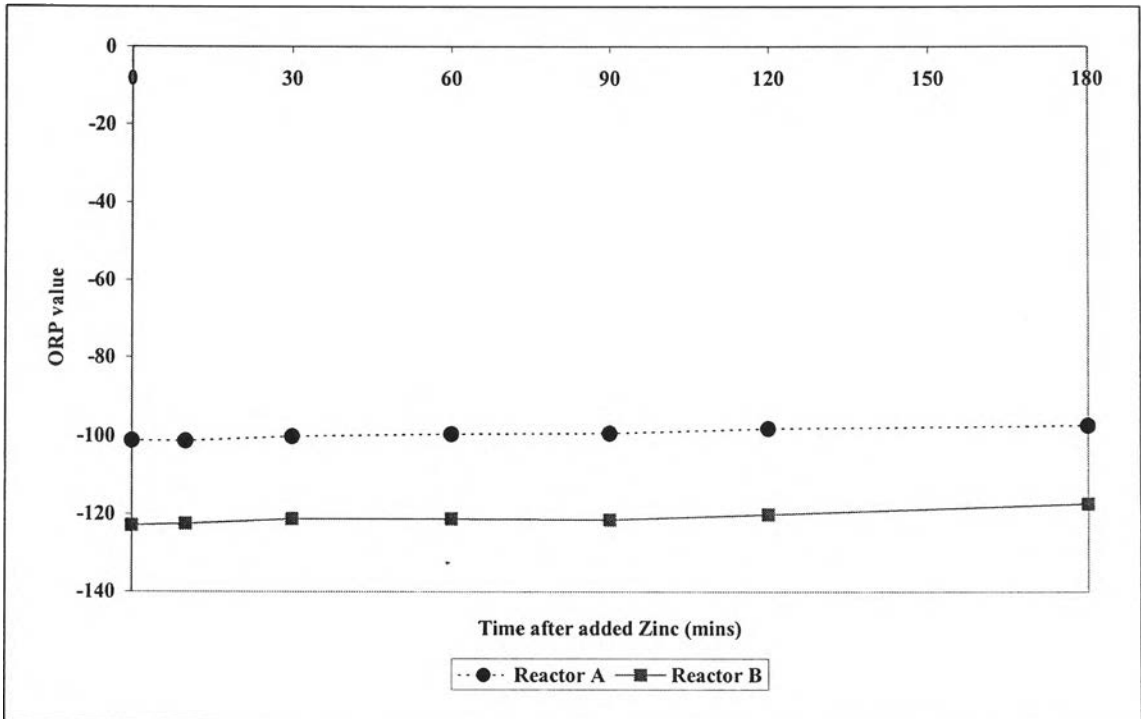


Figure 4.12(a) ORP values after the first addition of zinc (10mg/L) first 180 minutes

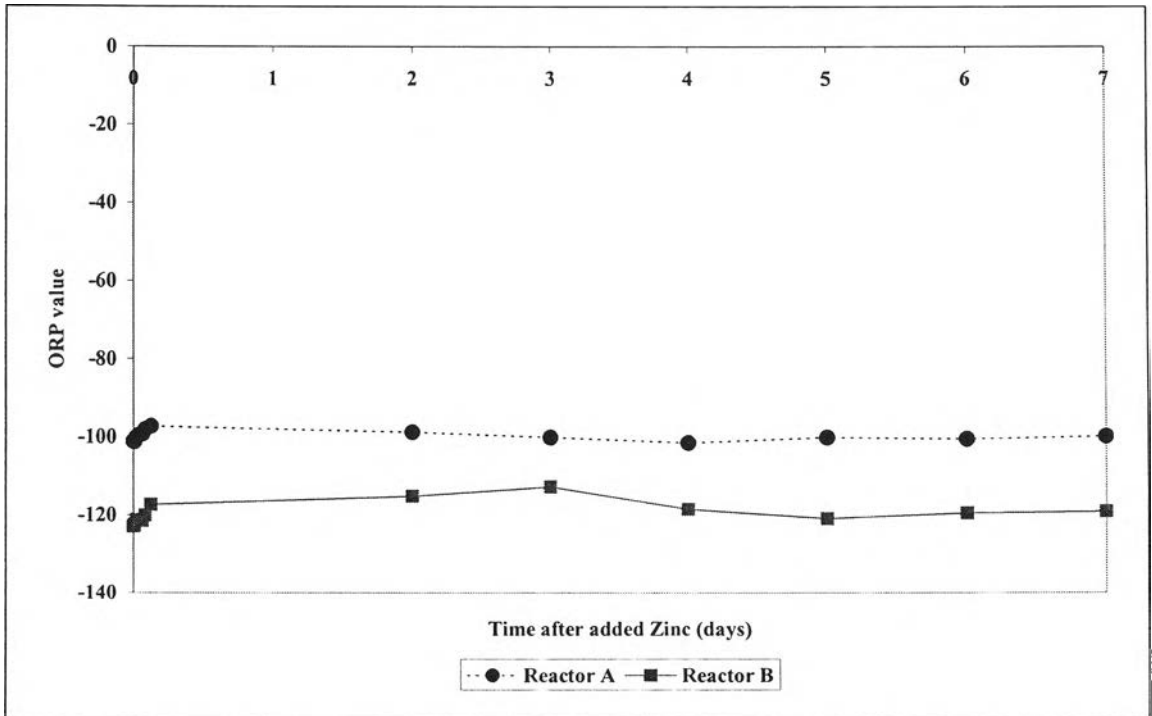
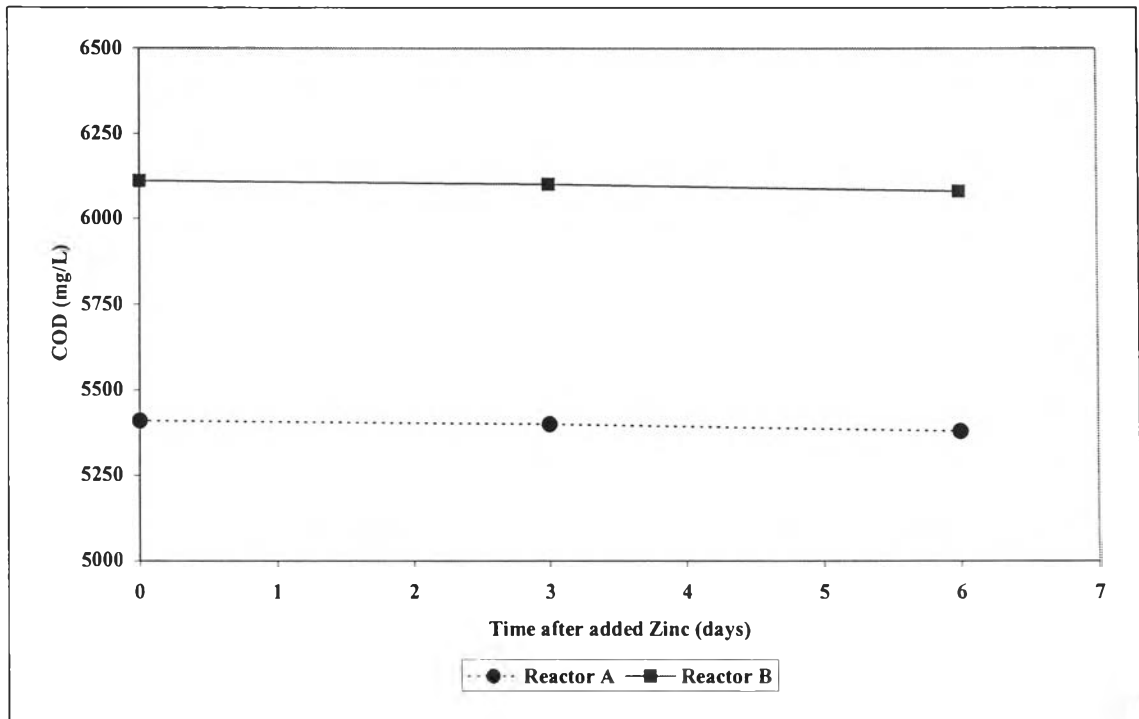


Figure 4.12(b) ORP values after the first addition of zinc (10mg/L) over the period of 7 days.

The COD values slowly decreased, as the carbon sources were used up by the SRB as shown in Figure 4.13.



**Figure 4.13** COD values after the first addition of zinc (10mg/L) over the period of 7 days.

The trend of the pH, alkalinity, and nutrients had shown after additions of 10 mg/L were similar to the startup experiment as shown in the Appendix D.

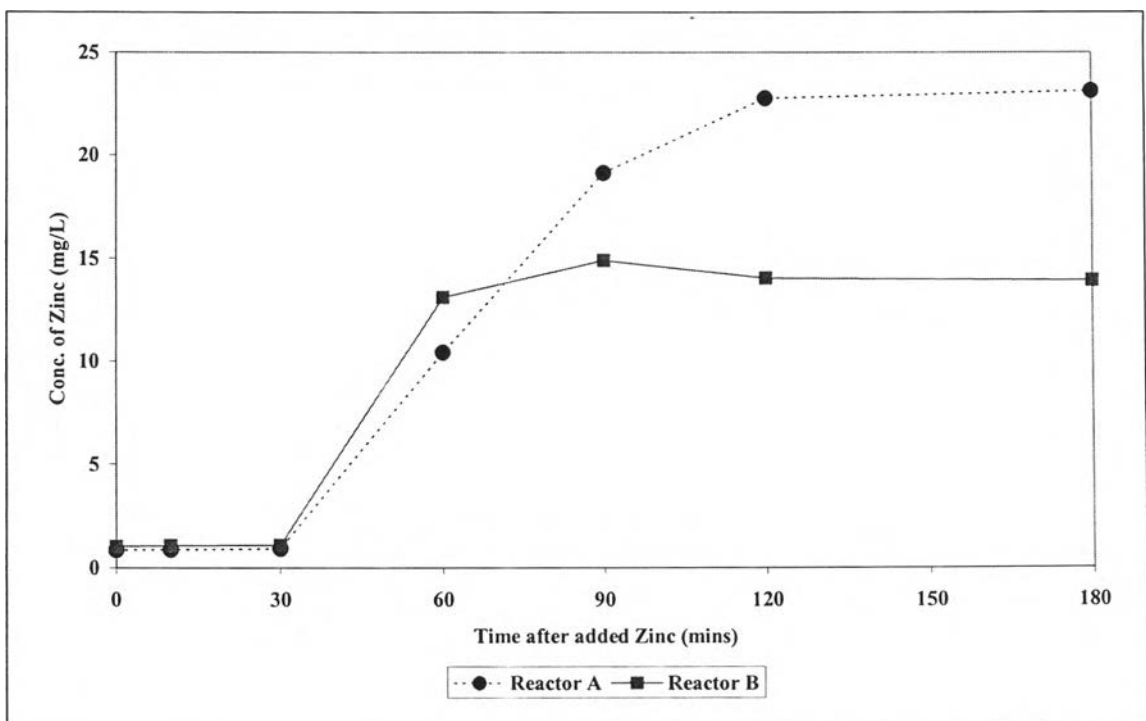
#### 4.2.2 Second addition of Zinc (50 mg/L).

The second dose of zinc (50 mg/L) with a volume of 200 ml was added to both reactor A and B on the day 39 of experiment.

The zinc concentrations had shown significant changes over the first 180 minutes after added the synthesized wastewater containing 50 mg/L. During the first 30 minutes, both of the reactors A and B had shown no changes. The possible reason for this was the wastewater was added from the top of the reactor, and required time for the zinc to flow through to the bottom of the reactor.

From the results after 30 minutes onward the zinc concentration increases until become stable. But in reactor A give a higher stable concentration than reactor B approximately 20 mg/L, as shown in the Figure 4.14 (a).

The zinc concentrations in reactor A had shown no changes over the experiment period of nine days. On the other hand, the zinc concentration of reactor B started to decrease and became almost constant after day 3 and day 4 as shown in Figure 4.14 (b). The reactor A had shown that zinc concentration remain unchanged, therefore this could be conclude that it fail. The possible reasons for the failure were; (1) toxicity to the sulfate reducing bacteria (SRR), and (2) the insufficient quantity of SRB due to the dead cause by the toxicity which lead to no further production of sulfide to form precipitate. The reactor B was assumed to be in the steady state after the day 4.



**Figure 4.14 (a)** Zinc concentrations after the second addition of 50 mg/L of zinc in the first 180 minutes

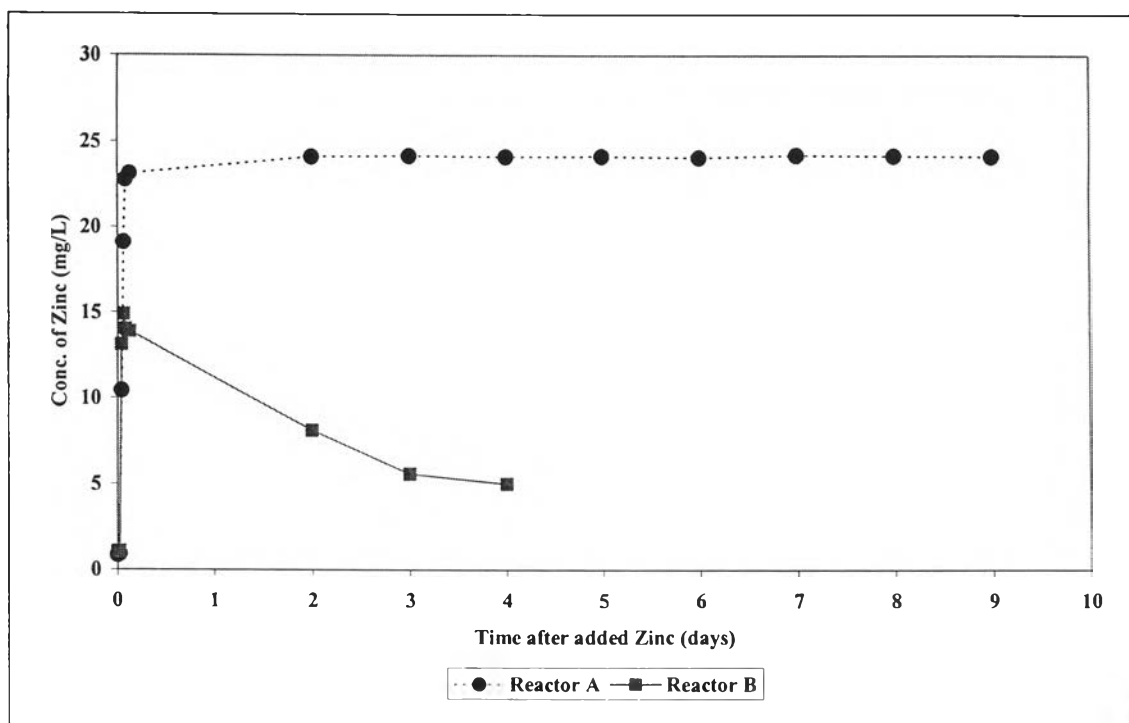
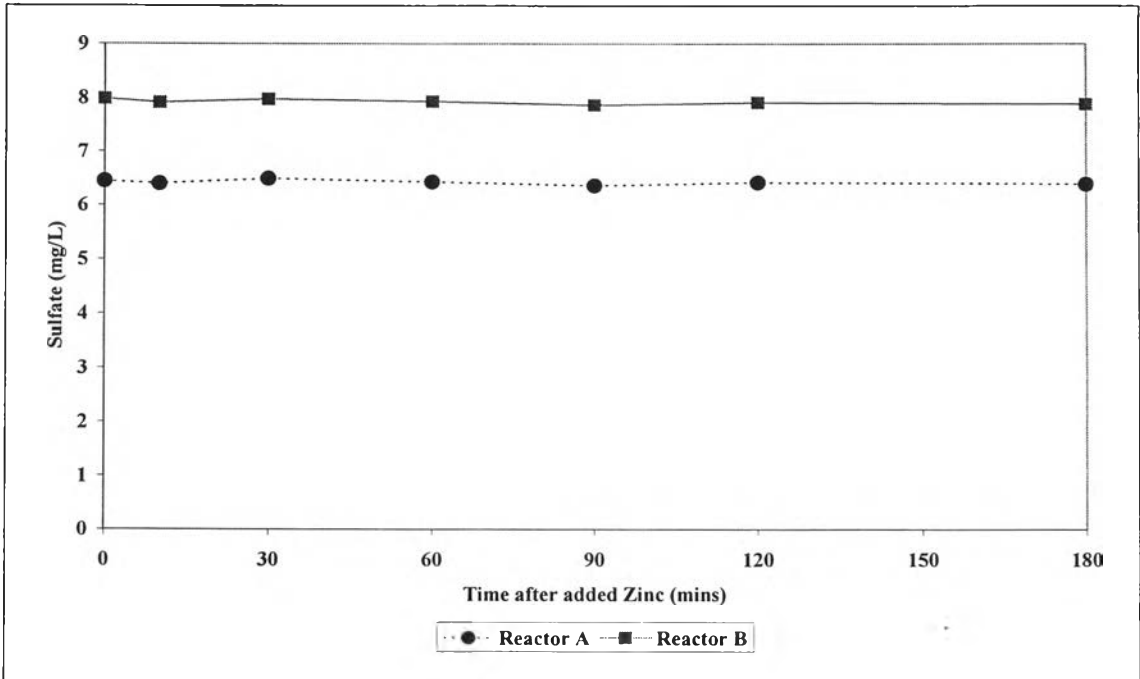


Figure 4.14 (b) Zinc concentrations after the second addition of 50 mg/L of zinc over the experiment period of nine days for reactor A and 4 days for reactor B.

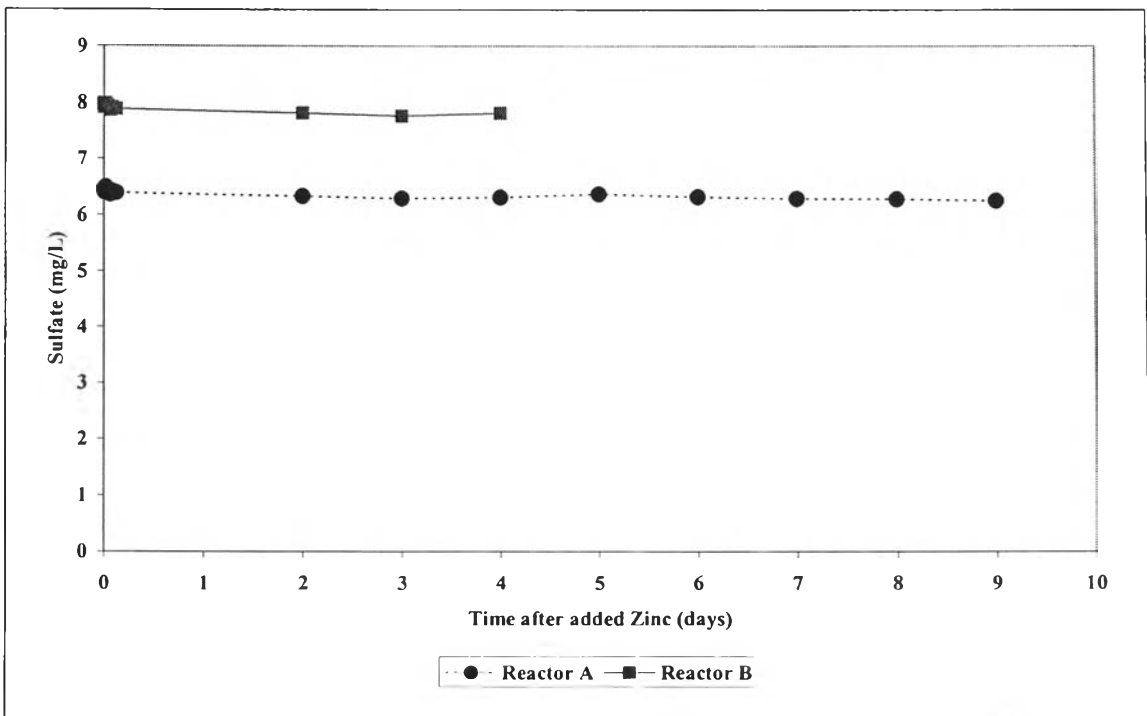
The amount of sulfate and sulfide had in reactor A shown that there was almost unchanged in the conversion from sulfate to sulfide, these could confirmed the assumption on the toxicity to the SRB. But in reactor B, there were some changes in the amount of sulfate and sulfide was likely to occur by the present of SRB in the reactor as shown in Figure 4.15 and 4.16. The amount of sulfate in reactor A and B were small fluctuates from 6.45 to 6.39 and 7.98 to 7.88 mg/L respectively in the first 180 minutes as shown in Figure 4.15 (a). The amount of sulfide in reactor A and B were slightly decreased from 11.49 to 11.13 and 24.12 to 24.01 mg/L respectively during the first 180 minutes as shown in Figure 4.16 (a).

The amount of sulfide in reactor of both reactor A and B were decreased from 11.49 to 11.13 and 24.12 to 24.01 mg/L respectively during the first 180 minutes. The decreased of sulfide was caused by the precipitation of zinc with sulfide. The amount of sulfide in reactor A was further decreased from 11.13 to 11.07 mg/L toward the day 9 after the second addition of zinc. But in reactor B, there was increased in the amount of sulfide from day 2 to day 4 in the amount of 24.01 to 24.29

mg/L as showed in Figure 4.16 (b). This showed that the reactor B still had the ability to produce of sulfide and resulting in further treatment of zinc in the reactor.



**Figure 4.15 (a)** Sulfates value after the second addition of 50 mg/L of zinc in the first 180 minutes.



**Figure 4.15 (b)** Sulfates value after the second addition of 50 mg/L of zinc over the experiment period of nine days for reactor A and 4 days for reactor B.

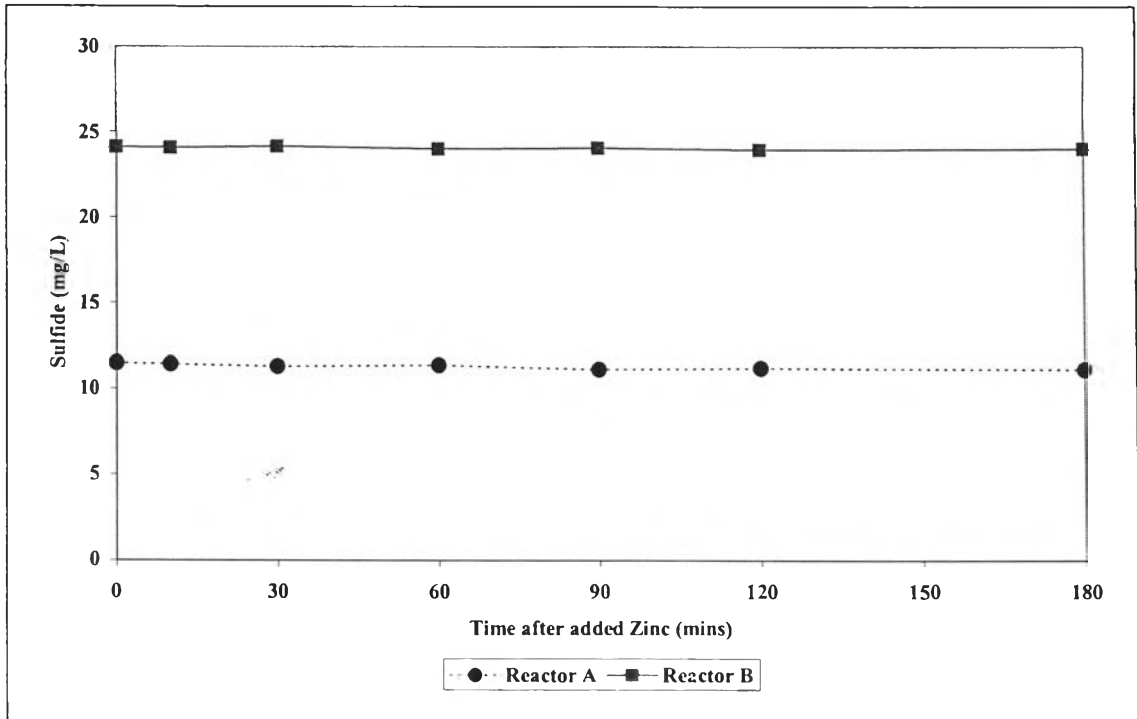


Figure 4.16 (a) Sulfide value after the second addition of 50 mg/L of zinc in the first 180 minutes.

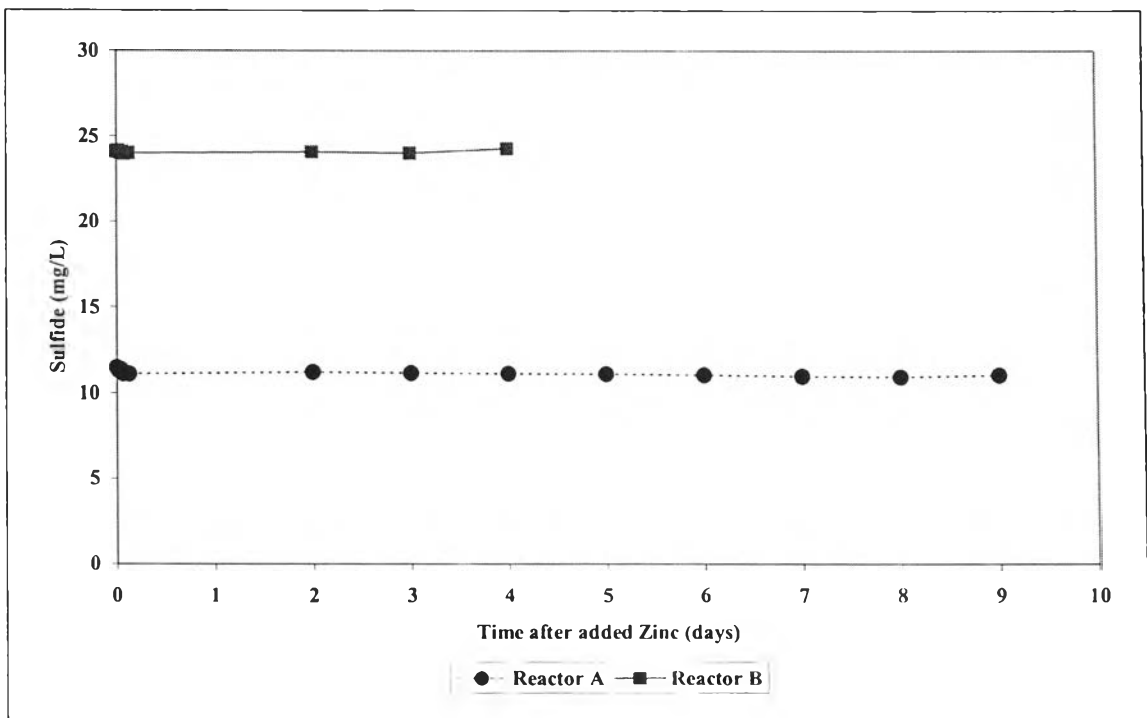
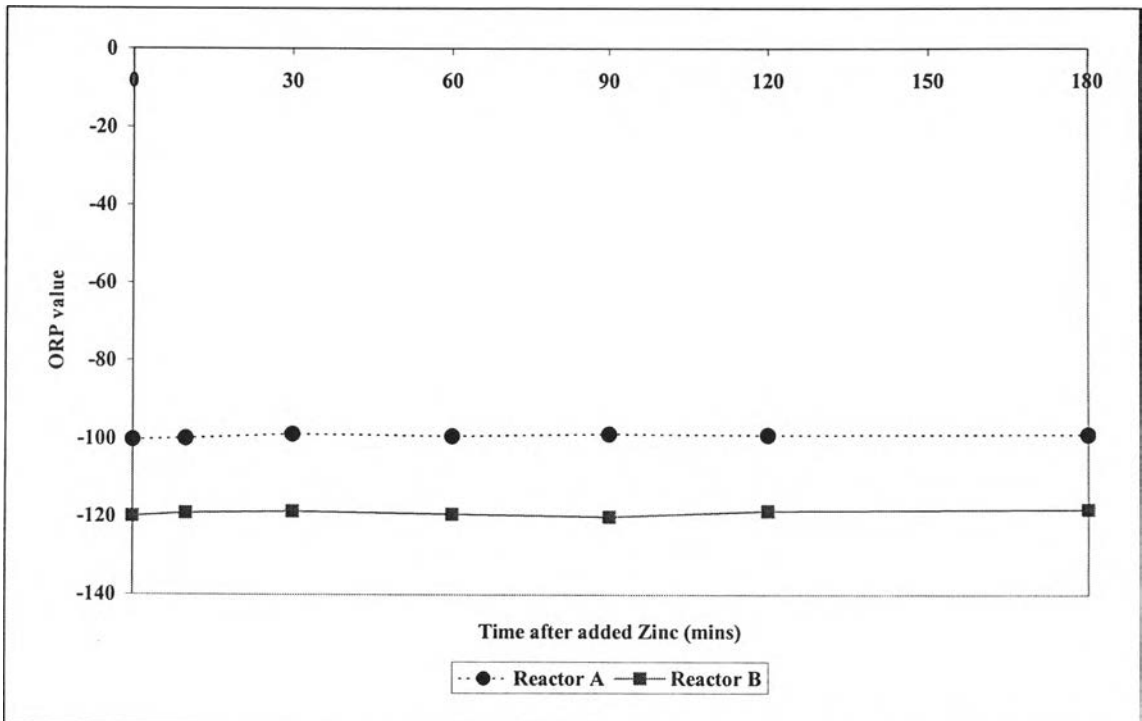


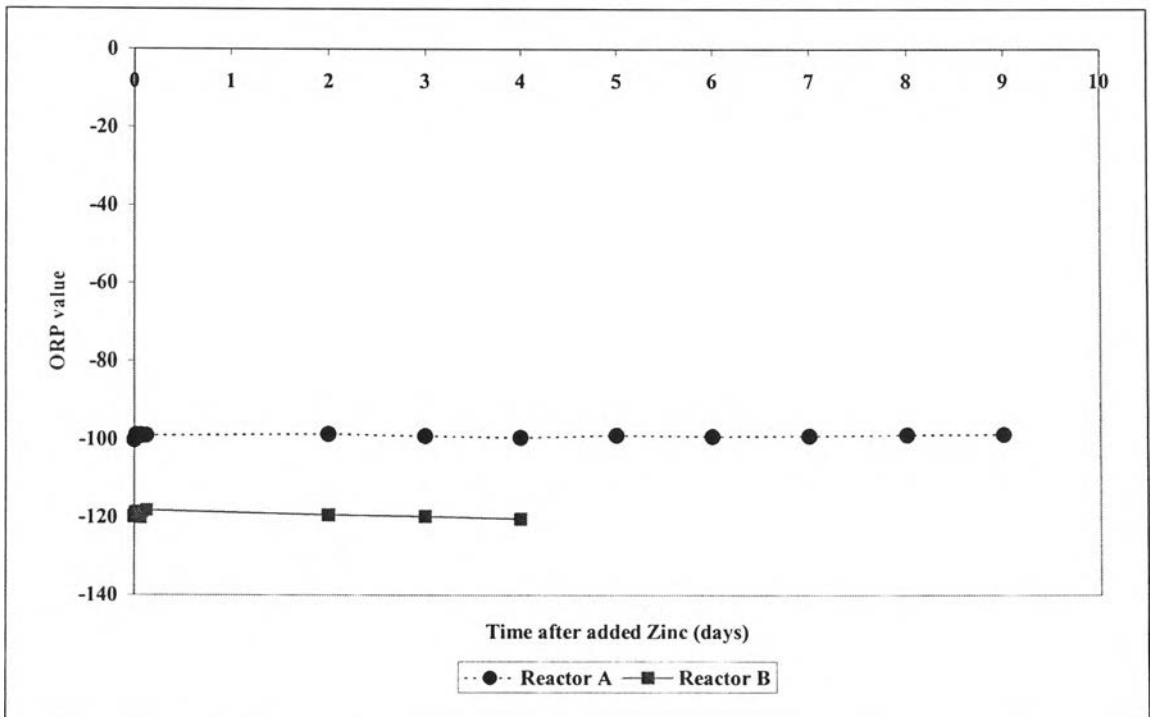
Figure 4.16 (b) Sulfide value after the second addition of 50 mg/L of zinc over the experiment period of nine days for reactor A and 4 days for reactor B.



The results of ORP values as shown in the Figure 4.17, shown small changes and also provided the similar conclusion as small production of sulfide.



**Figure 4.17 (a)** ORP value after the second addition of 50 mg/L of zinc in the first 180 minutes.



**Figure 4.17 (b)** ORP value after the second addition of 50 mg/L of zinc over the experiment period of nine days for reactor A and 4 days for reactor B.

The COD values were slightly decreased as shown in Figure 4.18 for both reactor A and B, as it was used by the SRB for carbon source.

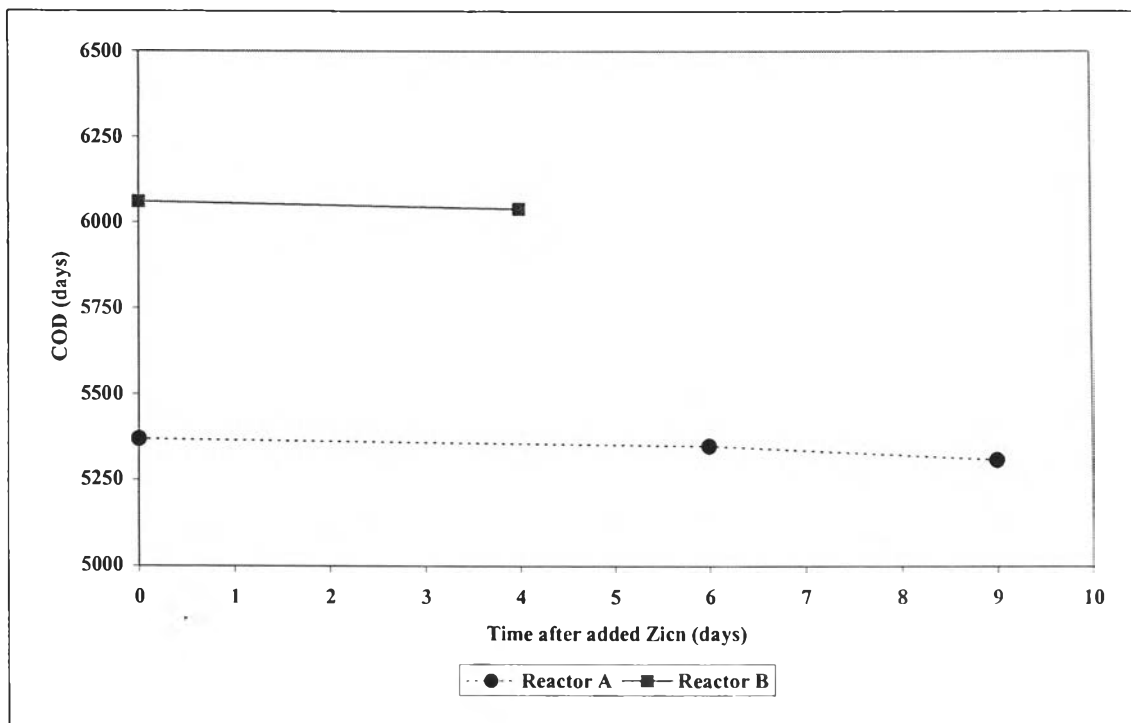
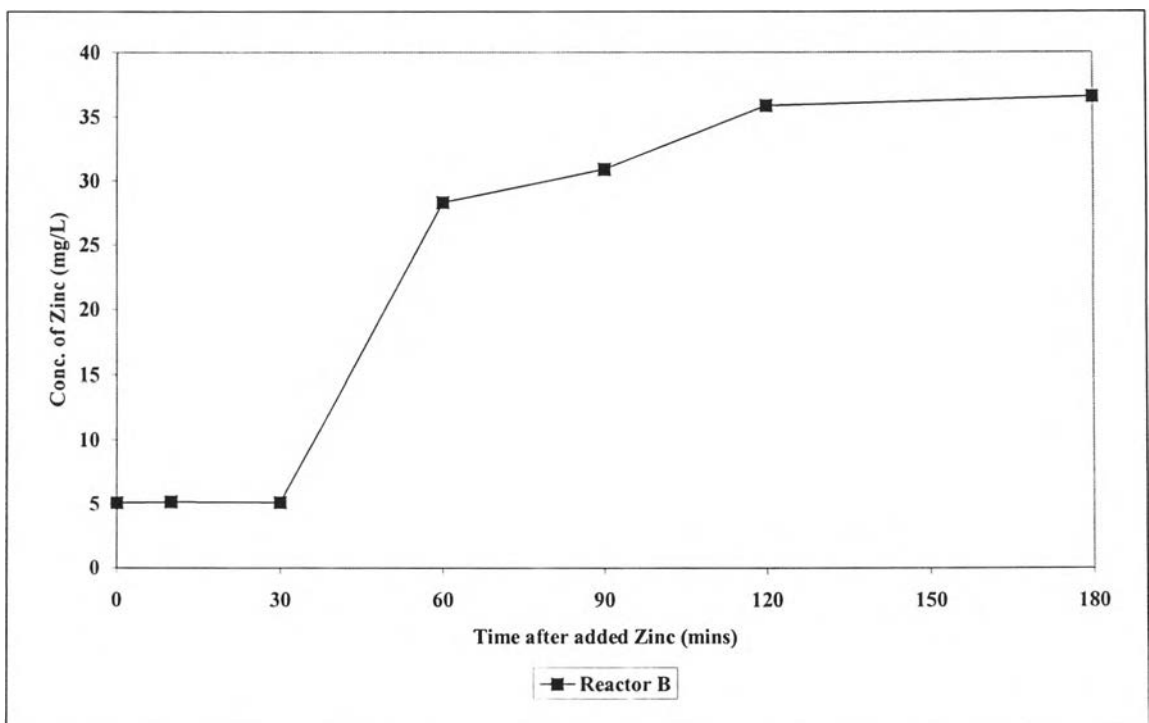


Figure 4.18 COD value after the second addition of 50 mg/L of zinc.

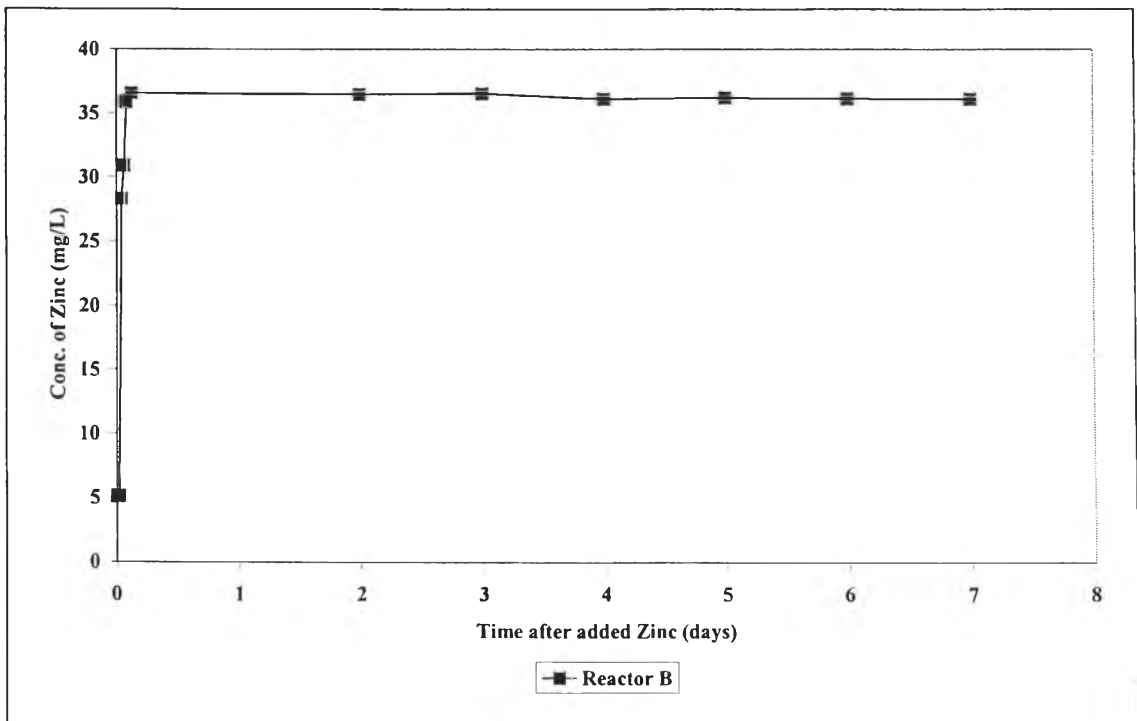
### 4.2.3 Third addition of Zinc for reactor B (50 mg/L)

The third dose of zinc (50 mg/L) with a volume of 200 ml was added to reactor B on the day 43 of experiment.

The zinc concentrations were remained unchanged during the first 30 minutes, and started to increase up to about 35.9 mg/L on the 120 minutes as shown in Figure 4.19(a). The zinc concentrations had shown no significant changes throughout the experiment period of 7 days. The unchanged in the zinc concentration could be concluded that there were no further precipitations due to the failure in the reactor as shown in Figure 4.19(b).



**Figure 4.19 (a)** Zinc concentrations after the third addition of zinc (50mg/L) First 180 minutes.



**Figure 4.19 (b)** Zinc concentrations after the third addition of zinc (50mg/L) over the period of 7 days.

The amount of sulfate in reactor B was increased during the first 180 minutes, but it remained constant after the first day to the end of experiment on day 7.

There was decreased in the sulfide from 24.15 to 17.89 mg/L during the first 180 minutes after the third addition of zinc as shown in Figure 4.21 (a). The decreased of sulfide had showed that it had been used up during the formation of zinc-sulfide precipitate.

In conclusion there was no further formation of sulfide by the reduction of sulfate as the amount of sulfate was increased but no increased in the sulfide. Therefore the SRB were not in the capability of produced further sulfide which cause the reactor to fail.

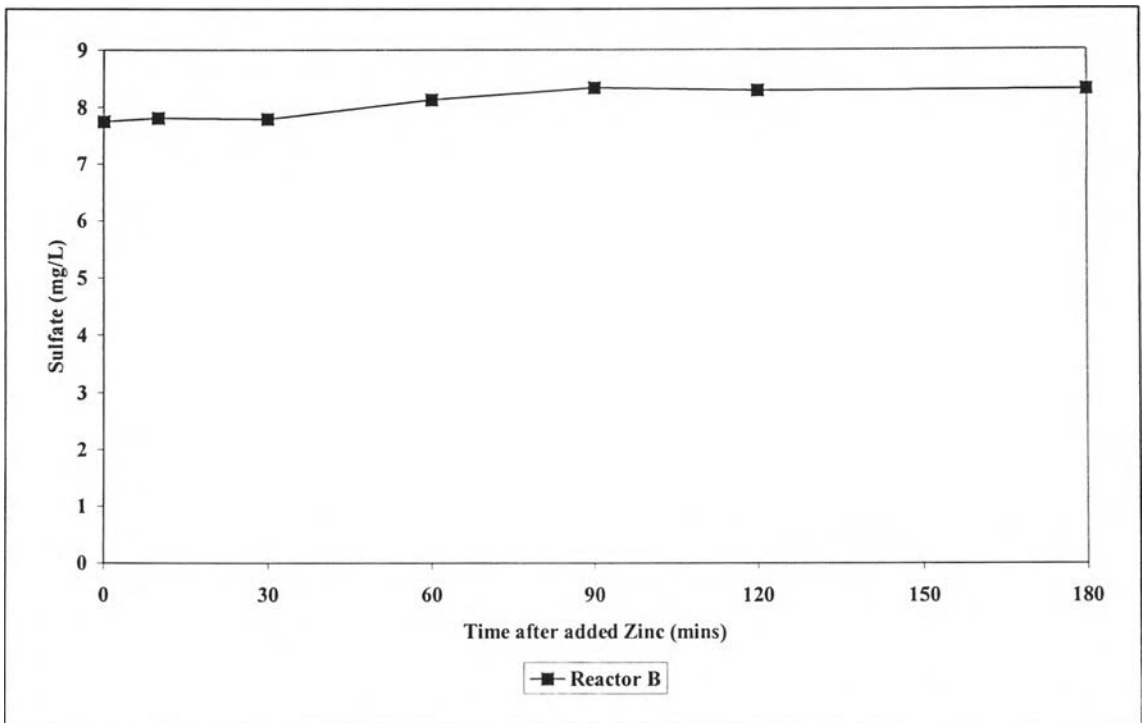


Figure 4.20 (a) Sulfate value after the third addition of zinc (50mg/L) first 180 minutes.

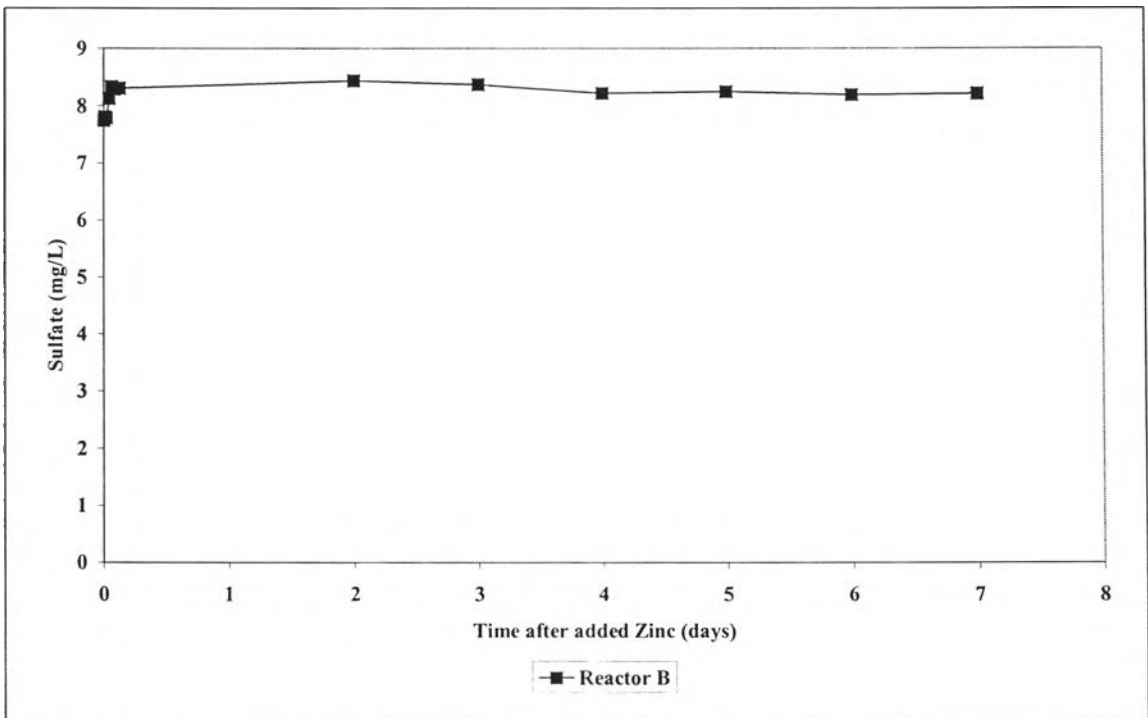
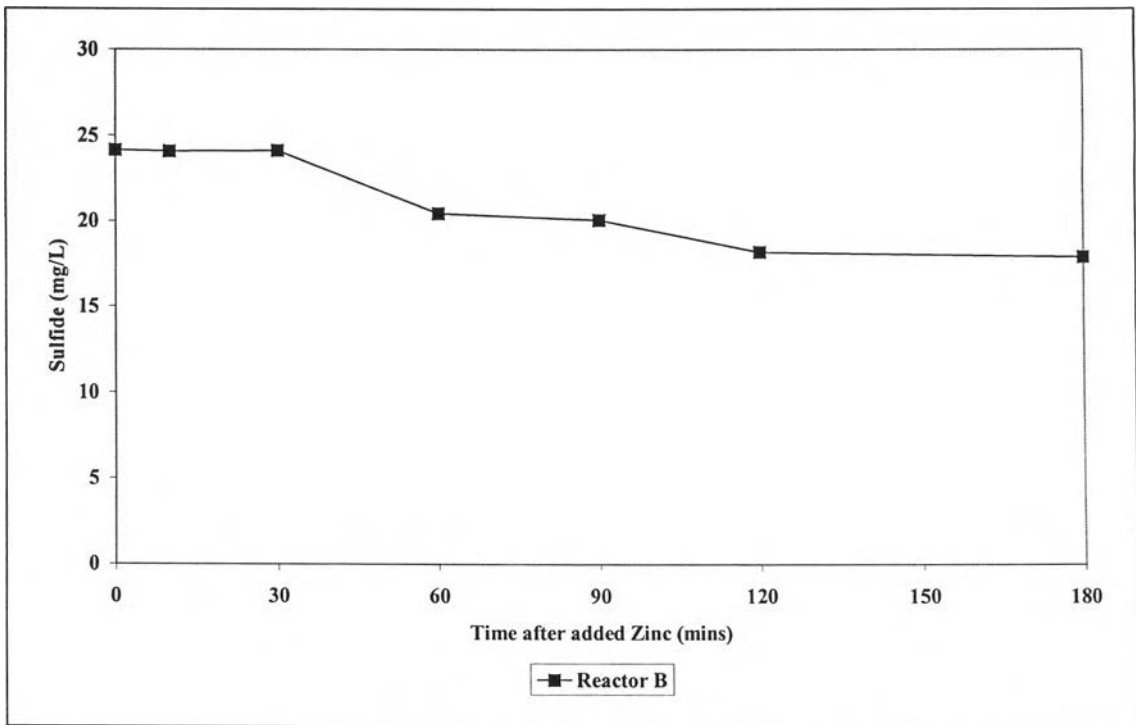
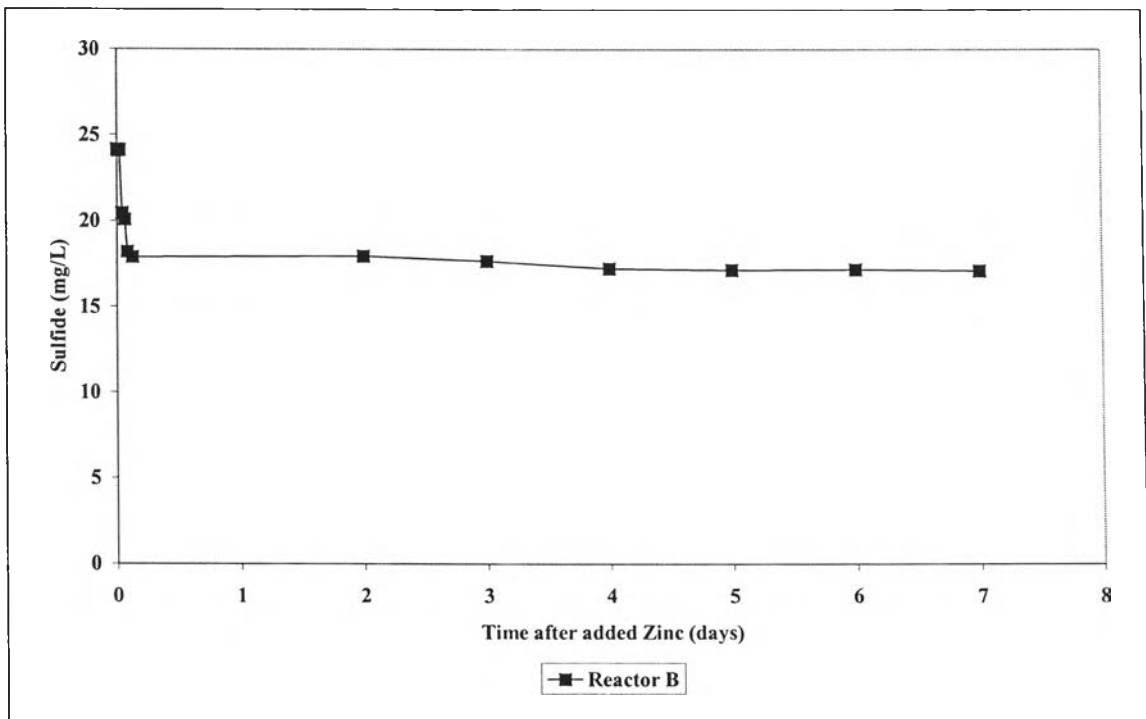


Figure 4.20 (b) Sulfate value after the third addition of zinc (50mg/L) over the period of 7 days.



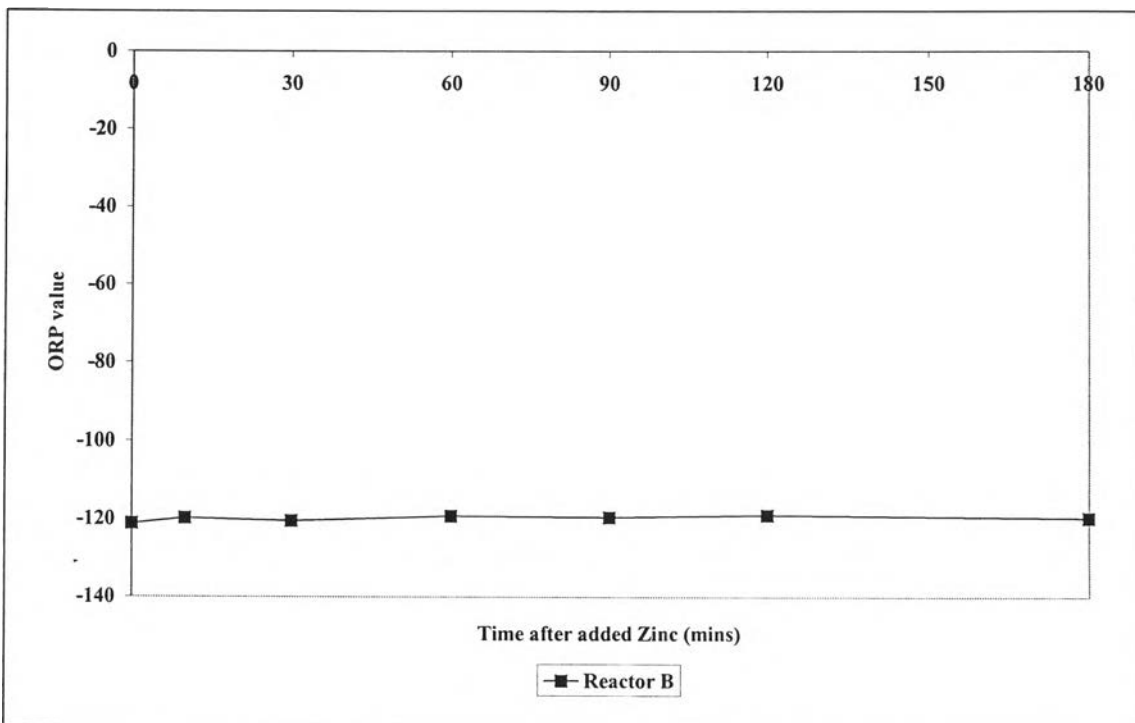
**Figure 4.21 (a)** Sulfide value after the third addition of zinc (50mg/L) first 180 minutes.



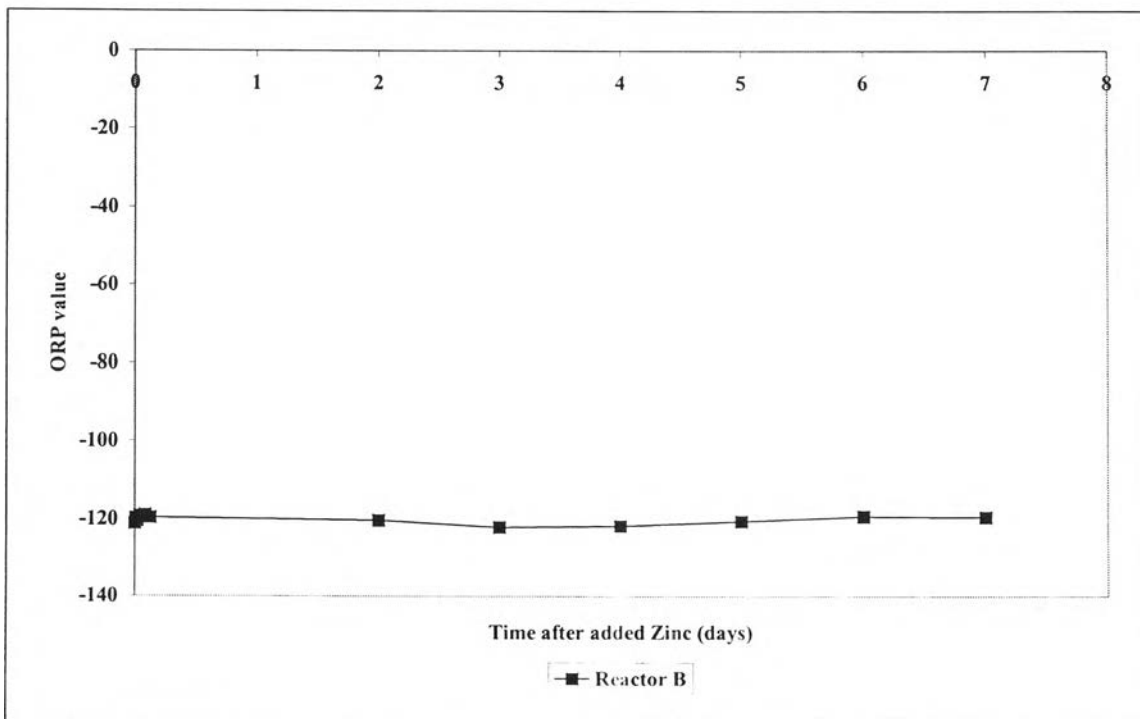
**Figure 4.21 (b)** Sulfide value after the third addition of zinc (50mg/L) over the period of 7 days.

The unchanged in the ORP value and slight changed in the COD value could lead to the conclusion of the SRB population in the reactor were low. As there

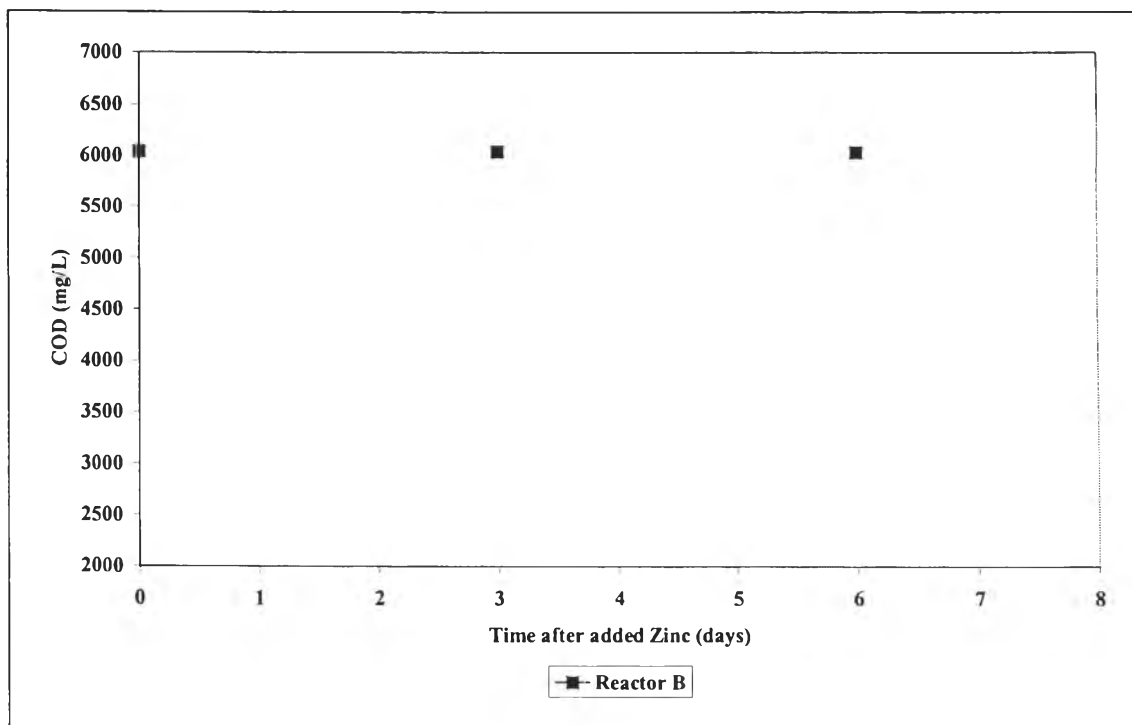
were slight increased in the ORP value during the day 4 which could lead to the conclusion of unsuitable condition for the SRB and cause further failure to the reactor as shown in Figure 4.22 (b) and 4.23, respectively.



**Figure 4.22 (a)** ORP value after the third addition of zinc (50mg/L) first 180 minutes.



**Figure 4.22 (b)** ORP value after the third addition of zinc (50mg/L) over the period of 7 days.



**Figure 4.23** COD value after the third addition of zinc (50mg/L).

The result of the remaining parameters that had tested was shown in Appendix F.



### 4.3 Mass Balance

#### Zinc mass balance

Initial mass = Initial concentration x Volume of water in reactor (0.8 L)

Mass of Zinc = Zinc concentration x Volume of water containing zinc added  
(0.2 L)

Effluent mass = Effluent concentration x Volume of water in reactor  
(Volume for fully mixed is 1.0 L and  
Volume for plugged flow is 0.2 L)

Mass Remain in System = Initial mass + Mass of Zinc added - Effluent mass

Efficiency (%) =  $\frac{\text{Mass Remain in System} \times 100}{\text{Initial} + \text{Zinc added}}$

After the first addition of Zinc (10 mg/L)

Initial mass (mg)	Mass of Zinc added (mg)	Effluent mass (mg)	Mass Remain in System (mg)	Efficiency (%)
Reactor A (Assumed to be Fully mixed condition)				
0.648	2	0.87	1.778	67.15
Reactor A (Assumed to be Plugged flow condition)				
0.648	2	0.174	2.474	93.43
Reactor B (Assumed to be Fully mixed condition)				
0.776	2	1.01	1.766	63.62
Reactor B (Assumed to be Plugged flow condition)				
0.776	2	0.202	2.574	92.72

The efficiency on the treatment of zinc were consider in two cases, 1) fully mixed and plugged flow condition.

Fully mixed condition:

The efficiency of zinc treatment after the first addition of zinc (10mg/L) in reactor A and B were 67.15 and 63.62%, respectively.

Plugged flow condition:

The efficiency of zinc treatment after the first addition of zinc (10mg/L) in reactor A and B were 93.43 and 92.72%, respectively.

After the first addition of zinc to both reactors A and B, they showed that the zinc treatment efficiency were quite high in the plugged flow condition and can work without any difficulty.

After the second addition of Zinc (50 mg/L)

Initial mass (mg)	Mass of Zinc added (mg)	Effluent mass (mg)	Mass Remain in System (mg)	Efficiency (%)
Reactor A (Assumed to be Fully mixed condition)				
0.68	10	24.15	-13.47	-126.12
Reactor A (Assumed to be Plugged flow condition)				
0.68	10	4.83	5.85	54.78
Reactor B (Assumed to be Fully mixed condition)				
0.824	10	5.02	5.804	53.62
Reactor B (Assumed to be Plugged flow condition)				
0.824	10	1.004	9.82	90.72

Fully mixed condition:

The efficiency of zinc treatment after the second addition of zinc (50mg/L) in reactor A and B were -126.12 and 53.62%, respectively.

Plugged flow condition:

The efficiency of zinc treatment after the second addition of zinc (50mg/L) in reactor A and B were 54.78 and 90.72%, respectively.

The efficiency of zinc treatment in the fully mixed condition was impossible as the efficiency from the calculation had showed a negative value. The efficiency of fully mixed condition had showed a contrast with the actual mechanism. On the other hand, in the plugged flow condition had showed a more prospective to reality.

The efficiency of zinc treatment in the reactor A and B were 54.78 and 90.72%. The reactor A had shown a maximum capacity on the treatment of zinc. As it showed that there were no changes in the reduction of zinc concentration since the second day and the treatment efficiency in reactor showed a dramatic drop from 93.43% to 54.78%. But in reactor B had shown a dramatic decreased in the zinc concentration since the start of day 1 to day 4. The reactor B still showed a promising successful treatment system as the treatment efficiency was slightly drop from 92.72% to 90.72% after the second addition of zinc. The sample of reactor B was stopped after the fourth day after the second addition, as it was assumed to be in a steady state.

After the third addition of Zinc (50 mg/L)

Initial mass (mg)	Mass of Zinc added (mg)	Effluent mass (mg)	Mass Remain in System (mg)	Efficiency (%)
Reactor B (Assumed to be Fully mixed condition)				
4.064	10	36.13	-22.066	-156.90
Reactor B (Assumed to be Plugged flow condition)				
4.064	10	7.226	6.838	48.62

Fully mixed condition:

The efficiency of zinc treatment after the third addition of zinc (50mg/L) in reactor B was -156.90%.

Plugged flow condition:

The efficiency of zinc treatment after the third addition of zinc (50mg/L) in reactor B was 48.62%.

The efficiency of zinc treatment in the fully mixed condition was indistinguishable as the efficiency from the calculation still showed a negative value. The efficiency of fully mixed condition had showed a contrast with the actual mechanism. On the other hand, in the plugged flow condition had showed a more promising to reality.

The efficiency of zinc treatment in reactor B was 48.62%. The percent reductions of sulfate were 89.99% for reactor B. The zinc concentration initially remained unchanged after the second day after the third addition of zinc (50mg/L) was added. Zinc sulfide (ZnS) precipitation was formed during electrochemical precipitation processes resulted in the decreased in zinc and sulfide concentration. The zinc treatment efficiency was intensely decreased from 90.72% to 48.62% after the third addition of zinc.

#### **4.4 Gas Analysis**

##### **4.4.1 Gas Production**

There were gas productions from both reactors. The gas production in reactor B seems to be slightly higher than that of reactor A, the reason for this was due to the condition and the amount of SRM in the reactor. The SRB in the reactor B required shorter period of time during the adaptation, as the leachate that fulfill the reactor was filtered from the anaerobic digested sludge obtained from treated wastewater from Nongkam wastewater treatment plant. The methane production from both reactors A and B through out the study was low in quantity and most of the time there were none. The possible reason for low to none methane production was that methane producing bacteria (MPB) had been out competed by the SRB as sulfate, and SRB food, is higher in concentration. From this it could be also concluded that the condition in the reactor was in a flavor environment for the SRB to work in the full capacity.

##### **4.5 Zinc sulfide Precipitation**

Zinc sulfide precipitate in the reactor was low in both reactor A and B. The low precipitation of zinc sulfide had shown a useful suggestion that the reactor would not fail due to the clogging of precipitation.